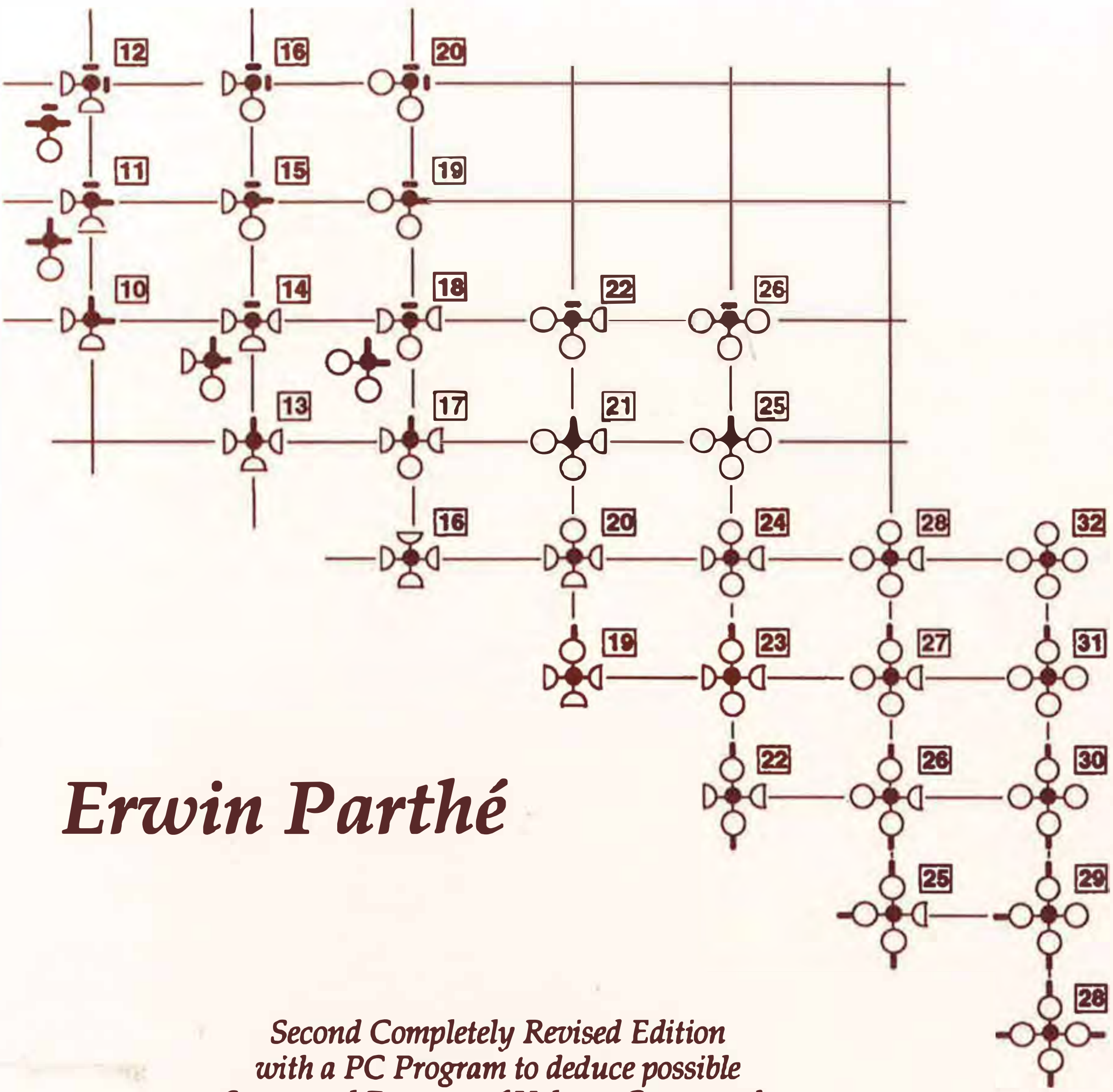
Elements of inorganic structural chemistry : selected efforts to predict structural features

Parthe, Erwin

Elements of Inorganic Structural Chemistry

Selected Efforts to predict Structural Features



Erwin Parthé

Second Completely Revised Edition
with a PC Program to deduce possible
Structural Features of Valence Compounds

Periodic table of the elements (L^* = lanthanides, A^* = actinides)

1A	*2A*	*3T*	*4T*	*5T*	*6T*	*7T*	*8T*	*9T*	*10T*	*1B*	*2B*	*3B*	*4B*	*5B*	*6B*	*7B*	*8B*
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*L**	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	*A**	Rf	Ha													

*L**	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
*A**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Electronegativity or Power of an atom to attract electrons to itself

H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1														

Numerical solutions for four related equations of crystal chemical interest

VEC_A	VEC	VEC'	$2{\cdot}n/m'$	8	7	6.667	6.5	6.4	6.333	6.286	6.25	6.222	6.2	6
AA			TT	0	1	1.333	1.5	1.6	1.667	1.714	1.75	1.778	1.8	2
$N'_{A/M}$	$N_{A/M}$	$N'_{A/M}$	$N'_{T/M}$	1	2	3	4	5	6	7	8	9	10	∞
(V-9)	(VI-10)	(VII-6)	(VII-11)											

ELEMENTS OF
INORGANIC STRUCTURAL CHEMISTRY

SELECTED EFFORTS TO PREDICT STRUCTURAL FEATURES

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SECOND COMPLETELY REVISED EDITION
WITH A PC PROGRAM TO DEDUCE POSSIBLE
STRUCTURAL FEATURES OF VALENCE COMPOUNDS

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About the author :
Born 1928 in Vienna, Austria, he obtained a Ph.D. in Physical Chemistry at the University of Vienna in 1954 under Professor Hans Nowotny. He spent five years at the Massachusetts Institute of Technology in Cambridge, USA as postdoctoral fellow and lecturer in the Metallurgy Department. From 1960 to 1970 he was Professor for Materials Science at the Laboratory for Research on the Structure of Matter at the University of Pennsylvania in Philadelphia, USA. In 1970 he accepted a call from the University of Geneva in Switzerland and founded the Laboratoire Interdisciplinaire de Cristallographie aux Rayons X. In the fall of 1993 when he retired from his post as Professeur Ordinaire de Cristallographie Structurale he was nominated Professeur Honoraire at the University of Geneva. He is continuing his scientific activity partly in the Department of Inorganic, Analytical and Applied Chemistry at the University of Geneva in Switzerland and partly in the Institute for Mineralogy and Crystallography at the Geozentrum of the University of Vienna in Austria.
He is the author of some 230 scientific publications, mostly on crystal chemistry and crystal structure determinations of inorganic and intermetallic compounds. This is his third book.
He has received a Dr.h.c. from the Université de Savoie, France in 1980. The mineral parthéite $Ca_2Al_4Si_4O_{15}(OH)_2{\cdot}4H_2O$ was named after him. In 1990 he was nominated Honorarprofessor für Strukturchemie at the University of Vienna. He is the recipient of the 1991 William Hume - Rothery award of the American Minerals, Metals & Materials Society.

Dedicated to

Katrin, Claudia and Sylvia

PREFACE FOR THE SECOND EDITION

This book deals with methods which can be used to predict possible simple structural features of inorganic compounds without relying on complicated time-consuming calculations.

This new edition represents a complete revision of a book published six years ago. The text has been rewritten so that it can be read, studied and understood alone without the guiding help of a lecturer. The volume has increased by more than two third, the chapters have been reorganized and the main subtitle changed to express more correctly the principal aim of this book. A chapter on the prediction of the deformation of coordination polyhedra has been added. The use of base tetrahedron electron numbers for the quick derivation of the possible atom linkage in anionic tetrahedron complexes is demonstrated here for the first time. New compound examples and instructive crystal chemical problems together with their solutions have been incorporated in the new text. They are often the result of questions students asked during the presentation of crystal chemistry courses based on the first edition of this book. The number of inorganic crystal structure types discussed has increased to nearly 400 of which a tenth had been published since 1970. A database with data sets representative for these structure types will be found on a floppy disk which is attached to this book as a supplement.

Many of the results of the methods to predict structural features which are discussed in this book can be obtained by mental arithmetics alone. However, to help the reader with the calculation of the parameters used for the crystal chemical analysis of a valence compound with tetrahedral structure or anionic tetrahedron complex, a PC program, labelled "VEC", has been written. It can also be found on the attached floppy disk. This program, based on the above results, makes a structure proposal, *i.e.* on the screen will be seen a possible crystal chemical formula together with graph drawings of the base tetrahedron(a) used for the construction of the tetrahedral anion complex.

It is my pleasant obligation to thank Prof. Hans Schmid at the Département de Chimie Minérale, Analytique et Appliquée, University of Geneva and Prof. Ekkehart Tillmanns at the Institut für Mineralogie und Kristallographie at the Geozentrum of the University of Vienna for graciously having provided me a working space in their institutes after my retirement from active service. I would like to thank here Dr. Karin Cenzual, Département de Chimie Minérale, Analytique et Appliquée and Dr. Roman Gladyshevskii, Département de Physique de la Matière Condensée, University of Geneva for their very helpful comments. Dr. Karin Cenzual collaborated on the preparation of the "VEC" program and the database. The author likes to thank also the Gmelin Institut for the permission to reproduce excerpts of TYPIX 1995 Database.

Vienna, August 1996.

ERWIN PARTHÉ

PREFACE FOR THE FIRST EDITION

The material treated in this textbook presents a selection of topics in inorganic structural chemistry, most of which are either not found in other textbooks or are only discussed there in a cursory manner. This applies particularly to the various valence electron rules and the prediction of the most probable structural features of tetrahedral structures and structures with anionic tetrahedron complexes. The structural features have been denoted, as far as possible, by crystal chemical formulae, which are very convenient in presenting predicted and observed structural information in a compact form. In all textbooks on inorganic crystal chemistry there is a certain arbitrariness on the subjects treated, provided it is really a textbook and not a lexicon on crystal structures. The main emphasis here is on the presentation and demonstration of simple rules which permit the prediction of the most probable structural features of various kinds of compounds. However, in all fairness, one has to admit that there remain many crystal structures which defy an easy interpretation and which we can neither explain nor predict.

This textbook is based on the updated version of my lecture notes for a crystal chemistry course which I have been giving during 20 years at the University of Geneva. It is intended to be used as supporting material for a lecture series on elements of inorganic structural chemistry which takes about twenty hours (*i.e.* a two-week-intensive course with two lecture hours per day). Only preliminary notions of crystallography are needed as a prerequisite. The course is thus suited for (advanced) undergraduates in chemistry, physics, mineralogy and metallurgy.

It is a great pleasure for me to acknowledge the help I received from Mrs. Christine Boffi, who typed the manuscript and from Mrs. Birgitta Künzler, who prepared the drawings. Furthermore, I would like to express my thanks for the technical assistance which was provided by the University of Geneva and for the financial support which I received from the Alfred and Hilde Freissler Fund.

Geneva, July 1990.

ERWIN PARTHÉ

CONTENTS

I. DEFINITION AND NOTATION OF STRUCTURE TYPES

Definition

Two structures are called (configurationally) isotypic if they have the same space group, the same number of atoms in the unit cell on the same Wyckoff sites with the same or similar positional coordinates (*x*, *y*, *z*) and the same or similar values of the unit cell axial ratios (*c/a*, *a/b*, *b/c*) and cell angles (α, β, γ). [I-1]

The space groups and their Wyckoff sites are listed in the International Tables for (X-Ray) Crystallography. [I-2] There are a few (unintended) differences between the 1952 and 1983 edition of the International Tables in the Wyckoff letters assigned to the Wyckoff sites and in the expressions for certain Wyckoff sites. Structure description ambiguities can be avoided if for each used Wyckoff site is listed not only the Wyckoff letter but also all three positional atom coordinates. [I-3]

Configurational isotypism does not necessarily indicate a similarity in the type of bonding or the possibility of forming solid solutions.

Example : In the case of octahedral structures with NaCl type (see Figure IV - 2) different bonding mechanisms can lead to the formation of this atom arrangement. The NaCl type is found for example not only with KCl (ionic) but also with TiC (metallic and covalent). There is no mutual solubility between KCl and TiC, however the two chlorides NaCl and KCl have a complete range of solid solubility. [I-4] There exists no valence electron rule valid for **all** compounds crystallizing with the NaCl type.
Differently, in the case of tetrahedral (adamantane) structures with ZnS (sphalerite) type (see Figure IV - 2) only one bonding mechanism occurs (*i.e.* overlapping of sp^3 hybridized orbitals). All isotypic compounds (such as GaAs or InP) are semiconductors and they form with few exceptions extended solid solutions. Since there is only one bonding mechanism it is possible to formulate a valence electron rule valid for all compounds which correlates structural features with the number of valence electrons.

The use of the term "isomorphic" for isotypic, occasionally found in the literature, is to be avoided. "Isomorphic" means literally having some crystal form or shape. The same crystal form can occur with different compounds having different crystal structure. For example, cubes are found with halite (NaCl) and pyrite (FeS_2).

I-1) Lima-de-Faria, J., Hellner, E., Liebau, F., Makovicky, E. & Parthé, E. (1990). Acta Cryst. ***A46****, 1 - 11.*

I-2) International Tables for X-Ray Crystallography (1952). Vol. I. Birmingham : Kynoch Press ; International Tables for Crystallography (1983). Vol. A. Dordrecht : Reidel.

I-3) Parthé, E., Gelato, L.M. & Chabot, B. (1988). Acta Cryst. ***A44****, 999 - 1002.*

I-4) See, for example, Figure 1 in Liu, L.-G., Bassett, W.A. & Liu, M.S. (1973). J. Phys. Chem. ***77****, 1695 - 1699.*

Inversely, the crystal form of a given compound may be different depending on the conditions during crystallization, although the atom arrangement, *i.e.* the crystal structure is the same.

Example : NaCl normally crystallizes in the form of cubes. However, if the aqueous salt solution is contaminated with urea $CO(NH_2)_2$ (urine in the original literature) then surprisingly NaCl octahedra are formed. This had been reported already in 1783 by Romé de l' Isle. [I - 5] The explanation for this change of crystal form is as follows : The {100} faces of a NaCl nucleus consist both of cations and anions (centred square mesh), while any given (111) face has alternatively only cations or only anions (triangular mesh). For electrostatic reasons the ions from the solution prefer normally to attach themselves on the {111} faces. In a pure salt solution a NaCl crystal nucleus grows thus faster along the ⟨111⟩ directions than the ⟨100⟩ directions. This has as consequence that the {111} faces eventually disappear from the growing crystal with the final crystal form being a cube. In a contaminated salt solution the polar urea molecules are adsorbed on the {111} faces of the nucleus, hindering the crystal growth along the ⟨111⟩ directions. The crystal now grows relatively faster along the ⟨100⟩ directions, the {100} faces will eventually disappear with the final crystal form being an octahedron.

According to the TYPIX 1995 database there are known for inorganic compounds (excluding oxides and halides) more than 3600 structure types. [I - 6] For example there exist

93 structure types for elements
210 types for binary equiatomic *AB* compounds (without SiC and ZnS polytypes)
235 types for binary AB_2 compounds.

The total number of known inorganic compounds is in a rough estimation about 10 times as large as the number of structure types.

Standardization of structure data

Structures are customarily described using the symmetry equivalent positions listed in the International Tables for (X-Ray) Crystallography. However there exist different but equivalent possibilities of describing a crystal structure due to a possible shift of the unit cell origin, a rotation or inversion of the coordinate system. As a consequence there are examples in the literature where identical crystal structures were not recognized as such but were considered as having different structure types. This could have been avoided in many cases if a standardized description of crystal structure data would have been used. [I - 7] The standardization of crystal structure data can be done by applying the STRUCTURE TIDY program. [I - 8]

In Table I - 1 is shown an example where the isotypism of two compounds is not obvious from the published structure data (and also remained unnoticed for a long time) but is easily recognizable from a comparison of the standardized data due to the similarity of cell parameters and positional atom coordinates. The $CeCu_2$ data are not changed during the standardization procedure, however, in the case of KHg_2, the a and *b* axes will be interchanged and the unit cell origin shifted by $^1/_4$ $^3/_4$ $^3/_4$.

I - 5) Romé de l' Isle, J.B. (1783). "Cristallographie". Second Edition. Vol.1, Footnote 277 on pages 377 and 379. Paris : Imprimerie de Monsieur.

I - 6) "TYPIX 1995 Database of Inorganic Structure Types". Distributed by Gmelin - Institut, Frankfurt. User's Guide by K. Cenzual, R.E. Gladyshevskii & E. Parthé (1995).

*I - 7) Parthé, E., Cenzual, K. & Gladyshevskii, R.E. (1993). J. Alloys Comp. **197**, 291 - 301.*

*I - 8) Gelato, L.M. & Parthé, E. (1987). J. Appl. Cryst. **20**, 139 - 143.*

Table I - 1 : Published and standardized structure data of $CeCu_2$ and KHg_2 (space group *Imma*)

Published data								Standardized data							
$CeCu_2$				KHg_2				$CeCu_2$				KHg_2			
a = 4.425, *b* = 7.057, *c* = 7.475				*a* = 8.10, *b* = 5.16, *c* = 8.77Å				*a* = 4.425, *b* = 7.057, *c* = 7.475				*a* = 5.16, *b* = 8.10, *c* = 8.77Å			
	x	*y*	*z*		*x*	*y*	*z*		*x*	*y*	*z*		*x*	*y*	*z*
Ce in 4(*e*)	0	1/4	0.5377	K in 4(*e*)	0	1/4	0.703	Ce in 4(*e*)	0	1/4	0.5377	K in 4(*e*)	0	1/4	0.547
Cu in 8(*h*)	0	0.051	0.1648	Hg in 8(*i*)	0.190	1/4	0.087	Cu in 8(*h*)	0	0.051	0.1648	Hg in 8(*h*)	0	0.06	0.163

Standardized data of all the structure types mentioned in this book are compiled in the EISC Database which is found on the floppy disk in a pocket in the hard cover (see Appendix D).

Notations of structure types

There are essentially two methods used to denominate a structure type.

1) The **chemical formula** (symbol) or **colloquial name** of the compound (element) where the particular atom arrangement was first found.

Some structure types were discovered independently at different places and were thus given different names by the different authors. Depending on who reads whose publications, the different structure type names are unfortunately carried on in the literature.

Example : $ThCr_2Si_2$ type (in western hemisphere) ≡ $CeAl_2Ga_2$ type (in eastern hemisphere)
The two original structure determinations had been published independently at the same time.

2) Notation after **Strukturbericht** (supplement to Zeitschrift für Kristallographie).

The notation consists of a letter and a number. The letter indicates the composition, whereas the number is a simple reference number without any (desirable) information on the structural features. The notation, which is still in use particularly with metallurgists, was not continued after 1945 in Structure Reports, the successor of Strukturberichte. Examples for the Strukturbericht notation of structure types can be found in Table I - 2.

Table I - 2 : Examples for the Strukturbericht notation of structure types

Letter	Composition	Examples of Strukturbericht notation (chemical formula or colloquial name)				
A	element	A1 (Cu),	A2 (W),	A3 (Mg),	A4 (diamond)	
B	*AB*	B1 (NaCl),	B2 (CsCl),	B3 (sphalerite),	B4 (wurtzite),	B8 (NiAs)
C	AB_2	C1 (CaF_2),	C14 ($MgZn_2$),	C15 ($MgCu_2$),	C36 ($MgNi_2$)	

Classification of structure types

Structure types can be classified by means of the Pearson code or according to space group and Wyckoff sequence.

1) **Pearson code** : The Pearson code consists of a small letter to indicate the crystal system (a = anorthic or triclinic, *m* = monoclinic, *o* = orthorhombic, *t* = tetragonal, *h* = hexagonal and trigonal, *c* = cubic), a capital letter to denote the type of Bravais lattice (*P*, *S* (for *A*, *B* or *C*), *R*, *F*, *I*) and finally a number which corresponds to the number of atoms in the unit cell.

The letter combinations for the 14 kinds of Bravais lattices are as follows :

aP--, mP--, mS--, oP--, oS--, oF--, oI--, tP--, tI--, hP--, hR--, cP--, cF--, cI--

Examples : Cu : *cF4*; α-Sm : *hR9*; W : *cI2*; ZnS (sphalerite) : *cF8*; ZnS (wurtzite) : *hP4*
Mg : *hP2*; As : *hR6* ; C (diamond) : *cF8*; NaCl : *cF8*; FeS_2 (pyrite) : *cP12*

Note that different structure types may have the same Pearson classification code, as for example, C (diamond), ZnS (sphalerite) and NaCl.
In the case of trigonal structures based on an *R* space group (examples above are α-Sm and As) [I - 9] the number of atoms refers in some data collections to the primitive rhombohedral unit cell but in others to the corresponding triple-hexagonal unit cell, and often they are mixed. The numbers given here always refer to the triple-hexagonal unit cells and must be thus multiples of 3.

2) **Space group** (number) and **Wyckoff sequence** : A much finer graded classification of the structure types is based on the space group (number) and the letter(s) of the used Wyckoff position(s), each letter with a trailing superscripted number (if > 1) which indicates how often a Wyckoff position is used. To obtain this so-called Wyckoff sequence one should, however, use standardized structure data since otherwise the Wyckoff sequence of isotypic structure might not be the same (see example in Table I - 1).

Examples : C (diamond) : *cF8 (227)* $Fd\bar{3}m$ *- a*
ZnS (sphalerite) : *cF8 (216)* $F\bar{4}3m$ *- ca*
NaCl : *cF8 (225)* $Fm\bar{3}m$ *- ba*
NiSbS (ullmannite) : *cP12 (198)* $P2_13$ - a^3
FeS_2 (pyrite) : *cP12 (205)* $Pa\bar{3}$ *- ca*
CO_2 : *cP12 (205)* $Pa\bar{3}$ *- ca*
Isotypic structures treated in Table I - 1 : $CeCu_2$ and KHg_2 : *oI12 (74) Imma - he*

Structures having the same space group and the same Wyckoff sequence are called **isopointal** structures. Isotypic structures are necessarily isopointal structures but not vice-versa.

Example : As seen in the list above FeS_2 (pyrite) and CO_2 are isopointal. A study of the two structures reveals that the positional parameters of the Fe atoms are different from those of the C atoms. The structural features are unrelated, *i.e.* three-dimensionally linked FeS_6 octahedra and S - S dumb-bells in pyrite (see Figure II - 5), but isolated linear O = C = O molecules in CO_2. The two structures are thus not isotypic but only isopointal.

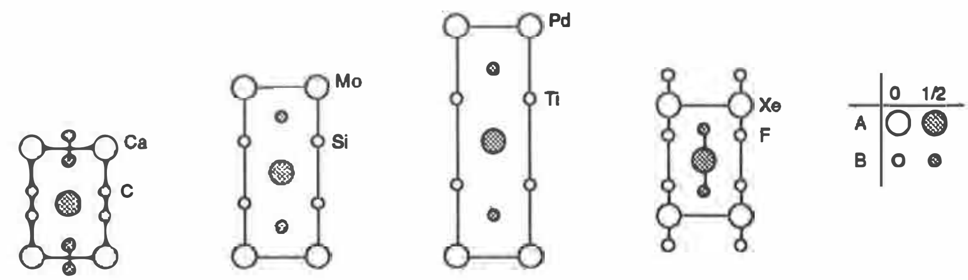
Structure type branches

The definition of certain structure types is not without problems. Even with moderate variations of the axial ratios and/or the positional coordinates, a change of the shape of the coordination polyhedra of the atoms may occur. Variations of a structure type with different shapes of the coordination polyhedra of the atoms are referred to as structure type branches. Note that there is no general agreement on the limits of the structure type branches.

I - 9) Trigonal space groups where all axes are either normal rotation axes (3 or $\bar{3}$) or screw axes (3_1 or 3_2) are P groups for which only a primitive hexagonal cell is used. In the R space groups 3 or $\bar{3}$ axes alternate with 3_1 or 3_2 axes. One finds in the International Tables both a description corresponding to the small primitive rhombohedral unit cell as well as one corresponding to the triple-hexagonal cell with a volume three times as large.

Example : CaC_2, $MoSi_2$, Ti_2Pd and XeF_2, shown in Figure I - 1, are isopointal : composition AB_2, space group *I4/mmm* , 2*A* in 2(*a*) : 000 + [$^1/_2$ $^1/_2$ $^1/_2$] and 4*B* in 4(*e*) : ± 00*z* + [$^1/_2$ $^1/_2$ $^1/_2$]. XeF_2 and CaC_2-type compounds have characteristic structural features, *i.e.* linear *B* - *A* - *B* molecules and *B* - *B* dumb-bells, respectively. It is justifiable to consider them as having individual structure types, but this is not so evident for the other isopointal compounds. The $MoSi_2$ branch differs from the Ti_2Pd branch in respect to the value of the *c / a* ratio and the size ratio between minority (*A*) and majority (*B*) atoms. The unusual case can happen that in one binary phase diagram two branches of the same structure type occur at inversed composition ratios. One example is the binary phase diagram Zr - Pd with one compound at composition Zr_2Pd (Ti_2Pd branch) and a second with composition $ZrPd_2$ ($MoSi_2$ branch).

CaC_2	$MoSi_2$	Ti_2Pd ($PdTi_2$)	XeF_2
c/a = 1.65	c/a = 2.45	c/a = 3.25	c/a = 1.62
z = 0.40	z = 0.33	z = 0.34	z = 0.28



Dumb-bells of *B* atoms	No dumb-bells	No dumb-bells	Linear molecule
	$r_A > r_B$	$r_A < r_B$	F - Xe - F
BaC_2, BaO_2	$ZrPd_2$, $ZrAu_2$	$PdZr_2$, $AuZr_2$	

Figure I -1 : Drawings of four branches of a tetragonal AB_2 type with space group I4/mmm, 2A in 2(a) : 000 and 4B in 4(e) : ± 00z.

Type and its antitype

In the case of an ionic compound the antitype corresponds to an atom arrangement where cations and anions have interchanged their sites. This concept becomes meaningless for equiatomic structure types such as NaCl, CsCl or ZnS (sphalerite) where cation and anion partial structures, with the exception of a shift, are identical.

Examples :

TYPE	BiF_3	CaF_2	Mn_2O_3	La_2O_3
ANTITYPE	Li_3Bi	Mg_2Si	Mg_3P_2	α-Mg_3Sb_2

Notations for stacking variants

A great number of socalled **polytypes** are known for certain compounds such as SiC or ZnS. These are geometrically closely related structure types which can be interpreted as stacking variants, all based on a common structural slab. For these polytypes a notation is needed to indicate how these slabs are stacked. We shall demonstrate these different notations on the close-packed element structure types where only five different stacking variants are known.

1) ***ABC* Notation** : Starting from the first slab in position *A* one denotes all other possible different stacking positions by capital letters (*B, C, D..*). The slab stacking sequence in the structure is expressed by a sequence of capital letters.

The close-packed element structures have as basic slab a close-packed hexagonal layer, shown in Figure I - 2a. There are three different stacking positions, denoted in Figure I - 2b by *A*, *B* and *C*. In a close-packed structure, where each atom has 12 equidistant neighbours, two successive layers have different position letters, so that the centers of the spheres in one layer fall directly over the centers of the triangular interstices of the other layer.

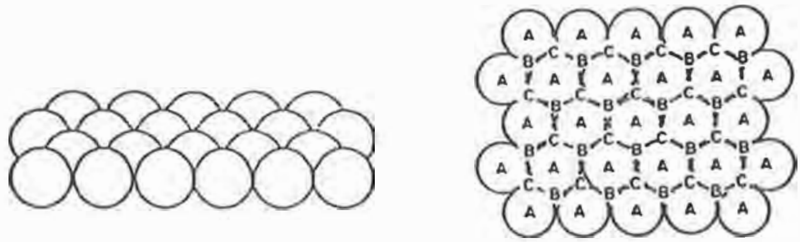
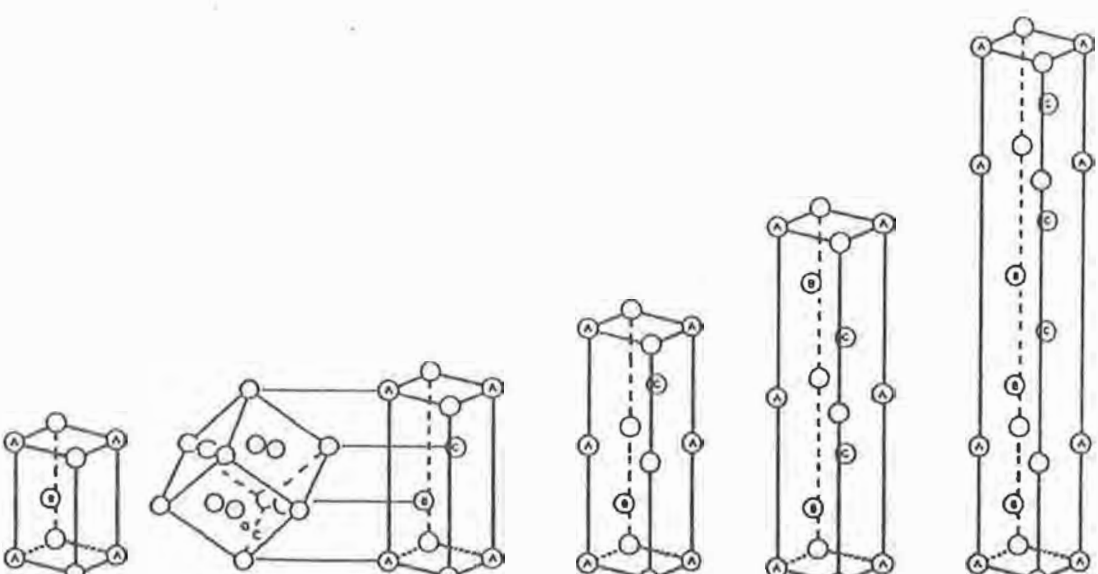


Figure I - 2 : The close-packed hexagonal layer which stacked in different ways will lead to the different close-packed element structure types. a) Layer seen in perspective; b) Layer seen from the top with the three different layer stacking positions indicated by letters A, B and C.

The distance between two layers in close packed structures is $d_L = a \cdot (2/3)^{1/2}$, which corresponds to the height of a regular tetrahedron with base length *a*. The ideal hexagonal *c / a* ratio for the different stacking variants is then given by

$$c/a \;=\; n \cdot d_L / a \;=\; n \cdot (2/3)^{1/2} \;=\; n \cdot 0.8165 \qquad \text{(I - 1)}$$

where *n* indicates the number of stacked close-packed hexagonal layers in one (triple-)hexagonal unit cell.



Mg, *hP2*	Cu, *cF4*	α-Nd, *hP4*	Tb *HP*, *hP6*	α-Sm, *hR9*
AB	*ABC*	*ABAC*	*ABCACB*	*ABABCBCAC*
c/a: $2 \cdot (2/3)^{1/2} = 1.63$	$3 \cdot (2/3)^{1/2} = 2.45$	$4 \cdot (2/3)^{1/2} = 3.27$	$6 \cdot (2/3)^{1/2} = 4.90$	$9 \cdot (2/3)^{1/2} = 7.36$

Figure I - 3 : The five known close-packed element structure types, ordered according to increasing n, the number of close-packed hexagonal layers in the (triple-)hexagonal unit cell, and their ideal hexagonal c / a values.

The five known close-packed element structure types, arranged according to increasing number of layers n in their (triple-)hexagonal cells, are presented in Figure I - 3. For each type is given the structure type name, the Pearson classification symbol, the *ABC* stacking symbol and the value of the ideal c/a ratio. *HP* stands for high pressure modification. To visualize that the Cu structure also belongs to the close-packed element structures it is necessary to make a unit cell transformation from the conventional face-centred cubic to a triple-hexagonal unit cell. Both unit cells are shown in Figure I - 3 and they are rotated to permit the recognition of corresponding atom sites. The matrix for the unit cell transformation from a face-centred cubic to a triple-hexagonal cell is given in Appendix A as equation (A - 14).

2) **Jagodzinski - Wyckoff Notation** : [I - 10] Applicable only to structures which allow not more than 3 stacking positions and where two subsequent slabs cannot have the same stacking position.

The notation consists of a sequence of small letters, ***h*** and ***c***, which are assigned to each slab depending on the side-wise displacements of the two neighbouring slabs, the one above and the one below.

h is assigned to each slab where the two neighbouring slabs are displaced side-wise in the same direction and for the same distance.

c is assigned to each slab where the two neighbouring slabs are displaced side-wise in opposite directions and for the same distance.

The number of ***h*** and ***c*** letters is often by a factor smaller than the number of *ABC* letters, *i.e.* the number of layers n in one (triple-)hexagonal unit cell. Optionally this factor can be added after the Jagodzinski - Wyckoff stacking formula as a subscript.

Example :	α-Sm	*A B A B C B C A C*		*ABC* notation for α-Sm
		c h h c h h c h h	= $(\boldsymbol{hhc})_3$,	Jagodzinski - Wyckoff notation

The Jagodzinski-Wyckoff stacking notation for the five close-packed element structure types :

Mg : $\boldsymbol{h}_2$ Cu : $\boldsymbol{c}_3$ α-Nd : $(\boldsymbol{hc})_2$ Tb *HP* : $(\boldsymbol{hcc})_2$ α-Sm : $(\boldsymbol{hhc})_3$

For an alternative interpretation of the ***h*** and ***c*** stacking based not on different side-wise displacements of the slabs but on their rotation for 180° or the lack of it, see Chapter 11.

3) **Zhdanov Notation** : [I - 11] Applicable only to structures which do not allow more than three stacking positions and where two subsequent slabs cannot have the same stacking position.

The notation consists of a sequence of numbers each of which represents the number of consecutive slabs with a given sign for the side-wise displacement with respect to the preceding slabs (1 for stacking ***h***, ∞ for stacking ***c***). Also here, the factor corresponding to the number of slabs in the triple-hexagonal cell can be added as a subscript.

Simple procedure for finding the Zhdanov stacking symbol : Starting from the Jagodzinski - Wyckoff stacking symbol divide it into sections, each section starting with the letter ***h***. The numbers of letters in each section correspond to the numbers used for the Zhdanov stacking symbol.

I - 10) Jagodzinski, H. (1954), Acta Cryst. 7, 17 - 25 and Neues Jb. Mineral. ***10****, 49 - 65.*

I - 11) Zhdanov, G.S. (1945). C.R. Acad. Sc. USSR ***48****, 39 - 42.*

Example : SiC *33R* $(h\ c\ c\ h\ c\ c\ h\ c\ c\ h\ c)_3$ Jagodzinski - Wyckoff notation

/ / / \ \ \ / / / \ \ $= (3_3 2)_3$ Zhdanov notation

The Zhdanov notation is even shorter than the Jagodzinski - Wyckoff notation. The number of layers in one (triple-)hexagonal unit cell can be obtained by summing up all numerals, properly multiplied by their subscripts.

The Zhdanov stacking notation for the five close-packed element structure types :

Mg : 1_2 Cu : ∞_3 α-Nd : 2_2 Tb *HP* : 3_2 α-Sm : $(21)_3$

⇒⇒⇒ Problem 1 in Appendix B

4) **Hexagonality or percentage of hexagonal stacking** : The hexagonality expresses the relative number of changes in the sign of the side-wise displacement of subsequent slabs. It can be calculated from the :

— Jagodzinski - Wyckoff stacking formula according to

$$[\text{(number of letters } h\text{) / (total number of letters)}] \cdot 100 \qquad \text{(I - 2a)}$$

— Zhdanov stacking formula according to

$$[\text{(number of numerals) / (sum of numerals)}] \cdot 100 \qquad \text{(I - 2b)}$$

The five known close-packed element structure types, ordered according to increasing hexagonality :

0%	33.3%	50%	66.7%	100%
Cu, c_3	Tb *HP*, $(hcc)_2$	α-Nd, $(hc)_2$	α-Sm, $(hhc)_3$	Mg, $(h)_2$

It will be seen in later chapters that the order of the element structure types based on hexagonality is crystallochemically more significant than an order based on the number of layers in the (triple-)hexagonal unit cell.

Examples for the application of the hexagonality parameter to rare-earth elements, ZnS polytypes and Laves phases

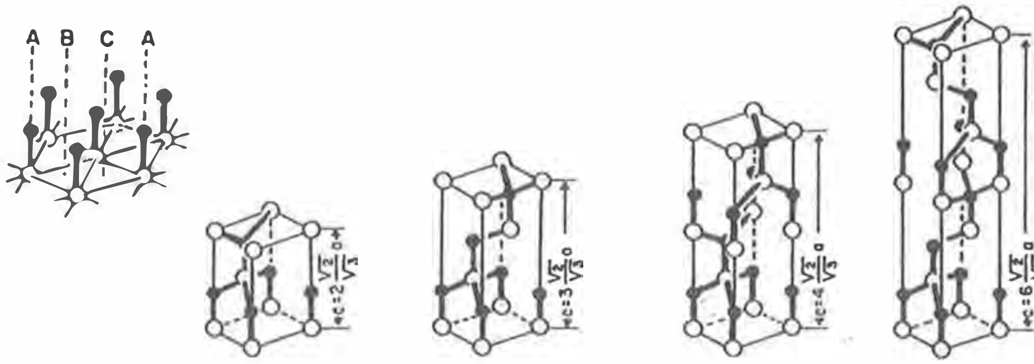
1) Decrease of the hexagonality of the close-packed structures of the rare-earth elements with an increase of pressure (see Figure X - 5) and the systematic change of the layer stacking in the structures of the inter-rare-earth alloys (see Table III - 1).

2) Increase of the birefringence Δ_n (difference between extreme values of the refractive index) with an increase of the hexagonality of a ZnS polytype.

The 196 properly identified ZnS polytypes [I - 12)] do not differ significantly in energy and cannot be transformed once they have formed (except for a possible change to the sphalerite type at high temperature). Various screw dislocations, some introduced by temperature gradients during formation, may be in part responsible for the formation of the many polytypes.

I - 12) Mardix, S. (1986). Phys. Rev. ***B33****, 8677 - 8684.*

In Figure I - 4 are shown four simple ZnS polytypes, described as a stacking of a common ZnS double layer which assumes different stacking positions denoted by *A, B* and *C*.

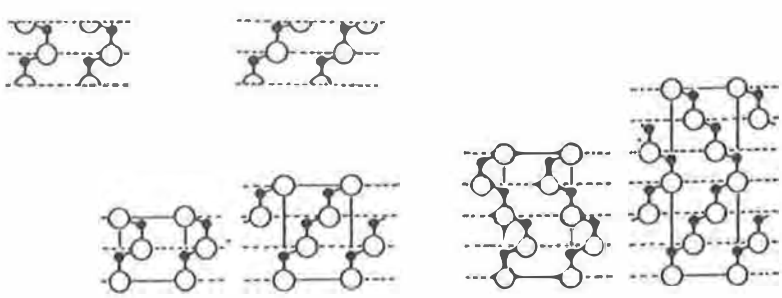


wurtzite, *hP4*	sphalerite, *cF8*	ZnS *4H*, *hP8*	ZnS *6H*, *hP12*
B4 type	B3 type	B5 type	B6 type
AB, ***h***$_2$	*ABC*, ***c***$_3$	*ABAC*, (***hc***)$_2$	*ABCACB*, (***hcc***)$_2$

Figure I - 4 : The basic double layer found in ZnS polytypes and four polytypes formed by stacking this double layer. The structure types are identified by the Pearson classification code, the Strukturbericht type code, the ABC stacking sequence and the Jagodzinski-Wyckoff stacking symbol. As in the case of the Cu type, a description of the cubic sphalerite type with a triple-hexagonal unit cell simplifies its comparison with the structures of the other polytypes.

In an alternative approach for the description of the ZnS polytypes, one can identify the different slabs presented in Figure I - 5. Each slab is three-atom-layers thick and is intergrown with neighboring slabs. The atoms at the interface belong half to one slab and half to the other slab, the overall composition of one slab being thus ZnS.

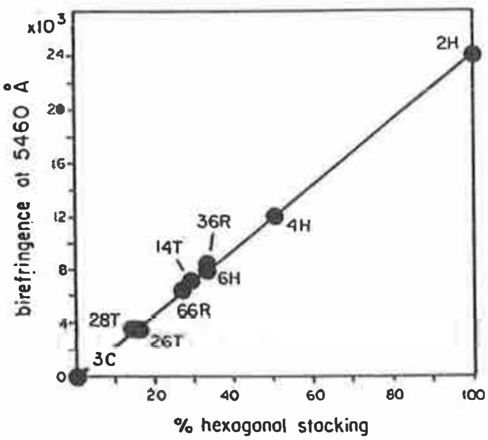
Differences in stacking are obtained by either rotating or by non-rotating the following intergrown slab by 180° around an axis through an atom in the interface. An infinite sequence of non-rotated intergrown slabs corresponds to the sphalerite structure with ***c*** stacking. An infinite sequence of successivly rotated intergrown slabs corresponds to the wurtzite structure with ***h*** stacking.



wurtzite sphalerite ZnS 4H ZnS 6H

*Figure I - 5 : Atom arrangement in the $(11\bar{2}0)$ planes of the same four ZnS polytypes, now interpreted as an intergrowth of a common slab. In the upper left are shown the two possibilities how two ZnS slabs can be intergrown, leading either to a **h** stacking (left) or to a **c** stacking (right). The traces of the interface planes are indicated by broken lines.*

In the following list of selected ZnS polytypes the structure types are also denoted by the simple **Ramsdell notation** [I-13] which consists of a number corresponding to the number of slabs in the hexagonal unit cell and a letter which indicates the crystal system (H = hexagonal, R = rhombohedral, *i.e.* trigonal with R Bravais lattice, T = trigonal with P Bravais lattice, C = cubic).
The cubic sphalerite is optically isotropic, *i. e.* its value of the birefringence is zero. The biggest value of the birefringence is found with wurtzite which has 100% hexagonal stacking. As seen in Figure I - 6 the birefringence value of a polytype increases linearly with its hexagonality.



Ramsdell	Jagodszinski - Wyckoff	hexagonality
$2H$	h_2	100
$4H$	$(hc)_2$	50
$6H$	$(hc_2)_2$	33.3
$36R$	$[hc_5(hc)_3]_3$	33.3
$14T$	$hc_4hc_3hchc_2$	28.6
$66R$	$[hc_6hc_2hchc_3(hc_2)_2]_3$	27.3
$26T$	$hc_{16}hc_3hchc_2$	15.4
$28T$	$(hc_8)_2(hc_4)_2$	14.3
$3C$	c_3	0

Figure I - 6 : The birefringence values of nine different ZnS polytypes, measured at 5460 Å, as a function of the hexagonality of the polytype (based on experimental data by Brafman & Steinberger [I-14] with additions). In the list on the right hand side the polytypes are identified according to Ramsdell notation, Jagodzinski - Wyckoff stacking formula and hexagonality.

3) Variation of the homogeneity ranges of Mg - based binary and pseudobinary Laves phase polytypes, characterized by their hexagonality, with the valence electron concentration *VEC*.
The Laves phases denote a large group (> 250) of binary or pseudobinary intermetallic compounds of general composition AB_2 where the A component is on the average about 20 % larger than the B component. They are not valence compounds and they are found with all except the very electronegative elements. Laves phases are known for example with KNa_2 (***A-A***), $CaIr_2$ (***A-T***), $CsBi_2$ (***A-B***), $NbCr_2$ *LT* (***T-T***) or $ZrZn_2$ (***T-B***). The classification of the elements used here corresponds to that of the Periodic Table on the inside front cover.

All twelve Laves phase polytypes with fully determined crystal structure can be interpreted as an intergrowth of one common slab which is stacked either with or without rotation for 180° around an axis perpendicular to the interface plane. The three most frequently found Laves phase polytypes, the C14 ($MgZn_2$) type with stacking $(h)_2$, the C36 ($MgNi_2$) type with stacking $(hc)_2$ and the C15 ($MgCu_2$) type with cubic stacking are shown in Figure I - 7. The cubic C15 type is presented with a triple-hexagonal unit cell to simplify its comparison with the other two types.

I - 13) Ramsdell, L.S. (1947). Amer. Mineral. **32**, 64 - 82.
I - 14) Brafman, O. & Steinberger, I.T. (1966). Phys. Rev. **143**, 501 - 505.

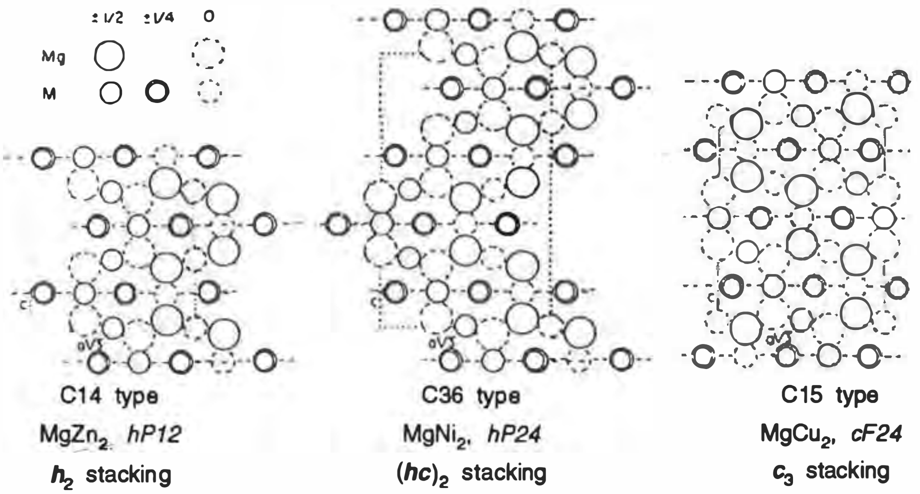


Figure I - 7 : Three common Laves phase polytypes, interpreted as an intergrowth of a common slab. The traces of the intergrowth planes are indicated by thicker broken lines.

To recognize better the relative orientations of the intergrown slabs, *i.e.* rotated or non-rotated in respect to each other, for each slab in C14 and C36 in Figure I - 7 only the atoms within one translation parallel to the intergrowth plane are shown. The outlines of these slabs are "left- or right-leaning" parallelograms. The reader should have no great difficulties to identify these slabs and their outlines also in the drawing of the C15 type, where all atoms in the unit cell are shown. The slabs in C15 are not rotated in respect to each other, *i.e.* all slab outlines in the drawing are "left-leaning" parallelograms.

In the pseudoternary system $MgZn_2$ - $MgCu_2$ - $MgNi_2$ different Laves phase stacking variants occur. Their homogeneity limits can be correlated with the so-called **valence electron concentration** ***VEC*** which for a ternary alloy $A(B_{1-x}B'_x)_2$ is defined by

$$VEC = [e_A + 2(1-x)\cdot e_B + 2x\cdot e_{B'}]/3 \quad \text{for } A(B_{1-x}B'_x)_2 \qquad (I - 3)$$

For metallic Laves phases one has to use for e_A : $e_{Mg} = 2$ and for e_B or $e_{B'}$: $e_{Zn} = 2$ or $e_{Cu} = 1$ or $e_{Ni} = 0$, *i.e.* only electrons outside the *d* shell are taken into consideration.

Examples :

alloy	$MgNi_2$	$MgCu_2$	MgNiZn	$MgZn_2$
VEC	0.67	1.33	1.33	2.0

In Figure I - 8 is shown the pseudoternary phase diagram $MgNi_2$ - $MgCu_2$ - $MgZn_2$ and the most probable homogeneity ranges of three Laves phase types, *i.e.* the C14 ($MgZn_2$), C36 ($MgNi_2$) and C15 ($MgCu_2$) types Experimental data on various pseudobinary sections by Laves & Witte [I - 15] and others have been used for the construction. The base line of the phase diagram triangle can serve here also as a linear *VEC* scale from 0.67 for $MgNi_2$ up to 2.0 for $MgZn_2$. One notes that each type occurs within a particular *VEC* range, but the C36 ($MgNi_2$) type has two separate ranges :

VEC range	0.67 - 1.0	1.05 - 1.70	1.80 - 1.90	1.97 - 2.0
Structure type	C36 ($MgNi_2$)	C15 ($MgCu_2$)	C36 ($MgNi_2$)	C14 ($MgZn_2$)

I - 15) Laves, F. & Witte, H. (1936). Metallwirtschaft 15, 840 - 842.

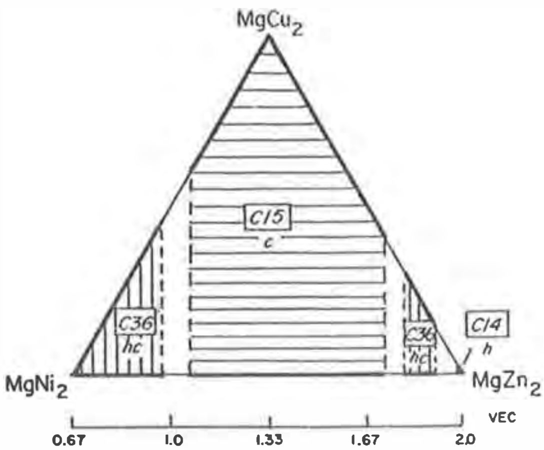


Figure I - 8 : Simplified version of the pseudoternary system $MgZn_2$ - $MgCu_2$ - $MgNi_2$ with the homogeneity ranges of the C14, C15 and C36 type phases indicated by different shading. In the ternary diagram the positions of all points with same VEC value are on vertical lines. A VEC scale is given below the base line of the phase diagram triangle.

Using (I - 3) one can calculate that the phase limit of the C15 type in the pseudobinary system $MgCu_2$ - $MgZn_2$ should be close to $Mg(Cu_{.45}Zn_{.55})_2$ and in the pseudobinary system $MgNi_2$ - $MgCu_2$ near to $Mg(Cu_{.575}Ni_{.425})_2$.

According to the more detailed studies of Komura & Kitano [I - 16] there exist many other Laves phase polytypes, mostly with very small homogeneity ranges. As shown in Figure I - 9, starting from the $MgZn_2$ type with *VEC* = 2 and 100% hexagonality, the hexagonality and the *VEC* parameter both decrease in steps untill *VEC* = 1.70 and 0% hexagonality. However, for *VEC* ≤ 1 one observes again an increase in hexagonality.

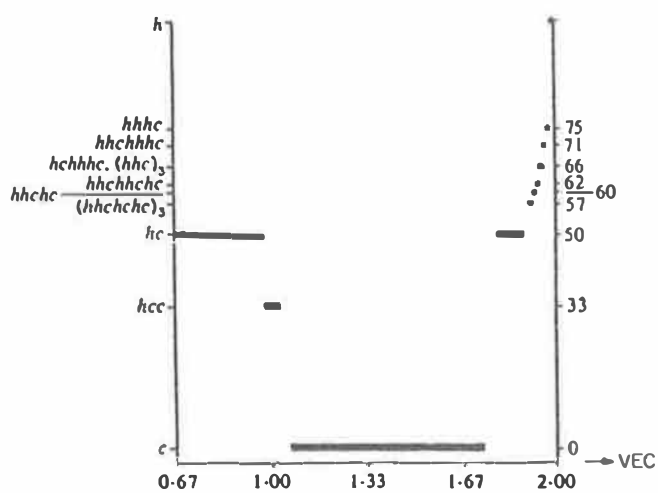


Figure I - 9 : The relation between the hexagonality of Laves phase polytypes and the valence electron concentration VEC (according to Komura & Kitano [I - 16]). On the left ordinate are indicated the Jagodzinski - Wyckoff stacking formulae of the polytypes and on the right ordinate the corresponding hexagonality values.

I - 16) Komura, Y. & Kitano, Y. (1977). Acta Cryst. B33, 2496 - 2501.

II. CRYSTAL CHEMICAL FORMULAE

The crystal chemical formulae are formulae which permit the notation of the essential structural features of simple inorganic structures in a very short symbolized form. This notation has been adopted and recommended for use by a commission of the International Union of Crystallography. [II - 1)] There exists a simple notation for the linkage of the overall structure, for the linkage of a partial structure and for the coordination of individual atoms. To this may be added a notation for non-bonding orbitals. We shall use this notation below to denote not only the experimentally observed but also the predicted structural features.

Notation for the linkage type of the overall structure

This notation will be useful for structures where there are pronounced differences in the bonds between the atoms. The usual chemical formula is preceded by a special symbol, *i.e.* :

$\overset{3}{\infty}$ for a three-dimensionally linked structure (often omitted)
$\overset{2}{\infty}$ for a layer structure
$\overset{1}{\infty}$ for a fiber structure
$\overset{0}{\infty}$ for a molecular structure.

The symbol for a molecular structure is rarely used. However, in this book one can easily recognize a molecular structure because in this case the chemical formulae will be surrounded by square brackets. By convention the formula has been multiplied so that the total number of atoms within the square brackets corresponds to the number of atoms of the molecule.

To characterize the shape of the molecule one can in addition use extra special symbols, which precede the opening square bracket. The following symbols are used :

^[···] for a chain molecule of finite length
O[···] for a cyclic molecule
●[···] for a cage molecule.

Note that in a cage molecule there are at least three different paths along the bonds to come back to the starting point. The simplest cage molecule is a tetrahedron.

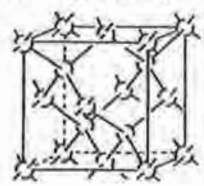
Occasionally it might be desired to characterize the molecule further by inserting a small number in the symbol for the molecular shape which then indicates the number of atoms which form the finite chain, ring or cage molecule, respectively. This is useful particularly in the case of a branched chain or ring and cage with side chains because the inserted number refers only to the number of atoms of the main part without the side chains. Examples for crystal chemical formulae for molecular structures with and without side chains can be found in Table II - 1.

II - 1) Lima-de-Faria, J., Hellner, E., Liebau, F., Makovicky, E. & Parthé E. (1990). Acta Cryst. ***A46****, 1 - 11.*

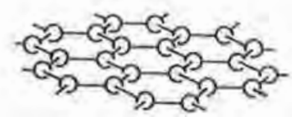
TABLE II - 1 : EXAMPLES FOR CRYSTAL CHEMICAL FORMULAE OF MOLECULAR STRUCTURES

Structures without side chains		Structures with side chains	
$\hat{4}$ [S_2Cl_2]	see Figure VI - 7	$\hat{4}$ [P_2I_4]	see Figure VI - 8
⑥[S_6]	cyclohexasulphur	⑥[C_6F_{12}]	perfluorocyclohexane
⑩[As_4O_6]	same as [P_4O_{10}] but without the four endstanding O atoms	⑩[P_4O_{10}]	same as the anionic tetrahedron complex in $Li_5P_2N_5$ (Figure VIII - 2)

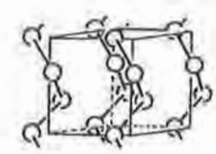
The crystal chemical formulae for selected element structures are presented in Figure II - 1. Note that the crystal chemical formula for iodine [I_2] can be simplified. A molecule consisting of two atoms cannot be anything else than a dumb-bell.



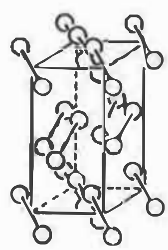
$^{3}_{\infty}$C, diamond *cF8*



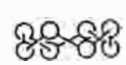
$^{2}_{\infty}$C, graphite



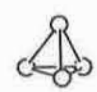
$^{1}_{\infty}$Se, fibrous selenium *hP3*



$\hat{2}$ [I_2] *oS8*



⑧[S_8] cyclooctasulphur

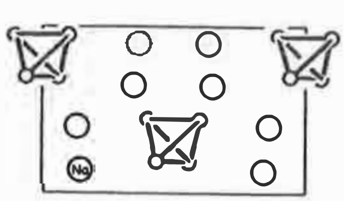


●[P_4], white phosphorus

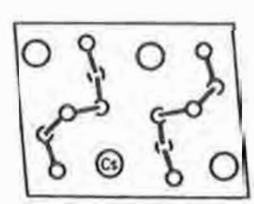
Figure II - 1 : Drawings and crystal chemical formulae of selected element structures. The Pearson classification code is given only when a complete unit cell is shown.

Notation for the linkage type of a partial structure

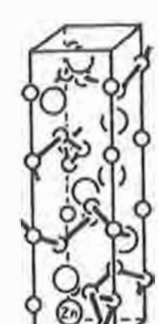
To indicate the linkage type which atoms of one kind have with atoms of the **same** kind, one uses the special symbols as listed above but now placed inside the chemical formula in front of the element's symbol. Examples are presented in Figure II - 2.



a) Na_4 ●[Si_4], *mS32*



b) Cs_2 $\hat{6}$ [S_6], *aP16*



c) Zn $^{1}_{\infty}P_2$ red, *tP24*

Figure II - 2 : Three structures with different anion partial structures : a) NaSi with isolated anion tetrahedra, b) CsS_3 with finite chains of six anions and c) red ZnP_2 with infinite anion chains. In the projection of NaSi are shown only half the atoms contained in one unit cell.

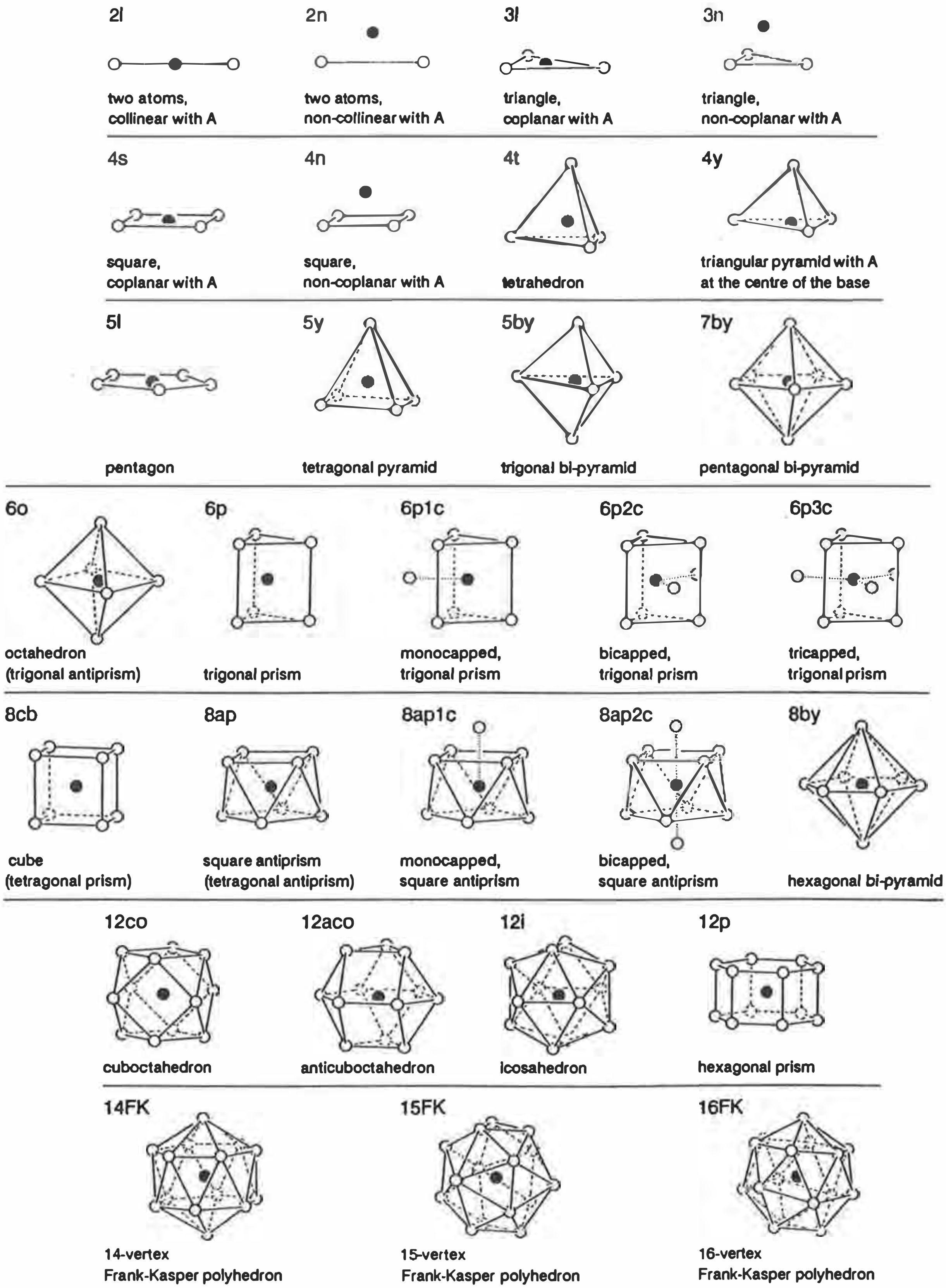


Figure II - 3 : Symbols for commonly observed coordination polyhedra.

Notation for the coordination of an individual atom

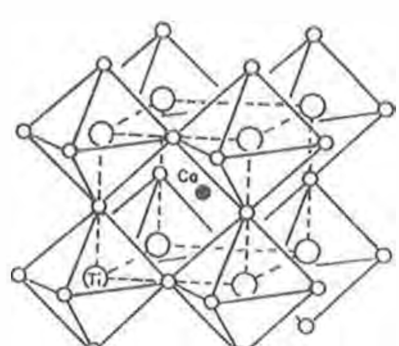
A set of symbols for the most commonly observed types of coordination polyhedra, presented in Figure II - 3, has been proposed. [II - 1] In the crystal chemical formulae these coordination symbols are placed inbetween square brackets and are added as trailing superscripts to the chemical symbols of the atoms. The superscripts consist of a number and letter(s). The numerical coefficient indicates the number of atoms coordinated to the central atom and the letter(s) characterize the type of coordination polyhedron. Drawings and crystal chemical formulae for simple binary structure types can be studied in Figure IV - 2.

It is desirable to differenciate in the coordination between **heteronuclear** neighbours (of different kind) and **homonuclear** neighbours (of the same kind). Within the square brackets the number on the left refers to the number of heteronuclear neighbours and the number on the right, always separated from the former by a **semi-colon**, to the number of homonuclear neighbours. If there are no homonuclear neighbours the semi-colon is often left out.

In the case of ternary (or generally multicomponent) compounds it will be also necessary to distinguish between the different kinds of heteronuclear neighbours of an atom. This is done by counting separately the numbers of neighbours of each kind. These numbers, separated by **commas**, are indicated within the square brackets (and to the left of the semi-colon if there is any). The order of the different neighbour elements considered will always be the same as the order of the elements in the chemical formula of the compound.

For a structure of composition $A_mB_nC_o$, the coordination of atom A is written as $A^{[x,y;a]}$ where x and y denote the numbers of B and C neighbours (*i.e.* always in the sequence given in the chemical formula) coordinated to atom A. These coordination numbers are separated by commas. The self-coordination number of A by A, denoted a, follows the semi-colon. The coordination of atom B is then written as $B^{[x',y';b]}$ where x', y' and b denote the numbers of atoms A, C and B around B, respectively, *etc.*.

As first example we consider a ternary crystal structure without homonuclear bonds, *i.e.* the idealized cubic perovskite $CaTiO_3$, [II - 2] shown in Figure II - 4, together with a complete crystal chemical formula and simpler versions of it.



$^3_\infty Ca^{[8cb,12co;0]}\,Ti^{[8cb,6o;0]}\,O_3^{[4s,2l;0]}$

$Ca^{[8,12co]}\,Ti^{[8,6o]}\,O_3^{[4s,2l]}$

$Ca^{[,12co]}\,Ti^{[,6o]}\,O_3^{[4,2]}$

$Ca^{[12co]}\,Ti^{[6o]}\,O_3$ (only coordination by O atoms)

Figure II - 4 : The crystal structure of idealized cubic perovskite $CaTiO_3$, cP5 and its crystal chemical formula with various degrees of simplifications.

II - 2) A structure redetermination has shown that the compound $CaTiO_3$ itself does not crystallize with the cubic perovskite type. It adopts instead the $GdFeO_3$ type, oP20, one of the deformation variants.

As second example we consider a structure with homonuclear bonds, *i.e.* the cubic pyrite FeS_2 with its characteristic S - S dumb-bells, shown in Figure II - 5. Each S atom is surrounded by a tetrahedron consisting of three Fe and one S atom.

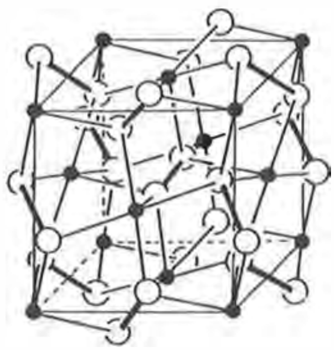


Figure II - 5 : Structure of pyrite FeS_2, cP12 and its crystal chemical formula in different versions. Fe atoms are represented by small filled circles.

$^{3}_{\infty}Fe^{[6o;0]}\ \overset{\wedge}{2}[S_2^{[(3;1)t]}]$

$Fe^{[6o]}\ S_2^{[(3;1)t]}$

$Fe^{[6o]}\ S_2^{[;1]}$ (only coordination by S atoms)

In Figure II - 2 were shown three structures with polyanions. Their crystal chemical formulae, given on page 14, can be complemented by adding the homonuclear atom coordination for each anion, as shown below. However, this is here superfluous since the number of homonuclear bonds of each anion can anyhow be derived from the known shape of the anion partial structure, sufficiently described by means of the special symbols.

a) $Na_4\ \bullet[Si_4^{[;3]}]$ b) $Cs_2\ \overset{\wedge}{6}[S_2^{[;1]}S_4^{[;2]}]$ c) $Zn\ ^{1}_{\infty}P_2^{[;2]}$

The most simplified crystal chemical formulae, where only the overall linkage type (if at all) and the coordination of the cations by the anions is considered, were introduced some 50 years ago by Felix Machatschki [II - 3]. They can be found mostly in mineralogy texts and apply to normal valence compounds where there are no homonuclear bonds (see chapter IV). Examples for four common minerals are :

Calcite $Ca^{[6o]}C^{[3l]}O_3$, Aragonite $Ca^{[9]}C^{[3l]}O_3$, Spinel $Mg^{[4t]}Al_2^{[6o]}O_4$, Garnet $Ca_3^{[8]}Al_2^{[6o]}Si_3^{[4t]}O_{12}$

Check of heteronuclear coordination numbers

There is a simple method to check if the heteronuclear coordination numbers agree with each other. For a structure of composition $A_m^{[x,y;a]}B_n^{[x',y';b]}C_o^{[x'',y'';c]}$ the total number of bonds, which radiate from all A and extend to the B atoms, must be equal to the total number of bonds which radiate from all B atoms and extend to the A atoms. The same reasoning applies to the other atom pairs. This result can formally be expressed by

$$m \cdot x = n \cdot x' \quad \text{and} \quad m \cdot y = o \cdot x'' \quad \text{and} \quad n \cdot y' = o \cdot y'' \qquad \text{for } A_m^{[x,y;a]}B_n^{[x',y';b]}C_o^{[x'',y'';c]} \qquad \text{(II - 1)}$$

One notes that self-coordination numbers do not appear in these formulae.

As a simple example for the application of (II - 1) one may regard the garnet structure for which a crystal chemical formula is given in the paragraph above. One finds that an O atom must be coordinated by four atoms, *i.e.* two Ca, one Al and one Si atom.

II - 3) Machatschki, F. (1947). Monatsh. Chem. 77, 334 - 342.

Notation for non-bonding orbitals

In the case of defect tetrahedral structures (chapters VI and VII) and tetrahedral anion complexes consisting of ψ-tetrahedra (chapter IX) it is possible to calculate the number of non-bonding orbitals per formula unit. These lone-electron pairs cannot be seen directly but their presence can be infered indirectly, for example, by the absence of an expected atom neighbour. To indicate in the crystal chemical formula that an element has one or more non-bonding orbitals attached to it one underlines its chemical symbol with one or more bars.

As example is presented in Figure II - 6 the *2H* stacking variant of GaSe, a layer structure with a very pronounced cleavage character. [II - 4] Single crystal platelets of GaSe can be cleaved easily by attaching adhesive tapes to both sides and pulling them in opposite directions parallel to the platelet surface. This anisotropic property of GaSe single crystals is due to the orientation of the Se non-bonding orbitals which extend perpendicular to the slab surface. While there exists strong covalent bonding within the slabs, there are only weak van der Waals' interactions between the slabs.

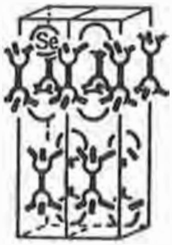


Figure II - 6 : Crystal structure of ε - GaSe 2H, hP8 and its crystal chemical formula in two versions.

$\overset{2}{\infty}\left(\overset{\wedge}{2}\left[\mathrm{Ga}_2^{[(3;1)^t]}\,\underline{\mathrm{Se}}_2^{[3n;0]}\right)\right.$

$\overset{2}{\infty}\,\mathrm{Ga}^{[(3;1)t]}\,\underline{\mathrm{Se}}^{[3n;]}$

General comments : Overloaded crystal chemical formulae are difficult to read and should be avoided as far as possible. It depends on the subject under discussion how complete a crystal chemical formula must be, but for most applications very simple versions are sufficient.

In certain cases it may not be possible to formulate a complete crystal chemical formula. Particularly with certain alloy structures there are difficulties in describing atom coordinations due to the presence of irregular polyhedra with coordinating atoms at different distances from the central atom. For these cases various methods have been devised to calculate weighted (non-integral) coordination numbers. [II - 5] However, the different methods do not always give the same result. It is further probable that certain atoms are not spherical but have the form of ellipsoids (see for example Figure X - 7). In this case lists of distances between atom centers alone are not sufficient for determining the number of coordinating neighbour atoms.

II - 4) At least six different kinds of stacking variants are known for GaSe, all based on the same kind of slab (see Figure VI - 2). The code 2H is the Ramsdell stacking symbol, explained in Chapter I.

*II - 5) Brunner, G.O. & Schwarzenbach, D. (1971). Z. Kristallogr. **133**, 127 - 133.*
*Brunner, G.O. (1977). Acta Cryst. **A33**, 226 - 227.*
*O'Keeffe, M. (1979). Acta Cryst. **A35**, 772 - 775.*

III. STRUCTURE OF THE ELEMENTS

The Hume - Rothery 8 - *N* rule

The Hume - Rothery 8 - *N* rule describes a structural feature of the elements on the right hand side of the Periodic Table : The number of next nearest neighbours of an atom is 8 - *N* where *N* is its number of electrons in the outer shell and its group number in the Periodic Table. Elements with structures which do **not** obey the 8 - *N* rule on the left of Figure III - 1, are separated from the elements on the right with structures which do, by a heavy line often referred to as **Zintl line**. As shown by (V - 11), the Hume - Rothery 8 - *N* rule is a special case of the generalized 8 - *N* rule.

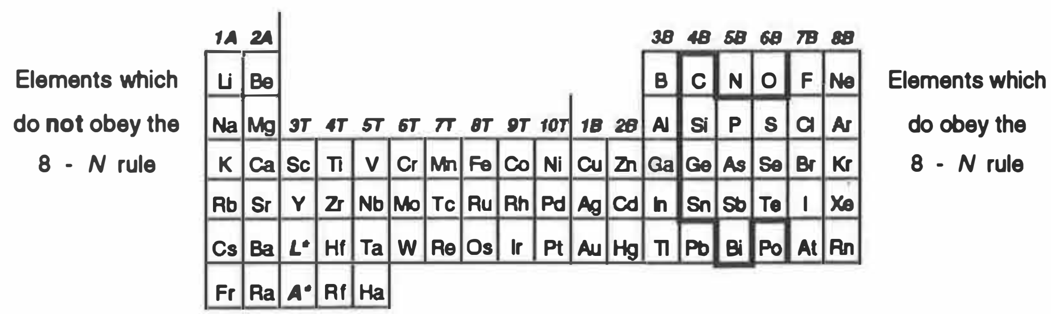


Figure III - 1 : The Hume - Rothery 8 - N rule and the Periodic Table of the elements.

Structures of elements which obey the 8 - *N* rule

In Figure III - 2 are shown selected element structures arranged according to increasing *N* value. The coordination superscripts in the crystal chemical formulae have the numerical value of 8 - *N*.

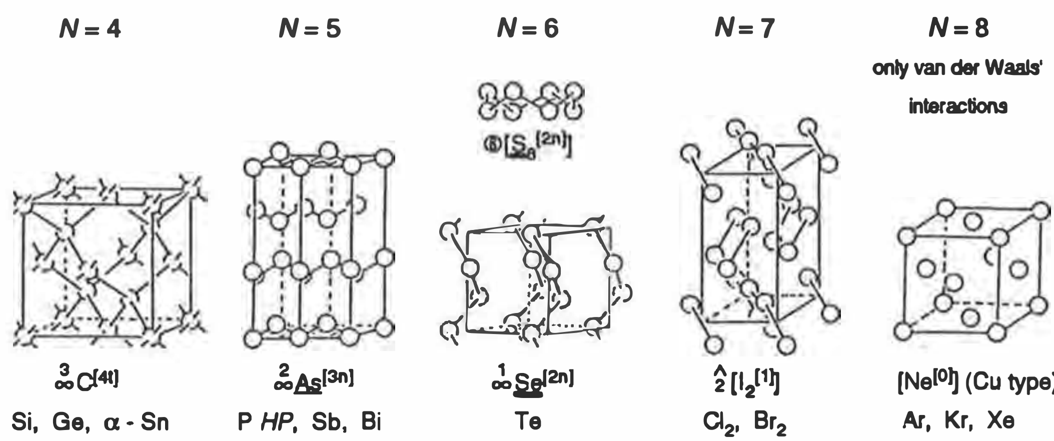


Figure III - 2 : A selection of element structures which obey the 8 - N rule.

Structures of elements which do not obey the 8 - *N* rule

Most of the elements to the left of the Zintl line are metallic and crystallize essentially with three simple structure types : A1, A2 and A3 (notation after Strukturbericht), shown in Figure III - 3. The distribution of these three types (at normal pressures and temperatures) can be studied in Figure III - 4 where only the left hand side of the Periodic Table is given.

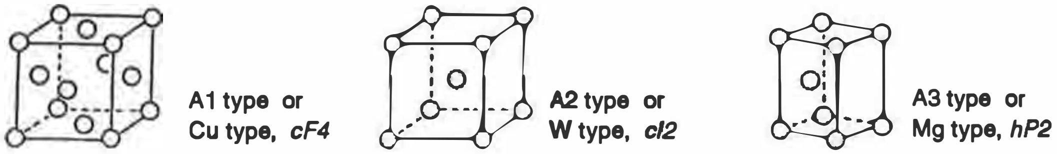


Figure III - 3 : The three most common structure types for elements to the left of the Zintl line.

Figure III - 4 : The distribution of the A1, A2 and A3 structure types for elements in the left hand part of the Periodic Table (see the inside cover of this book). An inscribed chemical symbol indicates that this element has a different structure.

1A	2A											3B	
A2	A3											B	
A2	A3	3T	4T	5T	6T	7T	8T	9T	10T	1B	2B	A1	
A2	A1	A3	A3	A2	A2	Mn	A2	A3	A1	A1	A3	Ga	
A2	A1	A3	A3	A2	A2	A3	A3	A1	A1	A1	A3	In	
A2	A2	L*	A3	A2	A2	A3	A3	A1	A1	A1	Hg	A3	A1

Structures of the rare-earth elements and of binary inter-rare-earth alloys

Most of the pure rare-earth elements crystallize with one of four close-packed structure types presented in Figure I - 3. [III - 1] As shown in the upper part of Table III - 1 the hexagonality of the structures increases successively from the early (left) to the late (right) rare-earth elements. In binary inter-rare-earth systems zero, one or two intermediate phases occur depending on the hexagonality of the end members. [III - 2] In Table III - 1 the lengths of the rectangular frames, each representing a different binary phase diagram, have been stretched or compressed so that the homogeneity ranges of the end members and of the intermediate phases come to lie in their proper structure type columns. In each phase diagram the hexagonality of consecutive phases increases from left to right.

TABLE III - 1 : STRUCTURES OF RARE-EARTH ELEMENTS AND BINARY INTER-RARE-EARTH ALLOYS

	Cu type 0%	α-Nd type 50%	α-Sm type 67%	Mg type 100%
Pure elements	Ce	Pr, Nd	Sm	Gd, Tb, Dy, Ho, Er
Ce - Gd	0 0 0 0 0	1/2 1/2 1/2 1/2 1/2 1/2	2/3 2/3 2/3 2/3 2/3 2/3	1 1 1 1 1
Ce - Sm	0 0 0 0 0	1/2 1/2 1/2 1/2 1/2 1/2	2/3 2/3 2/3	
Ce - Pr	0 0 0 0 0	1/2 1/2 1/2		
Nd - Gd		1/2 1/2 1/2	2/3 2/3 2/3 2/3 2/3 2/3	1 1 1 1 1
Nd - Sm		1/2 1/2 1/2	2/3 2/3 2/3	
Pr - Nd		1/2 1/2 1/2 1/2 1/2 1/2		
Sm - Gd			2/3 2/3 2/3	1 1 1 1 1
Gd - Tb				1 1 1 1 1 1 1 1 1 1 1

III - 1) The Tb HP type with 33 % hexagonality has not yet been found with other rare-earth elements or alloys.

III - 2) Gschneidner, K.A. (1985). J. Less-Common Met. 114, 29 - 42.

IV. NORMAL VALENCE COMPOUNDS

Stability of filled shells

In general in valence compounds all atoms either accept or provide and/or share valence electrons to obtain a stable octet configuration ns^2np^6, *i.e.* all s and p orbitals are completely filled or completely empty. An indication for the stability of a filled shell can be seen in the large amount of energy which is necessary to remove an electron from it. In Table IV - 1 are given different ionization potentials for the elements of the second period. It is relatively easy to remove an electron which is above the filled $1s^2$ shell, but much more energy is needed if it is an electron from the filled shell. In Table IV - 1 a heavy line marks the place where a particular large energy gap occurs from one to the next higher ionization potential indicating that now an electron from the stable inner shell has been forced outside.

TABLE IV - 1 : THE FIRST TO EIGHT IONIZATION POTENTIALS IN eV FOR THE ELEMENTS OF THE SECOND PERIOD.

	I	II	III	IV	V	VI	VII	VIII
Li	5.390	75.619	122.420					
Be	9.320	18.206	153.850	217.657				
B	8.296	25.149	37.920	259.298	340.127			
C	11.264	24.376	47.864	64.476	391.986	489.84		
N	14.54	29.605	47.426	77.450	97.863	551.925	666.83	
O	13.614	35.146	54.934	77.394	113.873	138.080	739.114	871.12
F	17.418	34.98	62.646	87.23	114.214	157.117	185.139	953.60

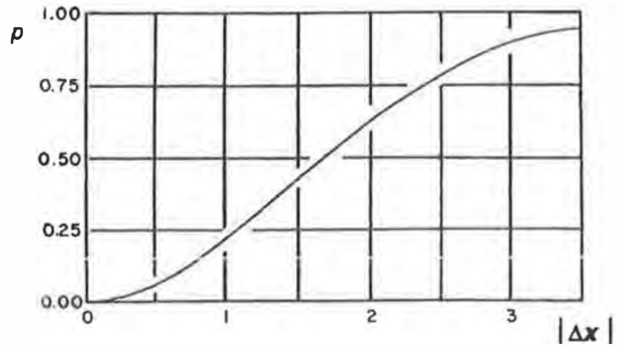
The octets of the atoms can be completed in two different ways :

1) Electrons are donated by one kind of atom (cation) to the other (anion) ⇒ **ionic bond**
2) Electrons are shared between the atoms ⇒ **covalent bond**

The degree of ionicity of an iono-covalent bond

Most valence compounds are iono-covalent compounds with a bonding intermediate between the two cases, *i.e.* using a pictorial model the electrons of the bond are neither only on the anions nor half-way between the atoms but closer to one of them. Following an idea of Linus Pauling [IV - 1)] the **degree of ionicity** of a bond, denoted by p, can be related to the magnitude of the **electronegativity difference** between the atoms, labelled $|\Delta x|$, as shown together with examples in Figure IV - 1. A list of electronegativity values of the atoms can be found on the inside cover of this book. It should be noted that the always used prototype for an ionic compound, *i.e.* NaCl has according to Figure IV - 1 only 68 % ionic bonding.

IV - 1) Pauling, L. (1960). "The Nature of the Chemical Bond". Third edition. Page 99. Ithaka : Cornell University Press.



Examples

	$\lvert\Delta x\rvert$	p
HCl	0.9	20%
NaCl	2.1	68%
Si^+C^-	0.7	13%
BAs	0	0%
Li^+H^-	1.1	25%

Figure IV - 1 : The relation between the degree of ionicity of a bond p and the magnitude of the electronegativity difference of the atoms $\lvert\Delta x\rvert$ after Pauling.

Definition and valence electron rule for normal valence compounds

In the historical development of the concept of a valence compound one has to distinguish two stages :

- The original concept due to Kossel (1916) and Lewis (1916) applies only to **normal valence compounds** (which are the topic of this chapter).
- The more general concept due to Mooser & Pearson (1956) and Pearson (1964) can also be applied to **polyanionic** and **polycationic valence compounds** (which shall be discussed in chapter V).

A compound C_mA_n is called a normal valence compound if the cations do not retain any but transfer all their valence electrons and if their number is correct for all the anions to be able to complete their octets without sharing electrons. This can be expressed by

$$m \cdot e_C = n \cdot (8 - e_A) \qquad \text{for } C_mA_n \qquad \text{(IV - 1)}$$

where e_C (e_A) is the number of valence electrons of the cation (anion) in the non-ionized state. If one introduces as new parameter the **partial valence electron concentration** in respect to the anion, labelled VEC_A and defined as

$$\boxed{VEC_A = (m \cdot e_C + n \cdot e_A) / n} \qquad \text{for } C_mA_n \qquad \text{(IV - 2)}$$

then equation (IV - 1) obtains the very simple form

$$\boxed{VEC_A = 8} \qquad \text{(IV - 3)}$$

which is the **valence electron equation for normal valence compounds.**

Compositions

The possible compositions of normal valence compounds can be obtained from (IV - 1) by inserting different numerical values for e_C and e_A. For the sake of simplicity we shall at first only consider the ***A*** and ***B*** group elements of the Periodic Table (see inside cover of the book). For these elements their number of valence electrons corresponds to their group number. Instead of denoting the elements by their chemical symbol we can group all those having the same number of valence electrons and identify them alone by their group number. This has been done in Table IV - 2 where are listed 19 numerical formulae for binary normal valence compounds with $e_A \geq 4$. If the electronegativity difference is large, *i.e.* $x_A - x_C >> 0$, the formation of a binary normal valence compound with this composition is probable. The special case of Cl_2O_7 (7_26_7) where the anion is from a lower group is discussed in Chapter VIII.

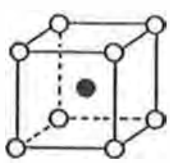
Table IV - 2 : Nineteen numerical formulae of binary normal valence compounds.

	$e_A = 4$	$e_A = 5$	$e_A = 6$	$e_A = 7$	
$e_C = 1$	$1_4 4$	$1_3 5$	$1_2 6$	17	Examples :
$e_C = 2$	$2_2 4$	$2_3 5_2$	26	27_2	*17*: NaCl, RbF
$e_C = 3$	$3_4 4_3$	35	$3_2 6_3$	37_3	*44*: SiC
$e_C = 4$	44	$4_3 5_4$	46_2	47_4	$3_2 6_3$: Al_2O_3, Ga_2S_3
$e_C = 5$			$5_2 6_5$	57_5	$2_3 5_2$: Zn_3P_2, Mg_3As_2
$e_C = 6$				67_6	

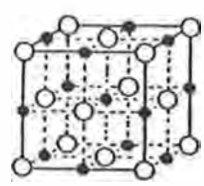
Structural features

In the structures of the normal valence compounds there are no shared electrons; thus there are neither cation - cation nor anion - anion bonds. Selected simple structure types for binary normal valence compounds of composition CA and CA_2 (or C_2A) are presented in Figure IV - 2. Details of the structural features of normal valence compounds can be rationalized using the **Pauling rules** and, more recently, the **bond valence concept.**

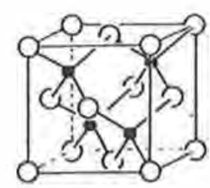
CA*: *17, 26, 35, 44



$Cs^{[8cb]}Cl^{[8cb]}$, *cP2*

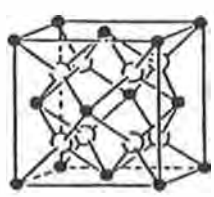


$Na^{[6o]}Cl^{[6o]}$, *cF8*

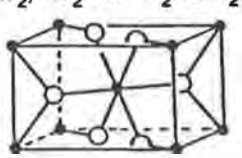


$Zn^{[4t]}S^{[4t]}$, *cF8*
sphalerite

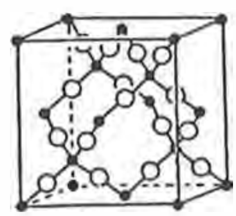
CA*$_2$: *27*$_2$, *46*$_2$ or *C*$_2$*A*: *1*$_2$*6*, *2*$_2$*4



$Ca^{[8cb]}F_2^{[4t]}$, *cF12*



$Ti^{[6o]}O_2^{[3t]}$, *tP6*
rutile



$Si^{[4t]}O_2^{[2n]}$, *cP24*
cristobalite

*Figure IV - 2 : Selected simple structure types for binary normal valence compounds with composition **CA** and **CA**$_2$.*

First Pauling rule

A coordination figure, consisting of a small cation coordinated by large anions, such as a triangle, a tetrahedron, an octahedron or a cube, becomes electrostatically unstable if the cation is so small that the anions touch each other. It exists thus, as formulated in (IV - 4), for each of the four coordination figures a minimum critical radius ratio r_C / r_A.

$$\boxed{C^{[3]}A_3 : r_C / r_A \geq 0.155} \quad \boxed{C^{[4t]}A_4 : r_C / r_A \geq 0.225} \quad \boxed{C^{[6o]}A_6 : r_C / r_A \geq 0.414} \quad \boxed{C^{[8cb]}A_8 : r_C / r_A \geq 0.732} \qquad \text{(IV - 4)}$$

The actual radius ratio r_C / r_A has to be bigger than the minimum critical value in order that a particular coordination figure can occur in the structure of a normal valence compound.
Based on the first Pauling rule it is possible to formulate for each of the six binary structure types, presented in Figure IV - 2, a range of r_C / r_A values where the type should be stable from an electrostatic point of view. These stability ranges coincide with the cation - anion contact ranges of the space filling curves, shown in Figure X - 3 and discussed in chapter X. Inversely, the ratio of the ionic radii of a given normal valence compound should allow one to predict the atom coordinations and the structure type. However, only about 50 % of the structures are predicted correctly. The reason for this is that the anions may not be hard spheres. Their electron clouds may be distorted, *i.e.* they may be polarized and there may be a greater proportion of covalent bonding. The first Pauling rule works best with fluorides and oxides due to the presence of small and rather incompressible anions.

Example : Predictions based on the first Pauling rule about the possible occurrence of Mg - O, Al - O, Si - O tetrahedra, octahedra and cubes in a structure.
Experimental evidence shows that Mg, Al, Si - O tetrahedra and octahedra are common, but AlO_8 and SiO_8 cubes do not occur. This is in agreement with predictions based on the first Pauling rule according to which cubes are possible only with MgO_8. For the calculation of the radius ratios it is necessary to use the **crystal ionic radii** (normalized to $r_{O^{2-}}$ = 1.26 Å) and not the traditional **effective ionic radii** (normalized to $r_{O^{2-}}$ = 1.40 Å). [IV-2] As can be seen in Table IV - 3 the radii increase with increasing coordination number *CN*. The radii listed for Al and Si with 8 coordination have been obtained by extrapolation from the corresponding radii values for lower coordination. The radius ratio values for different kinds of polyhedra are compiled in Table IV - 4. The values calculated for MgO_8 and SiO_8 are smaller that the minimum critical r_C / r_A value of 0.732, as given in (IV - 4). Thus the formation of MgO_8 and SiO_8 cubes in a structure is not expected.

TABLE IV - 3 : SELECTED CRYSTAL IONIC RADII NORMALIZED TO $r_{O^{2-}}$ = 1.26 Å

	CN = 4	*CN* = 6	*CN* = 8
$r_{Mg^{2+}}$	.71 Å	.86 Å	1.03 Å
$r_{Al^{3+}}$	.53 Å	.675 Å	(.79 Å)
$r_{Si^{4+}}$	.40 Å	.54 Å	(.65 Å)

TABLE IV - 4 : RADIUS RATIOS r_C / r_A FOR DIFFERENT MG, AL, AND SI - O POLYHEDRA

	$C^{[4t]}O_4$	$C^{[6o]}O_6$	$C^{[8cb]}O_8$
Minimum r_C / r_A	.225	.414	.732
C = Mg	.57 MgO_4	.68 MgO_6	.83 MgO_8
C = Al	.42 AlO_4	.54 AlO_6	.63 **no !**
C = Si	.32 SiO_4	.43 SiO_6	.53 **no !**

It might perhaps appear surprising for a few readers that according to Table IV - 4 SiO_6 octahedra are electrostatically stable. The great majority of the silicates is characterized by tetrahedrally coordinated Si atoms, however there exist also a number of compounds where the Si atoms are octahedrally coordinated (and these are not only high pressure modifications).
One example is the normal valence compound $Si_5P_6O_{25}$ ($Ge_5P_6O_{25}$ structure type) with crystal chemical formula $Si_2^{[4t]}Si_3^{[6o]}P_6^{[4t]}O^{[2Si]}O_{24}^{[1Si,1P]}$. For more details on the structure, see Problem 2 in Appendix B.

IV - 2) Compared to the traditional effective ionic radii the values of the anion radii in the list of crystal ionic radii are 0.14 Å smaller and those of the cations 0.14 Å larger.. Using either one of the two radius sets the sum of cation and anion radii has the same numerical value (thus either set can be used to derive interatomic distances), but the numerical result is different if a radius ratio is calculated. Correct results are obtained only when crystal ionic radii are used.. For a list of numerical values of both sets of radii, see Shannon, R.D. (1976). Acta Cryst. A32, 751 - 767.

Second Pauling rule or electrostatic valence sum rule

The spatial arrangement of the cations and anions should preferably be one where the anions receive the exact number of necessary valence electrons from cations of the coordination polyhedron. The second Pauling rule thus describes what one may call local electroneutrality.

The **electrostatic bond strength** of an electrostatic bond originating from a cation C, labelled s, can be obtained from the valence electron number of the cation e_C and the number of its anion neighbours $N(A \rightarrow C)$, according to

$$s = e_C / N(A \rightarrow C) \quad \text{for} \quad C_m^{[N(A \rightarrow C)]} A_n^{[N(C \rightarrow A)]} \qquad \text{(IV - 5)}$$

Pauling's electrostatic valence sum rule states that the sum of the bond strengths of all electrostatic bonds which originate from surrounding cations and reach a particular anion A_i should be equal to the (absolute value of the) charge of anion A_i which corresponds to $8 - e_{A_i}$.

$$\boxed{\sum_j s_{ij} = 8 - e_{A_i}} \qquad \text{(IV - 6)}$$

The summation leads over all the j *cation* neighbours of anion A_i which are considered as being bonded to it.

Example : Second Pauling rule applied to the three NaCl - type related modifications of $LiFe^{3+}O_2$.
The high temperature modification has the normal cubic NaCl type with Li and Fe atoms distributed at random on the Na sites. Of the two ordered tetragonal low temperature modifications, shown in Figure IV - 3, one is unstable because the second Pauling rule cannot be satisfied with this atom arrangement.

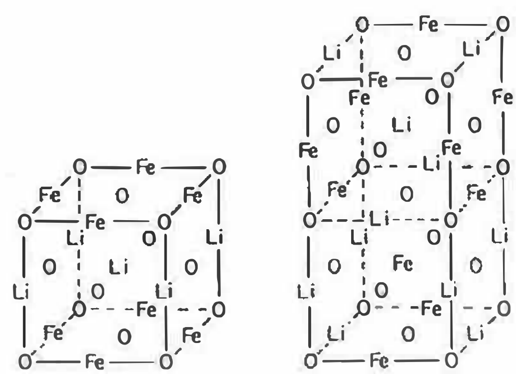


Figure IV - 3 : The unstable (left) and the stable (right) low temperature modification of $LiFeO_2$.

$LiFeO_2$ *LT*, unstable : Ordered pseudocubic substitution variant of the NaCl type. The chosen pseudocubic unit cell is not the smallest possible but is preferred for a structure comparison with NaCl. Two kinds of O atoms exist which have first coordination octahedra with **different** Li : Fe ratio.

Li : ½ ½ ½, 0 0 ½ Fe : ½ 0 0, 0 ½ 0 — O : 0 0 0, ½ ½ 0, 0 ½ ½, ½ 0 ½

$Li^{[6o]} Fe^{[6o]} O(i)^{[(2,4)o]} O(ii)^{[(4,2)o]}$

For O(i) $2 \cdot (1/6) + 4 \cdot (3/6) = \mathbf{2.33 \neq 8 - 6}$

For O(ii) $4 \cdot 1/6) + 2 \cdot (3/6) = \mathbf{1.67 \neq 8 - 6}$

$LiFeO_2$ *LT*, stable: Ordered tetragonal ($c/a = 2$) substitution variant of the NaCl type having double the cell volume of the pseudocubic $LiFeO_2$ *LT*. A study of the drawing in Figure IV - 3 reveals that all O atoms have here the **same** first coordination octahedron consisting of 3 Li and 3 Fe atoms.

$Li^{[6o]} Fe^{[6o]} O_2^{[(3,3)o]}$ — For O $3 \cdot (1/6) + 3 \cdot (3/6) = \mathbf{2 = 8 - 6}$

(Li,Fe)O *HT*: Cubic NaCl type with Li and Fe atoms distributed at random on Na sites.

(Li, Fe) : ½ ½ ½, 0 0 ½, ½ 0 0, 0 ½ 0 — O : 0 0 0, ½ ½ 0, 0 ½ ½, ½ 0 ½

Crystal chemical formula : $(Li^{1+},Fe^{3+})^{[6]} O^{[6]}$ — For O $6 \cdot \{[(1+3)/2] / 6\} = \mathbf{2 = 8 - 6}$

Break-down of the second Pauling rule and the distortion of coordination polyhedra

For certain structures and compositions the second Pauling rule in the form of (IV - 6) cannot be satisfied in a rigorous manner. If the bond strength sum does not correspond to the charge of the anion there remains as solution (provided there is no reconstruction leading to a different more stable atom arrangement, as reported, for example, with $LiFeO_2$ *LT*) the possibility to strengthen and to weaken individual ionic Coulomb interactions by changing individual cation - anion distances. If the anion charge is undercompensated by the bond strength sum the corresponding cation - anion distances will be shortened and if it is overcompensated they will be elongated.

As practical procedure for finding out whether or not the anion charges are properly compensated and which interatomic distances, if any, need to be changed, one starts by constructing first a **connectivity table.** In a connectivity table are recorded which atoms are having how many ionic bonds with which other atoms. Actually only cation - anion bonds are listed in such a table. Since we deal here with normal valence compounds there exist neither cation - cation nor anion - anion bonds. However, all crystallographically different atom sites and their (relative) multiplicities have to be considered. For simple structures the data needed for a connectivity table can be read directly from the crystal chemical formula (see Table IV - 5). For more complicated structures the crystal chemical formula has to be complemented to allow a clear distinction between crystallographically different sites (see *e.g.* Table IV - 6).

As second step one extends the simple connectivity table by multiplying the recorded values with the proper bond strength values obtained from (IV - 5) and then calculates the vertical and horizontal bond strength sums. If the connectivity table is arranged in such a way that the anions are listed on top and the cations on the side, then the horizontal bond strength sum corresponds exactly to the charge of the cation(s). This should not be surprising since this is a consequence of the definition of Pauling's bond strength according to (IV - 5). Of more interest is the vertical bond strength sum which may or may not agree with the (absolute value of the) charge of the anion(s). The consequences for the relevant interatomic distances are as follows :

> **If the vertical bond strength sum is smaller than the absolute value of the charge of the anion then the corresponding interatomic distances are shortened and vice versa.** IV - 3)

Examples for the construction of connectivity tables and the calculation of bond strength sums :

The three wurtzite related normal adamantane structure types, shown in the upper part of Figure VII - 2, are found with β-$NaFe^{3+}O_2$, $BeSiN_2$ (drawing on the left), Li_2SiO_3, Si_2LiN_3 (middle) and orthorhombic Cu_3AsS_4 (right). The second Pauling rule can be satisfied with the first two compounds and Cu_3AsS_4, but not with Li_2SiO_3 and Si_2LiN_3.

In Table IV - 5 are presented the crystal chemical formulae, the simple and the extended connectivity tables together with the horizontal and vertical bond strength sums for the three compounds where the second Pauling rule can be satisfied. The bond strength values are in *italics*. All vertical bond strength sums agree with the charges of the anions. Consequently changes of the interatomic distances are not to be expected and the coordination tetrahedra of the cations and the anions are undistorted.

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*IV - 3) When variations in distances are expected but not found experimentally this might be an indication that the chosen unit cell is **not** the correct one and that the derived interatomic distances correspond only to **average** values.*

TABLE IV - 5 : CRYSTAL CHEMICAL FORMULAE, SIMPLE (UPPER TABLES) AND EXTENDED (LOWER TABLES) CONNECTIVITY TABLES WITH BOND STRENGTH SUMS FOR β-$NaFeO_2$, $BeSiN_2$ AND Cu_3AsS_4.

$Na^{[4t]}Fe^{[4t]}O_2^{[2,2]}$

	2 O
Na	4
Fe	4

	2 O	
Na	$4\cdot{}^{1}/_{4}$	$\Sigma \equiv 1 = e_{Na}$
Fe	$4\cdot{}^{3}/_{4}$	$\Sigma \equiv 3 = e_{Fe}$
	$\Sigma = 4$	

$4=2(8-e_O)$

$Be^{[4t]}Si^{[4t]}N_2^{[2,2]}$

	2 N
Be	4
Si	4

	2 N	
Be	$4\cdot{}^{2}/_{4}$	$\Sigma \equiv 2 = e_{Be}$
Si	$4\cdot{}^{4}/_{4}$	$\Sigma \equiv 4 = e_{Si}$
	$\Sigma = 6$	

$6=2(8-e_N)$

$Cu_3^{[4t]}As^{[4t]}S_4^{[3,1]}$

	4 S
3 Cu	12
As	4

	4 S	
3 Cu	$12\cdot{}^{1}/_{4}$	$\Sigma \equiv 3 = 3e_{Cu}$
As	$4\cdot{}^{5}/_{4}$	$\Sigma \equiv 5 = e_{As}$
	$\Sigma = 8$	

$8=4(8-e_S)$

In Table IV - 6 is presented the same for Li_2SiO_3 and Si_2LiN_3 where the second Pauling rule cannot be satisfied. As seen in Figure IV - 4 the anions are not all equal, but can be divided into two groups which differ in the ratio of the two cations which make up the tetrahedral coordination polyhedron. Anions **(i)** have three majority and one minority cation neighbours, but anions **(ii)** two majority and two minority cation neighbours.

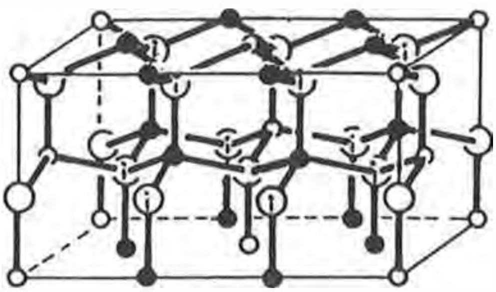

*Figure IV - 4 : The idealized structure of Li_2SiO_3 and Si_2LiN_3 with undistorted tetrahedra. Large circles represent O or N anions, small filled circles the majority cations and small open circles the minority cations. The letter **i** has been inscribed into anion circles which correspond to anions (i), while the anions (ii) are presented by unmarked circles.*

TABLE IV - 6 : CRYSTAL CHEMICAL FORMULAE (IN THE SECOND LINE SIMPLIFIED), SIMPLE CONNECTIVITY TABLES AND EXTENDED VERSIONS WITH BOND STRENGTH SUMS FOR Li_2SiO_3 AND Si_2LiN_3.

$Li_2^{[3O(i),1O(ii)]}Si^{[2O(i),2O(ii)]}O(i)_2^{[3Li,1Si]}O(ii)^{[2Li,2Si]}$

$Li_2^{[3,1]}Si^{[2,2]}O(i)_2^{[3,1]}O(ii)^{[2,2]}$

	2 O(i)	O(ii)
2 Li	6	2
Si	2	2

	2 O(i)	O(ii)	
2 Li	$6\cdot{}^{1}/_{4}$	$2\cdot{}^{1}/_{4}$	$\Sigma \equiv 2 = 2e_{Li}$
Si	$2\cdot{}^{4}/_{4}$	$2\cdot{}^{4}/_{4}$	$\Sigma \equiv 4 = e_{Si}$
	$\Sigma = 3.5<4$	$\Sigma = 2.5>2$	

$4=2(8-e_O)$ $2=1(8-e_O)$

$Si_2^{[3N(i),1N(ii)]}Li^{[2N(i),2N(ii)]}N(i)_2^{[3Si,1Li]}N(ii)^{[2Si,2Li]}$

$Si_2^{[3,1]}Li^{[2,2]}N(i)_2^{[3,1]}N(ii)^{[2,2]}$

	2 N(i)	N(ii)
2 Si	6	2
Li	2	2

	2 N(i)	N(ii)	
2 Si	$6\cdot{}^{4}/_{4}$	$2\cdot{}^{4}/_{4}$	$\Sigma \equiv 8 = 2e_{Si}$
Li	$2\cdot{}^{1}/_{4}$	$2\cdot{}^{1}/_{4}$	$\Sigma \equiv 1 = e_{Li}$
	$\Sigma = 6.5>6$	$\Sigma = 2.5<3$	

$6=2(8-e_N)$ $3=1(8-e_N)$

For both Li_2SiO_3 and Si_2LiN_3 the vertical bond strength sums do not agree with the charges of the anions. However, the deviations are **different** for both compounds. Thus the corresponding tetrahedra should be differently distorted. One expects for

Li_2SiO_3 : LiO_4 tetrahedra with **three short** (Li - O(i)) and **one long** bond (Li - O(ii))

Si_2LiN_3 : SiN_4 tetrahedra with **three long** (Si - N(i)) and **one short** bond (Si - N(ii)).

This has been verified experimentally. As a consequence the two structures are not really isotypic, as assumed originally. Due to the opposite distortion of the tetrahedra the two structures represent two different branches of the idealized structure type with undistorted tetrahedra, shown in Figure IV - 4.

Example for the construction of a connectivity table and the calculation of bond strength sums in the case of a structure with more (crystallographically different) atom sites :

The normal valence compound $Cu_4Ni^{2+}Si_2S_7$ with crystal chemical formula $Cu_4^{[4t]}\,Ni^{[4t]}\,Si_2^{[4t]}\,S_7^{[4t]}$ crystallizes with an ordered substitutuion derivative of the sphalerite type. There are two different Cu sites and four different S sites which all have to be considered individually. In the upper part of Table IV - 7 is written the extended crystal chemical formula which is needed for the construction of the connectivity table given in the lower part of the table. The four numbers in the coordination superscripts of the cations refer to the four kinds of S anions (S(i), S(ii), S(iii) and S(iv)) and, inversely, the numbers in the coordination superscripts of the S anions refer to the four kinds of cations (Cu(i), Cu(ii), Ni and Si).

TABLE IV - 7 : CRYSTAL CHEMICAL FORMULA AND EXTENDED CONNECTIVITY TABLE WITH HORIZONTAL AND VERTICAL BOND STRENGTH SUMS FOR $Cu_4NiSi_2S_7$. BOND STRENGTH VALUES ARE PRINTED IN *ITALICS*.

$Cu(i)_2^{[2,1,1,0]}\,Cu(ii)_2^{[0,2,1,1]}\,Ni^{[2,0,2,0]}\,Si_2^{[1,1,1,1]}\,S(i)_2^{[2,0,1,1]}\,S(ii)_2^{[1,2,0,1]}\,S(iii)_2^{[1,1,1,1]}\,S(iv)^{[0,2,0,2]}$

	2 S(i)	2 S(ii)	2 S(iii)	S(iv)	
2 Cu(i)	$4 \cdot \mathit{1/4}$	$2 \cdot \mathit{1/4}$	$2 \cdot \mathit{1/6}$	-	$\Sigma \equiv 2 = 2e_{Cu}$
2 Cu(ii)	-	$4 \cdot \mathit{1/4}$	$2 \cdot \mathit{1/4}$	$2 \cdot \mathit{1/4}$	$\Sigma \equiv 2 = 2e_{Cu}$
Ni	$2 \cdot \mathit{2/4}$	-	$2 \cdot \mathit{2/4}$	-	$\Sigma \equiv 2 = e_{Ni}$
2 Si	$2 \cdot \mathit{4/4}$	$2 \cdot \mathit{4/4}$	$2 \cdot \mathit{4/4}$	$2 \cdot \mathit{4/4}$	$\Sigma \equiv 8 = 2e_{Si}$
	$\Sigma = 4$	$\Sigma = 3.5<4$	$\Sigma = 4$	$\Sigma = 2.5>2$	
	$4 = 2(8-e_S)$	$4 = 2(8-e_S)$	$4 = 2(8-e_S)$	$2 = 1(8-e_S)$	

The vertical bond strength sums for S(ii) and S(iv) do not agree with the charges of the S anions. In the case of S(iv) the charge of the anion is overcompensated by 25% and consequently all distances involving S(iv) should be much longer than normal. This is verified with the experimental data.

In $Cu_4NiSi_2S_7$ the Si and S atoms form a $(Si_2S_7)^{6-}$ anionic tetrahedron complex (as shown *e.g.* in Figure VIII - 2 for $Li_6Si_2O_7$ in a planar graph presentation) consisting of two SiS_4 tetrahedra which share one anion, the so-called **bridging anion**. The S(iv) atom is that anion which forms the bridge. It is, according to the crystal chemical formula, the only S atom which forms bonds to two Si atoms.

In sorosilicates, pyrophosphates and corresponding sulfates occur the same kind of anionic double-tetrahedron complexes, *i.e.* $(Si_2O_7)^{6-}$, $(P_2O_7)^{4-}$ and $(S_2O_7)^{2-}$. In these complexes the distances from the bridging oxygen to the two neighbouring central atoms are generally found to be longer than other central atom - oxygen distances because the charges of the bridging oxygen ions are overcompensated.

⇒⇒⇒ Problem 2 in Appendix B

The bond valence method

The simple method based on bond strength sums gives only qualitative answers. To obtain quantitative results one relies on a method which uses bond valences. [IV - 4)]

According to the bond valence concept each bond is assigned a valence, labelled v, which is defined such, that

$$\boxed{\sum_j v_{ij} = V_i} \qquad \text{(IV - 7)}$$

where $V_i = e_{C_i}$ for cation C_i or $V_i = 8 - e_{A_i}$ for anion A_i. The summation leads over all the j anion neighbours of cation C_i or j cation neighbours of anion A_i which are considered as being bonded to it (irrespective of variations in distance).

Different from Pauling's bond strength values, the individual bond valences v_{ij} are not known at the start of the calculation. Only their sum V_i is known by definition. In the special case where the second Pauling rule is satisfied, the bond valences v_{ij} are numerically identical with the bond strength values s_{ij}, defined by (IV - 5). In the general case where the second Pauling rule is not satisfied, one can obtain the v_{ij} values of the bonds as follows :

One multiplies in a connectivity table the connectivity values with the (yet unknown) bond valences, denoted by α, β, γ *etc.*, and formulates all vertical and horizontal bond valence sums as linear equations of α, β, γ *etc.*. According to IV - 7 the value of each bond valence sum is known by definition. Under certain simplifying conditions, *i.e.* that **Brown's equal valence rule** [IV - 5)] is applicable, these simultaneous linear equations can be solved analytically for the individual bond valence values.

Example : Calculation of the numerical values of the bond valences in Li_2SiO_3 and Si_2LiN_3.

The simple connectivity tables have been presented in Table IV - 6. In Table IV - 8 the connectivity values are multiplied with symbolic bond valences. Four (framed) linear equations are formulated for each compound of which, however, only three are independent. Using as fourth equation Brown's equal valence rule, which has here the form $\alpha - \beta = \gamma - \delta$, it is possible to derive the numerical values of the four bond valences for both compounds (see lower part of Table IV - 8).

TABLE IV - 8 : CONNECTIVITY TABLES FOR Li_2SiO_3 AND Si_2LiN_3 EXTENDED WITH SYMBOLIC (UPPER TABLES) AND NUMERICAL (LOWER TABLES) BOND VALENCE VALUES. THE LATTER ARE PRINTED WITH BOLD-FACED CHARACTERS.

	2 O(i)	O(ii)	
2 Li	$6\cdot\alpha_1$	$2\cdot\beta_1$	$\Sigma=6\alpha_1+2\beta_1=2=2e_{Li}$
Si	$2\cdot\gamma_1$	$2\cdot\delta_1$	$\Sigma=2\gamma_1+2\delta_1=4=e_{Si}$
	$\Sigma=6\alpha_1+2\gamma_1=4$	$\Sigma=2\beta_1+2\delta_1=2$	
	$4=2(8-e_O)$	$2=1(8-e_O)$	

	2 N(i)	N(ii)	
2 Si	$6\cdot\alpha_2$	$2\cdot\beta_2$	$\Sigma=6\alpha_2+2\beta_2=8=2e_{Si}$
Li	$2\cdot\gamma_2$	$2\cdot\delta_2$	$\Sigma=2\gamma_2+2\delta_2=1=e_{Li}$
	$\Sigma=6\alpha_2+2\gamma_2=6$	$\Sigma=2\beta_2+2\delta_2=3$	
	$6=2(8-e_N)$	$3=1(8-e_N)$	

	2 O(i)	O(ii)	
2 Li	**6·3/10**	**2·1/10**	$\Sigma=2$
Si	**2·11/10**	**2·9/10**	$\Sigma=4$
	$\Sigma=4$	$\Sigma=2$	

	2 N(i)	N(ii)	
2 Si	**6·19/20**	**2·23/20**	$\Sigma=8$
Li	**2·3/20**	**2·7/20**	$\Sigma=1$
	$\Sigma=6$	$\Sigma=3$	

IV - 4) O'Keeffe, M. (1992). In "Modern Perspectives in Inorganic Crystal Chemistry". E. Parthé, editor. NATO ASI Series C382, pages 163 - 175. Dordrecht : Kluwer. O'Keeffe, M. (1989). Structure and Bonding 71, 161 - 190.

IV - 5) Bonds between like pairs of atoms should have valences as nearly equal as possible.

According to Pauling the length d_{ij} of a bond between atom i and one of its bonding neighbours j is related in first approximation to its bond valence v_{ij} :

$$d_{ij} \cong R_{ij} - b \cdot \ln v_{ij} \qquad \text{(IV - 8)}$$

where R_{ij} is the "bond valence parameter" and $b = 0.37$ Å, a "universal" constant.

The bond valence parameter for a given pair of atoms corresponds to the length of a single bond with bond valence $v_{ij} = 1$. The (nearly constant) values of R_{ij} for given pairs of atoms have been tabulated. IV - 6) In Figure IV - 5 can be read directly the numerical value of **- *b*·ln *v*** which has to be added to R_{ij} to obtain the interatomic distance for a known value of *v*.

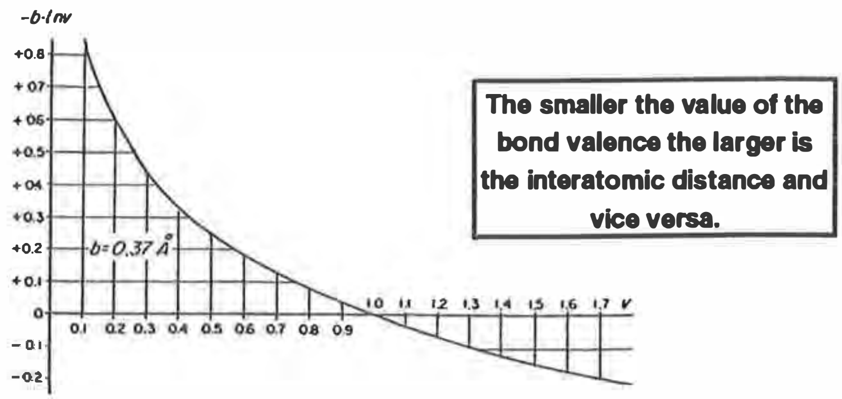

Figure IV - 5 : The numerical values of the additive factor - b·ln v for different values of v.

Steric constraints, "non-bonded" repulsions and other perturbing factors need to be considered as an explanation when there is no good agreement between calculated and observed distances. IV - 7) However, the method will account correctly for the presence of irregular coordination polyhedra.

Example : Calculation of the tetrahedron distortions in Li_2SiO_3 and Si_2LiN_3.

In the lower part of Table IV - 8 had been listed the calculated bond valences for Li_2SiO_3 and Si_2LiN_3 for which the corresponding values of - *b*·ln *v* can be read off in Figure IV - 5. To obtain the numerical values of the interatomic distances one needs to know the bond valence parameters R_{ij}. These parameters are, however, not needed, *i.e.* they cancel each other, if only distance differences between specified atom pairs are of interest. Using the anion labels of Figure IV - 4, the calculated (and observed) distortions of the anion tetrahedra centred by majority cations in Li_2SiO_3 and Si_2LiN_3 are as follows :

$d_{Li-O(II)} - d_{Li-O(I)} = -b \cdot \ln(^1/_{10}) - [-b \cdot \ln(^3/_{10})] = +0.40$ Å (experimentally + 0.244, + 0.233, + 0.220Å)

$d_{Si-N(II)} - d_{Si-N(I)} = -b \cdot \ln(^{23}/_{20}) - [-b \cdot \ln(^{19}/_{20})] = -0.07$ Å (experimentally - 0.056, - 0.059, - 0.068Å)

The signs of all distortions and the numerical values for the SiN_4 tetrahedron are predicted correctly. However, the observed distance differences in the case of the LiO_4 tetrahedron are much smaller than the calculated ones. If only the **sign** of a distortion is of interest, the much simpler qualitative method based on bond strength sums is sufficient.

IV - 6) Brown, I.D. & Altermatt, D. (1985). Acta Cryst. B41, 244 - 247.

IV - 7) Brown, I.D. (1992). Acta Cryst. B48, 553 - 572.

V. POLYANIONIC AND POLYCATIONIC VALENCE COMPOUNDS

Definition and valence electron rule for general valence compounds

General valence compounds are valence compounds where either the cations don't transfer all their valence electrons - they are used for bonds between them or are in non-bonding orbitals - or where the anions, due to bonds between themselves, don't need as many electrons from the cations to complete their octet shells. For a compound of composition C_mA_n

$$\underbrace{m \cdot (e_C - e_{CC})}_{\text{number of electrons the } m \text{ cations transfer to the n anions}} = \underbrace{n \cdot (8 - e_A - e_{AA})}_{\text{number of electrons the } n \text{ anions need to complete their octet shells}} \qquad \text{(V - 1)}$$

e_{CC} is the average number of valence electrons per cation which remain with the cation

e_{AA} is the average number of valence electrons per anion which the anions acquire by sharing covalent bonds with other anions.

The e_{CC} and e_{AA} values are experimentally inaccessible. In the common case that the interatomic bonds between cations or between anions are normal two-electron bonds, the e_{CC} and e_{AA} values can be replaced by the CC and AA parameters .

$$m \cdot (e_C - CC) = n \cdot (8 - e_A - AA) \qquad \text{(V - 2)}$$

CC is the **average** number per cation of cation - cation bonds and/or the average number of electrons which remain as non-bonding orbitals on the cations.

AA is the **average** number of anion - anion bonds per anion.

Cation - cation and anion - anion bonds in a structure can be recognized indirectly from a study of the distances between the atoms.

Introducing the partial valence electron concentration in respect to the anion VEC_A, which had been defined before in (IV - 2), equation (V - 2) can be rewritten as

$$\boxed{VEC_A = 8 + CC / (n/m) - AA} \quad \text{for } C_mA_n \qquad \text{(V - 3)}$$

This formula is known as the **generalized 8 - *N* rule**.

This equation, which relates the number of valence electrons with observable structural features, is derived under the assumption that all bonds are single two-electron bonds and additional electrons remain inactively in non-bonding orbitals of the cations or anions. Thus the compound should be a semiconductor. The applicability of this equation is not assured if the compound is metallic.

There is a well-known proverb which states that any good idea has many fathers, but a bad idea is an orphan. The generalized 8 - N rule and its variations are also known under the name **Mooser - Pearson rule** or **Zintl - Klemm concept**. V - 1) The compounds which obey the generalized 8 - N rule are often labelled **Zintl phases**. V - 2) The references listed below are not exhaustive. The version of the generalized 8 - N rule applied throughout this book which makes use of the three parameters : VEC_A, CC and AA was first introduced in 1973. V - 3)

Calculation of VEC_A allows the classification of a compound as normal, polyanionic or polycationic valence compound.

If $VEC_A = 8$: **Normal valence compound** with $CC = AA = 0$

If $VEC_A < 8$: **Polyanionic valence compound** with $AA > 0$

If $VEC_A > 8$: **Polycationic valence compound** with $CC > 0$.

The normal valence compounds with $VEC_A = 8$ have already been treated in Chapter IV.

Polyanionic valence compounds

A simple solution of (V - 3) is obtained if it is assumed that $CC = 0$ (which is nearly always the case). Then

$$\boxed{AA = 8 - VEC_A} \qquad \text{(V - 4)}$$

Replacing in (V - 4) the parameter VEC_A by (IV - 2) and solving for n / m one obtains (V - 5) which can be used to calculate the possible formulae of binary polyanionic compounds C_mA_n with specified AA value by inserting possible numerical values for e_C and e_A.

$$n / m = e_C / (8 - AA - e_A) \qquad \text{(V - 5)}$$

TABLE V - 1 : NUMERICAL FORMULAE FOR POSSIBLE POLYANIONIC VALENCE COMPOUNDS WITH AA = 1.

		e_A 5	6	7
	1	1_25	$\boxed{16}$	-
e_C	2	$\boxed{25}$	$\boxed{26_2}$	-
	3	3_25_3	$\boxed{36_3}$	-
	4	$\boxed{45_2}$	46_4	-

In Table V - 1 are listed the numerical formulae for possible polyanionic valence compounds with AA = 1 and $e_A \geq 5$ which have been calculated with (V - 5). A numerical formula is framed if a polyanionic valence compound with this composition is known. Examples for *16*, *25*, 26_2 and 45_2 compounds are discussed below in the text. An example for a 36_3 compound is $Ir^{3+}Se_3$.

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*V - 1) Pearson, W.B. (1964). Acta Cryst. **17**, 1 - 16; Hulliger, F. & Mooser, E. (1965). Progr. Solid State Chem. **2**, 330 - 377; Schäfer, H., Eisenmann, B. & Müller, W. (1973). Angew. Chem. Int. Edit. Engl. **12**, 694 - 712; von Schnering, H.G. (1981). Angew. Chem. Int. Edit. Engl. **20**, 33 - 51; Hulliger, F. (1981) In "Structure and Bonding in Crystals". Editors M. O'Keeffe & A. Navrotsky. Vol. 2, chapter 26, pages 297 - 352. New York : Academic Press.*

*V - 2) According to H. Schäfer (Annu. Rev. Mater. Sci. **15**, 1 - 41 and J. Solid State Chem. **57**, 97 - 111 (1985)) the term "Zintl phase" should be applied today to semimetallic or even metallic compounds where the underlying iono-covalent bonds play such an important role that chemically based valence rules, normally reserved for semi- or nonconducting compounds, can be used to account for the stoichiometry and the observed structural features.*

*V - 3) Parthé, E. (1973). Acta Cryst. **B29**, 2808 - 2815.*

The simplest geometrical interpretations for different AA values are as follows :

If $AA = 0$: isolated anions (*i.e.* a normal valence compound with $VEC_A = 8$)

$0 < AA < 1$: isolated anions and anion dumb-bells are both present

If $AA = 1$: anion dumb-bells $\Rightarrow C_mA_n^{[;1]}$ *i.e.* $C_{2m}[A_2]_n$

$1 \leq AA < 2$: finite anion chains

If $AA = 2$: infinite anion chains or rings $\Rightarrow C_mA_n^{[;2]}$ *i.e.* $C_m\,{}^1_\infty A_n$ or $C_mO[A_n]$

$2 < AA < 3$: anions with two and with three homonuclear bonds

If $AA = 3$: each anion with three homonuclear bonds $\Rightarrow C_mA_n^{[;3]}$

If AA is calculated to have a value between two integers, say between i and $i+1$, then one should find in the structures two kinds of anions, *i.e.* one kind with i and the other with $i+1$ homonuclear bonds. For a compound with crystal chemical formula $C_m\,A_{xn}^{[;i]}\,A_{(1-x)n}^{[;(i+1)]}$ the AA parameter corresponds to

$$AA = x \cdot i + (1-x) \cdot (i+1) \equiv i + 1 - x \qquad \text{(V - 6)}$$

The ratio of the number of anions with i homonuclear bonds to the number of anions with $i+1$ bonds, here labelled $^{M[;i]} / {}_{M[;(i+1)]}$, is given by

$$^{M[;i]} / {}_{M[;(i+1)]} \equiv {}^{x} / {}_{(1-x)} = [(i+1) - AA)] / (AA - i) \qquad \text{for } C_m\,A_{xn}^{[;i]}\,A_{(1-x)n}^{[;(i+1)]} \qquad \text{(V - 7)}$$

or more general for anions with i and j homonuclear bonds

$$^{M[;i]} / {}_{M[;j]} \equiv {}^{x} / {}_{(1-x)} = (j - AA) / (AA - i) \qquad \text{for } C_m\,A_{xn}^{[;i]}\,A_{(1-x)n}^{[;j]} \qquad \text{(V - 7a)}$$

Using (V - 7 or 7a) it will be possible to write a crystal chemical formula for any AA value.

In the following examples will be given for each compound first the parameters which can be calculated from the chemical formula, such as VEC_A, AA, and then, preceded by an arrow, a possible simple crystal chemical formula based on these parameters. The predicted structural features are further compared with the observed ones. The predicted simple anion linkage is often, but not always, observed in nature. However, even if a more complicated anion linkage is observed, the average number of anion - anion links per anion does agree with the calculated AA value. For a specified anion linkage there may exist various different spatial realizations which can lead to different unit cells and space groups. Thus it is not possible to make predictions on the unit cell or on the space group.

For **isoelectronic compounds** (same stoichiometry and same VEC_A (and AA) value but elements exchanged for others with different e_C and e_A values) one predicts identical structural features. In the following examples isoelectronic compounds will be discussed jointly. After the conventional chemical formulae for the isoelectronic compounds are written numerical formulae (surrounded by parentheses) where the element symbols are replaced by numerals which correspond to the valence electron contribution of the atoms.

Examples for polyanionic valence compounds with $6 \geq VEC_A \geq 5$ and $2 \leq AA \leq 3$.

Equation (V - 7), after inserting $i = 2$, becomes here $^{M[;2]} / {}_{M[;3]} = (3 - AA) / (AA - 2)$.

Red ZnP_2 : $VEC_A = 6$, thus $AA = 2$ (if CC = 0) $\Rightarrow Zn\,{}^1_\infty P_2^{[;2]}$ or $Zn_nO[P_{2n}]$

The structure of red ZnP_2, shown in Figure II - 2b, is characterized by infinite P - P chains. Infinite anion - anion chains are found also in the structures of compounds formed with homologous elements, such as α - CdP_2 or $ZnAs_2$ (Figure VI - 1), however, the mutual orientations of these chains are different. Black ZnP_2 is isotypic with $ZnAs_2$.

LiAs (*15*) : $VEC_A = 6$, thus $AA = 2$ (if $CC = 0$) ⇒ Li $\overset{1}{\infty}$As$^{[;2]}$ or $Li_nO[As_n]$
CaSi (*24*) : same as LiAs ⇒ Ca $\overset{1}{\infty}$Si$^{[;2]}$ or $Ca_nO[Si_n]$

Both isoelectronic compounds have infinite anion chains. CaSi crystallizes with the CrB type, shown in Figure XI - 2, which occurs also with metallic compounds where the generalized 8 - *N* rule is not valid.

BaP_3 : $VEC_A = 5.667$, thus $AA = {}^7/_3$ (if $CC = 0$), $^{N[;2]}/_{N[;3]} = 2$ ⇒ Ba $P_2^{[;2]}P^{[;3]}$

The P atom partial structure, presented in Figure V - 1, consists of an infinite chain formed of P_6 rings linked by P - P bonds. As predicted two-thirds of the P atoms have two, the remaining third three homonuclear bonds.

Figure V - 1 : The linkage of the P atoms in Ba $\overset{1}{\infty}(P_2^{[;2]}P^{[;3]})$

Ba_3Si_4 : $VEC_A = 5.5$, thus $AA = {}^5/_2$ (if $CC = 0$), $^{N[;2]}/_{N[;3]} = 1$ ⇒ $Ba_3\,Si_2^{[;2]}Si_2^{[;3]}$

The Si partial structure, shown in Figure V - 2, is a "butterfly" molecule which corresponds to a tetrahedron with one broken bond.

Figure V - 2 : The "butterfly" molecule of the Si atoms in $Ba_3[Si_2^{[;2]}Si_2^{[;3]}]$

NaSi : $VEC_A = 5$, thus $AA = 3$ (if $CC = 0$) ⇒ NaSi$^{[;3]}$

The structure of NaSi was shown in Figure II - 2a. A Si_4 tetrahedron is formed here with each Si atom having three homonuclear bonds. The crystal chemical formula of the observed structure is thus Na_4●$[Si_4]$.

$CaSi_2$, $SrSi_2$, $BaSi_2$: $VEC_A = 5$, thus $AA = 3$ (if $CC = 0$) ⇒ *C* $Si_2^{[;3]}$

In all three silicides the Si atoms have three homonuclear bonds, however, the Si partial structures, as shown in Figure X - 4, are all different, having even different dimensionality. The corresponding crystal chemical formulae are Ca $\overset{2}{\infty}Si_2^{[;3]}$, Sr$\overset{3}{\infty}Si_2^{[;3]}$ and Ba_2●$[Si_4^{[;3]}]$.

Examples for polyanionic valence compounds with $7 \geq VEC_A > 6$ and $1 \leq AA < 2$.
If $1 \leq AA < 2$ the anion partial structure consists in the most simple case of a finite non-cyclic chain. The number of atoms in this chain, labelled $N'_{A/M}$, can be related with *AA* (or VEC_A), as should become clear from a study of Figure V - 3. The two anions at the end of an unbranched chain participate each only on one homonuclear bond, all other anions in the chain, of which there are $N'_{A/M} - 2$ in number, have two homonuclear bonds. Thus the *AA* value for a chain of $N'_{A/M}$ atoms is

$$AA = [1 + 2\cdot(N'_{A/M} - 2) + 1] / N'_{A/M} \qquad (V - 8)$$

which can be rewritten as

$$\boxed{N'_{A/M} = 2 / (2 - AA)} \quad \text{for } 1 \leq AA \leq 2 \qquad (V - 9a)$$

or, using (V - 4), as

$$\boxed{N'_{A/M} = 2 / (VEC_A - 6)} \quad \text{for } 6 \leq VEC_A \leq 7 \qquad (V - 9b)$$

$N'_{A/M}$ stands for **number of atoms in the non-cyclic molecule formed by the anions.** The letter N is primed, *i.e.* N', to indicate that it refers **not** to the complete structure but only to the (charged) anion partial structure of the compound. Later we shall use also the unprimed parameter $N_{A/M}$ which relates then to **all** the atoms of a non-cylcic molecular structure.

Figure V - 3 : The relation between the number of anions in the chain, labelled $N'_{A/M}$, and the value of AA for different simple chains. In the case of an unbranched chain the value of $N'_{A/M}$ corresponds to the length of the chain.

chain type	$N'_{A/M}$	AA
	(1)	(0)
	2	1
	3	$4/3$
	4	$6/4$
	$N'_{A/M}$	$2(N'_{A/M}-1)/N'_{A/M}$
	(∞)	(2)

Since AA is the same for a branched or unbranched chain (provided the total number of atoms in the molecule is the same), (V - 9) applies also to branched chains (which can occur only when $N'_{A/M} \geq 4$). Equation (V - 9) is not valid if there exist both a finite chain (or an isolate atom) **and** an infinite chain (or a ring), as for example in $GeAs_2$ (see below).
Simple solutions of (V - 9) are tabulated in Table V - 2. They are also copied on the inside cover of this book.

TABLE V - 2 : THE SIMPLE NUMERICAL SOLUTIONS OF (V - 9) RELATING $N'_{A/M}$, THE NUMBER OF ATOMS IN THE FINITE ANION CHAIN, WITH THE AA AND VEC_A VALUES OF A COMPOUND.

VEC_A	(8)	7	$20/3$	$13/2$	$32/5$	$19/3$	$44/7$	$25/4$	$56/9$	$31/5$	(6)
AA	(0)	1	$4/3$	$3/2$	$8/5$	$5/3$	$12/7$	$7/4$	$16/9$	$9/5$	(2)
$N'_{A/M}$	(1)	2	3	4	5	6	7	8	9	10	(∞)

The following examples include also cases where less simple solutions are realized of which there are two kinds :
1) If AA is calculated to be an integer there exists always a simple solution where all anions have the same number of anion neigbours. However, it may occur that the calculated AA corresponds to an average $\langle AA \rangle$ of two integers. This happens with the structure of $GeAs_2$.
2) If $N'_{A/M}$ is calculated to be an integer the simple solution consists of one kind of anion chain. However, the calculated $N'_{A/M}$ may correspond to an average $\langle N'_{A/M} \rangle$ of two integers. Two kinds of finite anion chains are found with the structures of $LaAs_2$ *HT* and Ca_2As_3.

NaO (*16*) : $VEC_A = 7$, thus $AA = 1$ (if $CC = 0$), $N'_{A/M} = 2$ $\Rightarrow$ $Na_2[O_2]$
SrP (*25*) : same as NaO $\Rightarrow$ $Sr_2[P_2]$

Anion dumb-bells ($\equiv$ finite chains of two atoms) are observed in the two isoelectronic compounds which even adopt the same $Na_2[O_2]$ structure type.

BaO_2 (*26₂*) : $VEC_A = 7$, thus $AA = 1$ (if $CC = 0$), $N'_{A/M} = 2$ $\Rightarrow$ $Ba[O_2]$
$GeAs_2$ (*45₂*) : same as BaO_2 $\Rightarrow$ $Ge[As_2]$

BaO_2 crystallizes with the CaC_2 type (left hand side of Figure I - 1), characterized by anion - anion dumb-bells. [V-4)]

The structure of isoelectronic $GeAs_2$ does not correspond to the predicted simple crystal chemical formula. Instead of anion dumb-bells, as shown in Figure V - 4, isolated As atoms together with infinite As - As chains are found. But the average number of anion - anion links per anion, *i.e.* $(0 + 2) / 2 = 1$ is in agreement with the calculated *AA* value.

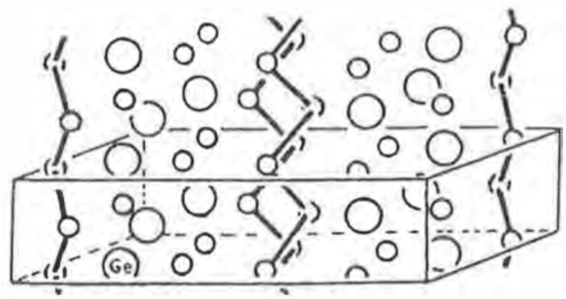


Figure V - 4 : The crystal structure of Ge $As^{[:0]}\,{}^{1}_{\infty}As^{[:2]}$, oP24.

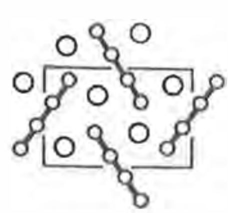
Sr_3As_4 : $VEC_A = 6.5$, thus $AA = 3/2$ (if $CC = 0$), $N'_{A/M} = 4$ $\Rightarrow$ $Sr_3\,\hat{4}\,[As_4]$

The predicted features, *i.e.* chains of four As atoms, are observed in the crystal structure.

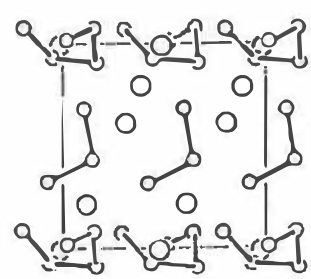
NaS_2 (16_2) : $VEC_A = 6.5$, thus $AA = 3/2$ (if $CC = 0$), $N'_{A/M} = 4$ $\Rightarrow$ $Na_2\,\hat{4}\,[S_4]$

$La^{3+}As_2$ (35_2) : same as NaS_2 $\Rightarrow$ $La_2\,\hat{4}\,[As_4]$

The structures of NaS_2 and of the low temperature modification of isoelectronic $LaAs_2$ ($NdAs_2$ type) have the expected finite anion chain consisting of four atoms. However, the high temperature modification of $LaAs_2$ (LaP_2 type), as shown on the right hand side of Figure V - 5, has two kinds of finite chains, *i.e.* one with three and the other with five As atoms. The average number of anion - anion links per anion, *i.e.* $(3\cdot 4/3 + 5\cdot 8/5) / 8 = 3/2$, is in agreement with the calculated *AA* value.



$La_2\,\hat{4}\,[As_4]$ *LT* ($NdAs_2$ type)



$La_4\,\hat{3}\,[As_3]\,\hat{5}\,[As_5]$ *HT* (LaP_2 type)

Figure V - 5 : The crystal structures of the low and high temperature modification of $LaAs_2$.

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*V - 4) The type defining compound CaC_2 itself does not agree with the generalized 8 - N rule because the bond between the C atoms is not a single but a C≡C triple bond. A comparative study of the carbides with group **2A** cations shows that also Mg_2C_3 with its finite linear chain of three carbon atoms does not agree with the 8 - N rule because of the double bonds between the C atoms. There is, however, agreement in the case of Be_2C, a normal valence compound, which crystallizes with the anti - CaF_2 type and where there are isolated C atoms. The formula of the gaseous hydrolysis products, i.e. acetylen HC≡CH for CaC_2, 17% propadiene $H_2C{=}C{=}CH_2$ and 83% propyne H_3C-C≡CH for Mg_2C_3 and finally methane CH_4 for Be_2C, gives an indication of the linkage and the type of bonding between the C atoms in the crystallized alkaline earth carbides.*

CsS_3 : $VEC_A = 6.333$, thus $AA = {}^5/_3$ (if $CC = 0$), $N'_{A/M} = 6$ $\Rightarrow$ $Cs_2\,\hat{6}\,[S_6]$

As seen in Figure II - 2b, finite chains of six S atoms occur in the structure.

Sr_2Sb_3 : $VEC_A = 6.333$, thus $AA = {}^5/_3$ (if $CC = 0$), $N'_{A/M} = 6$ $\Rightarrow$ $Sr_4\,\hat{6}\,[Sb_6]$

Ca_2As_3 : same as Sr_2Sb_3 $\Rightarrow$ $Ca_4\,\hat{6}\,[As_6]$

A chain of six anions is found in Sr_2Sb_3. In Ca_2As_3 two kinds of finite chains occur, *i.e.* one with four and the other with eight As atoms. The average number of anion - anion links per anion, *i.e.* $(4 \cdot {}^3/_2 + 8 \cdot {}^7/_4) / 12 = {}^5/_3$, is in agreement with the calculated *AA* value.

The crystal chemical formula corresponding to the observed structure is $Ca_8\,\hat{4}\,[As_4]\ \hat{6}\,[As_8]$.

Examples for polyanionic valence compounds with $8 > VEC_A > 7$ and $0 < AA < 1$

One should find here both isolated anions and anion dumb-bells. Equation (V - 7), after inserting $i = 0$, becomes $M_{[;0]} / M_{[;1]} = (1 - AA) / AA$. For the compounds listed below the observed structural features correspond to the predicted ones.

Ba_4P_3 : $VEC_A = 7.67$, thus $AA = {}^1/_3$ (if $CC = 0$), $M_{[;0]} / M_{[;1]} = 2$ $\Rightarrow$ $Ba_8P_4[P_2]$

$Th^{4+}_2S_5$: $VEC_A = 7.6$, thus $AA = {}^2/_5$ (if $CC = 0$), $M_{[;0]} / M_{[;1]} = {}^3/_2$ $\Rightarrow$ $Th_2S_3[S_2]$

$Eu^{2+}_5As_4$: $VEC_A = 7.5$, thus $AA = {}^1/_2$ (if $CC = 0$), $M_{[;0]} / M_{[;1]} = 1$ $\Rightarrow$ $Eu_5As_2[As_2]$

Li_7Ge_2 : $VEC_A = 7.5$, thus $AA = {}^1/_2$ (if $CC = 0$), $M_{[;0]} / M_{[;1]} = 1$ $\Rightarrow$ $Li_{14}Ge_2[Ge_2]$

Sr_5Si_3 : $VEC_A = 7.33$, thus $AA = {}^2/_3$ (if $CC = 0$), $M_{[;0]} / M_{[;1]} = {}^1/_2$ $\Rightarrow$ $Sr_5Si[Si_2]$

Derivation of the Hume-Rothery 8 - *N* rule as a special case of the generalized 8 - *N* rule

A limiting case for polyanionic valence compounds exists when the "anions" alone provide all the necessary electrons for the bonds formed between themselves. There are thus no "cations" needed, *i.e.* $m = 0$ and equation (IV - 2) simplifies to $VEC_A \equiv e_A$. Inserting this value into (V - 4) one obtains

$$AA = 8 - e_A \qquad \text{(V - 10)}$$

Since e_A corresponds to the group number *N* of the element in the Periodic Table one can write

$$\boxed{AA = 8 - N} \qquad \text{(V - 11)}$$

This is the well-known Hume-Rothery rule, introduced in Chapter 3, which states that in the structures of the elements on the right of the Periodic Table the number of close neighbours of an atom is 8 - *N* where *N* is its group number in the Periodic Table. *AA* is here the average number of bonds per atom which (under the assumption of single two-electron bonds) is equivalent to the number of close neighbours of an atom.

⇒⇒⇒ Problems 3, 4 and 5 in Appendix B

Polycationic valence compounds

The simplest solution of (V - 3) is obtained if it is assumed that $AA = 0$ (which is nearly always the case). Then

$$\boxed{CC = (n/m) \cdot (VEC_A - 8)} \qquad \text{for } C_mA_n \qquad \text{(V - 12)}$$

In analogy to (V - 5) one can derive (V - 13) which can be used to calculate the possible formulae for all binary polycationic compounds C_mA_n with specified CC value if one inserts all possible numerical values of e_C and e_A.

$$n/m = (e_C - CC) / (8 - e_A) \qquad \text{(V - 13)}$$

TABLE V - 3 : NUMERICAL FORMULAE FOR POSSIBLE POLYCATIONIC VALENCE COMPOUNDS WITH $CC = 1$.

		e_A 5	6	7
	1	-	-	-
e_C	2	2_35	2_26	$\boxed{27}$
	3	3_35_2	$\boxed{36}$	37_2
	4	$\boxed{45}$	$\boxed{4_26_3}$	$\boxed{47_3}$

In Table V - 3 are listed the numerical formulae for possible polycationic valence compounds with $CC = 1$ and $e_A \geq 5$ which have been calculated with (V - 13). A numerical formula is framed if a polycationic valence compound with this composition is known (see examples below).

The simplest geometrical interpretations for different CC values are as follows :

If $CC = 0$: isolated cations with no lone-electron pairs (*i.e.* a normal valence compound with $VEC_A = 8$)

If $CC = 1$: cation dumb-bells $\Rightarrow C_m^{[;1]}A_n$ *i.e.* $[C_2]_mA_{2n}$

If $CC = 2$: infinite cations chains or $\Rightarrow C_m^{[;2]}A_n$ *i.e.* $(^1_\infty C_m)A_n$
one lone pair on each cation $\Rightarrow \underline{C}_m^{[;0]}A_n$

If $CC = 3$: three cation - cation bonds per cation or $\Rightarrow C_m^{[;3]}A_n$
only one bond and one lone pair $\Rightarrow \underline{C}_m^{[;1]}A_n$

In the following examples the calculated parameters will be first given and then, preceded by an arrow, a possible crystal chemical formula based on these parameters. This formula is then compared with the experimentally observed structural features of the compound.

HgCl (*27*) : $VEC_A = 9$, thus $CC = 1$ (if $AA = 0$) $\Rightarrow [Hg_2]Cl_2$
GaSe (*36*) : same as HgCl $\Rightarrow [Ga_2]Se_2$
SiAs (*45*) : same as HgCl $\Rightarrow [Si_2]As_2$

All three structures are characterized by cation dumb-bells. In Hg_2Cl_2, known as calomel, linear Cl-Hg-Hg-Cl molecules are formed. The other compounds have tetrahedral structures. Drawings of ε - GaSe *2H* can be found in Figures II - 6 and VI - 2. Monoclinic GaTe is isotypic with isoelectronic SiAs for which a drawing of the atom linkage can be found in Figure VI - 4.

Si_2Te_3 : $VEC_A = 8.67$, thus $CC = 1$ (if $AA = 0$) $\Rightarrow [Si_2]Te_3$

The original proposal for the atom linkage in Si_2Te_3 assuming Si - Si dumb-bells, which is presented in Figure VI - 5, could be verified by a later crystal structure determination.

CCl_3 : $VEC_A = 8.33$, thus $CC = 1$ (if $AA = 0$) $\Rightarrow$ $[C_2]Cl_6$
There is a single two-electron C-C bond in hexachloroethane $Cl_3C\text{-}CCl_3$.

GeS : $VEC_A = 10$, thus $CC = 2$ (if $AA = 0$) $\Rightarrow$ $Ge^{[;2]}S$ or $\underline{Ge}^{[;0]}S$
The orthorhombic GeS structure, shown in Figure V - 6, and the trigonal α - GeTe structure, both corresponding to the second crystal chemical formula where each atom has one lone-electron pair attached to it, are ordered substitution variants of (isoelectronic) black phosphorus and arsenic, respectively.
A structure built up according to the first crystal chemical formula ought to be found with a compound where the two component elements have a much larger difference in electronegativity. In this case one would expect that the electrons (which according to the second formula are used for lone-electron pairs on the cations) are strongly attracted by the anions which tend to increase their number of non-bonding orbitals at the expense of the cations. Poorly crystallizing SiO might possibly have such a structure ($|\Delta x_{GeS}| = 0.7$, but $|\Delta x_{SiO}| = 1.7$). In Figure V - 7 is presented a model of a possible atom linkage in SiO, characterized by an infinite Si atom chain.

Figure V - 6 : Atom linkage in $^{2}_{\infty}\underline{Ge}^{[3;0]}\,\underline{S}^{[3]}$

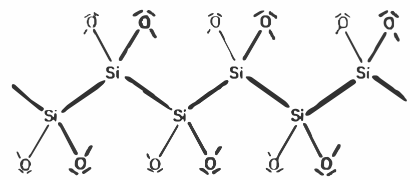
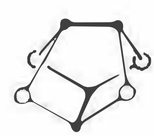


Figure V - 7 : Model for a possible atom linkage in $(^{1}_{\infty}Si^{[2;2]})\,\underline{O}^{[2]}$

PSe : $VEC_A = 11$, thus $CC = 3$ (if $AA = 0$) $\Rightarrow$ $P^{[;3]}Se$ or $\underline{P}^{[;1]}Se$
Two simple possibilities exist here, expressed by the two crystal chemical formulae. In PSe and homologous AsS the second formula is realized, *i.e.* each group ***5B*** element has one lone-electron pair and one homonuclear bond. In the "catena" modification of PSe one finds infinite chains of 7-atom cages linked by Se atom bridges according to $^{1}_{\infty}(\text{❼}[\underline{P}_4^{[2;1]}\,\underline{Se}_3^{[2]}]\,\underline{Se}^{[2]})$. The chains can close on themselves to form the 8-atom cage molecule, shown in Figure V - 8, which is observed with realgar ❽$[\underline{As}_4^{[2;1]}\,\underline{S}_4^{[2]}]$.
A cage molecule as in realgar is observed also in the homologous compound NS, but according to the electronegativity values the cation is now the S atom and the anion the N atom ($x_{As} = 2.0$, $x_S = 2.5$ and $x_N = 3.0$). Thus the lone electron pair and the homonuclear bond is now found on the S atom and the corresponding crystal chemical formula is ❽$[\underline{S}_4^{[2;1]}\,\underline{N}_4^{[2]}]$.

Figure V - 8 : The cage molecule in realgar ❽$[\underline{As}_4^{[2;1]}\,\underline{S}_4^{[2]}]$



The generalized 8 - *N* rule as a guide for checking experimental data

For the following compounds (with chemical formulae placed within quotation marks) the generalized 8 - *N* rule does not agree with the reported structural features. The lack of agreement between observation and expectation provided the motivation for a re-examination which led to corrected chemical formulae and/or corrected crystal structures in agreement with the 8 - *N* rule.

"Ca_3Pb" : VEC_A = 10, thus a polycationic valence compound with CC = $^2/_3$. However, in the observed structure there are neither Ca - Ca bonds nor lone-electron pairs on the Ca atoms. A re-examination has shown [V - 5)] that there are oxygen atoms present, the correct formula of the compound being Ca_3PbO. This formula corresponds to a normal valence compound with two kinds of anions ($CaO + Ca_2Pb = Ca_3PbO$) with VEC_A = 8 and CC = 0. The structure of the ternary compound is of the anti - $CaTi^{[6o]}O_3$ or anti - perovskite type (see Figure II - 4).

"Ca_2Sb" : VEC_A = 9, thus a polycationic valence compound with CC = $^1/_2$. However, as above, there are neither Ca - Ca bonds nor lone-electron pairs on the Ca atoms. The correct composition is Ca_4Sb_2O [V - 6)] which also corresponds to a normal valence compound with two kinds of anions ($CaO + Ca_3Sb_2 = Ca_4Sb_2O$) with VEC_A = 8 and CC = 0. The atom arrangement of the ternary compound is known as the anti - $K_2Ni^{[6o]}F_4$ structure type (see Figure XI - 1).

"K_4Ge_{23}" : VEC_A = 4.174, thus a polyanionic valence compound with AA = $^{88}/_{23}$ < 4. The structure of "K_4Ge_{23}" had been described as consisting of an Ge atom arrangement identical to that of diamond with K atoms positioned in the interstices. This cannot be correct because elementary Ge itself has all the necessary valence electrons to form a diamond type structure, *i.e.* there is no need for the extra valence electrons provided by the alkali atoms in the interstitial sites. Later studies have shown that the Ge partial structure is not exactly as diamond, one Ge site being in reality only partly occupied. With the composition corrected as $K_4Ge_{22}\square \equiv K_2Ge_{11}$ one calculates that VEC_A = 4.182 and AA = $^{42}/_{11}$. The corresponding crystal chemical formula is then $K_4Ge_4^{[;3n]}\square Ge_{18}^{[;4t]} \equiv K_2Ge_2^{[;3n]}Ge_9^{[;4t]}$ which agrees with the features of the corrected crystal structure.

Compounds with both cation - cation and anion - anion bonds

Compounds with structures where both cation - cation and anion - anion bonds occur are very rare. It is not possible to predict where these compounds occur, however, one can expect an agreement between experimentally determined CC and AA values with the number of available valence electrons as expressed by the generalized 8 - N rule in the form of (V - 3).

As an example we consider the structure of the "polyanionic" valence compound $Hg_9P_5I_6$.

$Hg_9P_5I_6$: For this two-anion compound with VEC_A = 7.727 = $^{85}/_{11}$ one obtains, when using (V - 4), the result that AA = $^3/_{11}$. For the derivation of (V - 4) it had been assumed that CC = 0 which is not the case here. The AA value in $Hg_9P_5I_6$ is larger than $^3/_{11}$, *i.e.* AA = $^4/_{11}$ as can be concluded from $Hg^{[;1]}\ Hg_8^{[;0]}\ P_4^{[;1]}{\cdot}P^{[;0]}\ I_6^{[;0]}$, the crystal chemical formula derived from the experimentally determined crystal structure. Writing the generalized 8 - N rule in the form given by (V - 3)

$$AA = 8 - VEC_A + CC\,/\,(n/m) \qquad \text{for } C_mA_n \qquad (V - 14)$$

and inserting a non-zero value for CC, that is CC = $^1/_9$ in agreement with the crystal chemical formula, one finds that the generalized 8 - N rule is satisfied for this compound :

$$^4/_{11} = {}^3/_{11} + (^1/_9)\,/\,(^{11}/_9) \qquad (V - 15)$$

V - 5) Widera, A. & Schäfer, H. (1980). J. Less-Common Met. ***77****, 29 - 36.*

V - 6) Eisenmann, B., Limartha, H., Schäfer, H. & Graf, H.A. (1980). Z. Naturforschung ***35b****, 1518 - 1524.*

VI. TETRAHEDRAL STRUCTURE COMPOUNDS

Definition and derivation of the tetrahedral structure equation

Tetrahedral structure compounds form a subset of the general valence compounds where each atom has at most four neighbours which are positioned at the corners of a surrounding tetrahedron. One distinguishes between

- **normal tetrahedral structures** where each atom in the structure has four tetrahedral neighbours and
- **defect tetrahedral structures** where some atoms have less than four neighbour atoms.

The tetrahedral structures are found with iono-covalent compounds which can be considered both as ionic and as covalent. For each hypothetical bonding state a valence electron rule can be formulated which allows certain structural features to be predicted.

In the **ionic bonding state** the atoms complete their octets by forming ions. The valence electron rule here is the generalized $8 - N$ rule, *i.e.* equation (V - 3), discussed in the previous chapter. The valence electron parameter used is the partial valence electron concentration in respect to the anion VEC_A, defined by (IV - 2).

In the **covalent bonding state** the atoms complete their octets by forming covalent two-electron bonds. Specifically, each atom first forms four tetrahedral sp^3 hybrid orbitals, occupied by one electron each, which then overlap with the sp^3 orbitals of the neighbouring atoms. Each orbital not used for bonding must for reasons of stability obtain a second electron. This non-bonding orbital can be detected experimentally under exceptionally favorable conditions as lone-electron pair, but its presence can be deduced from the absence of expected tetrahedral neighbour atoms.

The valence electron offer and need for the covalent bonding state can be formulated as follows

$$m \cdot e_C + n \cdot e_A = 4 \cdot (m + n) + (m + n) \cdot N_{NBO} \qquad \text{for } C_mA_n \qquad \text{(VI - 1)}$$

where N_{NBO} is a new parameter which expresses **the average number of non-bonding orbitals or lone-electron pairs per atom.**

The $(m + n)$ atoms in one formula unit need $4 \cdot (m + n)$ electrons to occupy their sp^3 hybrid orbitals. Since N_{NBO} is normalized to one atom, the number of extra electrons needed for all the lone-elctron pairs in one formula unit is $(m + n) \cdot N_{NBO}$.

It is convenient to use as valence electron parameter for the covalent bonding state - not the previously used partial valence electron concentration VEC_A, but - the **total valence electron concentration** VEC, defined as

$$\boxed{VEC = (m \cdot e_C + n \cdot e_A) / (m + n)} \qquad \text{for } C_mA_n \qquad \text{(VI - 2)}$$

The parameter VEC is closely related to VEC_A according to

$$VEC = VEC_A \cdot n/(m+n) \qquad \text{for } C_mA_n \qquad \text{(VI - 3)}$$

but both will be used below since they refer to different structural features.
Making use of (VI - 2) it is possible to rewrite (VI - 1) as

$$\boxed{VEC = 4 + N_{NBO}} \qquad \text{(VI - 4)}$$

which is the **tetrahedral structure equation**. VI - 1)

Calculation of the VEC value of a compound allows its classification as normal or defect tetrahedral structure compound.

If $VEC < 4$: Tetrahedral structure is not possible due to lack of valence electrons
If $VEC = 4$: **Normal tetrahedral structure compound** with $N_{NBO} = 0$
If $VEC > 4$: **Defect tetrahedral structure compound** with $N_{NBO} > 0$

Examples of normal and defect tetrahedral structure compounds

In the following examples the values will be given for each compound of the two valence electron parameters which can be calculated from the chemical formula, *i.e.* VEC and VEC_A, and the values derived from them, *i.e.* N_{NBO} and AA or CC, respectively. On the right hand side, preceded by an arrow, is presented a simple crystal chemical formula based on these parameters. For tetrahedral structures the sum of the number of neighbour atoms and the number of lone-electron pairs assigned to an atom must be four. The only possible coordination superscripts of the atoms in the crystal chemical formula are : [4t], [3n], [2n] and [1] (see Figure II - 3). The predicted structural features are now compared with the observed ones. Some of the compounds have already been discussed in chapter V under the aspect of the generalized 8 - N rule. Assuming that these compounds form tetrahedral structures their simple possible crystal chemical formulae can be filled in with more details.

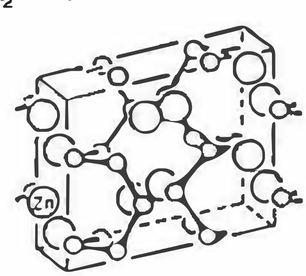
ZnP_2 : $VEC = 4$, thus $N_{NBO} = 0$ $\Rightarrow$ $Zn^{[4t]}\,{}^{1}_{\infty}P_2^{[(2;2)t]}$

$VEC_A = 6$, thus $AA = 2$ (if $CC = 0$) or $Zn_n^{[4t]}O[P_{2n}^{[(2;2)t]}]$

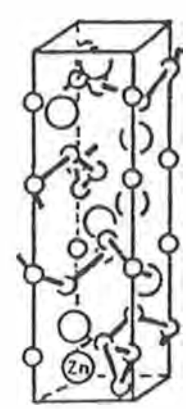
The structures of red ZnP_2 and of the two homologous compounds, shown in Figure VI - 1, are all normal tetrahedral structures with infinte anion chains (first crystal chemical formula).

Figure VI - 1 : The crystal structures of red ZnP_2 and of homologous compounds with the common crystal chemical formula $C^{[4t]}\,{}^{1}_{\infty}A_2^{[(2;2)t]}$.

α - CdP_2
parallel anion chains



$ZnAs_2$
anti-parallel anion chains



red ZnP_2
perpendicular anion chains

VI - 1) Parthé, E. (1963). Z. Kristallogr. **119**, 204 - 225. Parthé, E. (1972). "Cristallochimie des Structures Tétraédriques". Paris : Gordon & Breach.

GaSe (*36*) : *VEC* = 4.5, thus N_{NBO} = $^1/_2$ $\Rightarrow$ $[Ga_2^{[(3;1)t]}]\,\underline{Se}_2^{[3n]}$

VEC_A = 9, thus *CC* = 1 (if *AA* = 0)

SiAs (*45*) : same as GaSe $\Rightarrow$ $[Si_2^{[(3;1)t]}]\,\underline{As}_2^{[3n]}$

With N_{NBO} = $^1/_2$ there is one lone-electron pair per formula unit which can be assigned to the electronegative Se (or As) atom. All the GaSe polytypes (shown in Figure VI - 2), the two indium monochalcogenides (presented in Figure VI - 3) and also SiAs, together with isoelectronic and isotypic GaTe (Figure VI - 4), are built up in agreement with the given crystal chemical formula.

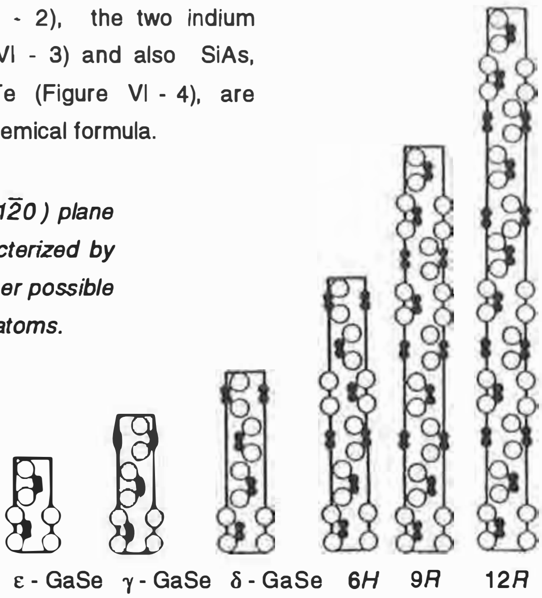


Figure VI - 2 : Atom arrangement in the (11$\bar{2}$0) plane of three known GaSe polytypes, characterized by parallel Ga - Ga dumb-bells, and three other possible stackings. Small filled circles represent Ga atoms.

The drawing of the (11$\bar{2}$0) plane of the ε - GaSe structure given here can be compared with Figure II - 6 where two complete hexagonal unit cells with all the atoms in perspective are shown.

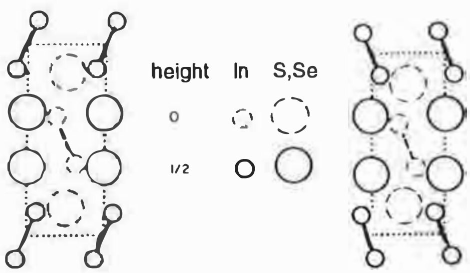


Figure VI - 3 : Projections of InS, oP8 (left) and InSe HP, mS8 (right).

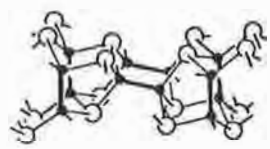


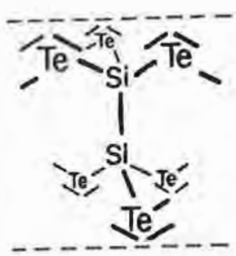
Figure VI - 4 : Atom linkage in SiAs and isotypic GaTe.

Si_2Te_3 : *VEC* ≈ 5.2, thus N_{NBO} = $^6/_5$ $\Rightarrow$ $[Si_2^{[(3;1)t]}]\,\underline{Te}_3^{[2n]}$

VEC_A = 8.67, thus *CC* = 1 (if *AA* = 0)

With N_{NBO} = $^6/_5$ and five atoms in one formula unit there are six lone-electron pairs which should be distributed over three anions, *i.e.* each Te atom carries two lone-electron pairs. The predicted crystal chemical formula was used to derive a model for a possible atom linkage in Si_2Te_3, shown in Figure VI - 5. This model was subsequently verified by a crystal structure determination. VI-2)

Figure VI - 5 : A proposal for the atom linkage in Si_2Te_3 based on the predicted crystal chemical formula.



VI-2) Ploog, K., Stetter, W., Nowitzki, A. & Schönherr, E. (1976). Mat. Res. Bull. **11**, *1147 - 1154.*

InTeCl : $VEC = 5.33$, thus $N_{NBO} = {}^{4}/_{3}$ $\Rightarrow$ $In^{[(2,2)t]}\ \underline{Te}^{[2n]}\ \underline{\underline{Cl}}^{[2n]}$

$VEC_A = 8$, thus $AA = CC = 0$ or $In^{[(3,1)t]}\ \underline{Te}^{[3n]}\ \underline{\underline{\underline{Cl}}}^{[1]}$

This is a simple case of a normal valence compound with two kinds of anions. Four lone-electron pairs have to be distributed over the two anions in one formula unit. Crystal chemical formulae are given for two of the possible distributions. There are no homonuclear bonds. The two numbers in the coordination superscript of the In atoms, separated by a comma, refer to the two kinds of anions. Because the Cl atoms are much more electronegative than the Te atoms, the formula where the Cl atoms have three lone-electron pairs is more probable and it is this second formula which corresponds to the observed crystal structure.

GaGeTe : $VEC = 4.33$, thus $N_{NBO} = {}^{1}/_{3}$ $\Rightarrow$ $Ga^{[(1,3)t]}\ Ge^{[(1;3)t]}\ \underline{Te}^{[3n]}$

$VEC_A = 6.5$, thus $AA = {}^{3}/_{2}$ (if $CC = 0$) or $Ga^{[(2;2)t]}\ Ge^{[(2;2)t]}\ \underline{Te}^{[(2;1)n]}$

or $Ga^{[(3,1)t]}\ Ge^{[(3;1)t]}\ \underline{Te}^{[(1;2)n]}$

This is a polyanionic valence compound with two kinds of anions. The single lone-electron pair per formula unit can be assigned to the more electronegative Te atom. There are different possibilities to distribute three anion - anion bonds over the two anions per formula unit. If one considers only the solutions where there are no Ge - Te bonds one can formulate the three crystal chemical formulae given above. It is necessary here to differenciate properly between commas and semi-colons in the coordination superscripts of the crystal chemical formulae (see chapter II). The observed crystal structure is a layer structure with features which correspond to the first crystal chemical formula. In Figure VI - 6 is shown a two-dimensional slab, about 10 Å thick, which can be recognized as a segment of the diamond structure.

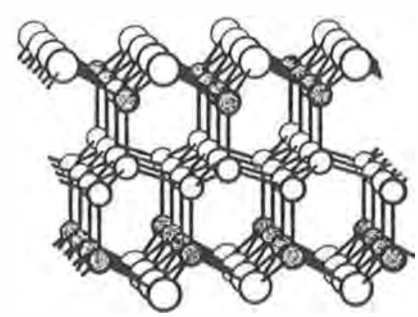


Figure VI - 6 : A slab of the layer structure of ${}^{2}_{\infty}Ga^{[(1,3)t;0]}\ Ge^{[(1,0;3)t]}\ \underline{Te}^{[(3,0)n;0]}$. *Ga : small shaded circles, Ge : small open circles, Te : large open circles. Drawing reproduced with the kind permission of Prof. Dr. H.G. von Schnering.* [VI-3)]

For more complicated structures, where not all atoms of the same kind have the same number of lone-electron pairs, it might be convenient to have available a simple algorithm to calculate the most probable distribution of the lone-electron pairs. We shall consider the case where all the lone-electron pairs are found only on the anions. This applies always to normal and polyanionic valence compounds, but also to the group of polycationic valence compounds where the electrons which remain with the cations are used only for cation - cation bonds.

The average <u>n</u>umber of <u>n</u>on-<u>b</u>onding orbitals par <u>a</u>nion, labelled N_{NBA}, is related to N_{NBO} as

$$N_{NBA} = N_{NBO} \cdot (m + n) / n \qquad \text{for } C_m A_n \qquad (VI - 5)$$

VI - 3) Fenske, D. & von Schnering, H.G. (1983). Angew. Chem. Int. Ed. Engl. ***22****, 407 - 408.*

If N_{NBA} is calculated to have a value between two integers, say between i and $i+1$, then one should find in the structure two kinds of anions, *i.e.* one kind with i non-bonding orbitals, denoted here by $A\{i\}$, and the other with $i+1$ non-bonding orbitals, denoted by $A\{i+1\}$. For a compound with crystal chemical formula $C_m\, A\{i\}_{yn}\, A\{i+1\}_{(1-y)n}$ the N_{NBA} parameter corresponds to

$$N_{NBA} = y \cdot i + (1-y) \cdot (i+1) \equiv i + 1 - y \qquad \text{(VI - 6)}$$

The ratio of the number of anions with i non-bonding orbitals to the number of anions with $i+1$ non-bonding orbitals, labelled $^{N\{i\}}/_{N\{i+1\}}$, is then given by

$$^{N\{i\}}/_{N\{i+1\}} \equiv {}^{y}/_{(1-y)} = [(i+1) - N_{NBA}] \,/\, (N_{NBA} - i) \qquad \text{for } C_m\, A\{i\}_{yn}\, A\{i+1\}_{(1-y)n} \qquad \text{(VI - 7)}$$

Using (VI - 7) it will be possible to formulate a crystal chemical formula for any N_{NBA} value. The derivation of the crystal chemical formula of Al_7Te_{10} serves as example.

Al_7Te_{10} : $VEC = 4.765$, $N_{NBO} = {}^{3}/_{17}$, $N_{NBA} = {}^{13}/_{10}$, $^{N\{1\}}/_{N\{2\}} = {}^{7}/_{3} \Rightarrow Al_6^{[4t]}\, Al^{[(3;1)t]}\, \underline{Te}_7^{[3n]}\, \underline{\underline{Te}}_3^{[2n]}$

$VEC_A = 8.1$, thus $CC = {}^{1}/_{7}$ (if $AA = 0$)

Since $N_{NBA} = {}^{13}/_{10}$ it follows that $i = 1$ and thus equation (VI - 7) has as solution $^{N\{1\}}/_{N\{2\}} = {}^{7}/_{3}$. Expressed in other terms, of the ten Te atoms in one formula unit seven have one and three two non-bonding orbitals. Further, with $CC = {}^{1}/_{7}$ we expect that one of seven Al atoms has one homonuclear bond. All this was used for the construction of the above given crystal chemical formula which agrees with the observed crystal structure.

For the following two polyanionic valence compounds both equations (VI - 7) and (V - 7) have to be used to obtain simple answers for the distribution of non-bonding orbitals and homonuclear bonds, respectively, over the anion sites. Three, or respectively two, different but equivalent crystal chemical formulae can be constructed with the values calculated for $^{N\{0\}}/_{N\{1\}}$ and $^{N[;2]}/_{N[;3]}$.

Ag_3P_{11} : $VEC = 4.142$, $N_{NBO} = {}^{2}/_{14}$, $N_{NBA} = {}^{2}/_{11}$, $^{N\{0\}}/_{N\{1\}} = {}^{9}/_{2} \Rightarrow Ag_3^{[4t]}\, P_3^{[(2;2)t]}\, \underline{P}_2^{[;3n]}\, P_6^{[(1;3)t]}$

$VEC_A = 5.273$, $AA = {}^{30}/_{11}$ (if $CC = 0$), $^{N[;2]}/_{N[;3]} = {}^{3}/_{8}$ or $Ag_3^{[4t]}\, \underline{P}^{[(1;2)n]} P_2^{[(2;2)t]} \underline{P}^{[;3n]} P_7^{[(1;3)t]}$

or $Ag_3^{[4t]}\, \underline{P}_2^{[(1;2)n]}\, P^{[(2;2)t]}\, P_8^{[(1;3)t]}$

In one formula unit there are two P atoms with one non-bonding orbital each. The three crystal chemical formulae differ in the number of homonuclear bonds of these two P atoms. The experimentally observed crystal structure of Ag_3P_{11} agrees with the first crystal chemical formula.

Cu_2P_7 : $VEC = 4.111$, $N_{NBO} = {}^{1}/_{9}$, $N_{NBA} = {}^{1}/_{7}$, $^{N\{0\}}/_{N\{1\}} = {}^{6}/_{1} \Rightarrow Cu_2^{[4t]}\, P_2^{[(2;2)t]}\, \underline{P}^{[;3n]}\, P_4^{[(1;3)t]}$

$VEC_A = 5.286$, $AA = {}^{19}/_{7}$ (if $CC = 0$), $^{N[;2]}/_{N[;3]} = {}^{2}/_{5}$ or $Cu_2^{[4t]}\, \underline{P}^{[(1;2)n]}\, P^{[(2;2)t]}\, P_5^{[(1;3)t]}$

Or derived from (V - 7a) and $^{N[;1]}/_{N[;3]} = {}^{1}/_{6} \Rightarrow Cu_2^{[4t]}\, \underline{P}^{[(2;1)n]}\, P_6^{[(1;3)t]}$

The difference between the two crystal chemical formulae is in the number of the homonuclear bonds of the single P atom which carries the non-bonding orbital. The experimentally observed crystal structure of Cu_2P_7 agrees with the first crystal chemical formula.

Molecular tetrahedral structures with *VEC* > 6

Compounds with *VEC* > 6 which crystallize with a tetrahedral structure form non-cyclic molecules for which the number of atoms can be calculated. One can rewrite the valence electron equation for tetrahedral structures as follows :

4	=	8 - *VEC*	+	N_{NBO}	(VI - 8)
total number of orbitals per atom		number of bonding orbitals per atom		number of non-bonding orbitals per atom	

If *VEC* > 6 it follows that the number of bonding orbitals per atom is smaller than 2, which means that one has a non-cyclic molecule with a finite number of atoms. **$N_{A/M}$, the average number of atoms in the non-cyclic molecule**, can be calculated from the *VEC* value. For a molecule with $N_{A/M}$ atoms one has $N_{A/M}$ - 1 bonds between the atoms. The ratio of the number of bonds to the number of atoms can have the values $^0/_1$, $^1/_2$, $^2/_3$ ... or in general $(N_{A/M} - 1) / N_{A/M}$. Because each bond is formed by the overlapping of two orbitals, the average number of bonding orbitals per atom is the double, *i.e.* $2 \cdot (N_{A/M} - 1) / N_{A/M}$. Thus

$$8 - VEC = 2 \cdot (N_{A/M} - 1) / N_{A/M} \qquad \text{(VI - 9)}$$

or

$$\boxed{N_{A/M} = 2 / (VEC - 6)} \qquad \text{if } VEC > 6 \qquad \text{(VI - 10)}$$

Simple solutions of (VI - 10) are tabulated in Table VI - 1. They are also copied on the inside cover of this book.

TABLE VI - 1 : THE SIMPLE NUMERICAL SOLUTIONS OF (VI - 10), RELATING $N_{A/M}$, THE NUMBER OF ATOMS IN THE MOLECULE, WITH THE *VEC* VALUE OF THE TETRAHEDRAL STRUCTURE COMPOUND.

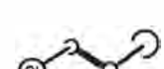
VEC	(8)	7	6.667	6.5	6.4	6.333	6.286	6.25	6.222	6.2	(6)
N_{NBO}	(4)	3	$^8/_3$	$^5/_2$	$^{12}/_5$	$^7/_3$	$^{16}/_7$	$^9/_4$	$^{20}/_9$	$^{11}/_5$	(2)
$N_{A/M}$	(1)	2	3	4	5	6	7	8	9	10	(∞)

Examples : For the following three molecular tetrahedral structures with 4, 6 and 8 atoms the longest atom chain consists of 4 atoms. According to Table II - 1 the number in the symbol preceding the opening square bracket of the crystal chemical formula refers to the length of the longest chain, while the number of atoms within the square bracket corresponds to the total number of atoms in the molecule. Crystal structure determinations have confirmed the presence of the predicted molecules.

SCl : *VEC* = 6.5, thus N_{NBO} = $^5/_2$ and $N_{A/M}$ = 4 $\Rightarrow$ $\hat{4}[\underline{S}_2^{[(1;1)n]}\underline{\underline{Cl}}_2^{[1]}]$

VEC_A = 13, thus *CC* = 5 (if *AA* = 0)

Figure VI - 7 : Structure of the $[S_2Cl_2]$ molecule.



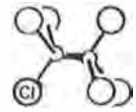
PI_2 : *VEC* = 6.33, thus N_{NBO} = $^7/_3$ and $N_{A/M}$ = 6 $\Rightarrow$ $\hat{4}[\underline{P}_2^{[(2;1)n]}\underline{\underline{I}}_4^{[1]}]$

VEC_A = 9.5, thus *CC* = 3 (if *AA* = 0)

Figure VI - 8 : Structure of the $[P_2I_4]$ molecule.

CCl_3 : *VEC* = 6.25, thus N_{NBO} = $^9/_4$ and $N_{A/M}$ = 8 $\Rightarrow$ $\hat{4}[C_2^{[(3;1)t]}\underline{Cl}_6^{[1]}]$
VEC$_A$ = 8.33, thus *CC* = 1 (if *AA* = 0)

Figure VI - 9 : Structure of the hexachloroethane $[C_2Cl_6]$ molecule.



$\Rightarrow\Rightarrow\Rightarrow$ Problems 6 and 7 in Appendix B

The tetrahedral structure equation as a guide for checking experimental data

For the following compound (with the chemical formula placed within quotation marks) there was no agreement between reported structural features and those expected from the tetrahedral structure equation. A reexamination led to a change of composition and an agreement with the valence electron rules.

"In_5S_4" : The reported crystal structure VI - 4) corresponds to a defect tetrahedral structure for which the structural features can be summarized by the crystal chemical formula : $In_4^{[(3;1)t]}\,In^{[;4t]}\,\underline{S}_4^{[3n;]}$. There are four lone-electron pairs in one formula unit consisting of nine atoms; thus N_{NBO} = $^4/_9$. Further, the five In atoms have together eight homonuclear bonds; thus *CC* = $^8/_5$. However, one obtains different values for these two parameters if one calculates them based on the reported composition :

"In_5S_4" : *VEC* = 4.333, thus N_{NBO} = $^1/_3$
VEC$_A$ = 9.75, thus *CC* = $^7/_5$ (if *AA* = 0)

Since the "In_5S_4" crystals had been prepared in a bath of liquid tin (used as a supposedly inert flux material) it was not unreasonable to consider the possibility that Sn atoms might have been incorporated involuntarily leading to a change in composition to In_4SnS_4 with a Sn atom substituting for one In atom in the formula unit. In and Sn are neighbouring elements in the Periodic Table and have similar scattering power for X-rays. Thus such an exchange would hardly have any great influence on the diffraction intensities. For the proposed new composition In_4SnS_4 one calculates N_{NBO} and *CC* values which agree with those derived from the reported crystal structure :

In_4SnS_4 : *VEC* = 4.444, thus N_{NBO} = $^4/_9$
VEC$_A$ = 10, thus *CC* = $^8/_5$ (if *AA* = 0) for a two-cation compound

More than 10 years passed before the "In_5S_4" puzzle was finally solved. According to a new synthesis and structure determination, VI - 5) a binary compound In_5S_4 does not exist. The atom sites in the crystal structure are correct, but the composition is In_4SnS_4 with one former In site occupied by a Sn atom. If one considers Sn here as an anion, then $In_4^{[1Sn,3S]}\,Sn^{[4In]}\,\underline{S}_4^{[3In]} \equiv In_4^{[(1,3)t]}\,Sn^{[(4,0)t]}\,\underline{S}_4^{[(3,0)n]}$ might be classified also as a normal valence compound with two kinds of anions where *VEC*$_A$ = 8 and *CC* = *AA* = 0.

In_4SnS_4 : *VEC* = 4.444, thus N_{NBO} = $^4/_9$
VEC$_A$ = 8, thus *CC* = *AA* = 0 for a two-anion compound

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*VI - 4) Wadsten, T., Arnberg, L. & Berg, J.E. (1980). Acta Cryst. **B36**, 2220 - 2223.*
*VI - 5) Deiseroth, H.J. & Pfeifer, H. (1991). Z. Kristallogr. **196**, 197 - 205.*

Tetrahedral anion partial structures in polyanionic valence compounds

The anionic partial structure in polyanionic valence compounds has often all the structural characteristics of a tetrahedral structure for which the above given valence electron rules can be applied with certain modifications. In a formalistic approach one assumes that the cations transfer all their valence electrons to the anions. The tetrahedral structure equation and the equation derived from it can then be applied to the charged anion partial structure. [VI - 6] To indicate that VEC, N_{NBO}, and also $N_{A/M}$, do not apply to the total structure but only to the (negatively charged) anion partial structure we shall use primed parameters, *i.e.* VEC', N'_{NBO} and $N'_{A/M}$.

In analogy to (VI - 2) one defines VEC' by

$$VEC' = (m \cdot e_C + n \cdot e_A) \; / \; n \qquad \text{for } C_mA_n \qquad \text{(VI - 11)}$$

The tetrahedral structure equation (VI - 4) becomes

$$VEC' = 4 + N'_{NBO} \qquad \text{(VI - 12)}$$

where N'_{NBO} is the average number of non-bonding orbitals per atom of the **charged** anion partial structure.

If $VEC' > 6$ one finds in analogy to (VI - 10)

$$N'_{A/M} = 2 \; / \; (VEC' - 6) \qquad \text{if } VEC' > 6 \qquad \text{(VI - 13)}$$

where $N'_{A/M}$ is the number of atoms in the non-cyclic molecular anion partial structure.

As an example we consider the structure of Sr_3As_4 which had already been treated in chapter V under the aspect of the generalized 8 - N rule.

Sr_3As_4 : $VEC = {}^{26}/_{7} < 4$

$VEC' = 6.5 > 6$ thus $N'_{NBO} = {}^{5}/_{2}$ and $N'_{A/M} = 4$

$VEC_A = 6.5 > 6$ thus $AA = {}^{3}/_{2}$ and $N'_{A/M} = 4$

Since VEC < 4 a tetrahedral structure involving all atoms is not possible for Sr_3As_4. However, for the charged anion partial structure $(As_4)^{6-}$ one calculates that $VEC' = 6.5$ which indicates that a non-cyclic molecular partial structure of four anions is possible. $[As_4]^{6-}$ is isoelectronic with $[S_2Cl_2]$ and both molecules are built in the same way, *i.e.* a chain of four atoms, as shown for $[S_2Cl_2]$ in Figure VI - 7. For Sr_3As_4 the same result had been obtained before using (V - 9).

In the particular case of binary polyanionic valence compounds the equations (VI - 11 to 13) do not provide any new structural insight beyond that which can be derived from the generalized 8 - N rule, because here $VEC' \equiv VEC_A$. However, the concept based on tetrahedral partial structures will be found useful for the understanding and interpretation of ternary and more component structures with anionic tetrahedron complexes, discussed in chapters VIII and IX.

VI - 6) Parthé, E. (1989). Z. Kristallogr. 189, 101 - 107.

VII. ADAMANTANE STRUCTURE COMPOUNDS

Definition

Adamantane structure compounds are normal valence compounds (see chapter IV) with tetrahedral structures (see chapter VI) where the cations and anions occupy the Zn and S sites, respectively, of the sphalerite or wurtzite structure (or a stacking variant of these) (see Figure I - 4). Thus the diffraction patterns of adamantane structure compounds are all similar to the patterns of sphalerite or wurtzite except for possible superstructure reflections due to the ordering of the substituting atoms. Sphalerite itself is an ordered substitution variant of the cubic diamond type, whereas the wurtzite structure can be considered an ordered substitution variant of the structure of the rare hexagonal diamond (lonsdaleite). The structural relationship to diamond is the origin for the term **adamantane structure**. [VII - 1)]

One distinguishes between

- **normal adamantane structures** with composition C_nA_n, $VEC = 4$ and $VEC_A = 8$ where all Zn and S sites are fully occupied and
- **defect adamantane structures** with composition $C_{n-u}\square_uA_n$, $VEC > 4$ and $VEC_A = 8$ where all S sites are occupied but some Zn sites are not. The symbol $\square$ is used for a vacancy. The number of vacancies is labelled u (unoccupied sites).

Derivation of the adamantane structure equation

By relating adamantane structures to the equiatomic ZnS structures we tacitly assumed that the number of (occupied and unoccupied) cation sites is equal to the number of anion sites. This can be verified by combing the equation for normal valence compounds $VEC_A = 8$ (IV - 3) with the tetrahedral structure equation $VEC = 4 + N_{NBO}$ (VI - 4).

We assume as a starting composition $C_{m-u}\square_uA_n$ where the number of (all occupied and unoccupied) cation sites (m) is a variable assumed to be independent of n. We observe that a vacancy $\square$ on a Zn site corresponds to four non-bonding orbitals, one on each of the four tetrahedrally coordinated anion neighbours of the unoccupied Zn site, thus

$$N_{NBO} = 4u\,/\,(m - u + n) \qquad \text{(VII - 1)}$$

With (VI - 4) one obtains

$$(m - u)\cdot e_C + n\cdot e_A = 4\cdot(m - u + n) + 4u \qquad \text{(VII- 2)}$$

and with (IV - 1)

$$(m - u)\cdot e_C + n\cdot e_A = 8n \qquad \text{(VII - 3)}$$

VII - 1) In earlier literature also denoted as adamantine structure.

Combining (VII - 2) with (VII - 3) leads to

$$4\cdot(m+n) = 8n \qquad \text{or} \qquad m = n \qquad \text{(VII - 4)}$$

Since the result is the same regardless of the value of u, the compositions of normal and defect adamantane structure compounds are C_nA_n and $C_{n-u}\square_u A_n$, respectively.
The proper equation for N_{NBO} is thus

$$N_{NBO} = 4u/(2n-u) \qquad \text{(VII - 5)}$$

which with (VI - 4) leads to

$$VEC = 8n/(2n-u). \qquad \text{(VII- 6)}$$

Rearranging (VII - 6) results in the **adamantane structure equation** VII - 2) :

$$\boxed{u/n = 2 - 8/VEC} \qquad \text{for } C_{n-u}\square_u A_n \qquad \text{(VII - 7)}$$

where $u/n \cdot 100$ is the percentage of unoccupied Zn sites. Adamantane structures are however stable only within the limits $4 \leq VEC \leq 4.923$ or $0 \leq u/n \leq 3/8$.

Example : Defect adamantane structure compounds where 1/4 of the Zn sites are unoccupied can occur only when $VEC = 8/(2 - 1/4) = 32/7 = 4.571$ (with $VEC_A = 8$ as precondition). Some known examples with $VEC = 4.571$ are α-$CdGa_2\square S_4$, β-$Ag_2Hg\square I_4$ or $Hg_2Sn\square Se_4$ (see Figure VII - 3).

VEC limits for adamantane structure compounds

Adamantane structures cannot exist with compounds where $VEC < 4$ because there are not enough valence electrons available for each atom to form sp^3 hybrid orbitals. But there is also an upper VEC limit. Experimental evidence indicates that adamantane structures can exist only up to a limit where three out of eight cation positions are not occupied, *i.e.* $C_5\square_3A_8$ with $u/n = 3/8$ to which corresponds $VEC = 4.923$ and $N_{NBO} = 12/13$. If more cations are removed the number of the remaining cation - anion bonds is insufficient to stabilize a defect adamantane structure. The structure of red HgI_2 ($VEC = 5.33$), shown in Figure VII - 1, serves as example. This is a tetrahedral structure but not an adamantane structure. There is no three-dimensional close-packed anion arrangement corresponding to the S atom arrangement in wurtzite or sphalerite.

Alternative formulation of the adamantane structure equation

In the early literature the valence electron condition for adamantane structure compounds was formulated as follows VII - 3) : **"The ratio of the total number of available valence electrons divided by the total number of sites (occupied plus unoccupied cation sites and anion sites) must be four."** Occasionally this was also expressed by stating that the "valence electron concentration" of the compound has to be four with the formal prescription that vacancies are counted as zero-valent atoms. The use of the term "valence electron concentration" for this ratio should be avoided. It is defined differently from the conventional VEC parameter we use throughout this book and it has been the source of some confusion in the literature.

VII - 2) Parthé, E. (1995). In "Intermetallic Compounds, Principles and Practice". Eds. J.H. Westbrook and R.L. Fleischer. Chapter 14, pages 343 - 362. Chichester (England) : John Wiley. Parthé, E. (1987). In "Ternary and Multinary Compounds". Edit. S.K. Deb and A. Zunger. Pages 3 - 17. Pittsburgh : Materials Research Society.

VII - 3) Pamplin, B.R. (1960). Nature 188, 136 - 137.

Rearranging the adamantane structure equation (VII - 7) as

$$[(2n - u) \cdot VEC] / 2n = 4. \qquad \text{(VII- 8)}$$

and replacing *VEC* by

$$VEC = [(n - u) \cdot e_C + n \cdot e_A] / (2n - u) \qquad \text{(VII - 9)}$$

yields an alternative formulation of the adamantane structure equation for $C_{n-u}\square_u A_n$:

$$\boxed{[(n - u) \cdot e_C + u \cdot 0 + n \cdot e_A] / [(n - u) + u + n] = 4} \quad \text{for } 0 \leq u/n \leq 3/8 \qquad \text{(VII - 10)}$$

occupied Zn sites — unoccupied Zn sites — S sites

Examples :

$Ga_2\square S_3$: $(2 \cdot 3 + 1 \cdot 0 + 3 \cdot 6) / (2 + 1 + 3) = 4$

$CdGa_2\square S_4$: $(1 \cdot 2 + 2 \cdot 3 + 1 \cdot 0 + 4 \cdot 6) / (1 + 2 + 1 + 4) = 4$

In Table VII - 1 are listed selected examples of adamantane structure compounds arranged according to increasing *VEC* and *u / n* values. The formula $(Ga_4Ge\square_3)Se_8$ on the second to last line, where *u / n* and *VEC* have the highest possible values for an adamantane structure, corresponds to the composition of the upper solubility limit of $GeSe_2$ (*VEC* = 5.33; a defect tetrahedral but not adamantane structure compound) in $Ga_2\square Se_3$ (*VEC* = 4.80; a defect adamantane structure compound). With *VEC* = 5.333 (last line of Table VII - 1) there are too many non-bonding orbitals (or, expressed differently, only two covalent bonds per anion) and an adamantane structure does not form.

TABLE VII - 1 : GENERAL FORMULAE FOR ADAMANTANE STRUCTURE COMPOSITIONS, CORRESPONDING *u / n* AND *VEC* VALUES AND EXAMPLES OF KNOWN COMPOUNDS WITH NUMERICAL FORMULAE WITHIN CURLY BRACKETS

Formula	*u / n*	*VEC*	Examples
C_nA_n	0	4.000	ZnS $\{26\}$, Cu_2ZnGeS_4 $\{1_2246_4\}$, $Cu_4NiSi_2S_7$ $\{1_424_26_7\}$, LiSiNO $\{1456\}$
$C_7\square A_8$	1/8	4.267	$Hg_5In_2Se_8$ $\{2_53_2\square 6_8\}$
$C_5\square A_6$	1/6	4.364	$Hg_3In_2Te_6$ $\{2_33_2\square 6_6\}$
$C_3\square A_4$	1/4	4.571	$CdGa_2Se_4$ $\{23_2\square 6_4\}$, $AgZnPS_4$ $\{125\square 6_4\}$, $AgIn_5Se_8$ $\{13_5\square_2 6_8\}$
$C_2\square A_3$	1/3	4.800	Ga_2Se_3 $\{3_2\square 6_3\}$, Si_2N_2O $\{4_2\square 5_26\}$, $(SiP)N_3$ $\{(45\square)5_3\}$
$C_5\square_3A_8$	3/8	4.923	$(Ga_4Ge)Se_8$ $\{(3_44\square_3)6_8\}$
$C\square A_2$	1/2	5.333	**Impossible**

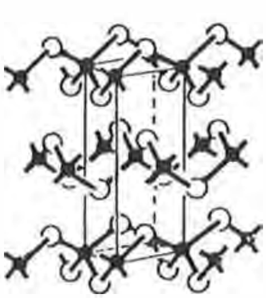


Figure VII - 1 : Structure of red $^2_\infty Hg^{[4t;]}I_2^{[2;]}$*, tP6. The small filled circles represent Hg atoms. This is a defect tetrahedral structure but not an adamantane structure.*

In Figure VII - 1 the defect tetrahedral layer structure of red HgI_2 is shown. This normal valence compound with *VEC* = 5.333 > 4.923 has too many non-bonding orbitals, *i.e.*

N_{NBO} = $^4/_3$ > $^{12}/_{13}$ to form an adamantane structure. One recognizes in the drawing slabs cut from the sphalerite structure, however these slabs are not connected by covalent *A - C - A* bonds and are vertically and horizontally displaced in respect to each other. The red HgI_2 structure can thus **not** be considered as a sphalerite structure with cation vacancies.

The prediction of the structures of the mercury dihalogenides is difficult because there is a competition between two kinds of Hg atom hybridizations. The HgX_2 compounds crystallize in five different structure types which can be subdivided into three groups according to the coordination of the Hg atoms :

1) HgX_4 tetrahedra (where Hg is sp^3 hybridized) occur in red HgI_2, *tP6* and orange HgI_2, *tI48*.
2) Linear *X*-Hg-*X* groups (where Hg is *sp* hybridized) are found with $HgCl_2$, *oP12* and $HgBr_2$, *oS12*. The latter type is found also with the third modification of HgI_2.
3) HgX_8 cubes are encountered in essentially ionic HgF_2 ($|\Delta x|$ = 2.1) which crystallizes with the CaF_2 type, *cF12* (drawing in Figure IV - 2).

Compositions

Two methods are available to calculate the possible compositititions of adamantane structure compounds : the cross-substitution method and the algebraic method.

1) Cross-substitution method

Following an original idea by Grimm & Sommerfeld [VII - 4)] the compositions can be derived from the *44* starting composition (which corresponds to SiC) by the repeated application of a procedure called "splitting" or "cross-substitution". This means the replacement of a pair of atoms of one kind by two different ones, one to the left and one to the right of group *4B* of the Periodic Table, while keeping constant the ratio of the number of valence electrons to the number of atoms. The method can be understood easily if one regards the direction of the arrows and the sequence of numerical formulae listed in Table VII - 2, an example of a cross-substitution table. All formulae in Table VII - 2 obtained by cross-substitution correspond to compositions of normal valence compounds with VEC_A = 8.

TABLE VII - 2: CROSS-SUBSTITUTION TABLE FOR THE DERIVATION OF ADAMANTANE STRUCTURE COMPOSITIONS

0	1	2	3	4	5	6	7	*VEC*	*u/n*	known examples
				$4_8 4_8$				4.0	0	SiC
			↙		↘					
			3_8		5_8			4.0	0	InP
		↙				↘				
		2_8				6_8		4.0	0	ZnS
	↙		↘			↓				
	1_4		3_4			6_8		4.0	0	$CuAlS_2$
↙		↘	↓			↓				
$□_2$		2_2	3_4			6_8		4.571	$^1/_4$	$CdGa_2□Se_4$
↓	↙		↘ ↓			↓				
$□_2$	1		3_5			6_8		4.571	$^1/_4$	$AgIn_5□_2Se_8$
↓ ↙			↓	↘		↓				
$□_3$			3_4	4		6_8		4.923	$^3/_8$	$(Ga_4Ge□_3)Se_8$

VII - 4) Grimm, H.G. & Sommerfeld, A. (1926). Z. Physik ***36****, 36 - 39.*

To derive compositions of defect adamantane structures where $VEC > 4$ it is necessary to extend by zero the list of valence electron numbers on the top line of Table VII - 2. An element with zero valence electrons can be considered as equivalent to a cation site vacancy □ in an adamantane structure.

2) Algebraic method
In this method one calculates possible solutions of the adamantane structure equation by changing systematically the numbers of the valence electrons of the atoms. This method is well suited for a systematic search of all possible element combinations for a given adamantane structure composition. An example is presented in Table VII - 4.

Binary adamantane structure compounds
In Table IV - 2 a list was given of 19 general compositions for binary normal valence compounds. In Table VII - 3 these formulae are taken up again but ordered according to increasing *VEC* value within the limits $2.67 \le VEC \le 5.33$. The six numerical formulae possible for binary adamantane structure compounds for which $4 \le VEC \le 4.923$ are :

$$\boxed{17 \quad 26 \quad 35 \quad 44 \quad 3_2\square 6_3 \quad 4_3\square 5_4} \qquad \text{(VII - 11)}$$

TABLE VII - 3 : NUMERICAL FORMULAE FOR BINARY NORMAL VALENCE COMPOUNDS ARRANGED ACCORDING TO INCREASING *VEC* VALUE. FORMULAE OF POSSIBLE ADAMANTANE STRUCTURE COMPOUNDS ARE FRAMED.

		$e_A = 4$	$e_A = 5$	$e_A = 6$	$e_A = 7$
	2.67	$2_2 4$	-	$1_2 6$	-
	3.2	-	$2_3 5_2$	-	-
	3.43	$3_4 4_3$	-	-	-
VEC	4	$\boxed{44}$	$\boxed{35}$	$\boxed{26}$	$\boxed{17}$
	4.57	-	$\boxed{4_3 5_4}$	-	-
	4.8	-	-	$\boxed{3_2 6_3}$	-
	5.33	-	-	46_2	27_2

Adamantane structure compounds are formed with group ***B*** elements (Cu always monovalent) but not group ***A*** elements with the exception of Li and Be. Also transition elements as, for example, two-valent Fe, Mn, Ni and three-valent Fe, are found as constituents.

In the case of compounds with numerical formula *26* we find the expected adamantane structure sulfides, for example, with BeS, ZnS, CdS and black HgS (metacinnabar). The last compound has, however, a second modification, *i.e.* red HgS (cinnabar) where the Hg atoms are (instead of sp^3) now *sp* hybridized, leading to linear S–Hg–S groups which are linked to form infinite zigzag chains.

Ternary normal adamantane structure compounds with two kinds of cations
These compounds with composition $C_{xn}\, C^*_{(1-x)n}\, A_n$ must be normal valence compounds. Thus

$$x \cdot e_C + (1-x) \cdot e_{C^*} = 8 - e_A \qquad \text{(VII - 12)}$$

which can be reformulated as

$$x/(1-x) = [e_{C^*} - (8 - e_A)] \,/\, [(8 - e_A) - e_C] \qquad \text{(VII - 13)}$$

The solutions of $^{x}/_{(1-x)}$ for different values of e_A, e_{C^*} and e_C (with $e_{C^*} > e_C$) are given in Table VII - 4. Of significance are, however, only the five solutions where $0 < {}^{x}/_{(1-x)} < \infty$.

Table VII - 4 : Solutions of equation (VII - 13) for cations and anions with different numbers of valence electrons. The five significant solutions of $^{x}/_{(1-x)}$ are framed.

	$e_A = 4$		$e_A = 5$			$e_A = 6$				$e_A = 7$
	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 4$	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 4$	$e_{C^*} = 5$	
$e_C = 1$	< 0	< 0	< 0	0	$\boxed{1/2}$	0	$\boxed{1}$	$\boxed{2}$	$\boxed{3}$	∞
$e_C = 2$		< 0		0	$\boxed{1}$		∞	∞	∞	< 0
$e_C = 3$					∞			< 0	< 0	< 0

To these five values of $^{x}/_{(1-x)}$ correspond five possible numerical formulae for ternary normal adamantane structure compounds with two kinds of cations :

$$\boxed{136_2 \quad 245_2 \quad 1_246_3 \quad 14_25_3 \quad 1_356_4} \qquad \text{(VII - 14)}$$

According to the ratio of the two kinds of cations these five compositions can be subdivided into three groups. For each group are known ternary wurtzite- and sphalerite-based substitution derivative structures for which drawings are presented in Figure VII - 2.

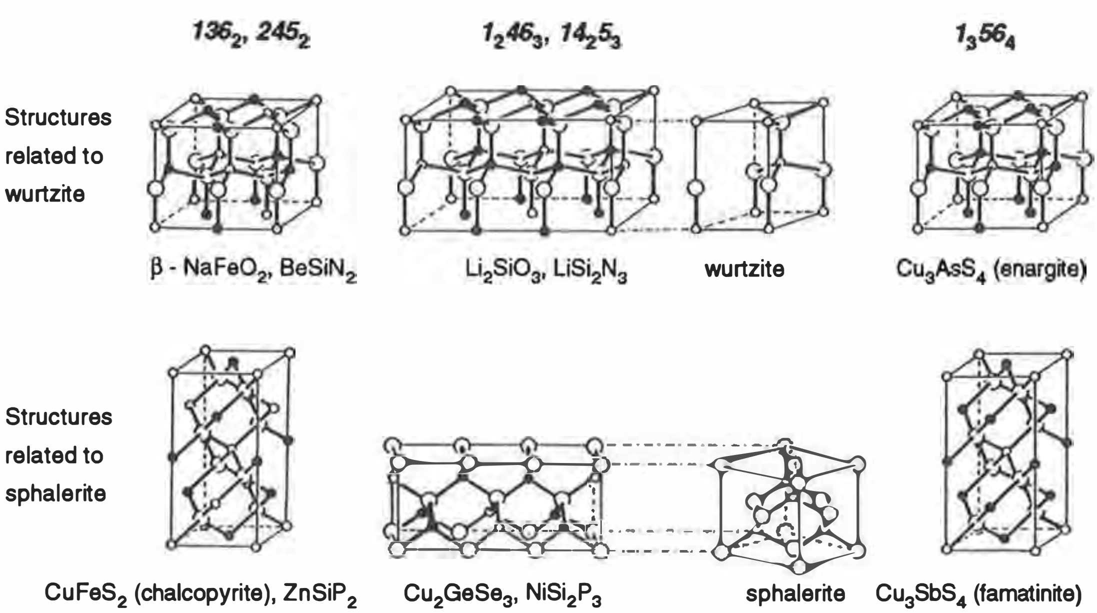


Figure VII - 2 : Ternary ordered wurtzite and sphalerite related normal adamantane structures with two kinds of cations. Cations are represented by small circles.

Li_2SiO_3 and Si_2LiN_3 (also Cu_2GeSe_3 and Si_2NiP_3) are not isotypic, as assumed previously, because the corresponding tetrahedra are distorted differently. See chapter IV for a discussion of the expected and observed changes of the interatomic distances which are due to the impossibility for an adamantane structure with this stoichiometry to satisfy the second Pauling rule.

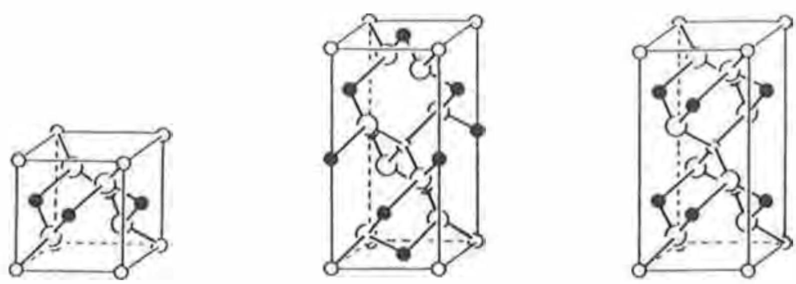
⇒⇒⇒ Problem 8 in Appendix B

Ternary ordered defect adamantane structures with general composition $C_2C^*\square A_4$

As can be proven by solving problem 8 in Appendix B, there are three possible numerical formulae for defect adamantane structures with $u / n = 1/4$, general composition $C_2C^*\square A_4$ and $e_C < e_{C^*} < e_A$:

$$\boxed{23_2\square 6_4 \quad 2_24\square 6_4 \quad 1_22\square 7_4} \qquad \text{(VII - 15)}$$

The sphalerite-related structure types of the $C_2C^*\square A_4$ compounds are shown in Figure VII - 3. It should not be too difficult for the reader to localize in the drawings the vacant sites, *i.e.* one in the unit cell of $CdIn_2Se_4$ and two sites each in the unit cells of the two other structure types.



$CdIn_2Se_4$ $\quad$ α - $CdGa_2S_4$ (thiogallate) β - Ag_2HgI_4 Hg_2SnSe_4 $\quad$ β - Cu_2HgI_4

Figure VII - 3 : Three ternary ordered adamantane structure types with composition $C_2C^*\square A_4$ which are vacancy and substitution derivatives of the sphalerite structure. Cations are presented by small circles of which 1/3 are blank and 2/3 filled.

The **possible homogeneity ranges of adamantane structure "line" compounds**

Depending on the elements involved the homogeneity range of a ternary adamantane structure may correspond to a single point or a straight line in the ternary diagram. The homogeneity range can be determined in the following way : One plots in a ternary phase diagram the line connecting points with $VEC_A = 8$ and also lines corresponding to $VEC = 4$ and $VEC = 4.923$, respectively. Adamantane structures are found on the line for $VEC_A = 8$ between the limits $4 \leq VEC \leq 4.923$. In most of these line compounds the cations and the vacancies occupy the Zn sites in random fashion. Ordering occurs only with a few particular compositions.

Example : In Figure VII - 4 are presented schematic diagrams for three ternary systems 1 - 2 - 6, 1 - 3 - 6 and 2 - 3 - 6. In each diagram lines are drawn which connect points where $VEC_A = 8$, $VEC = 4$ and $VEC = 4.923$, respectively. The compositions C_xA_{1-x} on the binary sides of the ternary diagrams which correspond to these parameters have been calculated using (VII - 16, 17 and 18) :

$$x / (1 - x) = (8 - e_A) / e_C \qquad \text{for } VEC_A = 8 \qquad \text{(VII - 16)}$$

$$x / (1 - x) = (e_A - 4) / (4 - e_C) \qquad \text{for } VEC = 4 \qquad \text{(VII - 17)}$$

$$x / (1 - x) = (e_A - 4.923) / (4.923 - e_C) \qquad \text{for } VEC = 4.923 \qquad \text{(VII - 18)}$$

In the 1 - 2 - 6 diagram an adamantane structure can occur only with a binary compound of composition *26*. Adamantane structures can be found in the 1 - 3 - 6 diagram on the short line between 136_2 and $3_2\square 6_3$, but in the 2 - 3 - 6 diagram on the long line between *26* and $3_2\square 6_3$. Ordered defect adamantane structures have been reported for compositions $23_2\square 6_4$ and $3_2\square 6_3$.

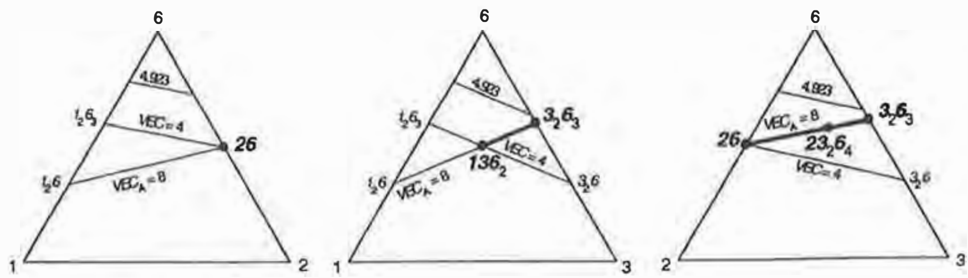


Figure VII - 4 : Three schematic ternary diagrams where the possible composition ranges of the line compounds with adamantane structure are indicated with heavy lines (or in the case of 1 - 2 - 6 by a thick point). Compositions where ordered adamantane structures are known have been written with larger characters.

Master diagram for homogeneity ranges of adamantane structure compounds.

The homogeneity ranges of adamantane structure compounds in binary and ternary phase diagrams can also be obtained by means of the master diagram, shown in Figure VII - 5. [VII - 5)] The valence electron numbers of the cations are given on bottom, those of the anions on top. By connecting appropriate points one obtains a triangle (in most cases non-equilateral) which corresponds to the ternary system of interest. The inscribed general formulae on the line for VEC_A = 8 correspond to possible binary normal valence compounds and those on the line for *VEC* = 4 to possible binary normal tetrahedral structure compounds. Adamantane structure compounds are found on the heavy short line for which VEC_A = 8 and $4 \leq VEC \leq 4.923$.

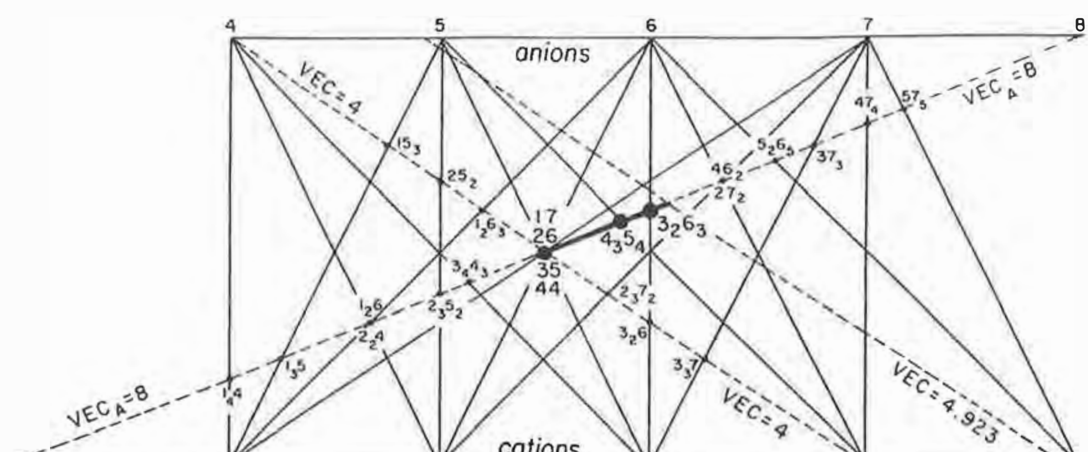


Figure VII - 5 : Master diagram to localize the possible homogenety ranges of adamantane structure compounds in binary and ternary phase diagrams.

Structure of the normal adamantane structure compound $Cu_{11.5}Zn_{23}Ga_{7.5}Ge_8As_{16}Se_{30}Br_4$.

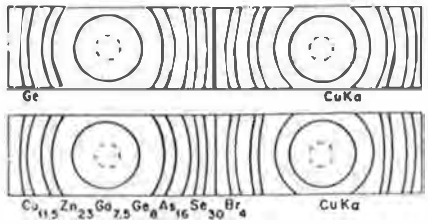
This compound was synthesized with the intention to test the validity of the valence electron rules. [VII - 6)] The proportion of the seven elements with 1 to 7 valence electrons (!) was chosen so that $VEC_A = 8$ and $VEC = 4$.

VII - 5) Parthé, E. & Paufler, P. (1991). Acta Cryst. B47, 886 - 891.

VII - 6) Parthé, E. (1972). "Cristallochimie des Structures Tétraèdriques". Paris : Gordon & Breach.

After three months in the furnace to assure a complete reaction, the Debye-Scherrer diagram of the reaction product, shown in Figure VII - 6, is virtually identical to that of Ge.

Figure VII - 6 : Debye-Scherrer X-ray diffraction diagram of Ge and $Cu_{11.5}Zn_{23}Ga_{7.5}Ge_8As_{16}Se_{30}Br_4$.



The compound has a sphalerite structure with Cu, Zn, Ga and Ge atoms on the Zn sites and the other atoms on the S sites. Since all the elements are from the same period there is virtually no difference between the expected sphalerite-type pattern and the diamond-type pattern, the sphalerite superstructure lines having here negligible intensities.

The adamantane structure equation as a guide for checking experimental data

A small excess or a small deficiency of bonding electrons from the expected *VEC* and VEC_A values (often caused intentionally by doping) will provoke changes in the electrical and optical properties of adamantane structure compounds which are of great technical importance for semiconductor applications. Minimal deviations from the expected *VEC* value in the range of $\Delta_{VEC} / VEC \approx 10^{-4}$ can be tolerated without a destabilization of the adamantane structure.

Experimental results on the homogeneity range of GaP with sphalerite structure :

The homogeneity range of GaP, a *35* compound, extends at 1000°C between $Ga_{.5001}P_{.4999}$ (VEC = 3.9998) and $Ga_{.5}P_{.5}$ (VEC = 4) and, close to the melting point, between $Ga_{.5002}P_{.4998}$ (VEC = 3.9996) and $Ga_{.5}P_{.5}$. [VII - 7] Thus $\Delta_{VEC} / VEC = 0.5 \cdot 10^{-4}$ or $1.0 \cdot 10^{-4}$, respectively, which lies in the tolerated range for a *VEC* deviation of an adamantane structure compound.

In the case of larger deviations from the expected *VEC* and VEC_A values the suspicion arises that either the composition is not correct or the structure is not an adamantane structure. For the following two compounds (with the chemical formula placed within quotation marks) there was no agreement between reported structural features and those predicted according to the adamantane structure equation. A reexamination led to a change of composition and an agreement with the valence electron rules.

"Cu_2SnSe_4" : This compound was reported to have a sphalerite type diffraction pattern which would indicate that two Cu and one Sn atom are distributed at random over four Zn sites. [VII - 8] Based on the reported composition one calculates that VEC = 4.286 and VEC_A = 7.5. However, the valence electron rules for adamantane structures require that VEC_A = 8. According to Figure VII - 5 adamantane structures can occur in the system 1 - 4 - 6 on the composition line from $1_2 4 6_3$ to $4 6_2$ up to VEC = 4.923 ($1_{1.33}4_{3.67}\square_3 6_8$). Possible compositions close to "Cu_2SnSe_4" are, for example, Cu_2SnSe_3 (VEC = 4, VEC_A = 8) [VII - 9] or $Cu_2Sn_{1.5}\square_{0.5}Se_4$ (VEC = 4.267 with u / n = 1/8, VEC_A = 8) or in between the two.

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*VII - 7) Jordan, A.S., von Neida, A.R., Caruso, R. & Kim, C.K. (1974). J. Electrochem.Soc. **121**, 153 - 158.*

*VII - 8) Bok, L.D.C. & de Wit, J.H. (1963). Z. anorg. allg. Chem. **324**, 162 - 167.*

VII - 9) For composition $1_2 4 6_3$ exist two sphalerite superstructure types : Cu_2GeSe_3 and new Cu_2SnS_3 (Chalbaud de Mogollon, L., Diaz de Delgado, G., Cenzual, K. & Delgado, J.M.; to be published in Mater. Res. Bull.)

"$Ni_{1.68}Si_{0.68}\square_{0.44}P_3$" : For this compound, which was reported with a sphalerite-related defect adamantane structure, [VII - 10] one calculates either $VEC_A = 6.733$ (assuming Ni^{1+}) or 7.293 (with Ni^{2+}), neither of these being in agreement with the expected value of 8. A recent redetermination [VII - 11] has shown that the correct composition is $Ni^{1+}Si_2P_3$ (with $VEC = 4$ and $VEC_A = 8$) and that the crystal structure (except for a different deformation of the tetrahedra) is the same as that of Cu_2GeSe_3, a normal adamantane structure, shown in Figure VII - 2.

Structure separation plots for adamantane structure compounds

The valence electron rules are a necessary, but not sufficient condition for the occurrence of an adamantane structure. Compounds are known for which the electron rules are satisfied but the structures occurring are not adamantane structures. To predict whether a compound (with a permitted composition) will actually crystallize with an adamantane structure one can make use of one of the several structure separation plots. In each plot one finds an area where adamantane structures occur and other regions where the formation of such a structure is unlikely. In Figure VII - 7 is presented the first plot due to Mooser & Pearson. [VII - 12] They use as ordinate $\bar{n}$, the average principal quantum number of the participating atoms, and as abscissa $|\Delta x|$, the magnitude of the difference of the electronegativity values. Other more elaborate separation plots have been proposed later by Phillips & Van Vechten, Zunger, Villars and Pettifor. [VII - 13]

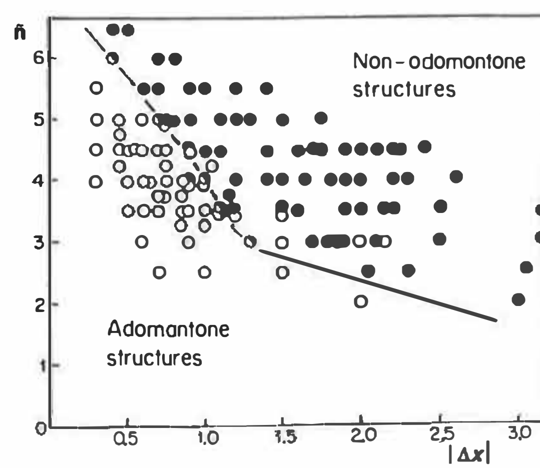

Figure VII - 7 : Structural separation plots for binary equiatomic normal valence compounds according to Mooser & Pearson. Points corresponding to normal adamantane structures are indicated with open circles, those of non-tetrahedral structures with filled circles.

Examples : $\bar{n}_{NaCl} = 3$, $|\Delta x|_{NaCl} = 2.1$

$\bar{n}_{ZnS} = 3.5$, $|\Delta x|_{ZnS} = 0.9$

See inside cover for Periodic Table and electronegativity values of the elements.

The shape of the structure separation line in Figure VII - 7 makes it evident that the tendency to form directional bonds, characteristic of tetrahedral structures, decreases with

- an increase of $\bar{n}$: With elements of higher periods a "dehybridisation" or "metallisation" occurs. The *d* and *f* orbitals have an energy which is comparable with that of the *s* and *p* orbitals and the first two may form non-tetrahedral combinations with the *s* and *p* orbitals.
- an increase of $|\Delta x|$: The electrons are now strongly attracted by the highly electronegative element and they do not anymore participate on the formation of sp^3 orbitals.

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*VII - 10) Il'nitskaya, O.N., Zavalii, P.Yu. & Kuzma, Yu.B. (1989). Dopov. Akad. Nauk Ukr. RSR Ser. B, **9**, 38 - 40.*

*VII - 11) Wallinda, J. & Jeitschko, W. (1995). J. Solid State Chem. **114**, 476 - 480.*

*VII - 12) Mooser, E. & Pearson, W.B. (1959). Acta Cryst. **12**, 1015 - 1022.*

VII - 13) Pettifor, D.G. (1995). In "Intermetallic Compounds, Principles and Practice". Edits. J.H. Westbrook & R.L. Fleischer. Volume 1. Chapter 18. Pages 419 - 438. Chichester: John Wiley & Sons.

VIII. NORMAL VALENCE COMPOUNDS WITH ANIONIC TETRAHEDRON COMPLEXES

Definition

More than one sixth of the known inorganic compounds have anionic tetrahedron complexes. As most simple general formula serves $C_m\,C'_{m'}\,A_n$ where the anionic partial structure, *i.e.* a tetrahedron complex is formed with all the C' (central atoms) and the electronegative A atoms (anions). The electropositive C atoms (cations), outside the complex and with a coordination different from tetrahedral, are assumed, according to a simple model, to transfer formally all their valence electrons to the tetrahedron complex.

One can distinguish between normal valence compounds with anionic tetrahedron complexes where $VEC_A = 8$ and general valence compounds where $VEC_A \neq 8$. The latter ones shall be discussed in chapter IX.

An example for a normal valence compounds with an anionic tetrahedron complex is forsterite Mg_2SiO_4, the Mg end member of the olivine series, shown in Figure VIII - 1. In olivines, as in all other nesosilicates, the anionic tetrahedron complex consists of an isolated centred tetrahedron.

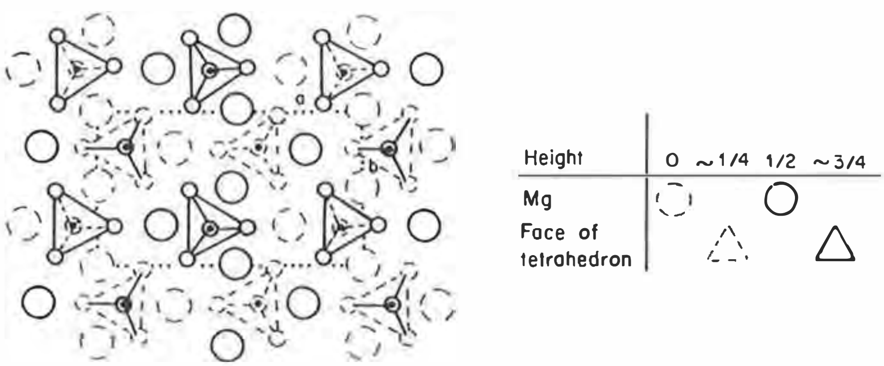


Figure VIII - 1 : Projection along the short c axis of orthorhombic forsterite Mg_2SiO_4, characterized by isolated $[SiO_4]^{4-}$ tetrahedra.

An isolated tetrahedron is the most simple anionic tetrahedron complex. In Figure VIII - 2 are shown, next to the simple tetrahedron, some examples for other anionic tetrahedron complexes which have been found with normal valence compounds. We use here in part perspective tetrahedron drawings and in part planar graph presentations of tetrahedra. The graph presentation offers the advantage of being more simple to draw without any loss of information important for our discussion. VIII - 1)

VIII - 1) The planar graph presentation of a tetrahedron suggests a certain order of the ligands, which is however irrelevant, all four ligands of a central atom in a tetrahedron being geometrically equivalent with respect to each other.

From the compositions of the five compounds, listed on top of Figure VIII - 2, we calculate values for the **total** valence electron concentration *VEC* as given on the second line. As these values are smaller than four, the formation of a tetrahedral structure involving **all** atoms, *i.e.* including the cations *C*, is, according to (VI - 4), not possible. But an anionic tetrahedron complex (third line) can be formed, because the valence electron concentration of the charged anionic tetrahedron complex, labelled *VEC'*, is equal or larger than 4 (fourth line).

The anionic tetrahedron complexes are negatively charged due to the transfer of the valence electrons of the cations *C*. The number of electrons accepted is just right for all atoms of the complex to complete their octets either by shared or lone electron pairs. In the drawings of the anionic tetrahedron complexes in Figure VIII - 2 (and all the later figures) the lone electron pairs on the anions are not shown. But it should be understood, that endstanding anions have three lone-electron pairs, anions shared between two tetrahedra two lone-electron pairs, *e.t.c.* The electrons used for these lone pairs are always included in the electron count when calculating the valence electron concentration (as can be verified by checking the listed *VEC'* values).

With the exception of $^{1}_{\infty}(AlAs_2)^{3-}$ in Na_3AlAs_2, all presented anionic tetrahedron complexes are molecular and their formulae are therefore placed within square brackets.

Ba_4SiAs_4	$Li_6Si_2O_7$	Na_5GeP_3	$Li_5P_2N_5$	Na_3AlAs_2
$VEC = {}^{32}/_{9} < 4$	$VEC = {}^{56}/_{15} < 4$	$VEC = {}^{24}/_{9} < 4$	$VEC = {}^{40}/_{12} < 4$	$VEC = {}^{16}/_{6} < 4$
$[SiAs_4]^{8-}$	$[Si_2O_7]^{6-}$	④$[Ge_2P_6]^{10-}$	⑩$[P_4N_{10}]^{10-}$	$^{1}_{\infty}(AlAs_2)^{3-}$
$VEC' = {}^{32}/_{5} = 6.4$	$VEC' = {}^{56}/_{9} = 6.22$	$VEC' = {}^{24}/_{4} = 6$	$VEC' = {}^{40}/_{7} = 5.71$	$VEC' = {}^{16}/_{3} = 5.33$

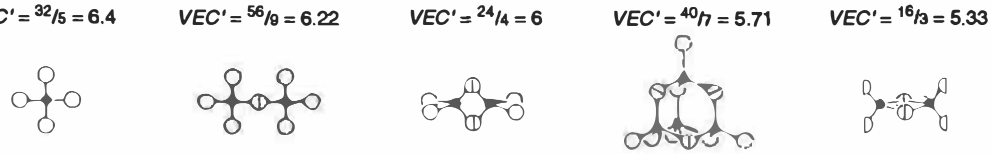


Figure VIII - 2 : Five examples of anionic tetrahedron complexes found with normal valence compounds. Central atoms are indicated by small black circles and anions by open circles.

An anion may be shared between two or more tetrahedra. Distinct from the isolated tetrahedron which has no shared anions, in the four other anionic tetrahedron complexes, shown on Figure VIII - 2, each tetrahedron has one, two, three or four anions shared with other tetrahedra. We distinguish between **corner**- and **edge-linked** tetrahedra depending whether one or two anions of a tetrahedron are shared with **one** other tetrahedron. In $Li_6Si_2O_7$ and $Li_5P_2N_5$ the tetrahedra are corner-linked, whereas in Na_5GeP_3 and Na_3AlAs_2 they are edge-linked. Note that a pair of edge-linked tetrahedra, as in Na_5GeP_3, can be considered also as a (smallest possible) tetrahedron ring. Face-linked tetrahedra (this corresponds to three anions shared between the two tetrahedra) are not to be expected because of the resulting too short distance between the central atoms.

As discussed above for the five examples presented in Figure VIII - 2, a tetrahedral structure involving all atoms is not possible because *VEC* < 4. We shall encounter below also compounds with anionic tetrahedron complexes where $VEC \geq 4$ and where thus a tetrahedral structure involving all atoms would be possible, but does not occur. It appears that this depends on the nature of the cation. The alkali atoms K, Rb, Cs, the alkaline earth atoms Ca, Sr. Ba and the ***3T*** group atoms have never been found in tetrahedral coordination, Na and Mg only exceptionally.

Valence electron rules for normal valence compounds with anionic tetrahedron complexes

The two valence electron rules used for compounds with tetrahedral structures, *i.e.* the generalized 8 - *N* rule (V - 3) and the tetrahedral structure equation (VI - 4) can also be applied to normal valence compounds with anionic tetrahedron complexes.

- **Generalized 8 - *N* rule**

One considers the charged anionic tetrahedron complex consisting only of central atoms (C') and anions (A). Each of the m cations C outside the complex has e_C valence electrons which are transferred to the complex. The negative charge of the anionic tetrahedron complex is thus $(m{\cdot}e_C)$-, *i.e.* the complex has the general formula $(C'_m, A_n)^{(m \cdot e_C)-}$.

One calculates first the partial valence electron concentration in respect to the anion, VEC_A, which, in analogy to (IV - 2), is defined as

$$\boxed{VEC_A = (m{\cdot}e_C + m'{\cdot}e_{C'} + n{\cdot}e_A) \; / \; n} \qquad \text{for } (C'_m, A_n)^{(m \cdot e_C)-} \qquad \text{(VIII - 1)}$$

Its value allows one to distinguish between normal and general valence compounds

The generalized 8 - *N* rule applied to the charged anionic tetrahedron complex of a normal valence compound has the simple form

$$\boxed{VEC_A = 8} \qquad \text{for } (C'_m, A_n)^{(m \cdot e_C)-} \qquad \text{(VIII - 2)}$$

In normal valence compounds one finds no bonds between anions, no bonds between cations or between central atoms and the lone electron pairs are only on the anions.

- **Tetrahedral structure equation**

At the end of chapter VI it has been shown that the tetrahedral structure equation can be applied to tetrahedral anion partial structures provided one includes for the calculation of *VEC* also the electrons which have been transferred from the cations and which are responsible for the negative charge of the partial structure. An anionic tetrahedron complex is a particular form of a tetrahedral structure, and consequently the same or related equations can be used. The here presented parameters VEC', N'_{NBO} and $N'_{A/M}$ refer to the **charged** anionic tetrahedron complex. In analogy to (VI - 11) we define VEC' by

$$\boxed{VEC' = (m{\cdot}e_C + m'{\cdot}e_{C'} + n{\cdot}e_A) \; / \; (m' + n)} \qquad \text{for } (C'_m, A_n)^{(m \cdot e_C)-} \qquad \text{(VIII - 3)}$$

The parameters VEC' and VEC_A are closely related and in analogy to (VI - 3)

$$VEC' = VEC_A \cdot n \, / \, (m' + n) \qquad \text{for } (C'_m, A_n)^{(m \cdot e_C)-} \qquad \text{(VIII - 4)}$$

The tetrahedral structure equation (VI - 4) applied to the charged anionic tetrahedron complex has the form

$$\boxed{VEC' = 4 + N'_{NBO}} \qquad \text{for } (C'_m, A_n)^{(m \cdot e_C)-} \qquad \text{(VIII - 5)}$$

where N'_{NBO} **is the average <u>n</u>umber of <u>n</u>on-<u>b</u>onding <u>o</u>rbitals per atom of the charged anionic tetrahedron complex.**

If *VEC'* > 6 one finds, corresponding to (VI - 13), that

$$\boxed{N'_{A/M} = 2\,/\,(VEC' - 6)} \qquad \text{if } VEC' > 6 \qquad \text{(VIII - 6)}$$

where $N'_{A/M}$ **is the average number of atoms in the non-cyclic molecular anionic tetrahedron complex.**

Simple solutions of (VIII - 6) are tabulated in Table VIII - 1. They are also copied on the inside cover of this book.

TABLE VIII - 1 : THE SIMPLE NUMERICAL SOLUTIONS OF (VIII - 6), RELATING $N'_{A/M}$, THE NUMBER OF ATOMS IN THE NON-CYCLIC MOLECULAR ANIONIC TETRAHEDRON COMPLEX, WITH THE *VEC'* VALUE OF THE COMPOUND.

VEC'	(8)	7	6.667	6.5	6.4	6.333	6.286	6.25	6.222	6.2	(6)
N'_{NBO}	(4)	3	$^8/_3$	$^5/_2$	$^{12}/_5$	$^7/_3$	$^{16}/_7$	$^9/_4$	$^{20}/_9$	$^{11}/_5$	(2)
$N'_{A/M}$	(1)	2	3	4	5	6	7	8	9	10	(∞)

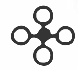
To test these rules on practical examples we study the two structures in Figure VIII - 2 with non-cyclic molecular tetrahedron complexes : Ba_4SiAs_4 and $Li_6Si_2O_7$. Counting all the lone electron pairs on the anions (not shown in the drawings) we find 12 for $[SiAs_4]^{8-}$ and 20 for $[Si_2O_7]^{6-}$. These values agree with the N'_{NBO} values calculated with (VIII - 5). Using (VIII - 6) one finds correctly that the molecular complexes of these two compounds consist of five and nine atoms, respectively. The two other molecular anionic tetrahedron complexes in Figure VIII - 2 have $VEC' \leq 6$ and are thus cyclic.

Construction of tetrahedron complexes with base tetrahedra

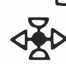
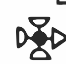
All anionic tetrahedron complexes can be imagined as being assembled of simple units, the so-called **base tetrahedra**, consisting each of one central atom *C'* surrounded by tetrahedrally arranged anion neighbours. The 12 kinds of possible base tetrahedra which can occur in normal valence compounds (assuming equipartition of the *C' - A - C'* bonds, to be discussed below) with compositions varying from $C'A_4$ to $C'A$ are shown in Table VIII - 2. Drawings of base tetrahedra which occur only in general valence compounds can be found in Chapter IX.
The most simple base tetrahedron is the isolated tetrahedron $C'A_4$, which by itself represents an anionic tetrahedron complex. The other base tetrahedra in Table VIII - 2 with general formula $C'A_{<4}$ are obtained from the simple tetrahedron by replacing one or more unshared anions by shared anions. An anion which is shared by two tetrahedra is represented in the drawings by a half circle, an anion shared by three or four tetrahedra by a triangle or square, respectively.
Alternatively, one can express the kind of anion sharing numerically by specifying the number of *C' - A - C'* bonds which pass through an anion once the base tetrahedra have been assembled. An unshared anion does not participate on any *C' - A - C'* bonds, an anion presented by a half-circle participates on one, an anion shown by a triangle on two bonds and an anion drawn as a square on three bonds.
The base tetrahedra in Table VIII - 2 are identified by two codes. The framed number on the upper right hand side of each base tetrahedron drawing represents the ***BEN*** value. Below each drawing is given between square brackets the (more detailed) base tetrahedron code. The formula on the top of each base tetrahedron drawing corresponds to that of an anionic tetrahedron complex built up only with that particular kind of base tetrahedron.

TABLE VIII - 2 : DRAWINGS OF THE 12 POSSIBLE BASE TETRAHEDRA FOR ANIONIC TETRAHEDRON COMPLEXES IN NORMAL VALENCE COMPOUNDS AND THE THREE TT VERSUS n/m' EQUATIONS.

Unshared anions and/or anions shared between two tetrahedra

Formula of complex	$C'A_2$	C'_2A_5	$C'A_3$	C'_2A_7	$C'A_4$	
$2 \le n/m' \le 4$	2	2.5	3	3.5	4	
Base tetrahedra	16	20	24	28	32	
						
	[- - 4]	[- - 3]	[- - 2]	[- - 1]	[- - 0]	
			$TT = 8 - 2\cdot(n/m')$			(VIII - 7a)

Anions shared between two and/or three tetrahedra

Formula of complex	C'_3A_4	C'_2A_3	C'_3A_5	C'_6A_{11}	$C'A_2$	
$4/3 \le n/m' \le 2$	1.333	1.5	1.667	1.833	2	
Base tetrahedra	$10^2/_3$	12	$13^1/_3$	$14^2/_3$	16	
						
	[- - 8]	[- - 7]	[- - 6]	[- - 5]	[- - 4]	
			$TT = 2\cdot[8 - 3\cdot(n/m')]$			(VIII - 7b)

Anions shared between three and/or four tetrahedra

Formula of complex	$C'A$	$C'_{12}A_{13}$	C'_6A_7	C'_4A_5	C'_3A_4	
$1 \le n/m' \le 4/3$	1	1.083	1.167	1.25	1.333	
Base tetrahedra	8	$8^2/_3$	$9^1/_3$	10	$10^2/_3$	
						
	[- - 12]	[- - 11]	[- - 10]	[- - 9]	[- - 8]	
			$TT = 3\cdot[8 - 4\cdot(n/m')]$			(VIII - 7c)

BEN value and base tetrahedron code used for identifying base tetrahedra

The *BEN* value, the **base tetrahedron electron number**, corresponds to the number of electrons needed for the formation of a particular base tetrahedron assuming that all atoms of the tetrahedron complete their octets. The following electron counting rules help us to derive the *BEN* numbers of the base tetrahedra found with normal valence compounds and shown in Table VIII - 2.

- An unshared anion (complete open circle) contributes 8 electrons each.
- A half-shared anion (half-circle) contributes 4 electrons to each base tetrahedron.
- An anion shared between three tetrahedra (triangle) contributes $8/3 = 2^2/_3$ electrons.
- An anion shared between four tetrahedra (square) makes a contribution of $8/4 = 2$ electrons.
- A central atom completes its octet by sharing one electron pair each with the four surrounding anions. Thus there is no contribution of the central atom to the electron count.

In Chapter IX shall be presented three complementary electron counting rules which apply to the special features of base tetrahedra which occur with general valence compounds.

The advantage of using the *BEN* value for the identification of a base tetrahedron lies in the simple numerical relation with the VEC_A value of a compound where the anionic tetrahedron complex is built up with the particular base tetrahedron. Generally valid for normal and general valence compounds is the following relation :

$$\boxed{BEN = VEC_A \cdot n/m' = (m \cdot e_C + m' \cdot e_{C'} + n \cdot e_A)\ /\ m'} \quad \text{for } (C'_{m'}A_n)^{(m \cdot e_C)-} \qquad \text{(VIII - 8)}$$

For the special case of a normal valence compounds (VIII - 8) simplfies to

$$\boxed{BEN = 8 \cdot n/m'} \quad \text{for } (C'_{m'}A_n)^{(m \cdot e_C)-} \qquad \text{(VIII - 9)}$$

Starting from the chemical composition of a compound and using (VIII - 9) or (VIII - 8) one can calculate a *BEN* value for its anionic tetrahedron complex. If it corresponds to a *BEN* value of a base tetrahedron in the table, the complex will probably be built up with that particular kind of base tetrahedron. If the numerical value calculated for the compound does not agree with that of a base tetrahedron, it must correspond to an average, *i.e.* <*BEN*>. Taking allowed *BEN* values from a base tetrahedron table, the most probable base tetrahedron mixture can then be obtained from the <*BEN*> value by a simple lever rule.

The use of the *BEN* parameter for the identification of base tetrahedra is to be preferred whenever tables with base tetrahedron drawings, identified by their framed *BEN* value, are readily avaible. When not, there remains as alternative method for the identification of the base tetrahedra the use of the **base tetrahedron code** which allows a complete description of a base tetrahedron, in principle comprehensible without the help of a drawing. Nevertheless, we have indicated below each base tetrahedron drawing the corresponding base tetrahedron code. The detailed description of the base tetrahedron code will be left for Chapter IX. For the moment we should take notice that the code for base tetrahedra found with normal valence compounds is very simple. Within the square brackets are two hyphens followed by the numerical value of the **tetrahedron sharing coefficient**, labelled *TT*. [VIII - 2] The tetrahedron sharing coefficient is the **total number of C' - A - C' bonds which originate from a central atom.** The *TT* value can be "read" directly from a base tetrahedron drawing. The numerical value of *TT*, which varies between 0 and 12, depends on the n/m' value, *i.e.* the ratio of the number of anions to the number of central atoms. The three different *TT* versus n/m' equations (VIIII - 7a, 7b and 7c), listed in Table VIII - 2, apply to three different n/m' ranges. In Chapter IX will be presented the derivation of these equations.

For the later discussion of the different tetrahedron complexes of normal valence compounds we shall use on some occasions the *BEN* values and on others the *TT* values. For normal valence compounds the numerical relation between *TT* and *BEN* values is obtained by combining (VIII - 7) with (VIII - 9). Which *BEN* value corresponds to which *TT* value can be read directly in Table VIII - 2.

Base tetrahedra with and without equipartition of the C' - A - C' bonds

Equipartition of the C' - A - C' bonds of a base tetrahedron means that **each** of the anions neighbours of a central atom is shared either by the **same** number of tetrahedra or, if not the same, then there is only a difference of **one**.

VIII - 2) Parthé, E. & Engel, N. (1986). Acta Cryst. ***B42****, 538 - 544.*

The tetrahedron sharing coefficient used here is, not the same but, related to the one introduced by T. Zoltaï (1960). Amer. Mineral. ***45****, 960 - 973.*

Expressed differently, in the case of equipartition there exist **no** base tetrahedra which have, for example, unshared anions (full circle) and also anions shared by three tetrahedra (triangle), or base tetrahedra with anions shared by two tetrahedra (half circle) together with anions shared by four tetrahedra (square). All the base tetrahedra shown in Table VIII - 2 and later tables are characterized by an equipartition of the $C' - A - C'$ bonds.
Anionic tetrahedron complexes built up of base tetrahedra without equipartition are rare. If there is **no** equipartition the equations (VIII - 7a to 7c) to calculate TT from the n / m' value can **not** be used. For the prediction of the structural features of anionic tetrahedron complexes we shall tacitly always assume that there is an equipartition of the $C' - A - C'$ bonds.

As one example of a normal valence compound with an anionic tetrahedron complex built up of base tetrahedra without equipartition we mention $Fe^{2+}Ga_2S_4$. The base tetrahedron drawing can be found in Figure VIII - 6. With $n / m' = 2$ one might have expected the presence of a base tetrahedron with equipartition where $BEN = 16$ and $TT = 4$. However, the observed base tetrahedron is characterized by one unshared anion and three anions shared between three tetrahedra. The BEN value is also 16, but the TT value is 6.

Tetrahedron complexes with compositions which agree with that of a base tetrahedron
If a tetrahedron complex of a normal valence compound has a composition which is the same as one of the base tetrahedra in Table VIII - 2 this means also that

- the numerical value calculated with (VIII - 9) corresponds to one of the framed BEN values
- the TT value calculated with (VIII - 7a, 7b or 7c) is an integer.

With few exceptions the anionic tetrahedron complex is constructed only with the particular base tetrahedron in Table VIII - 2 which carries the particular BEN value or TT value in the base tetrahedron code. All the compounds listed as examples in Tables VIII - 3 to 8 are built up in such a way.
However, the knowledge of the kind of base tetrahedron involved in the construction of a tetrahedron complex, is not always sufficient to define a unique tetrahedron complex. The base tetrahedra might be corner-linked or edge-linked or both. Examples for these different possibilities of assembling $\boxed{24}$, $\boxed{20}$ and $\boxed{16}$ base tetrahedra, respectively, can be studied in the first three drawings of Figures VIII - 4, 5 and 6, respectively.
The n / m' ratio of a tetrahedron complex which is constructed with only one kind of base tetrahedron is evidently identical with the n / m' value of the base tetrahedron. However, the charge of the tetrahedron complex varies and depends on the valence electron contributions of the central atom $e_{C'}$ and the anion e_A. The charge can be calculated using (VIII - 2). If the charge of the complex is calculated to be negative, there must be cations available outside the tetrahedron complex which provide the necessary electrons. If the charge is calculated to be zero, one has a neutral tetrahedron complex without cations, *i.e.* the structure is a (defect) tetrahedral structure. If the charge is formally calculated to be positive, then the formation of a tetrahedron complex with the chosen formula and element combination is not possible.
In Tables VIII - 3 to 7 are listed the possible numerical formulae and charges of tetrahedron complexes built up of $\boxed{32}$, $\boxed{28}$, $\boxed{24}$, $\boxed{20}$ and $\boxed{16}$ base tetrahedra, respectively. Here we also consider numerical formulae where the central atom comes from a group in the Periodic Table which is higher than that of the anion. These kind of compounds are formed only if the element

assumed to be the anion is more electronegative than the element which is central atom (or cation). Examples are $AgClO_4$ and OsO_4 in Table VIII - 3 or Cl_2O_7 in Table VIII - 4. VIII - 3)

- ***C'A₄* tetrahedron complex** : In Table VIII - 3 are listed the general numerical formulae of complexes consisting of isolated tetrahedra, the only possibility for $n/m' = 4$ (and $VEC_A = 8$).

TABLE VIII - 3 : GENERAL NUMERICAL AND CHEMICAL FORMULAE OF COMPOUND EXAMPLES WHERE ANIONIC TETRAHEDRON COMPLEXES $C'A_4$ CONSISTING OF ISOLATED $\boxed{32}$ BASE TETRAHEDRA WITH CODE [- - 0] ARE FOUND.

$C'A_4$	$e_A = 4$	$e_A = 5$		$e_A = 6$		$e_A = 7$	
$e_{C'} = 1$							
$e_{C'} = 2$				$(26_4)^{6-}$	Na_6ZnO_4	$(27_4)^{2-}$	Na_2BeF_4 γ'
$e_{C'} = 3$				$(36_4)^{5-}$	Na_5InS_4	$(37_4)^{1-}$	$LiAlCl_4$
$e_{C'} = 4$		$(45_4)^{8-}$	Ba_4SiAs_4	$(46_4)^{4-}$	$ZrSiO_4$	$(47_4)^{\pm0}$	- SiF_4
$e_{C'} = 5$		$(55_4)^{7-}$	Li_7PN_4	$(56_4)^{3-}$	$AlPS_4$	not	possible
$e_{C'} = 6$		$(65_4)^{6-}$	$Ba_3Mo^{6+}N_4$	$(66_4)^{2-}$	$CaSO_4$	not	possible
$e_{C'} = 7$				$(76_4)^{1-}$	$AgClO_4$	not	possible
$e_{C'} = 8$				$(86_4)^{\pm0}$	- $Os^{8+}O_4$	not	possible

There exist more general numerical formulae which can be derived from those in Table VIII - 3 by a partial anion substitution with other anions having different e_A value. One example is $(56_37)^{2-}$ derived from $(66_4)^{2-}$. Such an anionic tetrahedron complex is known to occur in the compound K_2PO_3F, an ordered anion substitution derivative of orthorhombic K_2SO_4.

- ***C'₂A₇* tetrahedron complex** : With $n/m' = 3.5$ one expects an anionic tetrahedron complex constructed with $\boxed{28}$ base tetrahedra. Two of them join to form a double tetrahedron as found, for example, with $Li_6Si_2O_7$ and shown in Figure VIII - 2. In Table VIII - 4 are presented the general numerical formulae of these complexes together with chemical formulae of compounds where these complexes are known to exist.

TABLE VIII - 4 : GENERAL NUMERICAL AND CHEMICAL FORMULAE OF COMPOUND EXAMPLES WHERE ANIONIC TETRAHEDRON COMPLEXES C'_2A_7 CONSTRUCTED WITH $\boxed{28}$ BASE TETRAHEDRA HAVING CODE [- - 1] ARE FOUND.

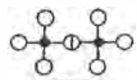
C'_2A_7	$e_A = 4$	$e_A = 5$	$e_A = 6$		$e_A = 7$	
$e_{C'} = 1$						
$e_{C'} = 2$					$(2_27_7)^{3-}$	$Li_2RbBe_2F_7$
$e_{C'} = 3$			$(3_26_7)^{8-}$	$Ba_4Ga_2S_7$	$(3_27_7)^{1-}$	KGa_2Cl_7
$e_{C'} = 4$			$(4_26_7)^{6-}$	$Li_6Si_2O_7$	not	possible
$e_{C'} = 5$			$(5_26_7)^{4-}$	$Hg_2P_2S_7$	not	possible
$e_{C'} = 6$			$(6_26_7)^{2-}$	$K_2S_2O_7$	not	possible
$e_{C'} = 7$			$(7_26_7)^{\pm0}$	- Cl_2O_7	not	possible

---

*VIII - 3) According to Table IV - 2 the numerical formula of the normal valence compound with **6B** and **7B** elements is 67_6 for which the stable SF_6 HT (isolated SF_6 octahedra) serves as example. However, if the element **6B** is more electronegative than element **7B** the formula changes to 7_26_7 for which Cl_2O_7 is an example. It is certainly unrealistic to assume here that the atoms which function as cations shed all their valence electrons to complete the octets of the anions. All atoms, i.e. cations and anions have here filled shells, but the atoms which function formally as cations have more **shared**-electron pairs and the anions more **lone**-electron pairs.*

Double tetrahedra are not the only possibility if one allows more than one kind of base tetrahedron. We consider $Ca_3Si_2O_7$ which has two modifications : rankinite and kilchoanite. As shown in Figure VIII - 3, rankinite has the corner-linked double tetrahedron, but in kilchoanite exist two different anionic tetrahedron complexes, *i.e.* an isolated tetrahedron and a finite tetrahedron chain consisting of three tetrahedra. Note, that <BEN> = 28 and <TT> = 1.

rankinite	$Ca_3Si_2O_7$	kilchoanite
$[Si_2O_7]^{6-}$	$VEC' = {}^{56}/_{9} = 6.22$	$[SiO_4]^{4-} + [Si_3O_{10}]^{8-}$
$TT = 1,\ N'_{A/M} = 9$		$<TT> = 1,\ <N'_{A/M}> = 9$



$\boxed{28}$

$1 \times \boxed{32} + 2 \times \boxed{28} + 1 \times \boxed{24}$

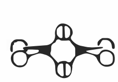
Figure VIII - 3 : The anionic tetrahedron complexes of the two modifications of $Ca_3Si_2O_7$: rankinite and kilchoanite and the base tetrahedra used for their construction.

- ***C'A*₃ tetrahedron complex** In Table VIII - 5 are listed general numerical formulae of anionic tetrahedron complexes $C'A_3$ and known examples. One expects that the complexes are built up with $\boxed{24}$ base tetrahedra. The first three drawings in Figure VIII - 4 show different possibilities of constructing anionic tetrahedron complexes with these base tetrahedra. In Na_5GeP_3 they are edge-linked, but in $Eu^{2+}GeS_3$ and Na_5SnSb_3 corner-linked. The fourth drawing in Figure VIII - 4 represents the tetrahedron complex of $La^{3+}GaS_3$ with a less simple solution consisting of a mixture of three different base tetrahedra, but <*BEN*> = 24 and <TT> = 2.

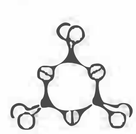
TABLE VIII - 5 : GENERAL NUMERICAL AND CHEMICAL FORMULAE OF COMPOUND EXAMPLES WHERE ANIONIC TETRAHEDRON COMPLEXES $C'A_3$ CONSTRUCTED WITH $\boxed{24}$ BASE TETRAHEDRA HAVING CODE [- - 2] ARE FOUND.

$C'A_3$	$e_A = 4$	$e_A = 5$		$e_A = 6$		$e_A = 7$	
$e_{C'} = 1$				$(16_3)^{5-}$	$BaLaCuS_3$	$(17_3)^{2-}$	K_2AgI_3
$e_{C'} = 2$				$(26_3)^{4-}$	Ba_2ZnO_3	$(27_3)^{1-}$	$CsBeF_3$
$e_{C'} = 3$		$(35_3)^{6-}$	Ca_3AlAs_3	$(36_3)^{3-}$	Rb_3InS_3	$(37_3)^{\pm 0}$	- $AlBr_3$
$e_{C'} = 4$		$(45_3)^{5-}$	Na_5GeP_3	$(46_3)^{2-}$	Li_2SiO_3	not	possible
$e_{C'} = 5$		$(55_3)^{4-}$	Ca_2PN_3	$(56_3)^{1-}$	$AgPS_3$	not	possible
$e_{C'} = 6$				$(66_3)^{\pm 0}$	- SO_3 γ	not	possible
$e_{C'} = 7$				not	possible	not	possible

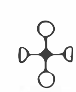
Na_5GeP_3	$Eu^{2+}GeS_3$	Na_5SnSb_3	$La^{3+}GaS_3$
④$[Ge_2P_6]^{10-}$	⑥$[Ge_3S_9]^{6-}$	$^1_\infty(SnSb_3)^{5-}$	$^1_\infty(GaS_3)^{3-}$
$VEC' = {}^{24}/_{4} = 6$	$VEC' = {}^{24}/_{4} = 6$	$VEC' = {}^{24}/_{4} = 6$	$VEC' = {}^{24}/_{4} = 6$



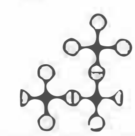
$\boxed{24}$



$\boxed{24}$



$\boxed{24}$



$\boxed{28} + \boxed{24} + \boxed{32}$

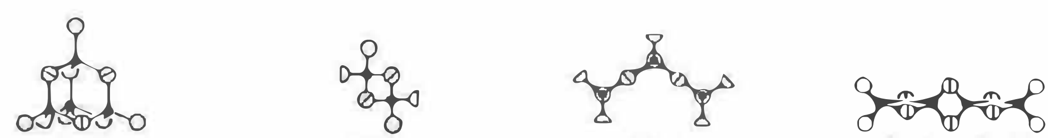
Figure VIII - 4 : Examples of anionic tetrahedron complexes observed with normal valence compounds where n / m' = 3, BEN or <BEN> = 24 and TT or <TT> = 2.

- C'_2A_5 tetrahedron complex : In Table VIII - 6 are presented general numerical and chemical formulae of compounds with tetrahedron complexes built up with $\boxed{20}$ base tetrahedra having three half-shared anions. The first three drawings in Figure VIII - 5 show three possibilities for an assembly, *i.e.* the molecular complex of $Li_5P_2N_5$, the one-dimensional tetrahedron complex of $Rb_4In_2S_5$ and the two-dimensional complex of $Na_2Ge_2Se_5$. The fourth tetrahedron complex found with $Cs_4Ga_2Se_5$ corresponds to a less simple solution with two kinds of base tetrahedra, but <*BEN*> = 20 and <*TT*> = 3.

TABLE VIII - 6 : GENERAL NUMERICAL AND CHEMICAL FORMULAE OF COMPOUND EXAMPLES WHERE ANIONIC TETRAHEDRON COMPLEXES C'_2A_5 CONSTRUCTED WITH $\boxed{20}$ BASE TETRAHEDRA HAVING CODE [- - 3] ARE FOUND.

C'_2A_5	$e_A = 4$	$e_A = 5$		$e_A = 6$		$e_A = 7$	
$e_{C'} = 1$							
$e_{C'} = 2$						$(2_2 7_5)^{1-}$	$CsBe_2F_5$ *RT*
$e_{C'} = 3$				$(3_2 6_5)^{4-}$	$Rb_4In_2S_5$	not	possible
$e_{C'} = 4$				$(4_2 6_5)^{2-}$	$Na_2Ge_2Se_5$	not	possible
$e_{C'} = 5$		$(5_2 5_5)^{5-}$	$Li_5P_2N_5$	$(5_2 6_5)^{\pm 0}$	- P_2O_5	not	possible
$e_{C'} = 6$				not	possible	not	possible
$e_{C'} = 7$				not	possible	not	possible

$Li_5P_2N_5$	$Rb_4In_2S_5$	$Na_2Ge_2Se_5$	$Cs_4Ga_2Se_5$
$^{0}_{\infty}[P_4N_{10}]^{10-}$	$^{1}_{\infty}(In_2S_5)^{4-}$	$^{2}_{\infty}(Ge_2Se_5)^{2-}$	$[Ga_4Se_{10}]^{8-}$
VEC' = $^{40}/_{7}$ = 5.71	*VEC'* = $^{40}/_{7}$ = 5.71	*VEC'* = $^{40}/_{7}$ = 5.71	*VEC'* = $^{40}/_{7}$ = 5.71



$\boxed{20}$	$\boxed{20}$	$\boxed{20}$	2 x $\boxed{16}$ + 2 x $\boxed{24}$

Figure VIII - 5 : Examples of anionic tetrahedron complexes observed with normal valence compounds where n / m' = 5/2, BEN or <BEN> = 20 and TT or <TT> = 3.

- $C'A_2$ tetrahedron complex : The general numerical formulae of anionic tetrahedron complexes built up with $\boxed{16}$ base tetrahedra having four half-shared anions are listed in Table VIII - 7.

TABLE VIII - 7 : GENERAL NUMERICAL AND CHEMICAL FORMULAE OF COMPOUND EXAMPLES WHERE ANIONIC TETRAHEDRON COMPLEXES $C'A_2$ CONSTRUCTED WITH $\boxed{16}$ BASE TETRAHEDRA HAVING CODE [- - 4] ARE FOUND.

$C'A_2$	$e_A = 4$	$e_A = 5$		$e_A = 6$		$e_A = 7$	
$e_{C'} = 1$				$(16_2)^{3-}$	$ErAgSe_2$		
$e_{C'} = 2$				$(26_2)^{2-}$	K_2ZnO_2	$(27_2)^{\pm 0}$	- HgI_2 red
$e_{C'} = 3$		$(35_2)^{3-}$	Na_3AlAs_2	$(36_2)^{1-}$	$KGaO_2$	not	possible
$e_{C'} = 4$		$(45_2)^{2-}$	Na_2SnAs_2	$(46_2)^{\pm 0}$	- SiS_2 I	not	possible
$e_{C'} = 5$		$(55_2)^{1-}$	$CsNb^{5+}N_2$	not	possible	not	possible
$e_{C'} = 6$				not	possible	not	possible
$e_{C'} = 7$		not	possible	not	possible	not	possible

In Figure VIII - 6 are presented three examples of anionic tetrahedron complexes constructed with this kind of base tetrahedron. In $BaGa_2S_4$ they are corner-linked, in Na_3AlAs_2 edge-linked and in $SrGa_2Se_4$ they are both. But the base tetrahedron used for the construction of the complex of $Fe^{2+}Ga_2S_4$ is quite different. It is one of the rare base tetrahedra where there is no equipartition of the $C'-A-C'$ bonds. The *BEN* value here is also 16, but the *TT* value is not 4 but 6.

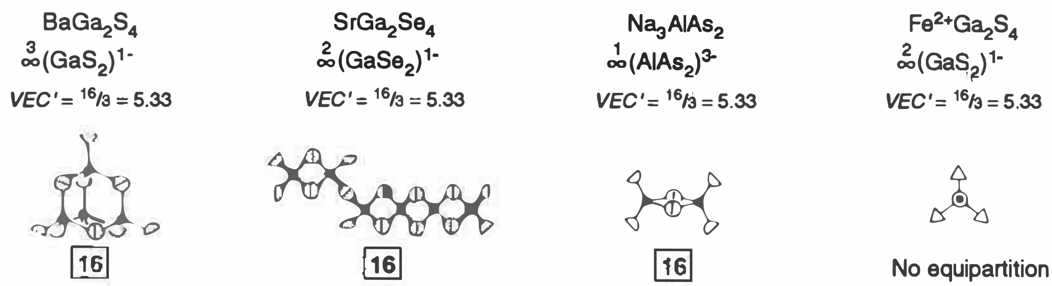


Figure VIII - 6 : Examples of anionic tetrahedron complexes observed with normal valence compounds where $n/m' = 2$ and BEN = 16.

- **C'_6A_{11}, C'_3A_5, C'_2A_3 and C'_3A_4 tetrahedron complexes where the anions are shared between two and three tetrahedra** : The formulae of these complexes can be found in Table VIII - 2. Thus it is possible to construct each complex with only one kind of base tetrahedron, *i.e.* the [- - 5], [- - 6], [- - 7] and [- - 8] base tetrahedron, respectively. In Table VIII - 8 are listed normal valence compounds for which these anionic tetrahedron complexes have been reported.

TABLE VIII - 8 : EXAMPLES OF NORMAL VALENCE COMPOUNDS WITH ANIONIC TETRAHEDRON COMPLEXES BUILT UP ONLY OF [- - 5], [- - 6], [- - 7] AND [- - 8] BASE TETRAHEDRA, RESPECTIVELY.

C'_6A_{11} [- - 5]	C'_3A_5 [- - 6]	C'_2A_3 [- - 7]	C'_3A_4 [- - 8]
$Na_3P_6N_{11}$	$Na_4Cd_3Se_5$ $AgGa_3Te_5$ *HP*	$Ca_3Al_2Ge_3$ $K_3In_2As_3$ $LiSi_2N_3$ $K_2Cd_2S_3$ - B_2O_3 II	$Cs_2Zn_3S_4$ - Si_3N_4

Tetrahedron complexes with compositions different from that of a base tetrahedron

If the <*BEN*> value calculated with (VIII - 9) does not agree with one of the framed *BEN* values in Table VIII - 2 or, expressed differently, if the *TT* value, calculated with (VIII - 7), is not an integer, then the anionic tetrahedron complex is built up of at least two different kinds of base tetrahedra. The ratio of their numbers can be determined by a lever rule as follows :
Assuming that <*BEN*> has a value between two allowed *BEN* values listed in Table VIII -2, denoted by $(BEN)_1$ and $(BEN)_2$, the ratio of their numbers is given by

$$N(BEN)_1 / N(BEN)_2 = [(BEN)_2 - \langle BEN\rangle] / [\langle BEN\rangle - (BEN)_1] \qquad \text{(VIII - 10a)}$$

A corresponding lever rule equation can be formulated for $\langle n/m'\rangle$ and $\langle TT\rangle$. If $\langle TT\rangle$ has a value between $(TT)_1$ and $(TT)_2$, the ratio of their numbers can be expressed by

$$N(TT)_1 / N(TT)_2 = [(TT)_2 - \langle TT\rangle] / [\langle TT\rangle - (TT)_1] \qquad \text{(VIII - 10b)}$$

The last equation is applicable only if the base tetrahedra are from the **same row** in Table VIII - 2.

In Figure VIII - 7 are given four examples for anionic tetrahedron complexes, built up of two kinds of base tetrahedra, where (VIII - 10b) can be applied. Note, that the <*TT*> values for the first three compounds have been calculated with (VIII - 7a), but for the last compound, where $n/m' < 2$, with (VIII - 7b).

$Na_5P_3O_{10}$ II	Amphiboles	$Na_7In_3Se_8$	$BaAl_4S_7$
$[P_3O_{10}]^{5-}$	$^1_\infty(Si_4O_{11})^{6-}$	$^1_\infty(In_3Se_8)^{7-}$	$^3_\infty(Al_4S_7)^{2-}$
$\langle TT \rangle = 1^1/_3$	$\langle TT \rangle = 2^1/_2$	$\langle TT \rangle = 2^2/_3$	$\langle TT \rangle = 5^1/_2$
$N(TT{=}1)/N(TT{=}2) = {}^2/_1$	$N(TT{=}2)/N(TT{=}3) = {}^1/_1$	$N(TT{=}2)/N(TT{=}3) = {}^1/_2$	$N(TT{=}5)/N(TT{=}6) = {}^1/_1$

2 x [- - 1] + 1 x [- - 2]	[- - 2] + [- - 3]	1 x [- - 2] + 2 x [- - 3]	[- - 5] + [- - 6]

Figure VIII - 7 : Four examples of normal valence compounds with anionic tetrahedron complexes which are constructed with two kinds of base tetrahedra and the prediction of these base tetrahedra and their ratio using (VIII - 10b). A detailed drawing of the base tetrahedron linkage in the amphiboles can be found in Figure VIII - 12.

Normal valence compounds with finite chains of corner-linked tetrahedra

For anionic tetrahedron complexes with $4 \geq n/m' > 3$ or $32 \geq \langle BEN \rangle > 24$ or $0 \leq \langle TT \rangle < 2$ there exists a different, more convenient, method to predict the possible linkage of the tetrahedra. We know from above that $TT = 1$ corresponds in the most simple case to a double tetrahedron and $TT = 2$ to an infinite chain or a ring of corner-linked base tetrahedra. For <*TT*> values in between one should find finite non-cyclic tetrahedron chains. Let us define a parameter $N'_{T/M}$ **which is the average number of tetrahedra per molecule of the anionic tetrahedron complex.** Making the same reasoning which led to the derivation of (V - 9) one can obtain a correlation between $N'_{T/M}$ and TT:

$$\boxed{N'_{T/M} = 2/(2 - TT)} \quad \text{for } 0 \leq TT < 2 \qquad \text{(VIII - 11a)}$$

which with (VIII - 7a) can be rewritten as

$$\boxed{N'_{T/M} = 1/[(n/m') - 3]} \quad \text{for } 3 < n/m' \leq 4 \qquad \text{(VIII - 11b)}$$

or

$$\boxed{N'_{T/M} = 2/[2\cdot(n/m') - 6]} \quad \text{for } 6 < 2\cdot(n/m') \leq 8 \qquad \text{(VIII - 11c)}$$

Simple solutions of (VIII - 11) are tabulated in Table VIII - 9. If, on the right hand side of (VIII - 11b), the parameter n/m' is replaced by $2\cdot(n/m')$, then equation (VIII - 11c) has algebraically the same form as (V - 9b) for which solutions are printed on the inside cover of this book.

TABLE VIII - 9: THE SIMPLE NUMERICAL SOLUTIONS OF (VIII - 11) RELATING THE NUMBER OF CORNER-LINKED TETRAHEDRA FORMING A FINITE CHAIN $N'_{T/M}$ WITH THE TT AND n/m' VALUE OF A COMPOUND.

n/m'	(4)	7/2	10/3	13/4	16/5	19/6	22/7	25/8	28/9	31/10	(3)
$2\cdot(n/m')$	(8)	7	20/3	13/2	32/5	19/3	44/7	25/4	56/9	31/5	(6)
TT	(0)	1	4/3	3/2	8/5	5/3	12/7	7/4	16/9	9/5	(2)
$N'_{T/M}$	(1)	2	3	4	5	6	7	8	9	10	(∞)

If $N'_{T/M}$ is calculated to be an integer one expects as most simple solution that the anionic tetrahedron complex consists of a finite non-cyclic chain of $N'_{T/M}$ corner-linked base tetrahedra. Short chains are unbranched but, when $N'_{T/M} \geq 4$, they can be also branched. Less probable is a solution where the calculated value corresponds to an average $<N'_{T/M}>$, *i.e.* the tetrahedron complex consists of two kinds of tetrahedron chains, one shorter and one longer than expected for the simple case.
Examples for anionic tetrahedron complexes consisting of finite tetrahedron chains with $N'_{T/M}$ = 3, 4 and 5 are shown in Figure VIII - 8. The general numerical formulae and examples for $N'_{T/M}$ = 1 and 2 can be found in Tables VIII - 3 and 4, respectively. A projection of one complete unit cell of $Na_3Mg_2P_5O_{16}$ ($N'_{T/M}$ = 5) is presented in Figure VIII - 9.

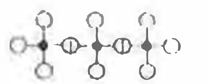
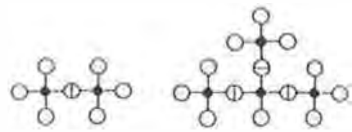
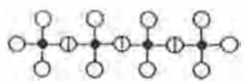
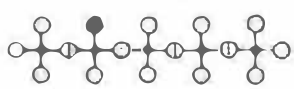
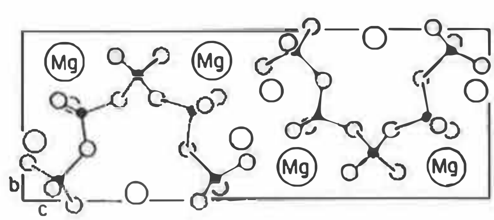
$N'_{T/M}$	numerical formula	formula of compounds with one kind of finite chains	formula of compound with two kinds of finite chains
3	$(4_36_{10})^{8-}$ $(5_36_{10})^{5-}$ $(6_36_{10})^{2-}$	$Na_2Ca_3Si_3O_{10}$ $Na_5P_3O_{10}$ II $K_2Cr^{6+}{}_3O_{10}$ 	$NaBa_3Nd_3Si_6O_{20}$ 
4	$(3_46_{13})^{14-}$ $(4_46_{13})^{10-}$ $(5_46_{13})^{6-}$ $(6_46_{13})^{2-}$	$Na_{14}Al_4O_{13}$ $Ag_{10}Si_4O_{13}$ $Ba_3P_4O_{13}$ *LT* $Rb_2Cr^{6+}{}_4O_{13}$ 	
5	$(3_56_{16})^{17-}$ $(4_56_{16})^{12-}$ $(5_56_{16})^{7-}$ $(6_56_{16})^{2-}$	$Na_{17}Al_5O_{16}$ $Na_4Sn_2Si_5O_{16} . H_2O$ $Na_3Mg_2P_5O_{16}$ $K_2S_5O_{16}$ 	

Figure VIII - 8 : Examples of anionic tetrahedron complexes with $N'_{T/M}$ = 3, 4 and 5. The complexes on the left hand side correspond to the simple solution, the one on the right to a more complicated solution with two kinds of tetrahedron chains, one being a branched chain.

Figure VIII - 9 : Projection of the structure of $Na_3Mg_2P_5O_{16}$ ($N'_{T/M}$ = 5).

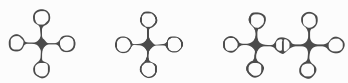


If the calculated value for $N'_{T/M}$ is not an integer, then it must correspond to an average, *i.e.* $<N'_{T/M}>$. If the value of $<N'_{T/M}>$ is between the integer i and j there will be finite chains with i tetrahedra and with j tetrahedra. The ratio of their numbers, labelled $N(iT) / N(jT)$, is given by

$$N(iT) / N(jT) = [j - <N'_{T/M}>] / (<N'_{T/M}> - i) \qquad \text{(VIII - 12)}$$

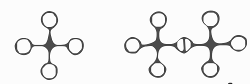
Examples of structures with anionic tetrahedron complexes consisting of two kinds of tetrahedron chains are presented in Figure VIII - 10.

$Na_2Ba_6Si_4O_{15}$
$(Si_4O_{15})^{14-}$
$<TT> = 1/2$, $<N'_{T/M}> = 4/3$
$N(1T) / N(2T) = 2/1$



1 x [- - 0] + 1 x [- - 1]

$Ag_7P_3S_{11}$
$(P_3S_{11})^{7-}$
$<TT> = 2/3$, $<N'_{T/M}> = 3/2$
$N(1T) / N(2T) = 1/1$



1 x [- - 0] + 2 x [- - 1]

Figure VIII - 10 : Two examples for compounds with anionic tetrahedron complexes consisting of two kinds of tetrahedron chains where $<TT>$ and $<N'_{T/M}>$ are not integers.

Normal valence compounds with finite chains of edge-linked tetrahedra

Edge-linked tetrahedra are never found with silicates, phosphates or sulphates, *i.e.* compounds with oxygen anions. One exception is fibrous SiO_2, a laboratory curiosity, isotypic with SiS_2, which forms an infinite straight chain of edge-linked tetrahedra isoster to the anionic tetrahedron complex in Na_3AlAs_2, shown in Figure VIII - 2.

When only edge-linked tetrahedra are allowed, then, assuming equipartition, only two kinds of base tetrahedra with *BEN* = 24 and 16 can occur, or expressed differently, base tetrahedra with codes [- - 2] and [- - 4]. With this restriction (VIII - 10b) changes to

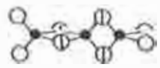
$$N(TT{=}2) \,/\, N(TT{=}4) = (4 - <TT>) \,/\, (<TT> - 2) \qquad \text{for } 2 \leq TT \leq 4 \qquad \text{(VIII - 13)}$$

The anionic tetrahedron complexes built up with these two base tetrahedra consist of straight chains of m' edge-linked tetrahedra. Their possible formulae are listed in Table VIII - 10 together with one known example for each case. Complete lists of possible general numerical formulae for m' = 2, 4 and ∞ can be found in Tables VIII - 5, 6 and 7, respectively.

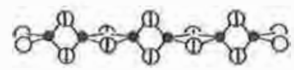
TABLE VIII - 10 : GENERAL FORMULAE AND EXAMPLES OF LINEAR MOLECULAR ANIONIC TETRAHEDRON COMPLEXES CONSTRUCTED WITH EDGE-LINKED TETRAHEDRA AS A FUNCTION OF THE NUMBER OF CENTRAL ATOMS.

m'	$C'_{m'} A_{2m'+2}$	$n/m' = 2 + 2/m$	$TT = 4(1 - 1/m')$	[- - 2] / [- - 4]	compound	complex	Figure
2	$[C'_2 A_6]$	3	2	2/0	Na_5GeP_3	$[Ge_2P_6]^{10-}$	VIII - 4
3	$[C'_3 A_8]$	2.67	2.67	2/1	$K_4Sn_3Se_8$	$[Sn_3Se_8]^{4-}$	VIII - 11
4	$[C'_4 A_{10}]$	2.5	3	1/1	$Cs_4Ga_2Se_5$	$[Ga_4Se_{10}]^{8-}$	VIII - 5
5	$[C'_5 A_{12}]$	2.4	3.2	2/3			
6	$[C'_6 A_{14}]$	2.33	3.33	1/2	$Cs_5Ga_3Se_7$	$[Ga_6Se_{14}]^{10-}$	VIII - 11
∞	$^1_\infty(C' A_2)$	2	4	0/2	Na_3AlAs_2	$^1_\infty(AlAs_2)^{3-}$	VIII - 2

The anionic tetrahedron complexes for m' = 3 and m' = 6 are presented in Figure VIII - 11. It remains unexplained why $K_4Sn_3Se_8$ (m' = 3) has only edge-linked tetrahedra, but $Na_7In_3Se_8$, shown in Figure VIII - 7, edge- and corner-linked base tetrahedra.



$[Sn_3Se_8]^{4-}$ in $K_4Sn_3Se_8$



$[Ga_6Se_{14}]^{10-}$ in $Cs_5Ga_3Se_7$

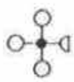
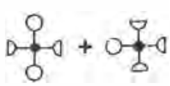
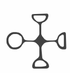
Figure VIII - 11 : Finite linear chains of edge-linked tetrahedra in the anionic complexes of $K_4Sn_3Se_8$ (m' = 3) and $Cs_5Ga_3Se_7$ (m' = 6).

⇒⇒⇒ Problem 9 in Appendix B

Silicates classified by means of the tetrahedron sharing coefficient

The TT value is an excellent parameter for a primary classification of silicates since it correlates composition, *i.e.* the $n\,/\,m'$ value, with structural features of the anionic tetrahedron complex. All silicates are normal valence compounds and the tetrahedra in the anionic complexes are practically always corner-linked. The base tetrahedra corresponding to the simplest solutions of (VIII - 7a) and (VIII - 2) are, with few exceptions, the ones used to construct the observed tetrahedron complex. In Table VIII - 11 a very simple version of a silicate classification system is presented. Many more subdivisions can be made for silicates with non-integer TT values.

TABLE VIII - 11 : CLASSIFICATION OF SILICATES BASED ON THE TETRAHEDRON SHARING COEFFICIENT TT. THE LAST COLUMN REFERS TO TETRAHEDRON COMPLEXES FORMED BY EDGE-LINKED TETRAHEDRA; SUCH TETRAHEDRON COMPLEXES DO NOT OCCUR WITH SILICATES.

$TT = 0$	$n/m' = 4$ 	**NESOSILICATES** with isolated tetrahedra olivines garnet $Ca_3Al_2[SiO_4]_3$	
		corner-linked	edge-linked
$TT = 1$	$n/m' = 7/2$ 	**SOROSILICATES** with double tetrahedra thortveitite $Sc_2[Si_2O_7]$	—
$TT = 2$	$n/m' = 3$ 	**INOSILICATES** with simple tetrahedron chains pyroxenes enstatite $Mg\,{}^{1}_{\infty}(SiO_3)$ **CYCLOSILICATES** with tetrahedron rings beryl $Be_3Al_2[Si_6O_{18}]$	double tetrahedra (Figure VIII - 4)
$TT = 5/2$	$n/m' = 11/4$ 	**INOSILICATES** with double chains amphiboles tremolite	—
$TT = 3$	$n/m' = 5/2$ 	**PHYLLOSILICATES** with sheets (or ribbons or cages) micas kaolinite $Al_2(OH)_4\,{}^{2}_{\infty}(Si_2O_5)$	chains of four tetrahedra (Figure VIII - 5)
$TT = 4$	$n/m' = 2$ 	**TECTOSILICATES** with three-dimensional frameworks quartz SiO_2 felspar $Na\,{}^{3}_{\infty}(AlSi_3O_8)$	infinite chains (Figure VIII - 6)

Problems to classify the silicates based on their n / m' value do occur when the function of the participating elements as cations or as central atoms is not evident. In certain alumino-silicates the Al atoms are cations outside the complex, however, in others they substitute for the tetrahedrally coordinated Si atoms and have to be considered as central atoms (as for example in felspar $NaAlSi_3O_8$). There are also problems when some of the oxygen atoms present do not participate on the formation of the tetrahedron complex *i.e.* they are not bonded to the Si atoms (as for example in epidote $Ca_2Al_2Fe^{3+}O(OH)\ [SiO_4]\ [Si_2O_7]$).

Examples are also the different aluminium silicates with same chemical formula Al_2SiO_5. In kyanite (≡ disthen) $Al_2^{[6]}O[SiO_4]$ one oxygen atom per formula unit is outside the complex which consists of isolated SiO_4 tetrahedra (TT = 0). But in sillimanite $Al^{[6]}\ {}^{1}_{\infty}(Al^{[4]}SiO_5)$ half of the Al atoms participate on the one-dimensional tetrahedron chain, an anionic tetrahedron complex where TT = 3.

Examples of physical measurements which provide structural information

1) Measurement of the angle between cleavage planes to distinguish between pyroxene and amphibole infinite-chain silicates.

To distinguish between pyroxenes and amphiboles, both characterized by infinite chains but of different width (see Figure VIII - 12a), one measures the angle between the pronounced cleavage planes. A projection along the direction of the chains, as presented in Figure VIII - 12b, indicates the different widths of the chain-outlining trapezoids. The pyroxenes and amphiboles structures can be presented schematically as a stacking of these trapezoids with cations inbetween the chains. For cleavage to occur, one has to select planes where neither silicon - oxygen nor cation - oxygen bonds will be broken. As demonstrated in Figure VIII - 12c, the (apparent) angle between possible cleavage planes is about 87° in the pyroxenes, but about 124° in the amphiboles.

Pyroxenes with simple chains (n / m' = 3)

Amphiboles with double chains (n / m' = $^{11}/_4$)

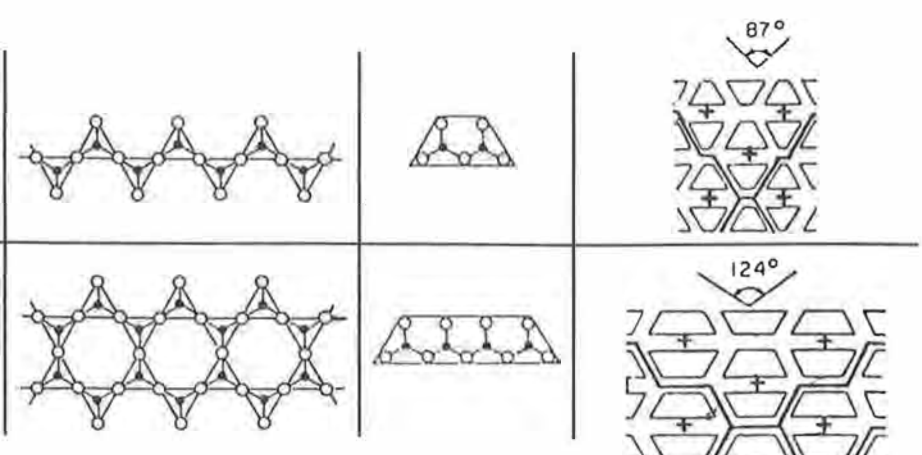


Figure VIII - 12a : Projection perpendicular to the direction of a tetrahedron chain.

Figure VIII - 12b : A projection parallel to the direction of a tetrahedron chain.

Figure VIII - 12c : Structure represented schematically as a stacking of the chain-outlining trapezoids. The ✦ symbols indicate the positions of cations in between the chains.

2) Chromatography experiments to separate different finite-chain phosphates.

When phosphates with finite anionic tetrahedron chains are dissolved in water the anionic complex is to a certain degree conserved in the aqueous solution. Since the adsorption (and desorption) rate on cellulose depends on the size and shape of the anion group, a chromatography experiment can be devised to separate anionic tetrahedron complexes with different chain length, *i.e.* $[PO_4]^{3-}$ ($N'_{T/M} = 1$), $[P_2O_7]^{4-}$ ($N'_{T/M} = 2$), $[P_3O_{10}]^{5-}$ ($N'_{T/M} = 3$), *e.t.c.*. [VIII - 4)]

Subclassification by means of the linkedness and connectedness parameters

The classification based on the tetrahedron sharing coefficient corrélates composition with base tetrahedra but does not differenciate whether these base tetrahedra are corner- or edge-linked (or both). Unfortunately these differences in linkage cannot be predicted but they seem to depend on subtle differences in the environment.

One particularly illustrating example is provided by the different anionic tetrahedron complexes of two compounds which differ only by the presence or absence of crystalline water, *i.e.* Na_2GeS_3 and $Na_2GeS_3{\cdot}7H_2O$. From $n/m' = 3$ one obtains $BEN = 24$ or $TT = 2$ and, as the most simple solution, the anionic tetrahedron complex is expected to be built up of only [- - 2] base tetrahedra. This is the case, but in the first compound these are corner-linked, forming an infinite chain (as in Na_5SnSb_3, see Figure VIII - 4), while in the second they are edge-linked, forming a cyclic molecule $[Ge_2S_6]^{4-}$ (as in Na_5GeP_3, also Figure VIII - 4). The water molecules occupy interstitial sites and do not contribute to the valence electron pool, but they influence the linkage of the GeS_4 tetrahedra.

It is the purpose of the subclassification to characterize the different kinds of base tetrahedron linkages which may occur with the different structures constructed with the same base tetrahedra. Liebau [VIII - 5)] proposed for silicates (and other normal valence compounds) two subclassification parameters, called ***L*** (linkedness) and ***s*** (connectedness), which are defined as follows :

L = **linkedness is the number of anions shared between a given tetrahedron with one of its adjacent tetrahedra.**

s = **connectedness is the (total) number of tetrahedra that share anions with the given tetrahedron.**

Example : The ***L*** and ***s*** values of the [- - 2] base tetrahedra in Na_2GeS_3 and $Na_2GeS_3{\cdot}7H_2O$.

For a corner-linked base tetrahedron in an infinite chain : ***L*** = 1, ***s*** = 2.

For an edge-linked base tetrahedron in the cyclic molecule : ***L*** = 2, ***s*** = 1.

Following the recommendation of an IUCr commission [VIII - 6)] the ***L*** and ***s*** values are written within a pair of Japanese brackets (Japanese quotation marks) and separated by a semi-colon 「***L***; ***s***」. If all adjacent tetrahedra are linked in the same way it is sufficient to write only one ***L*** value. However, if the base tetrahedron is both corner- and edge-linked, then all individual L_1, L_2, values, each one applying to one adjacent tetrahedron, have to be given. They will be separated by commas : 「L_1, L_2; ***s***」.

Examples : The ***L*** and ***s*** values of the base tetrahedra used for the construction of the anionic tetrahedron complexes of the four structures with TT or $\langle TT \rangle = 3$, presented in Figure VIII - 5.

$Li_5P_2N_5$	$Rb_4In_2S_5$	$Na_2Ge_2Se_5$	$Cs_4Ga_2Se_5$
「1; 3」	「2,1; 2」	「1; 3」	「2; 1」 + 「2; 2」

VIII - 4) Aurenge, J., Degeorges, M. & Normand, J. (1964). Bull. Soc. Chim. Fr. ***1964****, 508 - 511.*

VIII - 5) Liebau, F. (1985). "Structural Chemistry of Silicates". Berlin : Springer.

VIII - 6) Lima-de-Faria, J., Hellner, E., Liebau, F., Makovicky, E. & Parthé, E. (1990). Acta Cryst. ***A46****, 1 - 11.*

Although one has to know the crystal structure before one can write down the particular ***L*** and ***s*** values of the base tetrahedra, the value of the product (or the average of the products) corresponds to *TT* or <*TT*> which can be calculated alone from the composition. If the tetrahedron complex is built up only with one kind of base tetrahedron then (VIII - 14a) is valid.

$$TT = \langle L \rangle \cdot s \qquad \text{(VIII - 14a)}$$

where <*L*> is the average of all the *L* values (referred to all the tetrahedra which are adjacent to the base tetrahedron considered).

If there are more base tetrahedra involved, then

$$\langle TT \rangle = \langle [\langle L \rangle \cdot s] \rangle \qquad \text{(VIII - 14b)}$$

As example we come back to the four structures shown in Figure VIII - 5 with *TT* = 3 for which the ***L*** and ***s*** values of the base tetrahedra have been given a few lines above. That the product of **L** and ***s*** agrees with the *TT* value can be verified for the first three structures by using (VIII - 14a) and for $Cs_4Ga_2Se_5$ by applying (VIII - 14b).

Limits for the use of the valence electron rules

For the application of the rules presented in this chapter the assumption was made that an anionic tetrahedron complex is formed. It is not possible to state precisely when a tetrahedron complex occurs. If the central atom and the anion are from the second period of the Periodic Table then, instead of a tetrahedron complex, a planar triangular molecular complex may form, as for example with $[BO_3]^{3-}$, $[CO_3]^{2-}$ or $[NO_3]^{1-}$. Tetrahedron complexes are rarely found if the central atom is from a very high period. Central atoms from periods in between generally form tetrahedral complexes, but there are exceptions.

Example of an unexpected change of the anionic complex with homologous compounds :
One might expect that the two isoelectronic normal valence compounds Na_5GeP_3 and Cs_5GeP_3 have structures characterized by an anionic tetrahedron complex constructed with base tetrahedra having code [- - 2]. This is the case for Na_5GeP_3 where one finds edge-linked double tetrahedra (see Figure VIII - 4). Surprisingly, homologeous Cs_5GeP_3 has no tetrahedron complex, but a molecular anionic triangle complex $[Ge^{[3]}P_3]^{5-}$, isoster to $[CO_3]^{2-}$. It is surprising that the hybridization of Ge changes from sp^3 to sp^2 when the period number of the cation is increased.

The valence electron contribution of the main group elements essentially corresponds to their group number. Exceptions are the cations Tl^+, Sn^{2+} and Pb^{2+} (however Sn used as a central atom provides all four valence electrons). Early transition elements like Ti, Zr or V usually contribute all their valence electrons, but not the late transition elements. When Fe functions as cation it is mostly two-valent, but as tetrahedral central atom mostly three-valent.

For compounds with *VEC* ≥ 4 it is in principle possible that all participating elements, *i.e.* including the cations *C*, participate on the formation of a tetrahedral structure. Experimental evidence shows that ***1A***, ***2A*** and ***3T*** elements from the fourth period up are hardly ever sp^3 hybridized and are thus outside the tetrahedron complex.

IX. GENERAL VALENCE COMPOUNDS WITH ANIONIC TETRAHEDRON COMPLEXES

Definition

The general valence compounds with anionic tetrahedron complexes differ from the corresponding normal valence compounds by having either anion - anion bonds or central atom - central atom bonds and/or lone-electron pairs on the central atoms. Of the three anionic tetrahedron complexes, shown in Figure IX - 1, the first belongs to a **polyanionic valence compound**, characterized by a covalent anion - anion bond, the second and the third to a **polycationic valence compound** with a covalent central atom - central atom bond or a lone-electron pair replacing an anion neighbour, respectively. A tetrahedron where the central atom carries a lone-electron pair is called a **ψ (psi) - tetrahedron**. In analogy to compounds presented in Figure VIII- 2, also here the formation of a tetrahedral structure involving all atoms is not possible because *VEC* < 4. However, an anionic tetrahedron complex can be formed because the parameter *VEC* ', the valence electron concentration of the charged anionic tetrahedron complex, is equal or larger than 4. Below the drawings of the anionic tetrahedron complexes are shown the base tetrahedra used for their construction. For the simple examples chosen only one kind of base tetrahedron is needed for each complex and all the anions are unshared.

Na_3SiSe_4	K_3SiTe_3	Na_3AsS_3
$VEC = {}^{31}/_{8} < 4$	$VEC = {}^{25}/_{7} < 4$	$VEC = {}^{26}/_{7} < 4$
$[Si_2Se_8]^{6-}$	$[Si_2Te_6]^{6-}$	$[AsS_3]^{3-}$
$VEC_A = {}^{31}/_{4}$, $VEC' = {}^{31}/_{5}$	$VEC_A = {}^{25}/_{3}$, $VEC' = {}^{25}/_{4}$	$VEC_A = {}^{26}/_{3}$, $VEC' = {}^{26}/_{4}$

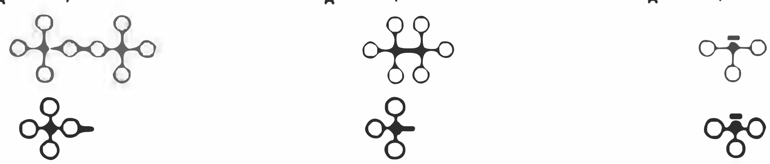


Figure IX - 1 : Three examples of anionic tetrahedron complexes in general valence compounds and the base tetrahedra needed for their construction. Central atoms are indicated by small black circles and anions by open circles. A thick line represents the homonuclear bond between anions or between central atoms or indicates the lone-electron pair on the central atom.

Valence electron rules for general valence compounds with anionic tetrahedron complexes

The two principal parameters for the application of the generalized 8 - *N* rule and of the tetrahedral structure equation to general valence compounds with anionic tetrahedron complexes are VEC_A, defined by (VIII - 1), and *VEC*', expressed by (VIII - 3).

- **Generalized 8 - *N* rule**

The C cations outside the complex do not retain any valence electrons but transfer **all** of them to the complex. Thus, the original generalized 8 - *N* rule, as given by (V - 3), has for the application to charged anionic tetrahedron complexes the slightly different form : *IX - 1)*

$$VEC_A = 8 + C'C' \,/\, (n \,/\, m') - AA \qquad \text{for } (C'_{m'} A_n)^{(m \cdot e_C)-} \qquad (IX - 1)$$

$n \,/\, m'$ is the ratio of the number of anions to the number of central atoms,

$C'C'$ is the **average** number of C' - C' bonds per central atom and/or the **average** number of valence electrons per central atom which rest inactively with the central atom in lone-electron pairs,

AA is the **average** number of A - A bonds per anion.

It is convenient to operate here with parameters which are normalized to one tetrahedron as reference unit (and not to only one atom of the tetrahedron). The parameter $C'C'$ refers by definition to one central atom. But since each tetrahedron has only one central atom, this parameter refers also to one tetrahedron. However, AA needs to be replaced by $N_{A\text{-}A}$, **the average number of anion - anion bonds per tetrahedron**, to be obtained from AA with

$$N_{A\text{-}A} = AA \cdot (n \,/\, m') \qquad (IX - 2)$$

The new formulation of the generalized 8 - *N* rule is now

$$VEC_A = 8 + [1 \,/\, (n \,/\, m')] \cdot [C'C' - N_{A\text{-}A}] \qquad \text{for } (C'_{m'} A_n)^{(m \cdot e_C)-} \qquad (IX - 3)$$

For our application it is necessary to decompose the $C'C'$ parameter in its two parts, *i.e.* the number of electrons used for lone-electron pairs and the number used for central atom - central atom bonds. The two new parameters to be used are labelled N_{lep} and $N_{C'C'}$.

N_{lep} is the average number of lone-electron pairs on the central atom per tetrahedron.

$N_{C'\text{-}C'}$ is the average number of central atom - central atom bonds per tetrahedron.

These parameters are related with $C'C'$ according to

$$C'C' = 2\, N_{lep} + N_{C'C'} \qquad (IX - 4)$$

The final version of the generalized 8 - *N* rule is thus

$$\boxed{VEC_A = 8 + [1 \,/\, (n \,/\, m')] \cdot [2\, N_{lep} + N_{C'C'} - N_{A\text{-}A}]} \qquad \text{for } (C'_{m'} A_n)^{(m \cdot e_C)-} \qquad (IX - 5)$$

Based on the VEC_A value we distinguish, as before, between a polyanionic, normal and polycationic valence compound.

If $VEC_A < 8$: **Polyanionic valence compound** where

$$\boxed{N_{A\text{-}A} = (n \,/\, m') \cdot (8 - VEC_A)} \qquad \text{if } N_{lep} = N_{C'\text{-}C'} = 0 \qquad (IX - 6)$$

If $VEC_A = 8$: **Normal valence compound** where $N_{lep} = N_{C'\text{-}C'} = N_{A\text{-}A} = 0.$

If $VEC_A > 8$: **Polycationic valence compound** where

$$\boxed{C'C' \equiv 2\, N_{lep} + N_{C'\text{-}C'} = (n \,/\, m') \cdot (VEC_A - 8)} \qquad \text{if } N_{A\text{-}A} = 0 \qquad (IX - 7)$$

Note that there are bonds between and/or lone-electron pairs on the **central atoms** C' but **not** the **cations** C. The label "polycationic" is kept for historic reasons.

IX - 1) Parthé, E. & Chabot, B. (1990). Acta Cryst. B46, 7 - 23.

- Tetrahedral structure equation

All what has been stated in Chapter VIII on the application of the tetrahedral structure equation to normal valence compounds with anionic tetrahedron complexes is equally valid for general valence compounds.

Referring, for example, to the general valence compounds of Figure IX - 1, one calculates, based on the listed *VEC'* values and (VIII - 6), that the non-cyclic molecular anionic tetrahedron complexes consist of 10, 8 and 4 atoms, respectively. Note should be taken, that the lone-electron pair attached to the central atom of a ψ-tetrahedron is included in the value calculated for N'_{NBO}. Thus, in the case of $[AsS_3]^{2-}$ (third drawing in Figure IX - 1), one obtains with (VIII - 5) that $N'_{NBO} = {}^{10}/_4$, *i.e.* there are ten lone-electron pairs per isolated ψ-tetrahedron.

Base tetrahedra for general valence compounds

In Figure IX - 2 is presented a gallery of graph drawings of all 40 possible base tetrahedra for general and normal valence compounds with unshared anions and/or anions shared between two tetrahedra (assuming equipartition). The drawings are arranged on a grid with an *n / m'* scale as abscissa and with an $(n / m') \cdot (VEC_A - 8)$ scale as ordinate. According to (IX - 7) the positive values on the ordinate scale can be reinterpreted as *C'C'* values and the negative values, corresponding to (IX - 6), as $N_{A\text{-}A}$ values. On the horizontal middle line where $(n / m') \cdot (VEC_A - 8) = 0$, *i.e.* $VEC_A = 8$ are aligned the base tetrahedra for normal valence compounds (which were shown before in the top part of Table VIII - 2). In the upper half of Figure IX - 2 are found the base tetrahedra needed for the construction of complexes of polycationic valence compounds and in the lower half those used for complexes of polyanionic valence compounds. The base tetrahedra drawings have been positioned in Figure IX - 2 so that the black circles representing the central atoms are on a grid position which corresponds to the *C'C'* or $N_{A\text{-}A}$ value and the *n / m'* value of the base tetrahedron. There are, however, four exceptions, *i.e.* there exist four pairs of base tetrahedra, each pair having same *C'C'* and *n / m'* value although the base tetrahedra are different. One base tetrahedron drawing of each pair is at the correct grid point [IX - 2] and the second displaced to the lower left.

***BEN* values and base tetrahedron codes**

All the base tetrahedra shown in Figure IX - 2 can be identified by their *n / m'* values and the *BEN* numbers which are written within a rectangular frame on the upper right of each drawing. To derive the *BEN* value of the new base tetrahedra shown in Figure IX - 2, the electron counting rules of Chapter VIII, have to be extended with three complementary rules :

- An anion which extends a covalent bond to another anion contributes only 7 electrons to its base tetrahedron.
- A central atom which carries a lone-electron pair contributes two electrons.
- A central atom which extend one covalent bond to another central atom contributes one electron.

As an example we calculate the *BEN* numbers of the three base tetrahedra, shown in Figure IX - 1. One obtains the *BEN* values 31, 25 and 26, respectively. Drawings of these base tetrahedra can be found in Figure IX - 2 at the proper $N_{A\text{-}A}$ or *C'C'* and *n / m'* grid points.

IX-2) At n/m' = 1 with C'C' = 3 and 4, further at C'C' = 2 with n/m' = 1.5 and 2.

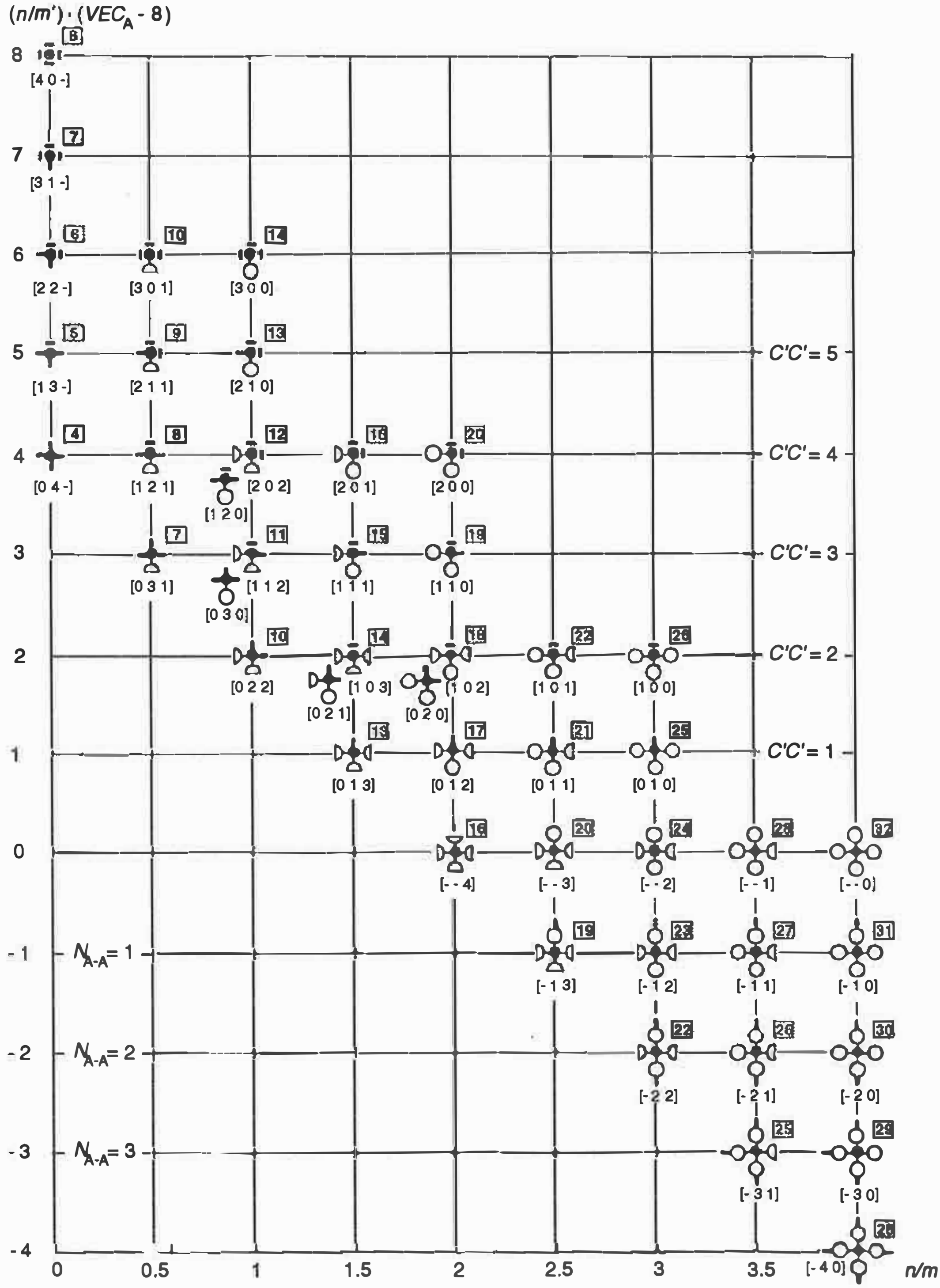


Figure IX - 2 : Drawings of the 40 possible base tetrahedra with unshared anions and/or anions shared between two tetrahedra (together with 5 degenerated base tetrahedra at n / m' = 0), the BEN values and the base tetrahedron codes. The positions of the filled circles (central atoms) of the base tetrahedron drawings on the (n / m') · (VEC$_A$ - 8) [≡ BEN - 8 (n / m')] versus n / m' grid correspond to the parameter values of the base tetrahedra. Two base tetrahedra are possible for BEN = 11, 12, 14 (at n / m' = 1.5) and 18. For each pair the drawing on the lower left should coincide with the one on the upper right which is positioned at the proper grid point.

The base tetrahedra used with normal valence compounds can be unambiguously identified with their *BEN* numbers alone. However, for proper identification within the much larger gallery of base tetrahedra graph drawings in Figure IX - 2 one needs to register both the *BEN* number and the n/m' ratio. This is necessary because there exist different base tetrahedra with same *BEN* numbers but different n/m' ratios. For four pairs of base tetrahedra even this is not enough. A distinction between both members of each pair which have same *BEN* number and n/m' value will be possible only with the base tetrahedron codes, to be discussed below.
The *BEN* values in Figure IX - 2 are all integers because only base tetrahedra with unshared anions and/or anions shared between two tetrahedra are considered. The *BEN* values vary, vertically, for a given n/m' in regular steps of one and, horizontally, in regular steps of four. This makes the *BEN* number, calculated with (VIII - 8), a convenient parameter to use when searching for the kind of base tetrahedra involved in the construction of an anionic tetrahedron complex. Particularly for general valence compounds there is one simple method for doing this and it is based on *BEN* numbers and tables with base tetrahedron drawings.

In the following paragraph will be presented a summary of the numerical relations between the *BEN* number and the different parameters which are used to describe the geometrical features of a base tetrahedron. The reader in a hurry can skip this paragraph. He can see all the features of base tetrahedra by looking at the drawings in Figure IX - 2.

For a normal valence compound with VEC_A [$\equiv BEN / (n/m')$] = 8 :

$$BEN = 32 - 4\,TT \qquad \text{for } TT \leq 4 \qquad \text{(IX - 8)}$$

For a polyanionic valence compound with VEC_A [$\equiv BEN / (n/m')$] < 8 :

$$BEN = 32 - N_{A\text{-}A} - 4\,TT \qquad \text{for } TT \leq 4 - N_{A\text{-}A} \qquad \text{(IX - 9)}$$

For a polycationic valence compound with VEC_A [$\equiv BEN / (n/m')$] > 8 :

$$BEN = 32 - 6\,N_{lep} - 7\,N_{C'\text{-}C'} - 4\,TT \qquad \text{for } TT \leq 4 - N_{lep} - N_{C'\text{-}C'} \qquad \text{(IX - 10)}$$

The total number of lone-electron pairs of a base tetrahedron can be obtained from the *BEN* number :

$$N'_{NBO} \cdot (n + m') / m' = \text{BEN} - 4 \cdot [(n/m') + 1] \qquad \text{(IX - 11)}$$

Equations (IX - 8 to 10) are valid only for base tetrahedra with unshared anions and/or anions shared between two tetrahedra, but (IX - 11) for all kinds of base tetrahedra.

The base tetrahedra can alternatively be described with base tetrahedron codes which, compared to *BEN* numbers, are more elaborate but relate more to the structural features of base tetrahedra. Below each drawing in Figure IX - 2 is given the base tetrahedron code which can be identified by the surrounding square brackets. IX - 3) Three kinds of code versions have to be considered, depending on the number of hyphens within the square brackets.

[- - *TT*] is the code for a base tetrahedron without an anion - anion or central atom - central atom bond and without a lone-electron pair on the central atom. The single numeral within the square brackets after the two hyphens corresponds to the *TT* value. These base tetrahedra are the only ones which occur in the anionic tetrahedron complexes of normal valence compounds where VEC_A = 8.

IX - 3) The notation of the base tetrahedra presented here differs from the notation used in the first edition of this book. The new notation relates more directly to the features of a base tetrahedron.

[- $N_{A\text{-}A}$ TT] is used for a base tetrahedron where there exists an anion - anion bond, which is indicated in the drawing by a tangling heavy line originating from an open circle. The two parameters within the square brackets after the hyphen are the $N_{A\text{-}A}$ and TT value. Base tetrahedra with these codes are found with polyanionic valence vompounds where $VEC_A < 8$.

[N_{lep} $N_{C'\text{-}C'}$ TT] represents the code for a base tetrahedron with a lone-electron pair and/or a central atom - central atom bond. In the drawings the lone electron pair is shown by a thick short line associated to the filled circle, while the central atom - central atom bond is represented by a tangling heavy line originating from a filled circle. The three parameters within the square bracket are the N_{lep}, $N_{C'\text{-}C'}$ and TT values. The $C'C'$ value of each base tetrahedron is determined by (IX - 4). Base tetrahedra carrying the [N_{lep} $N_{C'\text{-}C'}$ TT] code are found with polycationic valence compounds for which $VEC_A > 8$. IX - 4) TT has no value in the five degenerated base tetrahedra with $n/m' = 0$.

Here follows a summary of the equations which can be used to derive the base tetrahedron codes from known BEN and n/m' values (anions unshared and/or shared between two tetrahedra and equipartition).

For a base tetrahedron with code [- - TT] where $VEC_A \equiv BEN/(n/m') = 8$:

$$TT = 8 - BEN/4 \qquad \text{for } 0 \le TT \le 4 \qquad \text{(IX - 12)}$$

For a base tetrahedron with code [- $N_{A\text{-}A}$ TT] where $VEC_A \equiv BEN/(n/m') < 8$:

$$N_{A\text{-}A} = 8(n/m') - BEN \qquad \text{for } 0 < N_{A\text{-}A} \le 4 - TT \qquad \text{(IX - 13)}$$

$$TT = 8 - (BEN + N_{A\text{-}A})/4 \qquad \text{for } 0 \le TT \le 4 - N_{A\text{-}A} \qquad \text{(IX - 14)}$$

For a base tetrahedron with code [N_{lep} $N_{C'\text{-}C'}$ TT] where $VEC_A \equiv BEN/(n/m') > 8$:

$$N_{lep} = [BEN - 8(n/m')]/2 \qquad \text{when } BEN - 8(n/m') \text{ even} \qquad \text{(IX - 15a)}$$

or

$$N_{lep} = [BEN - 8(n/m')]/2 - 1/2 \qquad \text{when } BEN - 8(n/m') \text{ odd} \qquad \text{(IX - 15b)}$$

$$N_{C'\text{-}C'} = BEN - 8(n/m') - 2N_{lep} \qquad \text{for } 0 \le N_{C'\text{-}C'} \le 4 - N_{lep} \qquad \text{(IX - 16)}$$

$$TT = 8 + 6(n/m') - BEN - N_{C'\text{-}C'} \qquad \text{for } 0 \le TT \le 4 - N_{lep} - N_{C'\text{-}C'} \qquad \text{(IX - 17)}$$

If $N_{lep} > 0$ the calculation of (IX -16) and (IX - 17) has to be repeated with a N_{lep} value which is smaller by 1, then with N_{lep} smaller by 2, and further in steps of one down to $N_{lep} = 0$. Only those solutions can be accepted which are within the specified limits

Three examples for the calculation of the base tetrahedron codes :

1) $BEN = 18$ and $n/m' = 2$: $BEN/(n/m') = 9 > 8$; $N_{lep} = 1$.

Calculation with $N_{lep} = 1$	Calculation with $N_{lep} = 0$
$N_{C'\text{-}C'} = 0$; $TT = 2 \Rightarrow$ [1 0 2]	$N_{C'\text{-}C'} = 2$; $TT = 0 \Rightarrow$ [0 2 0]

In Figure IX - 2 the two base tetrahedra at $BEN = 18$ and $n/m' = 2$ have the codes [1 0 2] and [0 2 0].

2) $BEN = 12$ and $n/m' = 1$: $BEN/(n/m') = 12 > 8$; $N_{lep} = 2$.

Calculation with $N_{lep} = 2$	Calculation with $N_{lep} = 1$	Calculation with $N_{lep} = 0$
$N_{C'\text{-}C'} = 0$; $TT = 2 \Rightarrow$ [2 0 2]	$N_{C'\text{-}C'} = 2$; $TT = 0 \Rightarrow$ [1 2 0]	$N_{C'\text{-}C'} = 4$; $TT = -2 \Rightarrow$ **Impossible**

The TT value calulated for $N_{lep} = 0$ is negative. Thus only [2 0 2] and [1 2 0] are solutions.

IX - 4) The term "polycationic valence compound" is not fully appropriate but it has been retained here for historic reasons. It would have been more correct to state that this is compound where the central atom keeps electrons which are not used for bonding with the anions. The original term should have been used when only [0 $N_{C'\text{-}C'}$ TT] base tetrahedra are involved.

3) BEN = 29 and n/m' = 3.5 : $BEN/(n/m') = 8^2/_7 > 8$; $N_{lep} = 0$.

Calculation with $N_{lep} = 0$

$\boxed{N_{C'-C'} = 1;\ TT = -1 \Rightarrow \text{Impossible}}$

Since TT is calulated to have a (not allowed) negative value a base tetrahedron with this code **cannot** exist and is **not** found in Figure IX - 2.

To derive the equations above we have used relations for the tetrahedron sharing coefficient TT for which the proof has not yet been given. This will be done now. The reader not interested in these derivations can jump immediatly to the next subchapter written with normal size characters.

General relation between a polyhedron sharing coefficient and the n/m' ratio of a complex

We consider an anion complex $C'_{m'}A_n$ built up of C' centered polyhedra of a not specified kind (tetrahedra, prisms, octahedra *etc.*). We define as the **polyhedron sharing coefficient** PP the average number of $C' - A - C'$ links which originate from the central atom of a polyhedron. The value of PP depends on

- $N_{C'-A}$: the average number of anion neighbours of a central atom and
- n/m' : the ratio of the anions to the central atoms.

A relation between PP and n/m' is obtained by combining the following three equations : IX - 1)

$$N_{C'-A} = N_0 + N_1 + N_2 + N_3 + \qquad \text{(IX - 18)}$$
$$n/m' = N_0 + {}^1/_2 \cdot N_1 + {}^1/_3 \cdot N_2 + {}^1/_4 \cdot N_3 \qquad \text{(IX - 19)}$$
$$PP = N_1 + 2 \cdot N_2 + 3 \cdot N_3 + \qquad \text{(IX - 20)}$$

- N_0 is the mean number of "unshared" anions per polyhedron
- N_l is the mean number of shared anions per polyhedron which participate on l $C' - A - C'$ links to other polyhedra.

To simplify the results we assume **equipartition** of the $C' - A - C'$ links over the anion corners of a polyhedron. This means there is either no or only a difference of one in the number of $C' - A - C'$ links on which the different anions of a polyhedron participate. For the case of equipartition only one (or two) value(s) of N_l are not zero, *i.e.* N_k (or N_k and N_{k+1}). Combining (IX - 18 to 20) the N values drop out and it results (IX - 21) which relates PP to n/m' for the case of equipartition.

$$PP = k \cdot [2 \cdot N_{C'-A} - (k+1) \cdot (n/m')] \quad \text{with } k < [N_{C'-A}/(n/m')] \le k+1 \qquad \text{(IX - 21)}$$

The parameter k corresponds to the number of $C' - A - C'$ links on which each anion of the polyhedron participates or - if the number of the links is not the same for all anions - to the larger number (which for the case of equipartition differs from the smaller number only by 1). Examples of k values for combinations of anion ligands, which are permitted by equipartition, are shown in Figure IX - 3.

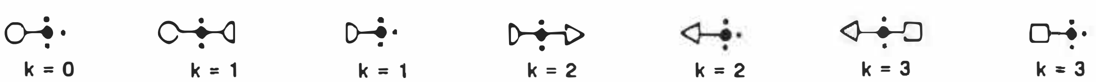


Figure IX - 3 : Anion ligand combinations for the case of equipartition and the corresponding k values. The points around the central atoms indicate other ligands of the same kind as the ligand(s) drawn.

Below will be used versions of (IX - 21) with particular numerical values inserted for the k parameter :

$k = 0$	$PP = 0$	for $N_{C'-A} = n/m'$	(IX - 21a)
$k = 1$	$PP = 1 \cdot [2 \cdot N_{C'-A} - 2 \cdot (n/m')]$	for $N_{C'-A} \ge n/m' \ge N_{C'-A}/2$	(IX - 21b)
$k = 2$	$PP = 2 \cdot [2 \cdot N_{C'-A} - 3 \cdot (n/m')]$	for $N_{C'-A}/2 \ge n/m' \ge N_{C'-A}/3$	(IX - 21c)
$k = 3$	$PP = 3 \cdot [2 \cdot N_{C'-A} - 4 \cdot (n/m')]$	for $N_{C'-A}/3 \ge n/m' \ge N_{C'-A}/4$	(IX - 21d)

Depending on the numerical value inserted for $N_{C'-A}$ one can formulate equations relating different sharing coefficient to the n/m' ratio of the compound. For the **tetrahedron sharing coefficient** TT one inserts $N_{C'-A} = 4$ (see below), but $N_{C'-A} = 6$ for the **octahedron sharing coefficient** OO. IX - 5)

IX - 5) The equation for the octahedron sharing coefficient OO for k = 1, using (IX - 21b), is $OO = 12 - 2 \cdot n/m'$. An example of a structure with isolated octahedra is - $[S^{[6o]}F_6]$ HT (OO = 0) and with corner-linked octahedra : - ${}^1_\infty(U^{[6o]}F_5)$ alpha (OO = 2), ${}^2_\infty(Fe_2^{[6o]}Cl_9)^{3-}$ in trigonal $Cs_3Fe_2Cl_9$ (OO = 3), ${}^2_\infty(Ni^{[6o]}F_4)^{2-}$ in K_2NiF_4 (OO = 4), ${}^2_\infty(Ti_2^{[6o]}O_7)^{6-}$ in $Sr_3Ti_2O_7$ (OO = 5) and ${}^3_\infty(Ti^{[6o]}O_3)^{2-}$ in $CaTiO_3$ (OO = 6). For OO = 4, 5, 6 see Figure XI - 1.

Equations for the tetrahedron sharing coefficient *TT*

In normal and polyanionic valence compounds with anionic tetrahedron complexes each central atom has four anion neighbours, thus $N_{C'-A} = 4$. Inserting this value into (IX - 21b to 21d) one obtains the three *TT* versus n / m' equations for normal valence compounds (VIII - 7a to 7c), presented in Table VIII - 2. These equations are equally valid for polyanionic valence compounds because also here $N_{C'-A} = 4$.
In polycationic valence compounds, however, the value of $N_{C'-A}$ is smaller than four as some anion neighbours of the central atom have been replaced by lone-electron pairs and/or $C' - C'$ bonds. Thus

$$N_{C'-A} = 4 - N_{lep} - N_{C'-C'} \qquad \text{(IX - 22)}$$

The number of unknowns can be reduced from two to one by introducing $C'C'$ in the form of (IX - 4) :

$$N_{C'-A} = 4 - {}^1/_2 \cdot (C'C' + N_{C'-C'}) \qquad \text{(IX - 23)}$$

For the further discussions we shall limit ourselves to the case where the anions are unshared and/or shared between two tetrahedra, *i.e.* $k = 1$. Inserting (IX - 23) into (IX - 21b) results in

$$\boxed{TT + N_{C'-C'} = 8 - 2\cdot(n / m') - C'C'} \text{ for } 4 - {}^1/_2\cdot(C'C' + N_{C'-C'}) \geq n / m' \geq {}^1/_2\cdot[4 - {}^1/_2\cdot(C'C' + N_{C'-C'})] \qquad \text{(IX - 24)}$$

The right hand side of (IX - 24) can be calculated from the composition of the compound, however, there are different solutions for *TT*, varying between TT_{min} and TT_{max}, depending on the value of $N_{C'-C'}$.

A simplification of (IX - 24) is possible. The experimental evidence shows that with few exceptions the anionic tetrahedron complexes are built up with only the minimum number of different kinds of base tetrahedra. Complexes with *BEN* and n / m' values for which in Figure IX - 2 a base tetrahedron can be found will with high probability be constructed only with this base tetrahedron. With polycationic complexes there is, however, the problem that for four particular *BEN* and n / m' values there exist two different base tetrahedra in Figure IX - 2. If we ignore these cases we note that base tetrahedra with $C'C' = 1$ have one $C' - C'$ bond, with $C'C' = 2$ one lone-electron pair, with $C'C' = 3$ one $C' - C'$ bond and one lone-electron pair and with $C'C' = 4$ two lone-electron pairs. This regularity allows us to formulate also for polycationic valence compounds *TT* versus n / m' equations without unknowns.

$$TT = 6 - 2 \cdot n / m' \begin{cases} \text{For } C'C' = 1 \text{ with } N_{lep} = 0,\ N_{C'-C'} = 1 \text{ and } n / m' = {}^3/_2,\ 2,\ {}^5/_2,\ 3 \\ \text{For } C'C' = 2 \text{ with } N_{lep} = 1,\ N_{C'-C'} = 0 \text{ and } n / m' = {}^5/_2,\ 3 \end{cases} \qquad \text{(IX - 25a)}$$

$$TT = 4 - 2 \cdot n / m' \begin{cases} \text{For } C'C' = 3 \text{ with } N_{lep} = 1,\ N_{C'-C'} = 1 \text{ and } n / m' = {}^3/_2,\ 2 \\ \text{For } C'C' = 4 \text{ with } N_{lep} = 2,\ N_{C'-C'} = 0 \text{ and } n / m' = {}^3/_2,\ 2 \end{cases} \qquad \text{(IX - 25b)}$$

Two examples where (IX - 25a) cannot be used because n / m' is outside the permitted range :

- $Li_2Cu^{2+}{}_3Se_4O_{14}$: $C'C' = 1$, $n / m' = {}^7/_2$ and $BEN = 29$. For these values exists no base tetrahedron. Thus the complex must consist of two different ones. See Figure IX - 6 and 7.
- SiI_2 and SeO_2: $C'C' = 2$, $n / m' = 2$ and $BEN = 18$. As seen in Figure IX - 2 two different base tetrahedra are possible for these values. SiI_2 is built up with [0 2 0] base tetrahedra, but isoelectronic SeO_2 with [1 0 2] base tetrahedra.

How to find the possible base tetrahedra of an anionic tetrahedron complex

To find the possible base tetrahedron(a) which might be used for the construction of an anionic tetrahedron complex one proceeds in the following way :
As first step, starting from the known chemical composition of the compound, one calculates VEC_A, using (VIII - 1) and with (VIII - 8) the value of *BEN*.

If $VEC_A = 8$ then the compound is a normal valence compound. By means of (VIII - 7) one can obtain the value of TT. The complete gallery of base tetrahedra for tetrahedron complexes of normal valence compounds is presented in Table VIII - 2. If no base tetrahedron is found in the table which has the same TT or BEN values as the compound, then the calculated values must be average values. The appropriate base tetrahedron mixture can be obtained with the help of (VIII - 10a) or (VIII - 10b).

If $VEC_A \neq 8$ then the compound is a general valence compound. Depending on the value of VEC_A one calculates either $N_{A\text{-}A}$ with (IX - 6) or $C'C'$ with (IX - 7). The $N_{A\text{-}A}$ or $C'C'$ value corresponds in Figure IX - 2 to the ordinate and the n / m' value to the abscissa of a point which represents the compound. This compound point will be marked with the BEN value of the compound, calculated with (VIII - 8). The following possibilities have to be considered :

A) The compound point has an integral BEN value and coincides with the position of a central atom of a base tetrahedron drawing in Figure IX - 2.

A1) The most probable and most common solution is the one where the anionic tetrahedron complex is constructed with only that kind of base tetrahedron. In the four cases where two base tetrahedra are possible for a given BEN and n / m' value, *i.e.* at BEN = 11, 12, 14 (when $n / m' = 1.5$) and 18, the anionic tetrahedron complexes can be built up with either one and they are equally probable.

A2) A less probable solution is one where different kinds of base tetrahedra occur although there is one base tetrahedron in the gallery which has the same BEN value as the one calculated for the compound and with which it would have been possible to construct alone the anionic tetrahedron complex. The average of the BEN values of the different base tetrahedra involved in the construction of the tetrahedron complex will correspond to the BEN value calculated from the composition of the compound. If there are only two kinds of base tetrahedra involved, then a straight line connecting these two base tetrahedron points in Figure IX - 2 must pass through the compound point. The ratio of the numbers of the two different kinds of base tetrahedra can be determined using a lever rule based on BEN values which can be expressed formally by (VIII - 10a).

B) The compound point does not coincide with the position of a central atom of a base tetrahedron drawing in Figure IX - 2. In most cases the calculated BEN value will not be an integer. More than one kind of base tetrahedron must be involved in the construction of the anionic tetrahedron complex.

B1) The most probable and most common solution is the one where a minimum number of different kinds of base tetrahedra is involved. If the compound point in Figure IX - 2 is on a connecting line between two base tetrahedron points, then these two base tetrahedra will be used for the construction of the tetrahedron complex. The ratio of their numbers can be obtained from the ratio of the distances between the compound point and the base tetrahedron points by means of the lever rule using BEN values (VIII - 10a). If it is possible to draw other connecting lines between other base tetrahedron points, which also pass also through the compound point, then these base tetrahedron pairs have also to be considered as a possibility for the construction of the tetrahedron complex of the compound. If the compound point is not on a connecting line between two base tetrahedron points, then at least three different kinds of base tetrahedra are necessary.

B2) The less probable solution is one where more than the minimum number of different kinds of base tetrahedra are involved in the construction of the anionic tetrahedron complex.

Calculation of the base tetrahedron ratios for complexes with three kinds of base tetrahedra

If there are three different base tetrahedra present, the lever rule using *BEN* values is not sufficient to determine the ratio of the numbers of the base tetrahedra. The coordinates of a compound point in Figure IX - 2 are expressed in terms of $\langle n/m'\rangle$ and $\langle C'C'\rangle$ or $\langle N_{A\text{-}A}\rangle$ values for which additional lever rules can be formulated. In analogy to (VIII - 10a) one finds for the number ratios of base tetrahedra with different n/m', $C'C'$ or $N_{A\text{-}A}$ values, the following equations :

$$N(n/m')_1 / N(n/m')_2 = [(n/m')_2 - \langle n/m'\rangle] / [\langle n/m'\rangle - (n/m')_1] \qquad \text{(IX - 26)}$$

and

$$N(C'C')_1 / N(C'C')_2 = [(C'C')_2 - \langle C'C'\rangle] / [\langle C'C'\rangle - (C'C')_1] \qquad \text{(IX - 27a)}$$

or

$$N(N_{A\text{-}A})_1 / N(N_{A\text{-}A})_2 = [(N_{A\text{-}A})_2 - \langle N_{A\text{-}A}\rangle] / [\langle N_{A\text{-}A}\rangle - (N_{A\text{-}A})_1] \qquad \text{(IX - 27b)}$$

Within the three different base tetrahedra there are always two which either have the same n/m' or $C'C'$ (or $N_{A\text{-}A}$) value or they are equally far apart from the average value calculated for the compound.

We present as a demonstration the calculation for $K_6Sn_3As_5$.

$K_6Sn_3As_5$: $VEC_A = 8^3/_5$, $C'C' = 1$, $\langle n/m'\rangle = {}^5/_3$, $\langle BEN\rangle = 14^1/_3$

Simple solution (not observed) with two kinds of base tetrahedra :

$N(BEN{=}13) / N(BEN{=}17) = 2$ from (VIII - 10a)

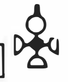
More complicated solution (observed) with three kinds of base tetrahedra, *i.e.* $BEN = 13$, 14 and 16. The base tetrahedra with $BEN = 13$ and 14 have same n/m' value and those with $BEN = 14$ and 16 have an average of $\langle C'C'\rangle = 1$.

$[N(BEN{=}13) + N(BEN{=}14)] / N(BEN{=}16) = 2$ from (IX - 26)

$N(BEN{=}14) / N(BEN{=}16) = 1$ from (IX - 27a)

Thus $N(BEN{=}13) / N(BEN{=}14) / N(BEN{=}16) = 1 : 1 : 1$

TABLE IX - 1 : POLYANIONIC VALENCE COMPOUNDS WHERE THE ANIONIC TETRAHEDRON COMPLEX IS CONSTRUCTED OF ONLY ONE KIND OF BASE TETRAHEDRON.

	$n/m' = 2.5$	$n/m' = 3$	$n/m' = 3.5$	$n/m' = 4$
$N_{A\text{-}A} = 1$	19  [-13] $(3_25_5)^{7-}$ $Na_7Al_2Sb_5$	23  [-12] $(35_3)^{5-}$ $Ca_5Ga_2As_6$ $(46_3)^{1-}$ $CsSiTe_3$	27  [-11] $(4_26_7)^{4-}$ $Cs_4Sn_2Te_7$	31  [-10] $(46_4)^{3-}$ Na_3SiSe_4 $(66_4)^{1-}$ KSO_4
$N_{A\text{-}A} = 2$		22  [-22] $(45_3)^{3-}$ $AlSiP_3$ $(36_3)^{1-}$ $Tl^{+}BS_3$		30  [-20] $(46_4)^{2-}$ Cs_2GeSe_4
$N_{A\text{-}A} = 3$			25  [-31] $(3_26_7)^{2-}$ $Na_2B_2Se_7$	

Polyanionic tetrahedron complexes having unshared and/or half-shared anions

A1) The *BEN* value calculated from the composition of the compound agrees with a framed *BEN* value in Figure IX - 2. The anionic tetrahedron complex is built up only of one kind of base tetrahedron. A list of general numerical formulae of the different polyanionic tetrahedron complexes together with one known example is given in Table IX - 1. The only non-cyclic molecular tetrahedron complex occurs with *BEN* = 31 and consists of 10 atoms (*VEC'* = 6.2).

B1) The *BEN* value does not agree with a *BEN* value listed in Table IX - 2. For the construction of the tetrahedron complex two different base tetrahedra are selected from the gallery such that their average corresponds to the value calculated for the compound. The method is demonstrated in Figure IX - 4 with $Na_5In_2Te_6$ and $Tl^+{}_3B_3S_{10}$.

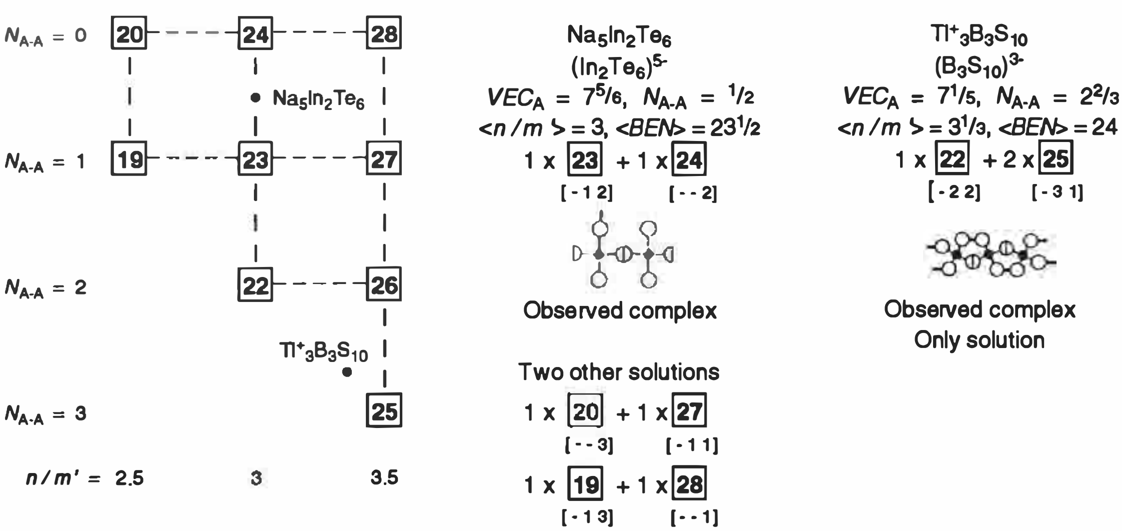


Figure IX - 4 : Positions of compound points for $Na_5In_2Te_6$ and $Tl^+{}_3B_3S_{10}$ on the $(n/m') \cdot (VEC_A - 8)$ versus n/m' grid, the selection of possible base tetrahedron pairs using a lever rule and the observed tetrahedron complexes. The two other base tetrahedron pair solutions for $Na_5In_2Te_6$, given in the lower part, differ only in the distribution of the anions shared between two tetrahedra.

Polycationic tetrahedron complexes having unshared and/or half-shared anions

A1) The *BEN* value calculated from the composition of the compound agrees with a framed *BEN* value in Figure IX - 2. The anionic tetrahedron complex is built up of only one kind of base tetrahedron. A list of general numerical formulae of the different polycationic tetrahedron complexes together with one known example each is given in Table IX - 2. For two *BEN* values exist two different kinds of base tetrahedra, *i.e.* for *BEN* = 14 : [1 0 3] and [0 2 1] and for *BEN* = 18 : [1 0 2] and [0 2 0]. Non-cyclic molecular tetrahedron complexes occur with *BEN* = 25 ($N'_{A/M}$ = 8), 26 ($N'_{A/M}$ = 4), 22 ($N'_{A/M}$ = 7), 19 ($N'_{A/M}$ = 6), 20 ($N'_{A/M}$ = 3) and 16 ($N'_{A/M}$ = 5).

A2) The calculated *BEN* value agrees with a value in Figure IX - 2, but a less probable solution is realized where two tetrahedra are involved for which <*BEN*> corresponds to the calculated value. In Figure IX - 5 are presented as example the complexes of three compounds with *BEN* = 22 and n/m' = 5/2. The complex of $NaSn_2F_5$ is built up with only one base tetrahedron, but for $K_2S_2O_5$ and $Ba_2As_2Se_5$ two different ones are used.

TABLE IX - 2 : POLYCATIONIC VALENCE COMPOUNDS WITH COMPLEXES BUILT UP WITH ONLY ONE KIND OF BASE TETRAHEDRON. THE LETTER L OR R BEFORE THE CHEMICAL FORMULAE LISTED UNDER *BEN* = 14 AND 18 INDICATES THAT THE LEFT OR RIGHT BASE TETRAHEDRON IS USED FOR THE CONSTRUCTION OF THE COMPLEX.

	n/m' = 1.5		n/m' = 2		n/m' = 2.5		n/m' = 3	
$C'C'$ = 4	$\boxed{16}$	[2 0 1]	$\boxed{20}$ $(76_2)^{1-}$ $(67_2)^{\pm 0}$	[2 0 0] $NaClO_2$ - SCl_2				
$C'C'$ = 3	$\boxed{15}$	[1 1 1]	$\boxed{19}$ $(56_2)^{2-}$ $(66_2)^{1-}$ $(57_2)^{\pm 0}$	[1 1 0] K_2AsTe_2 $NaSO_2$ - PI_2				
$C'C'$ = 2	$\boxed{14}$ [1 0 3] $(3_26_3)^{\pm 0}$	[0 2 1] L - As_2S_3	$\boxed{18}$ [1 0 2] $(35_2)^{5-}$ $(46_2)^{2-}$ $(56_2)^{1-}$ $(66_2)^{\pm 0}$ $(47_2)^{\pm 0}$	[0 2 0] R $Ca_5Ga_2N_4$ L $BaSnS_2$ R $CsPO_2$ aq L $KAsSe_2$ L - SeO_2 R - SiI_2	$\boxed{22}$ $(5_26_5)^{4-}$ $(6_26_5)^{2-}$ $(4_27_5)^{1-}$	[1 0 1] $Sr_2Sb_2S_5$ aq $ZnSe_2O_5$ $NaSn_2F_5$	$\boxed{26}$ $(56_3)^{3-}$ $(66_3)^{2-}$ $(76_3)^{1-}$ $(47_3)^{1-}$ $(57_3)^{\pm 0}$	[1 0 0] Ag_3AsS_3 Na_2SO_3 $KClO_3$ $CsSnCl_3$ - $AsBr_3$
$C'C'$ = 1	$\boxed{13}$ $(3_26_3)^{2-}$ $(4_26_3)^{\pm 0}$	[0 1 3] $Na_2Ga_2Se_3$ - Si_2Te_3	$\boxed{17}$ $(45_2)^{3-}$	[0 1 2] $Sr_3Si_2As_4$	$\boxed{21}$ $(4_26_5)^{4-}$	[0 1 1] $Ba_2Ge_2Te_5$	$\boxed{25}$ $(46_3)^{3-}$ $(56_3)^{2-}$ $(66_3)^{1-}$ $(37_3)^{1-}$ $(47_3)^{\pm 0}$	[0 1 0] K_3SiTe_3 $HgPS_3$ KSO_3 $LiGaBr_3$ - CCl_3

B1) The calculated *BEN* value corresponds to an average because it does not agree with a *BEN* value in Figure IX - 2. Two or more base tetrahedra are involved in the construction of the anionic tetrahedron complex. The ratio of their numbers can be determined by the lever rules (VIII - 10a), (IX - 26) and (IX - 27a).

$NaSn_2F_5$	$K_2S_2O_5$	$Ba_2As_2Se_5$
$(Sn_2F_5)^{1-}$	$(S_2O_5)^{2-}$	$(As_2Se_5)^{4-}$
VEC_A = 8 4/5, $C'C'$ = 2	VEC_A = 8 4/5, $\langle C'C' \rangle$ = 2	VEC_A = 8 4/5, $C'C'$ = 2
n/m' = 5/2, BEN = 22	$\langle n/m' \rangle$ = 5/2, $\langle BEN \rangle$ = 22	$\langle n/m' \rangle$ = 5/2, $\langle BEN \rangle$ = 22
$\boxed{22}$	1 x $\boxed{19}$ + 1 x $\boxed{25}$	1 x $\boxed{18}$ + 1 x $\boxed{26}$
[1 0 1]	[1 1 0] [0 1 0]	[1 0 2] [1 0 0]

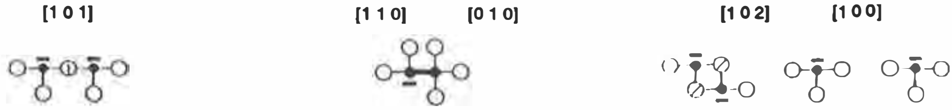


Figure IX - 5 : Graph drawings of the observed anionic tetrahedron complexes of three compounds with BEN = 22 and n / m' = 5/2. The simple solution with only one kind of base tetrahedron occurs with $NaSn_2F_5$ (also $ZnSe_2O_5$ and $Sr_2Sb_2S_5$ aq).

Of the three examples shown in Figure IX - 6 the compound $Li_2Cu^{2+}{}_3Se_4O_{14}$ is unusual because the *BEN* value calculated from the composition is an integer, but for this *BEN* and n/m' value exists no base tetrahedron in Figure IX - 2. There is only one possible solution which consists of two base tetrahedra, *i.e.* an isolated normal tetrahedron and a ψ-tetrahedron. The average number of atoms per molecule is $4^1/2$. This is also the value for $N'_{A/M}$ calculated from *VEC'* with (VIII - 6).

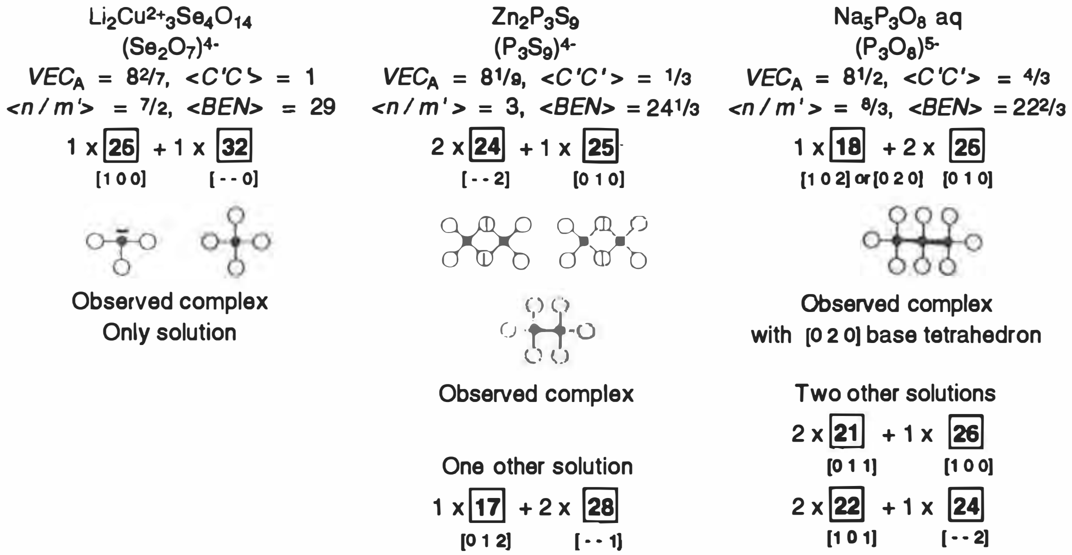


Figure IX - 6 : The possible base tetrahedron combinations for $Li_2Cu^{2+}{}_3Se_4O_{14}$, $Zn_2P_3S_9$ and $Na_5P_3O_8$. 14 H_2O and graph drawings of the observed anionic tetrahedron complexes.

For $Zn_2P_3S_9$ and $Na_5P_3O_8$. 14 H_2O exist more possibilities for selecting base tetrahedra. Figure IX - 7 is of help to see immediatly what kind of base tetrahedron pairs can be chosen. However, in the first solution for $Na_5P_3O_8$. 14 H_2O with *BEN* = 18 and 25 there has to be made for *BEN* = 18 also a choice between the [1 0 2] and the [0 2 0] base tetrahedron. The latter occurs in the observed tetrahedron complex which is non-cyclic molecular and consists of 11 atoms in agreement with *VEC'* = $6^2/11$.

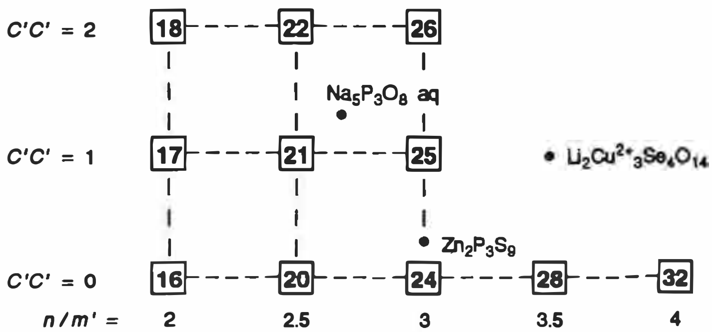


Figure IX - 7 : Positions of compound points for $Li_2Cu^{2+}{}_3Se_4O_{14}$, $Zn_2P_3S_9$ and $Na_5P_3O_8$. 14 H_2O on the $(n/m')\cdot(VEC_A - 8)$ versus n/m' grid. This presentation is helpful for the selection of possible base tetrahedron pairs by means of a lever rule.

⇒⇒⇒ Problems 10 and 11 in Appendix B

B2) The calculated *BEN* value is not an integer and thus the tetrahedron complex must be constructed of two kinds of base tetrahedra. However, the experimentally observed complex involves more base tetrahedra that is needed in a simple solution.

As example we consider $K_6Sn_3As_5$ for which the calculations have already been done on page IX - 86.

$K_6Sn_3As_5$: VEC_A = 8³/₅, $C'C'$ = 1, $<n/m'>$ = ⁵/₃, $<BEN>$ = 14¹/₃

According to Figure IX - 2 and (VIII - 10a) one expects as simple solution a mixture of base tetrahedra with *BEN* = 13, code [0 1 3] and base tetrahedron with *BEN* = 17, code [0 1 2] in the ratio 2 to 1. Observed is, however, a complex built up of three kinds of base tetrahedra in equal proportions, *i.e.* *BEN* = 13, code [0 1 3] and *BEN* = 14, code [1 0 3] and *BEN* = 16, code [- - 4]. It had been shown above that this mixture agrees with (IX - 26) and (IX - 27a).

The valence electron rules for general valence compounds with anionic tetrahedron complexes as a guide for checking experimental data

In Table IX - 3 are given the data for two pairs of structures which on casual inspection might appear to be isotypic but actually are not. The space group and Wyckoff sequence for each pair are the same. The unit cell dimensions and the positional atom coordinates are nearly similar, but the VEC_A values of the "isotypic" compounds are different. A closer analysis of the positional atom coordinates brings out the structural differences which are to be expected from the different VEC_A values.

TABLE IX - 3 : DATA OF STRUCTURE PAIRS WHICH ON CASUAL INSPECTION APPEAR TO BE ISOTYPIC BUT ARE NOT.

Compound	$Ca_5Ga_2As_6$	$Ca_5Sn_2As_6$
Formula of complex	$(GaAs_3)^{5-}$	$(SnAs_3)^{5-}$
Space group, Wyckoff sequence	*(55) Pbam - h³g³a*	*(55) Pbam - h³g³a*
Unit cell parameters (in Å)	11.357 13.224 4.138	11.830 13.643 4.121
VEC_A n/m' $<BEN>$	7.67 3 $\boxed{23}$	8 3 $\boxed{24}$
Base tetrahedron code	[- 1 2]	[- - 2]
Compound	$K_2Co^{2+}Se_2O_6$	$K_2CaC_2O_6$ (buetschliite)
Formula of complex	$(SeO_3)^{2-}$	$(CO_3)^{2-}$
Space group, Wyckoff sequence	*(166)* $R\overline{3}m$ *- hc²a*	*(166)* $R\overline{3}m$ *- hc²a*
Unit cell parameters (in Å)	5.516 5.516 18.520	5.3822 5.3822 18.156
VEC_A n/m' $<BEN>$	8.67 3 $\boxed{26}$	8 3 **no**
Base tetrahedron code	[1 0 0] ψ-tetrahedron	planar triangular group

$Ca_5Sn_2As_6$ is a normal valence compound, but $Ca_5Ga_2As_6$ is polyanionic. The Ga atoms are displaced toward each other so that Ga - Ga pairs are formed. This displacement is not observed with the corresponding Sn atoms.

$K_2Ca(CO_3)_2$ (buetschliite) is a normal valence compound, but $K_2Co^{2+}(SeO_3)_2$ is polycationic. There is a difference in the positional atom coordinates of C and of Se. The C atom is sp^2 hybrized and is located in the centre of a (nearly) planar CO_3 group, while the SeO_3 ψ-tetrahedron is non-planar with the Se atom above the plane of the oxygen atom triangle.

X. STRUCTURE CHANGES UNDER PRESSURE

Volume decrease as determining parameter for any change under increasing pressure
All structure changes under increasing pressure are necessarily accompagnied by a decrease in volume. This is one of the consequences of the **principle of le Chatelier**. X - 1)

The volume of a unit cell depends on

- the volume of the atoms,
- the way the atoms are arranged within the unit cell and
- the geometrical shape or form of the atoms.

It is obvious that the unit cell volume depends on the volume of the atoms because the atoms are in contact with each other and thus the unit cell dimensions are determined by their sizes. There has, however, also to be considered how the atoms are arranged in space. Atoms don't completely fill the space of a unit cell. With a different atom arrangement the unoccupied cell space might be smaller. This second factor can be expressed by the **space filling parameter** ϕ, a geometrical factor which is independent of the volume of the atoms. It is defined by

$$\phi = (\text{sum of volumes of atoms in cell}) \ / \ (\text{volume of unit cell}) \qquad (X-1)$$

The space filling can be changed, however, not only by rearranging the atoms or changing their positions within the unit cell, but also by modifying the shape of the atoms (without changing their volume). It is easy to understand, to use a trivial example, that a cubical box can be packed much more efficiently with (properly oriented) cubes than with spheres. The change of the shape of the atoms in a structure is not so easy to describe and to quantify. Practically, to simplfy the results of numerical calculations for the space filling parameter it is assumed that the atoms during structure transformation do not change their shape. Often it will be further assumed that the atoms are spherical which may not correspond to reality. With all these simplifications it should not be left out of sight that the only what really counts is the volume decrease during transformation.

In Figure X - 1 is shown a two-dimensional model structure with an arrangement of circles in square packing. The two-dimensional unit cell area can be decreased by 13.4% in three different ways:

a) Rearrangement of the circles from a square to a hexagonal packing without changing the circle size. By this procedure the space filling increases from ϕ = 0.785 to 0.907.

b) Decrease of the circle radius from r to 0.93 r without changing the arrangement of the circles.

c) Deformation of the circles to octagons with same surface area without changing the original square packing. This change from a circle to an octagon leads to an increase of the space filling or, expressed differently, to a decrease of the unoccupied cell space.

X - 1) If in a system under equilibrium occurs a modification of a factor which determines the equilibrium, the system reacts in such a way as to minimize the effect of this modification.

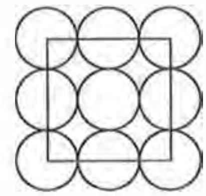
Original structure (4 circles / cell)

square arrangement of circles

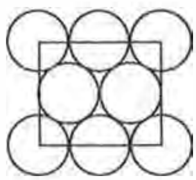
circle area = $r^2 \pi$

cell surface area = $(4r)^2$

$\phi = \pi / 4 = 0.785$



Three variants of original structure with surface area decreased by 13.4%



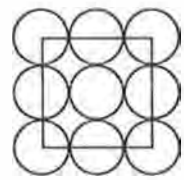
a)

hexagonal arrangement of circles

circle area = $r^2 \pi$

cell surface area = $4r \cdot 2\,(3)^{1/2}\,r$

$\phi = \pi \;/\; [2\,(3)^{1/2}] = 0.907$



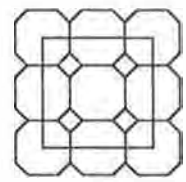
b)

square arrangement of circles

circle area = $(0.93\ r)^2 \pi$

cell surface area = $[4\ (0.93\ r)]^2$

$\phi = \pi / 4 = 0.785$



c)

square arrangement of octagons

octagon area $\equiv r^2 \pi$

cell surface area = $[4\ (0.93\ r)]^2$

$\phi = 0.907$

Figure X - 1 : Decrease of the unit cell area of a two-dimensional model structure by 13.4% due to three different procedures : a) rearrangement of the circles from a square to a hexagonal packing, b) decrease of the circle size without changing the circle arrangement and c) change of the circles to octagons with same surface area to increase space filling.

In conclusion, any change due to pressure can be related to a volume decrease expressed by

$$-(\Delta V / V) = (\Delta\phi / \phi) - (\Sigma\, \Delta V_{atom} / \Sigma\, V_{atom}) \qquad (X - 2)$$

The volume decrease can be attributed to one or more of the following :

- an increase of the space filling parameter (due to a rearrangement of the atoms and/or due to a change of the atom shape - without changing volume - to better fill space)
- a decrease in the volume of the atoms.

We shall first discuss structure changes under pressure which can be correlated essentially with an increase of the space filling due to a rearrangement of the atoms, then structure changes where the space filling is not primarily effected, and, finally the rare cases where during the pressure transformation the atoms become so much smaller in volume that, surprisingly, even a more open structure with smaller ϕ value can be formed.

Pressure-induced structure changes with a rearrangement of the atoms and an increase of the space filling

The majority of the structure transformations under pressure of ionic and covalent compounds can be attributed to an increase in the space filling due to a rearrangement of the atoms. We shall calculate in the following the space filling parameters of a few element and binary structure types. We shall find that there are difficulties with the determination of the exact value of the space filling parameter for the case that the atoms are not spherical and/or have different compressibilities (for binary or multicomponent compounds). To simplify we shall finally substitute "**increase of atom coordination**" for "**increase of space filling**".

Space filling parameters of element structure types

Assuming the atoms to be rigid spheres which are in contact, the unit cell (and thus also the unit cell volume) can be expressed in terms of the atomic radius. For this case one obtains with (X - 1) a value for ϕ which is independent of the actual size and volume of the atoms. It depends only on the arrangement of the atoms in the unit cell.

An example we calculate with the help of (X - 1) the space filling parameter of the cubic Cu (A1) type and the hexagonal Mg (A3) type with $c_h / a_h = 2 \cdot (2/3)^{1/2}$ (see Figures I - 3 and III - 3). The result is 0.74 for both structure types :

General equation for Cu type	$\phi = 4 \cdot (4\pi r_{Cu}^3 / 3) \; / \; a_c^3$	(X - 3)
Cu - Cu contact, therefore $a_c = 2 \cdot 2^{1/2} \cdot r_{Cu}$	$\phi_{Cu\text{-}Cu} = \pi / (18)^{1/2} = \mathbf{0.740}$	(X - 3a)
General equation for Mg type	$\phi = 2 \cdot (4\pi r_{Mg}^3 / 3) \; / \; [a_h^2 \cdot (3/4)^{1/2} \cdot c_h]$	(X - 4)
Mg - Mg contact, therefore $a_h = 2\, r_{Mg}$	$\phi_{Mg\text{-}Mg} = \pi / (18)^{1/2} = \mathbf{0.740}$	(X - 4a)

In Table X - 1 are presented the space filling values of a selection of common element structures. As can be expected the close-packed element structures have the highest space filling values. However, in the case of the non-cubic close-packed structures the maximum possible value of $\phi = 0.740$ is obtained only for the ideal c/a ratios (last line of Figure I - 3).

TABLE X - 1 : SPACE FILLING VALUES OF SELECTED ELEMENT STRUCTURES

element	type	*c / a*	ϕ	element	type	*c / a*	ϕ
Cu	Cu	-	0.740	α-Po	Po		0.523
Mg	Mg	1.63	0.740	Bi	As	2.60	0.446
W	W	-	0.680	As	As	2.80	0.385
Zn	Mg	1.86	0.650	Te	Se		0.364
β-Sn	Sn		0.535	C	diamond	-	0.340
α-U	U		0.534	C	graphite		0.171

Examples of pressure-induced structure changes of ***4B*** elements are given in Table X - 2. The results can be expressed in an approximate manner by a simple "historic" rule :

> **Pressure - Homologue Rule** : *X - 2)* For the elements of group ***4B*** to ***7B*** and within one column, the high-pressure structure corresponds to the normal-pressure structure of a homologous element from a higher period.

TABLE X - 2: EXAMPLES FOR PRESSURE - INDUCED STRUCTURE CHANGES WITH ***4B*** ELEMENTS WHERE THE SPACE FILLING INCREASES.

structure type		ϕ	C	Si	Ge	Sn
graphite	C[3]	0.17	↓			
diamond	C[4]	0.34		↓	↓	
β-tin	Sn[4+2]	0.54				↓
tungsten	W[8cb]	0.68				

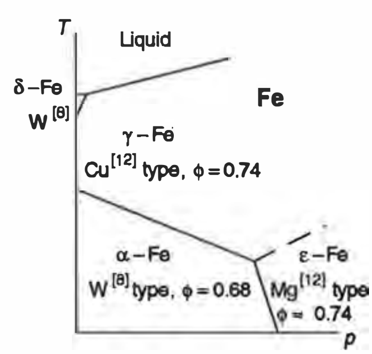


Figure X - 2 : The p - T phase diagram of Fe.

X - 2) Neuhaus, A. (1964). Chimica 18, 93 - 103.

The rule that in the normal case the space filling should increase with pressure serves also as a guide to check in p - T phase diagrams the direction of the slope of the lines separating different phase fields.
As an example we consider the p -T diagram of Fe, shown in Figure X - 2 The structure type in each phase field X - 3) is identified by its crystal chemical formula and ϕ value. The line separating α - Fe from γ - Fe must slope down with increasing pressure as shown in Figure X - 2 because otherwise would be observed with increasing pressure a transition from a phase with high space filling to a phase with lower space filling.

Space filling parameters of binary structure types

The space filling parameter is not a constant but varies with the atom radius ratio $\varepsilon = r_C / r_A$. In the general case the space filling curve consists of three branches depending on which atoms are in contact. The calculation of the space filling curves of the NaCl type serves as an example.

The equation for the space filling parameter ϕ for the NaCl type in its more general form (X - 5) has three special solutions, *i.e.* (X - 5a) valid for ε (= r_{Na} / r_{Cl}) > 2.414 when there are contacts between the atoms on the Na sites, (X - 5b) for 0.414 < ε < 2.414 when Na - Cl contacts occur and finally (X - 5c) for ε < 0.414 when only atoms on the Cl sites are in mutual contact. It possible to express the lattice constant a_c in (X - 5) in terms of the radii of the atoms which are in contact and one obtains three equations for ϕ which depend only on the radius ratio ε (always assuming spherical atoms).

General equation for NaCl type	$\phi = [4 \cdot (4\pi / 3) \cdot (r_{Na}^3 + r_{Cl}^3)] \ / \ a_c^3$	(X - 5)
Na - Na contact, therefore $a_c = 2 \cdot (2)^{1/2} \cdot r_{Na}$	$\phi_{Na\text{-}Na} = [\pi / (3 \cdot 2^{1/2})] \cdot [(\varepsilon^3 + 1) / \varepsilon^3)]$	(X - 5a)
Na - Cl contact, therefore $a_c = 2 \cdot (r_{Na} + r_{Cl})$	$\phi_{Na\text{-}Cl} = (2\pi / 3) \cdot [(\varepsilon^3 + 1) / (\varepsilon + 1)^3)]$	(X - 5b)
Cl - Cl contact, therefore $a_c = 2 \cdot (2)^{1/2} \cdot r_{Cl}$	$\phi_{Cl\text{-}Cl} = [\pi / (3 \cdot 2^{1/2})] \cdot (\varepsilon^3 + 1)$	(X - 5c)

In Figure X - 3 are shown space filling curves for simple AB and AB_2 types which occur with normal valence compounds (in ϕ - ε diagrams with a double-logarithmic scale). X - 4)

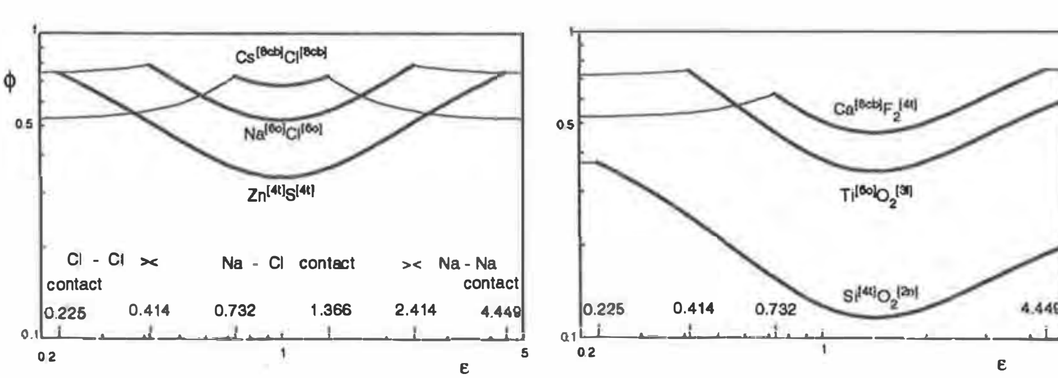


Figure X - 3 : log ϕ - log ε diagrams for AB and AB_2 types found with normal valence compounds. Sphalerite and wurtzite type with $c / a = (8 / 3)^{1/2} \equiv 1.633$ have overlapping space filling curves.

X - 3) No distinction is made in Figure X - 2 between ferromagnetic α - Fe (below Curie temperature) and paramagnetic β - Fe (above Curie point). Both have the same body-centred atom arrangement of the cubic W-type. However, if also the spins and their orientations are considered then the true symmetry of α - Fe is tetragonal.

*X - 4) Parthé, E. (1961). Z. Kristallogr. **115**, 52 - 72.*

According to the first Pauling rule an ionic structure type is stable only in the ε range where cations and anions can be in contact. This range corresponds for each type to the range of the middle curve in the space filling diagram. The ε values at the intersections of the middle curve with the two other space filling curve branches are the critical radius ratios for each type. The lower ε limit ($\varepsilon < 1$) corresponds to the critical radius ratio of the cation-centred anion coordination figure and the upper one ($\varepsilon > 1$) to the critical radius ratio for the anion-centred cation coordination figure. From the crystal chemical formulae of the structure types in Figure X - 3 one obtains the cation and anion coordinations and with the help of (IV - 4) the corresponding critical radius ratio values. Thus the ε values where space filling curve branches intersect can be determined easily. If $\varepsilon < 1$ it has the same value as the one listed in (IV - 4) and when $\varepsilon > 1$ it is its reciprocal.

For the $Ca^{[8cb]}F_2^{[4t]}$ type, as example, the ε range of the space filling curve where Ca and F atoms are in contact is $0.732 \le \varepsilon \le 1 / 0.225 = 4.449$. According to (IV - 4) 0.732 is the value of the critical radius ratio for cubic coordination and 0.225 the corresponding value for tetrahedral coordination.

⇒⇒⇒ Problem 12 in Appendix B

According to the diagrams in Figure X - 3 an increase of the space filling can be obtained within certain ε ranges by a transformation to another structure type for which the space filling curve for cation - anion contact is positioned higher up. The predictions for the sequence of structure types with increasing pressure are thus :

for *AB* compounds $Zn^{[4t]}S^{[4t]} \rightarrow Na^{[6o]}Cl^{[6o]} \rightarrow Cs^{[8cb]}Cl^{[8cb]}$
for *AB*$_2$ compounds $Si^{[4t]}O_2^{[2n]} \rightarrow Ti^{[6o]}O_2^{[3l]} \rightarrow Ca^{[8cb]}F_2^{[4t]}$

Important is the observation that in both structure type series the increase of the space filling is coupled with an increase of the coordination of the cations and anions.

In Table X - 3 are listed examples of observed pressure-induced structure changes with equiatomic normal valence compounds. There has been included in Table X - 3 also the $B^{[3l]}N^{[3l]}$ type as first member of the above given high-pressure structure type series.

TABLE X - 3 : EXAMPLES OF PRESSURE-INDUCED STRUCTURE CHANGES OF EQUIATOMIC NORMAL VALENCE COMPOUNDS WITH $VEC_A = 8$ WHERE SPACE FILLING AND ATOM COORDINATION NUMBER INCREASE.

Compounds	$B^{[3l]}N^{[3l]}$ type	$Zn^{[4t]}S^{[4t]}$ type	$Na^{[6o]}Cl^{[6o]}$ type	$Cs^{[8cb]}Cl^{[8cb]}$ type
BN	——	——→		
AgI, ZnO, ZnS, ZnSe, CdS, CdTe, InP, InAs		——	——→	
KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CaO, SrO, $Eu^{2+}O$			——	——→

No distinction is made here between the sphalerite and the wurtzite type (ideal *c / a* ratio of 1.63) since they are only stacking variants with same crystal chemical formula and overlapping space filling curves.

The application of ϕ - ε diagrams for the exact prediction of the structures of high-pressure phases is, however, limited for the following reasons :

- The ε value of a compound may change gradually with an increase of pressure because the compressibility of the different atoms in a binary or multicomponent structure may not be the same. Thus the exact ε value at the structure transition is not known.
- Non-cubic structure types may have variable axial ratios and if there are also adjustable positional parameters they may change gradually. All this influences the space filling value of a structure.
- The simple calculation of the space filling parameters is based on the assumption that the atoms are spherical which is not necessarily the case.
- The increase of space filling due to a rearrangement of the atoms is only one of the factors to be considered (the possible change of the atom shapes and/or the volume decrease of the atoms being ignored).

Pressure-induced structure changes with a rearrangement of the atoms and an increase of the atom coordination

In view of the above mentioned difficulties with the calculation and the application of the space filling parameter their remains the observation that in increase of space filling is coupled with an increase of the atom coordination. This is the content of another simple "historic rule" :

> **Pressure - Coordination Rule** : *X - 2)* Pressure-induced structure changes can be correlated with an increase of the coordination number of the atoms.

This rule is not free from conceptional difficulties because the term "atom coordination" is not well defined. But atom coordination is commonly used as ordering parameter for the sequence of structures types with increasing pressure. Examples are presented in Tables X - 4 and 5.

According to Table X - 4 the structure type sequence for dioxides and dihalides contains at least 12 types including also the three AB_2 types discussed above which were derived from space filling considerations. Within the series the cation coordination increases from 4 to 10. Two parallel structure type sequences are shown (having partially the same types). One sequence applies to dioxides and difluorides where the anions are small and rather incompressible, and the second to other dihalides with larger and more compressible anions. Not all these types occur with all the ionic norrnal valence compounds of AB_2 composition.

TABLE X - 4 : STRUCTURE TYPE SEQUENCE WITH INCREASING PRESSURE FOR IONIC NORMAL VALENCE COMPOUNDS WITH FORMULA AB_2. *X - 5)* THE TYPES ARE IDENTIFIED WITH PEARSON CODE AND WYCKOFF SEQUENCE.

Structure type sequence for dioxides and difluorides with small and rather incompressible anions

$Si^{[4t]}O_2$ → $Ti^{[6o]}O_2$ → $Ca^{[6]}Cl_2$ → α-$Pb^{[6+2]}O_2$ → $Zr^{[7]}O_2$ * → $Ca^{[8cb]}F_2$ → $Pb^{[9]}Cl_2$

$Si^{[4t]}O_2$	$Ti^{[6o]}O_2$	$Ca^{[6]}Cl_2$	α-$Pb^{[6+2]}O_2$	$Zr^{[7]}O_2$ *	$Ca^{[8cb]}F_2$	$Pb^{[9]}Cl_2$
hP9, P3₁21 - ca	*tP6, P4₂/mnm - fa*	*oP6, Pnnm - ga*	*oP12, Pbcn - dc*	*mP12, P2₁/c - c³*	*cF12, Fm-3m - ca*	*oP12, Pnma - c³*

Structure type sequence for other dihalides with larger and more compressible anions

$Hg^{[4t]}I_2$ →	$Cd^{[6o]}Cl_2$ or	$Ca^{[6]}Cl_2$ →	$Sr^{[7]}I_2$ or	$Sr^{[7,8]}Br_2$ →	$Pb^{[9]}Cl_2$ →	$Pb^{[10]}Cl_2$ *HP***
tP6, P4₂/nmc - db	*hR9, R-3m - ca*	*oP6, Pnnm - ga*	*oP24, Pbca - c³*	*tP30, P4/n - g³cba*	*oP12, Pnma - c³*	*mP24, P2₁/c - e⁸*

* This ZrO_2 modification is known as baddeleyite type. ** Also labelled postcotunnite type.

X - 5) Léger, J.M., Haines, J. & Atouf, A. (1996). J. Phys. Chem. Solids ***57***, *7 - 16. Haines, J., Léger, J.M. & Hoyau, S. (1995). J. Phys. Chem. Solids* ***56***, *965 - 973. Beck, H.P. (1979). Z. anorg. allg. Chem.* ***459***, *72 - 80. Seifert, K.F. (1968). Fortschr. Miner.* ***45***, *214 - 280. For AB_3 halides see Peterson, J.R. (1995). J. Alloys Comp.* ***223***, *180 - 184.*

The sequence of structure types with increasing pressure is not necessarily the same when the pressure is relaxed because then there may be formed metastable phases. In earlier papers the distinction between phases forming with increasing and those forming with decreasing pressure was not always made which led to conflicting results.

Examples of pressure-induced structure changes with ternary normal valence compounds are presented in Table X - 5. The average of the cation and central atom coordination numbers increases parallel with the sequence of structure types under increasing pressure.

TABLE X - 5: EXAMPLES OF PRESSURE-INDUCED STRUCTURE TYPE SEQUENCES OF TERNARY NORMAL VALENCE COMPOUNDS. FOR EACH TYPE IS INDICATED THE AVERAGE OF THE CATION AND CENTRAL ATOM COORDINATION NUMBERS.

$\boxed{C_2C^*A_4}$	4 $Cd^{[4t]}Ga_2{}^{[4t]}S_4$ type thiogallate, *tI14* $Be_2{}^{[4t]}Si^{[4t]}O_4$ type phenakite, *hR126*	→	5.33 $Mg^{[4t]}Al_2{}^{[6o]}O_4$ type spinel, *cF56* $Mg_2{}^{[6o]}Si^{[4t]}O_4$ type forsterite *oP28*, olivine	→	6 $Mo_2{}^{[6o]}Co^{[6o]}S_4$ type *mS14*
$\boxed{CC^*A_3}$	5 $Mg^{[6]}Si^{[4t]}O_3$ type enstatite *oP40*, pyroxene	→	6 $Ti^{[6o]}Fe^{[6o]}O_3$ type ilmenite, *hR30*	→	9 $Ca^{[12co]}Ti^{[6o]}O_3$ type idealized perovskite, *cP5*
	4.5 $Ca^{[6o]}C^{[3t]}O_3$ type calcite, *hR30*	→	6 $Ca^{[9]}C^{[3t]}O_3$ type aragonite, *oP20*		

The recently developed image-plate detectors for angle-dispersive powder diffraction studies with synchrotron radiation have so much improved the traditionally poor quality of the high-pressure powder patterns that it became possible for the first time to refine positional atom coordinates and to determine how these coordinates and interatomic distances vary as function of pressure. The new results which contradict certain parts of the older literature have led McMahon & Nelmes [X - 6)] to reformulate the systematics for the pressure sequence of the structure types found with group *4B* elements and *26* and *35* semiconductor compounds. Their results are presented in Table X - 6 in a simplified version where not all structure types are mentioned.

The structure type formulae in Table X - 6 are surrounded by different frames. A double frame indicates that both the relative unit cell dimensions and the positions of the atoms within the structure are fixed by symmetry. A simple frame means that one of both is fixed, *i.e.* for example, the atom sites in the β-Sn, NiAs types and the simple hexagonal structure (SH) while the *c / a* ratio can be changed. In structure types without frames both positional atom coordinates and axial ratios can vary. [X - 7)]

X - 6) McMahon, M.I. & Nelmes, R.J. (1995). J. Phys. Chem. Solids 56, 485 - 490.

X - 7) The reader can verify the proper assignment of the frames by referring to the Wyckoff sequence listed below each type formula in Table X - 6 and checking in the International Tables for Crystallography for each Wyckoff site whether or not the atoms have adjustable positional coordinates.

TABLE X - 6 : SEQUENCES OF STRUCTURE TYPES WITH INCREASING PRESSURE FOR GROUP *4B* ELEMENTAL SEMICONDUCTORS AND FOR *26* AND *35* BINARY SEMICONDUCTORS WITH AN IONIC BONDING CONTRIBUTION. THE TYPES ARE IDENTIFIED WITH PEARSON CODE AND WYCKOFF SEQUENCE.

Structure type sequence for covalently bonded group *4B* elements

$\boxed{C^{[4t]}}$	→	$\boxed{\beta\text{-}Sn^{[4+2]}}$	→	$Si^{[-6]}$ XI	→	$\boxed{(SH)^{[6+2]}}$ *	→	$\boxed{Mg^{[12]}}$	or	$\boxed{\alpha\text{-}Nd^{[12]}}$	or	$\boxed{Cu^{[12]}}$
cF8, Fd-3m - a		*tI4, $I4_1/amd$ - b*		*oI4, Imma - e*		*hP1, P6/mmm - a*		*hP2, $P6_3/mmc$ - c*		*hP4, $P6_3/mmc$ - ca*		*cF4, Fm-3m - a*

Structure type sequence for *26* and *35* semiconductors with an ionic bonding contribution

$\boxed{Zn^{[4t]}S^{[4t]}}$	→	CdTe trig.**	→	$\boxed{Na^{[6o]}Cl^{[6o]}}$	or	$\boxed{Ni^{[6o]}As^{[6p]}}$	or	$Zn^{[-6]}$Te III
cF8, F-43m - ca		*hP6, $P3_121$ - ba*		*cF8, Fm-3m - ba*		*hP4, $P6_3/mmc$ - ca*		*oS8, Cmcm - c^2*

* (*SH*) stands for simple hexagonal structure ($HgSn_6$ type) where each atom has 6 + 2 neighbours.
** CdTe trig. is often called cinnabar type, but it is a cinnabar branch with different atom coordination.

To the last category belong

- the Si XI type in the upper part of Table X - 6 between the β-Sn and (*SH*) types and
- the trigonal CdTe ("cinnabar") type in the lower part intermediate between ZnS and NaCl types.

With increasing pressure these intermediate phases change gradually their axial ratios and/or the positional coordinates of certain atoms (which their neighbouring phases with the framed structure type formulae can not do). The Si XI and the trigonal CdTe type structures are intermediate in the sense that the gradual rotations and/or deformations of certain parts in these structures within their homogeneity ranges correspond - within geometrical limits - to gradual structural changes from the atom arrangement of the neighbouring lower pressure type to an arrangement of the neighbouring higher pressure type. All these gradual structure changes with increasing pressure are evidently always connected with a gradual volume decrease.

Pressure-induced structure transformation with general valence compounds

In the case of general valence compounds the structural features of both the normal and the high-pressure structure are in agreement with the generalized 8 - *N* rule, as given by (V - 3), provided the pressure is not excessive. [X - 8)]

In Table X - 7 are presented examples of pressure-induced structure changes of polyanionic valence compounds of composition CA_2 with different VEC_A and *AA* values. For a comparison there has been added also one normal valence compound where VEC_A = 8 and *AA* = 0. The structural changes with increasing pressure can be summarized as follows :

- the atom coordination increases
- the number of non-bonding orbitals decreases
- only those structure types occur under high pressure which have structural features in agreement with the *AA* value calculated from VEC_A. That means, that the generalized 8 - *N* rule is also valid for high-pressure modifications.

The in Table X - 7 mentioned pressure-induced transformation from the ZnP_2 type (see Figure VI - 1) to the $CaSb_2$ type [X - 9)] is a prediction which requires an experimental verification. High-pressure experiments on the compound $ZnAs_2$ did not give the expected result. Unexpectedly, the compound decomposes according to $ZnAs_2$ → ZnAs + As.

X - 8) Parthé, E. (1984). High Temp. - High Press. 16, 553 - 557.

X - 9) For more details on this type see the corresponding entry in the database which is described in Appendix D.

TABLE X - 7 : EXAMPLES OF PRESSURE INDUCED STRUCTURE CHANGES OF POLYANIONIC VALENCE COMPOUNDS AND ONE NORMAL VALENCE COMPOUND WITH COMPOSITION CA_2.

VEC_A	AA	crystal chemical formula of low pressure form	structure type		crystal chemical formula of high pressure form	structure type
8 isolated anions	0	$Si^{[4]}\underline{O}_2^{[;0]}$	SiO_2 quartz	$\longrightarrow$	$Si^{[6]}\underline{O}_2^{[;0]}$ stichovite	TiO_2 rutile
7 dumb-bells (simple solution) or isolated anion and anion chains	1	$Si^{[4]}\underline{As}^{[;0]}\underline{As}^{[;2]}$	$GeAs_2$	$\longrightarrow$	$Si^{[6]}As_2^{[;1]}$	$Fe[S_2]$ pyrite
6 infinite anion chains	2	$C^{[4]}A_2^{[;2]}$	$Zn\,{}^1_\infty P_2$	$\longrightarrow$?	$C^{[6]}A_2^{[;2]}$	$Ca\,{}^1_\infty Sb_2$
5 each anion with 3 bonds to other anions	3	$Ca^{[6]}Si_2^{[;3]}$ $Sr^{[\sim8]}Si_2^{[;3]}$ $Ba^{[\sim9]}Ge_2^{[;3]}$	$Ca\,{}^2_\infty Si_2$ $Sr\,{}^3_\infty Si_2$ $Ba_2\bullet[Si_4]$	$\longrightarrow$ $\longrightarrow$ $\longrightarrow$	$Ca^{[12]}Si_2^{[;3]}$ $Sr^{[12]}Si_2^{[;3]}$ $Ba^{[12]}Ge_2^{[;3]}$	$Th\,{}^3_\infty Si_2$ $Th\,{}^3_\infty Si_2$ $Th\,{}^3_\infty Si_2$

In Figure X - 4 are shown the three different disilicide or digermanide structures, listed in the lower part of Table X - 7, where each Si or Ge atom has three homonuclear bonds. All these compounds transform under high pressure to the tetragonal $ThSi_2$ type which - as expected - Is also characterized by three anion - anion bonds per anion.

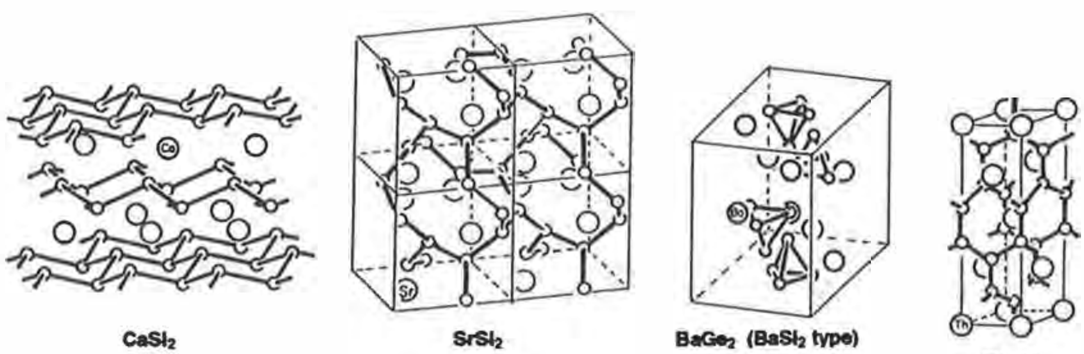


Figure X - 4 : Structures of $CaSi_2$, $SrSi_2$ and $BaGe_2$ at normal pressure and the atom arrangement of their isotypic high-pressure structures with $ThSi_2$ type.

The validity of the generalized 8 - *N* rule is not guaranteed If the compound contains a transition element. In other words, if the polyanionic valence compound contains a transition element, the rule that *AA* is the same for normal and high-pressure structure is not necessarily valid. The application of high pressure may provoke the insertion of a valence electron into an inner shell. Thus the number of valence electrons transfered from the cation to the anions decreases and consequently the anions, in order to complete their octets, have to form more shared-electron bonds between themselves, *i.e.* *AA* increases. One example is found with the compound IrS_2.

IrS_2 crystallizes under normal pressure with the $IrSe_2$ type characterized by the crystal chemical formula $Ir^{[6o;]}\underline{S}^{[3n;0]}S^{[(3;1)t]}$ and AA = 1/2. The Ir atom, a group *9T* transition element, transfers three valence electrons to the two S atoms for the completion of their octets. Six electrons remain in the *d* shell of the transition element (d^6 configuration). Under pressure is formed a pyrite type structure (see Figure II - 5) with crystal chemical formula $Ir^{[6o;]}S_2^{[(3;1)t]}$ *HP* where AA = 1. The increasing pressure provokes the insertion of one extra electron in the *d* shell, *i.e.* Ir changes to a d^7 configuration . Only two valence electrons are available for transfer to the S atoms. The latter in order to complete their octets have to increase the average number of their homonuclear bonds. If only the outer valence electrons and the linkage of the anions are considered then the structure change of IrS_2 under pressure corresponds to a normally not found transformation from the $La^{3+}S_2$ structure to the $Zn^{2+}S_2$ structure (both structures being treated in Problem 3 of Appendix B).

Pressure-induced structure changes without a change of the atom coordination

The most well known examples are the rare-earth elements which at ambient pressures and room temperature are all close-packed with 12 next-nearest neigbours and ϕ = 0.74 (or close to it for non-cubic structures) (see Table III - 1). Under pressure a change to another close-packed structure with a smaller percentage of hexagonal stacking is observed. The structure types change with increasing pressure in the following sequence :

$$\text{Mg type } (h)_2 \rightarrow \alpha\text{-Sm type } (hhc)_3 \rightarrow \alpha\text{-Nd type } (hc)_2 \rightarrow \text{Cu type } (c)_3$$

In Figure X - 5 are presented the *p* - *T* phase diagrams for Gd, Sm and Nd where pressure-induced phase transformations are observed in agreement with the above given sequence. For Y the complete structure type series has been reported, *i.e.* increasing pressure leads from $(h)_2$ to $(hhc)_3$, further to $(hc)_2$ and finally to $(c)_3$. [X - 10)] It remains to be investigated if there exists also an intermediate phase with the Tb *HP* type $(hcc)_2$ having 33% hexagonality.

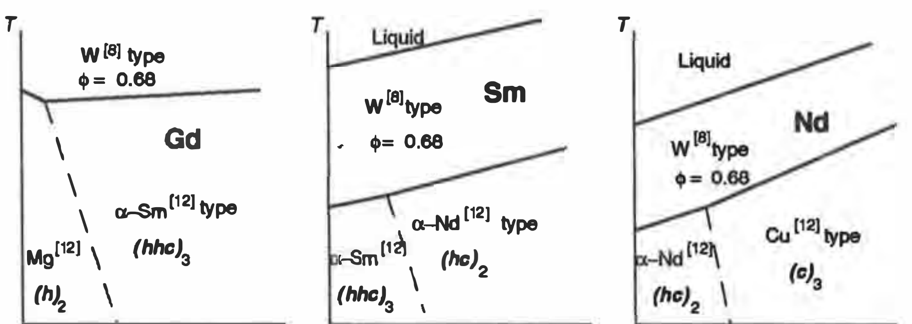


Figure X - 5 : The p - T phase diagrams of the rare-earth elements Gd, Sm and Nd. The diagrams are schematic. Lines separating phase fields are presented by straight lines only.

The Mg, α-Sm and α-Nd type structures before and after transformation have *c / a* ratios close to their ideal values (listed in Figure I - 3) and the single adjustable positional atom parameter (*z*) in α-Sm is close to its ideal value for close packing. The volume decrease during the pressure-induced transformation is thus essentially due to a change of the size and/or shape of the atoms.

X - 10) Grosshans, W.A., Vohra, Y.K. & Holzapfel, W.B. (1982). J. Magn. Magn. Mat. 29, 282 - 286.

An example of a pressure-induced change which beyond doubt is related with a change of the size of the atom is provided by Ce for which the *p* - *T* phase diagram is shown in Figure X - 6. In the same system there is a second pressure-induced structure transformation which can be explained by a change of the shape of the atoms.

In the lower left corner of the *p* - *T* diagram of Ce can be seen two phases with Cu [12] type. The one on the left has a lattice constant of *a* = 5.16 Å while the one on the right a = 4.48 Å. The change of the cubic cell volume with increasing pressure is related to an electronic transition of the Ce atoms which decrease their size. The line separating these two phases ends at higher temperatures in a critical point. Above this point there is no difference between these two Cu-type phases.

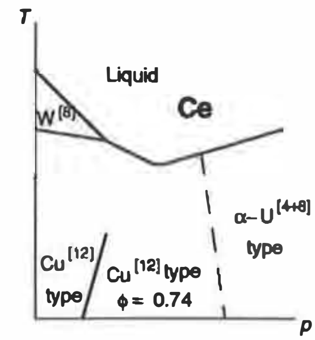
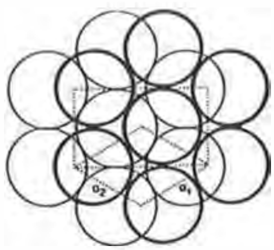


Figure X - 6 : The p - T diagram of Ce.

At very high pressures Ce [12] transforms to the orthorhombic α-U type, where each Ce has 4 close and 8 distant neighbours. This structure can be interpreted, as shown in Figure X - 7, as a hexagonal close packing of irregular ellipsoids. *X - 11)* The Ce atoms are thus not anymore spherical.

Mg[12]
hP2, P6$_3$/mmc



α-U[4+8]
oS4, Cmcm

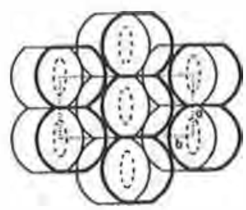
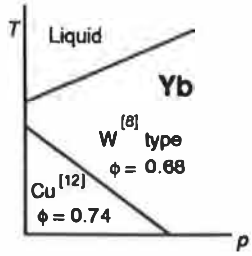


Figure X - 7 : The packing of spheres in the Mg type structure and the α-U type structure interpreted as a packing of irregular ellipsoids arranged as in the Mg type.

Pressure-induced structure changes with a decrease of the atom coordination

For these unexpected transformations the decrease of the volume of the atoms cannot be ignored. In effect, the decrease of the atom volume may be so great under the effect of pressure, that a more open structure with a smaller space filling parameter and a smaller atom coordination is formed. There are only a few examples known.



Yb with Cu[12] type (ϕ = 0.74) transforms under pressure, as seen in the *p* - *T* phase diagram in Figure X - 8, into the W[8] type (ϕ = 0.68). The high pressure leads to a change of the electronic configuration of Yb ($Yb^{2+} \rightarrow Yb^{3+}$) with three electrons in the conduction band. The decrease of the atom radius during the structure transformation amounts to more than ten percent.

Figure X - 8 : The p - T diagram of Yb.

X - 11) The theoretical possibilities for the densest packing of regular ellipsoids have been studied by Matsumoto, T. & Nowacki, W. (1966). Z. Kristallogr. 123, 401 - 421.

Ti and Zr crystallize at normal pressure in the $Mg^{[12]}$ type, the hexagonal close-packed element structure type with $\phi \approx 0.74$, supposedly the highest space filling value for an element structure. As seen in the *p* - *T* phase diagram for Ti in Figure X - 9, under pressure a new phase is formed, the so-called ω-phase, which has an even higher space filling. The structure of the ω-phase, which occurs also with Zr, is shown in Figure X - 10. This atom arrangement is found frequently with binary intermetallic compounds at ambiant pressures and is known as the AlB_2 type. In the ω-phase all sites are occupied by one kind of atoms, *i.e.* two thirds of the Ti (Zr) atoms are now smaller than the remaining third. With atoms of two different sizes a space filling with $\phi > 0.74$ is possible. The crystal chemical formula of the ω-phase is $Ti^{[12p]}Ti_2^{[3+6]}$, *i.e.* the average coordination number of the atoms is now smaller than 12.

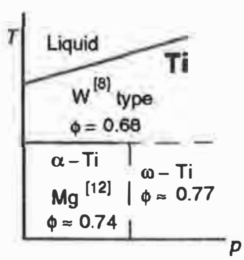


Figure X - 9 : The p - T diagram of Ti.

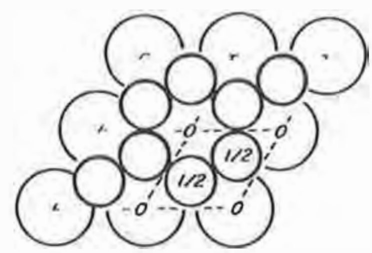


Figure X - 10 : Structure of ω - Ti (hP3, a = 4.62₅Å, c = 2.81₃Å). Inscribed is the atom height above the projection plane.

SnTe supposedly changes under high pressure from the $Na^{[6o]}Cl^{[6o]}$ type (Figure IV - 2) to the $Ge^{[3n]}S^{[3n]}$ type (Figure V - 6). In the course of this unexpected transformation not only the atom coordinations decrease but also the electrical resistance of SnTe increases by 360%, as shown in Figure X - 11. *X - 12)*

Since SnTe is isoelectronic with phosphorus it is of interest to compare the low and high pressure structures of SnTe with the different structures known for P. $Sn^{[6o]}Te^{[6o]}$ with NaCl type, the normal pressure modification, is metallic and its structure can be considered as an ordered substitution variant of the metallic high-pressure modification of phosphorus with $Po^{[6o]}$ type where $\phi \approx 0.523$. $Sn^{[3n]}Te^{[3n]}$ *HP* with GeS type is a semiconductor and its structure can be considered as an ordered substitution variant of the non-metallic low-pressure modification of black phosphorus $P^{[3n]}$ where $\phi \approx 0.285$. The structure change with increasing pressure reported for SnTe is thus directly opposite to that known for phosphorus.

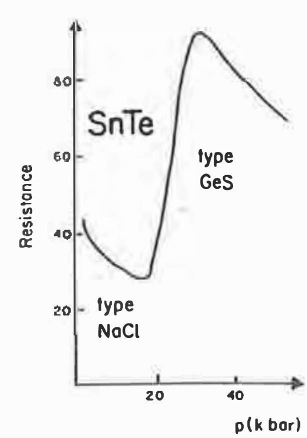


Figure X - 11 : The unexpected increase of the electrical resistance of SnTe with increasing pressure.

X - 12) Kafalas, J.A. & Mariano, A.N. (1964). Science 143, 952. Nomura, M., Kuroda, K. Inoue, M. & Fujiwara, H. (1985). In "Solid State Physics under Pressure. Recent Advances with Anvil Devices". Edit. S. Minomura. Pages 171 - 175. Dordrecht : Reidel.

XI. THE INTERGROWTH CONCEPT AND ITS APPLICATIONS

General definition

The term intergrowth structure is applied to a structure which consists of a periodic intergrowth of segments of (simple) parent structures. The segments can be (two-dimensional) slabs or (one-dimensional) columns or (zero-dimensional) bricks. In order to be intergrown two segments must have identical outer interfaces with the same atom arrangement and the same two-dimensional mesh parameters. In many cases is it possible to construct different structures with the same kinds of structure segments, cut from of the same parent structures, but mixed in different proportions. These structures can be grouped in an intergrowth structure series for which a common general formula can be given.

Ruddlesden and Popper [XI - 1)] were one of the first who recognized this kind of structural relationship in the case of the ternary Sr titanites Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ where there is an intergrowth of slabs cut from SrO having NaCl-type with slabs cut from $SrTiO_3$ with (idealized) $CaTiO_3$-type. We shall demonstrate on the Ruddlesden - Popper phases the periodic structure intergrowth and the intergrowth structure series. Ruddlesden - Popper phases have incidently become quite well known recently because they have certain structural similarities with the superconducting high T_c Cu oxide phases.

Ruddlesden - Popper phases, an intergrowth of NaCl- and $CaTiO_3$-type slabs

The Ruddlesden - Popper phases are ternary normal valence compounds with the general formula $C_{n+1}T_n^{[,6o]}A_{3n+1}$ where one NaCl-type slab with formula CA is intergrown with n perovskite-type slabs, each with formula CTA_3. The NaCl-type slab consists only of a lower and an upper interface layer which, referred to the NaCl structure drawing in Figure IV - 2, corresponds to the $(001)_{NaCl}$ plane at $z = 0$ and $z = {}^1/_2$, respectively. The atom arrangement on the interface can be described as a checkerboard arrangement of C and A atoms. Lower and upper interface layers are identical except that C and A atoms interchange sites. The perovskite-type slab has three layers, *i.e.* this slab is about twice as thick as the NaCl-type slab. The lower and the upper interface layers have the same checkerboard arrangement of C and A atoms (without interchange). Referred to the drawing of the perovskite structure in Figure II - 4, these interface planes correspond to the $(001)_{perovskite}$ planes at $z = {}^1/_2$ and $z = {}^3/_2$, respectively. The middle layer of the slab is identical with the $(001)_{perovskite}$ plane at $z = 1$. The NaCl- and $CaTiO_3$-type slabs can be intergrown as shown in Figure XI - 1. The slab labels and the traces of their interface planes, marked by dashed lines, can be found on the right hand side of each drawing.

XI - 1) Ruddlesden, S.N. & Popper, P. (1958). Acta Cryst. 11, 54 - 55.

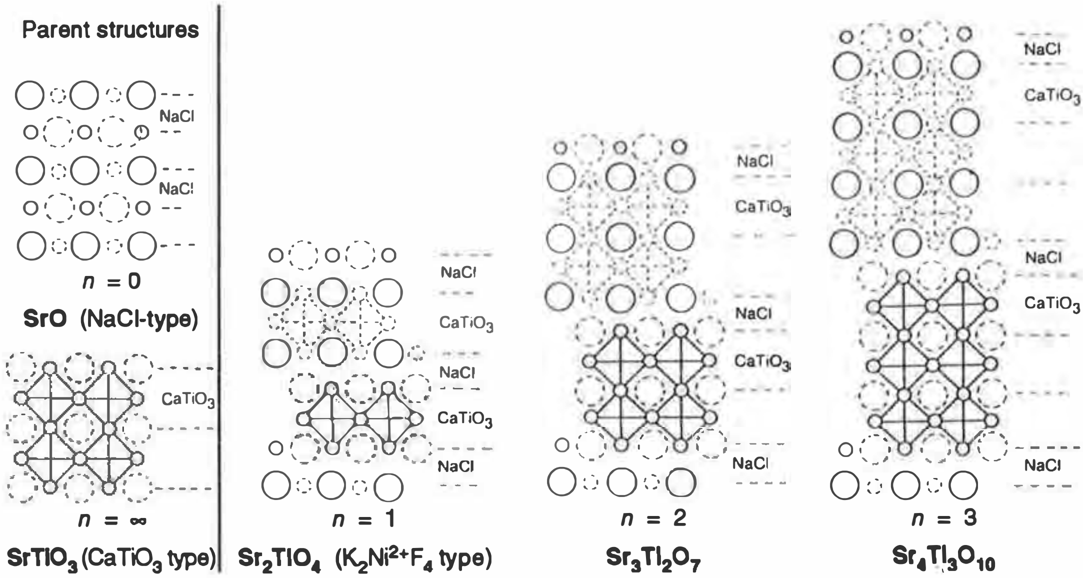


Figure XI - 1 : Schematic drawings of Ruddlesden - Popper phases $C_{n+1}T_n^{[,6o]}A_{3n+1}$ with n = 1, 2 and 3 together with the two parent structures. Large circles represent Na, K, Sr or Ca and small circles the anions. Circles drawn with full lines differ from those with dashed lines by a shift of one half in height. The transition metal centred anion octahedra are indicated by squares with small circles at the corners which correspond to the four anions in the middle plane of an octahedron. The transition metal atom in the centre of the square and the anion above and the one below the transition metal atom are not shown.

In Figure XI - 1 are presented the projections of the structures of the Ruddlesden - Popper phases with n = 0, 1, 2, 3 and ∞. Other members of this structure series are $Ba_5Hf_4S_{13}$ with n = 4 and $Ba_6Hf_5S_{16}$ with n = 5. It can not be excluded that more members do not exist. Given that the general formula of the intergrowth structure series is available, one knows the possible formulae of the compounds beforehand. Since the positions of the atoms within each kind of slab are also known, it becomes possible to calculate the ideal positions of all atom sites in a structure belonging to this intergrowth structure series. It is only necessary to specify the value of n. [XI - 2)]

Classification of intergrowth structures

Periodic Intergrowth structures are found not only with valence compounds but also with intermetallic compounds. Intermetallic compounds have quite often not only complicated compositions which are difficult to memorize but also complicated crystal structures which defy an easy interpretation. The valence concept fails here. Crystal chemists interested in intermetallic compounds - they devised the classification of intergrowth structures - use the intergrowth concept as a possible key for an understanding of composition and structure. [XI - 3)]

XI - 2) The ideal structures belonging to this intergrowth structure series with $0 < n < \infty$ have Pearson code tI(10n + 4) and space group I4/mmm. However, with certain compounds only pseudotetragonal symmetry is observed. This is due to a tilting of the transition metal centred anion octahedra.

*XI - 3) Grin', Yu.N., Yarmolyuk, Ya.P. & Gladyshevskii, E.I. (1982). Sov. Phys. Cryst. **27**, 413 - 417. Parthé, E., Chabot, B. & Cenzual, K. (1985). CHIMIA **39**, 164 - 174. Pani, M. & Fornasini, M.L. (1990). Z. Kristallogr. **190**, 127 - 133. Grin', Yu.N. (1992). In "Modern Perspectives in Inorganic Crystal Chemistry". E. Parthé, editor. NATO ASI Series C382, pages 77 - 96. Dordrecht : Kluwer.*

One distinguishes between

- linear, two-dimensional or three-dimensional structure series. In a **linear structure series** the segments are infinite slabs which are stacked in one direction, *i.e.* in a direction perpendicular to the interface planes. In a **two-dimensional structure series** the segments are infinite columns which are stacked in two dimensions. Finally, in a **three-dimensional structure series**, the segments are blocks which are stacked in three dimensions.

- homogeneous, quasi-homogeneous or inhomogeneous structure series. In a **homogeneous series** there is only one kind of parent structure. In a **quasi-homogeneous series** there are different parent structures but they are geometrically closely related (for example, as site occupation variants and/or as deformation variants). In **inhomogeneous series** the different parent structures are different in construction.

Concerning the compositions of the members of a structure series three cases may occur :
- all have the same composition if all parent structures have the same composition
- for a linear structure series with parent structures of different composition the compositions of the members of the structure series can be expressed by a **linear structure series formula,** *i.e.* in the subscripts of the general formula of the structure series appear only linear relations. The $R_{m+n}T_{5m+3n}M_{2n}$ structure series in Table XI - 3 is an example.
- for a two-dimensional structure series with parent structures of different composition, the compositions of the members of the series can be expressed by a **quadratic structure series formula**, *i.e.* in the subscripts of the general formula appear squares. As example serves the $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ structure series (Figure XI - 12).

As general rule interface planes are always selected in such a way that they contain atoms. Each atom on the interface is sliced, one part belonging formally to one slab and the other part to the neighbouring slab.. During intergrowth both parts are then formally united to form one complete atom.

To identify the atom arrangement in the interface plane it is best to refer to a drawing of one unit cell of the parent structure, to state the Miller indices of the corresponding plane and also the distance of this plane from the origin of the unit cell.

Linear homogeneous structure series

Three examples of linear homogeneous structure series have already been mentioned before :
- the close-packed element structures, shown in Figure I - 3,
- the ZnS and SiC polytypes, presented in Figures I - 4 and 5, and
- the Laves phases in Figure I - 7.

These stacking variants can be described in two alternative ways, as had been demonstrated above in detail for the ZnS polytypes. According to the older approach stacking variants are constructed of (not-intergrown) slabs (as shown for example on the upper left of Figure I - 4) with a side-wise displacement of consecutive slabs either in one or in an opposite direction parallel to the slab plane. This method can be also used for close-packed element structure types (the not-intergrown slab consisting here of a single close-packed atom layer as shown in Figure I - 2). But for the Laves-phase polytypes this approach is not suited very well. It is necessary in addition to the side-wide displacement of the slabs also to rotate of certain slabs for 180° around an axis perpendicular to the slab plane.

In the second method the slabs are delimited differently and they are intergrown (as shown for example on the upper part of Figure I - 5). The intergrown slabs can be stacked either rotated (by 180° around an axis perpendicular to the slab plane) in respect to the neighbouring slab or are stacked without rotation. It is the newer approach based on intergrown rotated and /or unrotated slabs which can be applied more widely and which we prefer for further applications.

In the drawings of the three Laves phases stacking variants in Figure I - 7 have already been indicated the intergrown slabs and their interfaces. This was not done in Figure I - 3 for the close-packed element structure types. The common intergrown slab is here very simple, consisting only of two interface layers. The slab corresponds to the ZnS type slab of Figure I - 5 but without the atoms inside the slab.

The interfaces of all the mentioned slabs are straight planes. However, it is possible to apply the intergrowth concept also to stacking variants where buckled înterface planes exist. The CrB - FeB stacking variants are one example.

CrB - FeB stacking variants, a linear homogeneous structure series with buckled interface planes

The basic construction element of the CrB - FeB stacking variants is a trigonal prism formed of the large atoms which is centred by a smaller atom. Each prism shares two rectangular faces with neighbouring prisms in such a way that parallel infinite prism columns are formed which are traversed lengthwise by infinite zig-zag chains of the smaller atoms. The different stacking variants differ in the way these infinite prism columns are connected with each other.

The conventional unit cell drawings of the two base types FeB and CrB in Figure XI - 2 .give no direct indication that these two structures might be considered as stacking variants.

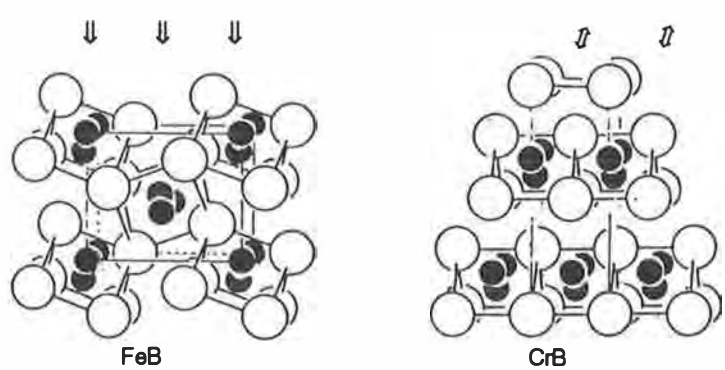


Figure XI - 2 : Perspective drawings of the FeB and CrB structures.

It is possible to slice both structures into identical slabs which - different from above - have buckled interface planes. The slabs are perpendicular to the plane of projection and they are parallel to the arrows on top of the drawings. In Figure XI - 3 are presented the slabs and the two ways how they can be intergrown. On the left hand side is shown a double slab where the intergrown upper slab is rotated in respect to the lower slab, *i.e.* rotated by 180° around an axis perpendicular to the slab plane,. This kind of stacking of two intergrown slabs was labelled ***h*** stacking in the case of the ZnS stacking variants (left hand drawing on the upper part of Figure I - 5). The drawing on the right hand side of Figure XI - 3 shows a double slab with intergrown iso-oriented unrotated slabs. This kind of stacking was labelled ***c*** stacking in Figure I - 5.

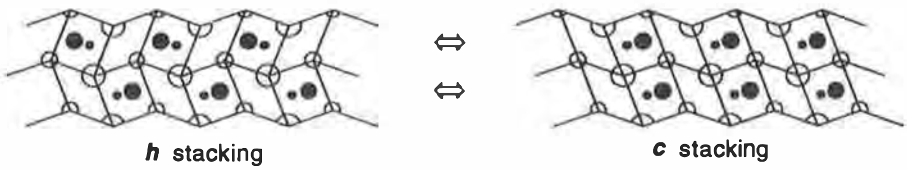


Figure XI - 3 : The two ways how the slabs found in CrB - FeB stacking variants can be intergrown, i.e. ***h*** *stacking (left) with the slabs rotated in respect to each other or* ***c*** *stacking (right) with iso-oriented slabs. Open circles are large atoms and shaded circles small atoms. For each kind the larger circles are at height 1/2 and the smaller ones at height 0.*

We shall use the term ***h*** and ***c*** stacking also for the CrB - FeB stacking variants, although the base structures are not anymore hexagonal or cubic. In the orthorhombic FeB structure all slabs are ***h*** stacked and in the equally orthorhombic CrB structure ***c*** stacked. The essentail point behind the new interpretation of the Jagodzinski - Wyckoff stacking letters **h** and ***c*** is whether or not the next slab is rotated or not With this new interpretation it becomes possible to treat stacking variants with straight and buckled interface planes in the same way. The redefined term **hexagonality** mean now the ratio of the number of interface planes (buckled or not) where the intergrown upper and lower slabs are rotated in respect to each other to the total number of interface planes.

Sixteen CrB - FeB stacking variants are known of which a selection is presented in Figure XI - 4. They are arranged according to increasing hexagonality.

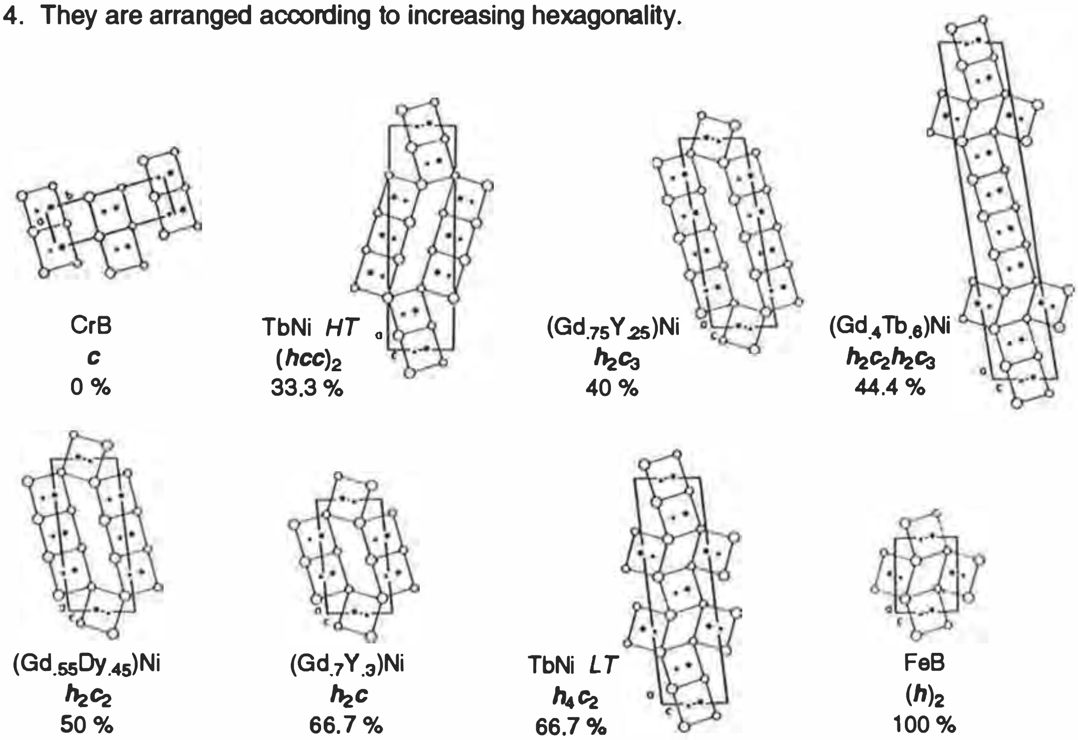


Figure XI - 4 : Examples of CrB - FeB stacking variants. Open circles correspond to large atoms and filled circles to small atoms. Larger circles of each kind are 1/2 in height above the small ones.

In Figure XI - 4 the drawings have been rotated in such a way that the intergrown slabs are horizontal. Thus it becomes possible to "read" vertically in the drawings the sequence of Jagodzinski - Wyckoff stacking letters for each stacking variant. For each variant is given in the last line the hexagonality value.
All CrB - FeB stacking variants have monoclinic or orthorhombic unit cells of different dimensions and originally the geometrical relationship between them was not seen immediatly. There are a number of systems where several CrB - FeB stacking variants occur. The hexagonality of the CrB - FeB stacking variants is found to be an ordering parameter for the sequence of these phases. As example we present in Table XI - 1 the different CrB - FeB stacking variants which occur in the pseudobinary $Gd_{1-x}R'_xNi$ systems.

TABLE XI - 1 : HOMOGENEITY RANGES OF THE CRB - FEB STACKING VARIANTS IN $GD_{1-x}R'_xNI$ AT 1070°K. XI - 4)

GdNi	CrB type 0 %	44 %	50 %	67 %	67	TbNi
GdNi	CrB type 0 %	50%	67 %	FeB type 100 %		DyNi
GdNi	CrB type 0 %	67 %	FeB type 100 %			HoNi
GdNi	CrB type 0 %	40%	67 %	FeB type 100 %		ErNi
GdNi	CrB type 0 %	67%	FeB type 100 %			ErNi
GdNi	CrB type 0 %	FeB type 100 %				LuNi

The numbers inscribed in Table XI - 1 are the hexagonality values of the stacking variants. These values can be used to find the drawings of the stacking variants in Figure XI - 4. To distinguish between the two different structures with 66.7 % hexagonality one of them will be underlined, *i.e.* 67 will be assigned to the TbNi *LT* type with stacking h_4c_2.
The hexagonality of all the stacking variants in Table XI - 1 increases within one row from left to the right. This is an useful observation for which a theoretical explanation is missing. The number of the intermediate phases and their homogeneity ranges vary with the rare-earth partners of the Gd element. Intermediate stackings between CrB and FeB may be even completely missing as it is in the case of $Gd_{1-x}Lu_xNi$. The hexagonality depends, however, also ón temperature as can be seen in Figure XI - 4 by the hexagonality difference between TbNi *LT* (67 %) and TbNi *HT* (33 %).

Linear inhomogeneous structure series

The efforts undertaken In the last 10 to 15 years to reinterpret many of the older already known crystal structures as well as the new ones as intergrowth structures were quite successful any many new linear inhomogeneous structure series have been found. For an overview see Volume 1 of the TYPIX book (Reference Book list in Chapter on Bibliography).
The recognition of the parent structures and determination of the Miller indices of their slab interfaces is not always as simple as it was for the Ruddlesden - Popper phases in Figure XI - 1. Depending on what kind of parent structures should be intergrown the slabs might have to be sliced in a different manner to have suitable interface planes.

XI - 4) Klepp, K. & Parthé, E. (1982). J. Less-Common Met. 85, 181 - 194.

For example in the Ruddlesden - Popper phases the NaCl-type slabs had $(001)_{NaCl}$ interface planes. If a NaCl-type slab is to be intergrown with a slab of a hexagonal structure for which the most common interface plane is the hexagonal base plane with a simple hexagonal mesh then the NaCl-type slab must be different, *i.e.* one needs a NaCl-type slab which is sliced parallel to $(111)_{NaCl}$ at $x,y,z = 0$ and $x,y,z = 1/3$. This slab has the thickness of one third of the cubic space diagonal. [XI - 5)] Examples for the intergrowth of these kinds of NaCl-type slabs with hexagonal parent structures are presented in Figure XI - 5. If it is not possible to find planes with identical atom arrangement in the two parent structures an intergrowth structure can not form.

In Figure XI - 5 are shown the structures which can be interpreted as an intergrowth of NaCl-type slabs with WC-type slabs (left) [XI - 6)] and CdI_2-type slabs (right), respectively. In the drawings of Figure XI - 5 not all the atoms in the hexagonal unit cells can be seen, but only those which are positioned on the $(11\bar{2}0)$ planes of their hexagonal unit cells. By imaging the atoms which are before and behind the $(11\bar{2}0)$ plane the reader will find out readily that in the

WC-type slab : atoms drawn with small open circles are trigonal prismatically coordinated,
NaCl-type slab : atoms shown as small black circles are octahedrally coordinated, and
CdI_2-type slab : atoms drawn represented by small open circles have a triangular non-coplanar coordination.

In one unit cell of the NiAs and Ti_2CS structures there are two WC-type slabs which are rotated in respect to each other by 180 ° around an axis perpendicular to the interface which is the hexagonal base plane.

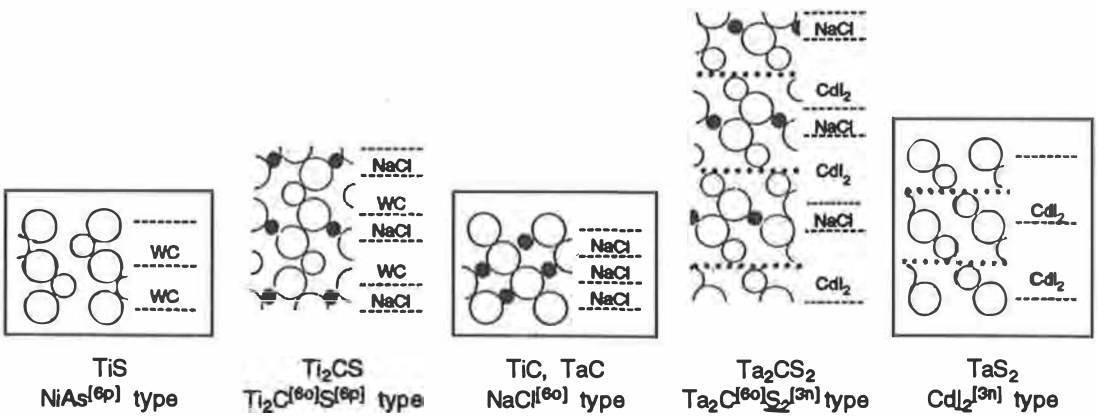


Figure XI - 5 : Linear inhomogeneous intergrowth structures based on slabs sliced from an hexagonal parent structure with WC or CdI_2 type, respectively, and on slabs with NaCl type. The size ratio of the circles does not correspond to the size ratio of the atoms. The dashed lines to the right of the drawings are the traces of the slab interface planes. The dotted lines inside the CdI_2-type slabs are the traces of horizontal cleavage planes which are not crossed by directed covalent bonds.

XI - 5) If one starts with a NaCl-type structure described with its triple-hexagonal cell (see Problem 14 in Appendix B) the interface planes of the new NaCl-type slab are the hexagonal (00.1) base planes at $z = 0$ and $z = 1/3$.

XI - 6) The unit cells of the WC and the CdI_2 (C6 type) structures contain only two and three atoms, respectively. The thickness of the WC- and of the CdI_2-type slabs corresponds to the height of their hexagonal cells.

In the chosen binary transition metal compounds the C atoms prefer an octahedral coordination and the S atom a trigonal prismatic coordination or - if there is a non-bonding electron pair attached to the S atom - a triangular non-coplanar coordination. In the ternary compounds these elements have the same coordination, as the ternary structures are built up of intergrown slabs sliced from the corresponding binary structures.

Linear intergrowth of binary and ternary Laves-type and $CaCu_5$-type slabs.
More than 30 (!) structure types exist with binary and ternary intermetallic compounds having in part grotesque stoichiometries which can be "read" and understood as an intergrowth of Laves-type and $CaCu_5$-type slabs.
The Laves-type slabs correspond to those shown in Figure I - 7. Their interface planes are parallel to $(00.1)_{MgZn_2}$ and their thickness is $c/2$ referred to hexagonal $MgZn_2$ (or $c/3$ referred to the triple-hexagonal cell of $MgCu_2$). The atom arrangement on the hexagonal base plane - different from the simple hexagonal mesh of WC and CdI_2 - has a so-called Kagomé mesh, seen in Figure XI - 6. Kagomé is originally the name of a three-way bamboo weave used in the Far East for making baskets (kago = basket and mé = eye in Japanese). A Kagomé mesh is the repetetive pattern obtained if points are placed where bamboo reeds cross each other.

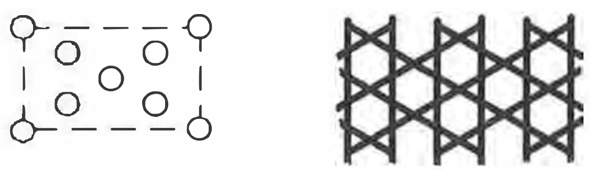


Figure XI - 6 : The atom arrangement with Kagomé mesh at the interfaces of the Laves-type and $CaCu_5$-type slabs (left) and the Kagomé weave pattern (right).

With the kind of binary and ternary rare-earth (*R*) - transition metal (*T*) - main group (*M* = B, Ga, Si, Ge) compounds, which we want to discuss in more details, one finds not only binary Laves-type slabs with general formula R_2T_4, but also ternary, substituted Laves-type slabs with formula R_2T_3M, which can be compared with each other in the upper part of Figure XI - 7. The interface planes are always occupied by *T* atoms only, the substitution of *T* by *M* occurs inside the slab.

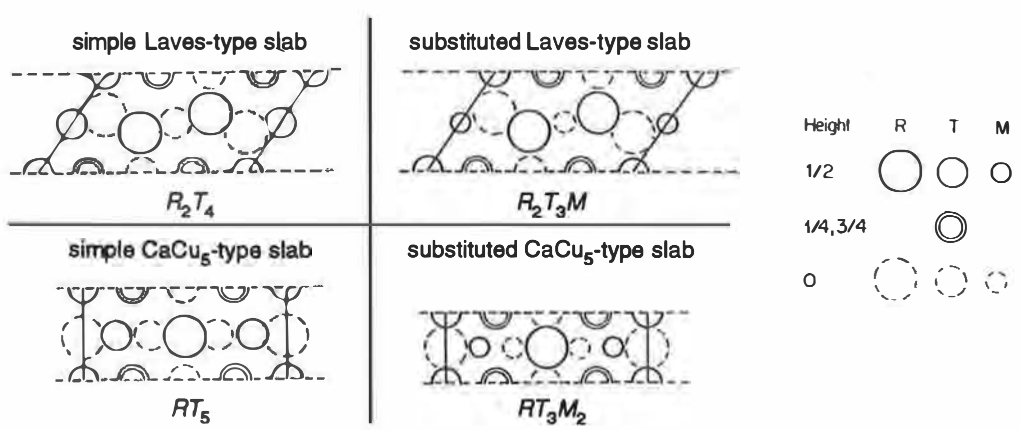


Figure XI - 7 : The simple binary and the substituted ternary Laves- and $CaCu_5$-type slabs.

The compounds with hexagonal $CaCu_5$-type structure have in the hexagonal base plane also a transition metal arrangement with Kagomé mesh. We have to consider also here binary slabs of general formula RT_5 and ternary, substituted slabs with general formula RT_3M_2, both slabs being shown in the lower part of Figure XI - 7. The substituted slab is generally not as thick as the unsubstituted slab but this detail will be ignored for the further considerations.
In Figure XI - 8 is shown a ternary *R - T - M* diagram and in it, framed by heavy lines, the composition field where structures with intergrown Laves-type and/or $CaCu_5$-type slabs occur. At the four corners of this frame are the formulae which correspond to the four kinds of slabs of Figure XI -7. Small symbols, *i.e.* rectangles and parallelograms have been added to these formulae. Instead of writing the slab formula we shall find it more convenient further on to identify the slabs by these small symbols which copy the slab outlines in Figure XI - 7. The symbols corresponding to ternary slabs have stripes inside, while symbols for binary slabs are without stripes.

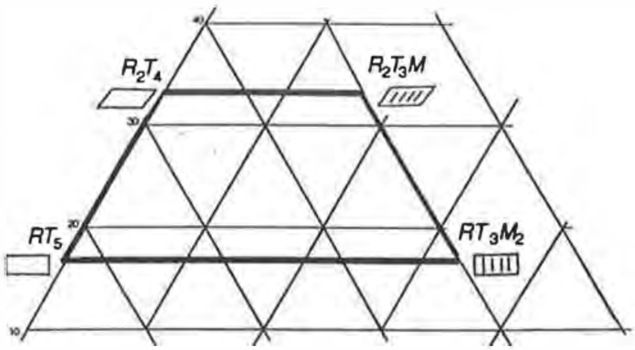


Figure XI - 8 : The composition field of intergrowth structures with Laves-type and/or $CaCu_5$-type slabs in a R - T - M diagram. The very small numbers on the left refer to the horizontal lines and indicate the atom percentage of rare-earth element.

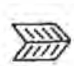
The different structure series which can be formed by an intergrowth of these four slabs can be divided into three groups according to the compositions of its members, *i.e.*

1) - all members of the series have the same general formula
2) - all members of the series have the same percentage of rare-earth element and
3) - the members of the series have different formulae.

1) Structure series where members have the same general formula

These are linear homogeneous structure series with only one kind of slab. Successive slabs are intergrown with or without rotation by 180° around an axis perpendicular to the interface plane. Examples of rare-earth compounds with composition R_2T_4 and R_2T_3M, respectively, built with binary and ternary Laves-type slabs, respectively, are shown in Table XI - 2. Different from the Laves-type slabs, both binary and ternary $CaCu_5$-type slabs are invariant to a rotation by 180°. Therefore a homogeneous structure series with these slabs is not possible.

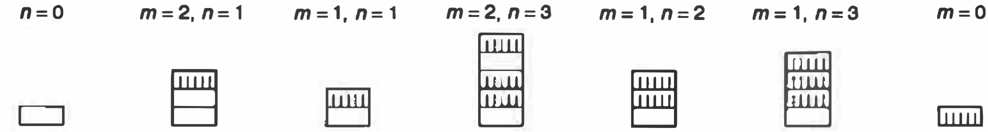
TABLE XI - 2 : EXAMPLES OF MEMBERS OF THE HOMOGENEOUS R_2T_4 AND R_2T_3M STRUCTURE SERIES.

R_2T_4 structure series		R_2T_3M structure series	
			
$HoOs_2$ ($MgZn_2$ type)	$PrOs_2$ ($MgCu_2$ type)	Sc_2Co_3Si (Mg_2Cu_3Si type)	Y_2Rh_3Ge (Mg_2Ni_3Si type)

2) Structure series where members have the same percentage of rare-earth element

In these linear quasihomogeneous structure series is observed an intergrowth of binary and substituted ternary slabs of the same kind. The structure series with 16.7 at.% R where there is an intergrowth of m binary RT_5 slabs with n ternary RT_3M_2 slabs has $R_{m+n}T_{5m+3n}M_{2n}$ as general formula. All the examples listed in Table XI - 3 are prototypes of individual structure types except for $SmCo_5$ which crystallizes with $CaCu_5$ type. Representatives for the second possible quasihomogeneous structure series with 33.3 at.% R where binary and ternary Laves-type slabs are intergrown have not yet been found.

TABLE XI - 3 : EXAMPLES OF MEMBERS OF THE QUASIHOMOGENEOUS $R_{m+n}T_{5m+3n}M_{2n}$ STRUCTURE SERIES WITH 16.7 AT.% R.



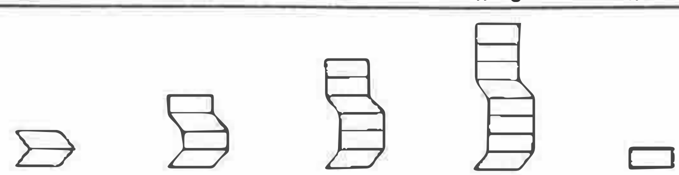
$n=0$	$m=2, n=1$	$m=1, n=1$	$m=2, n=3$	$m=1, n=2$	$m=1, n=3$	$m=0$
$SmCo_5$	$Nd_3Ni_{13}B_2$	$CeCo_4B$	$Lu_5Ni_{19}B_6$	$Ce_3Co_{11}B_4$	$Ce_2Co_7B_3$	$CeCo_3B_2$

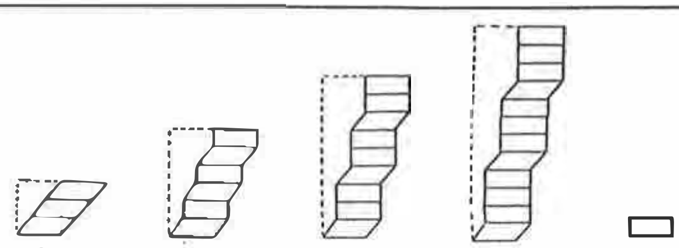
3) Structure series where members have different formulae

In these linear inhomogeneous structure series there is an intergrowth of Laves-type and $CaCu_5$-type slabs. Of the different possibilities which exist we want to discuss only two, *i.e.* all slabs are binary only or they are all ternary substituted slabs. The compositions of the members of the first and second series, respectively, are on the left and right border line, respectively, of the marked composition field in the R - T - M diagram in Figure XI - 8.

The structure series where one binary Laves-type slab R_2T_4 is intergrown with n binary $CaCu_5$-type slabs RT_5 has the general formula $R_{2+n}T_{4+5n}$. There exist two branches of this series, as seen in Table XI - 4, which differ in respect to the rotation of successive Laves-type slabs, *i.e.* being rotated as in $MgZn_2$ or not rotated as in $MgCu_2$.

TABLE XI - 4 : EXAMPLES OF MEMBERS OF THE BINARY INHOMOGENEOUS $R_{2+n}T_{4+5n}$ STRUCTURE SERIES

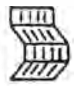
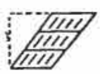
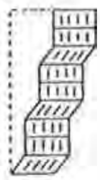




	$n=0$	$n=1$	$n=2$	$n=3$	$n=\infty$
Laves-type slabs stacked as in $MgZn_2$	$HoOs_2$	$CeNi_3$	Ce_2Ni_7	Sm_5Co_{19}	$SmCo_5$
Laves-type slabs stacked as in $MgCu_2$	$PrOs_2$	$PuNi_3$	Gd_2Co_7	Ce_5Co_{19}	$SmCo_5$

The structure series where one ternary substituted Laves-type slab R_2T_3M is intergrown with n ternary $CaCu_5$-type slabs RT_3M_2 has the general formula $R_{2+n}T_{3+3n}M_{1+2n}$. Again there are two branches depending on the rotation of the Laves-type slabs. The examples are presented in Table XI - 5.

TABLE XI - 5 : EXAMPLES OF MEMBERS OF THE TERNARY INHOMOGENEOUS $R_{2+n}T_{3+3n}M_{1+2n}$ STRUCTURE SERIES

	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = \infty$
Laves-type slabs stacked as in $MgZn_2$	 Sc_2Co_3Si	 YRh_2Si	 $Y_4Ir_9Si_5$		 $CeCo_3B_2$
Laves-type slabs stacked as in $MgCu_2$	 Y_2Rh_3Ge		 $Y_4Rh_9Si_5$		 $CeCo_3B_2$

Examples of intergrowth structures which are positioned inside the composition field of Figure XI - 8 are treated in Appendix B.

⇒⇒⇒ Problem 13 in Appendix B

Ternary $R_rT_tM_m$ compounds with a linear intergrowth of other kinds of slabs

For many R - T - M systems there seems to exist a limited number of elementary, binary and ternary parent structures which have essentially a simple atom arrangement. Intermetallic compounds with a composition which is inbetween the compositions of the parent structures can often be interpreted as an intergrowth of segments of two or three parent structures. If the composition of the $R_rT_tM_m$ compound is outside the composition field in Figure XI - 8 then the slabs have to be sliced from different parent structures. We consider the section of the ternary R - T - M diagram which is shown in Figure XI - 9.

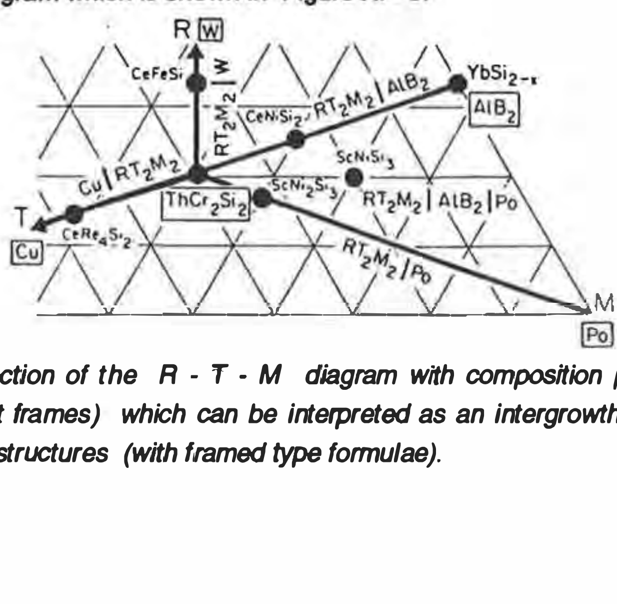


Figure XI - 9 : Section of the R - T - M diagram with composition points of five ternary compounds (without frames) which can be interpreted as an intergrowth of slabs sliced from two or three parent structures (with framed type formulae).

As elemental parent structures serve the W, α-Po and Cu types, as binary parent structure the AlB_2 type and the $ThCr_2Si_2$ type as ternary parent structure. The structures and slabs sliced from them are shown in Figure XI - 10.

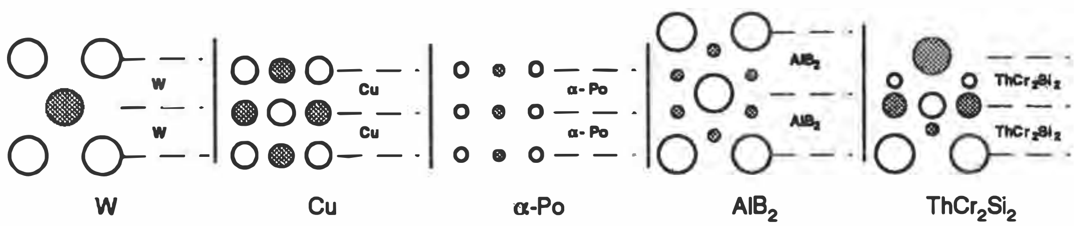


Figure XI - 10 : The five parent structures and the slabs sliced from them which are used for intergrowth in the structures shown in Figure XI - 11.

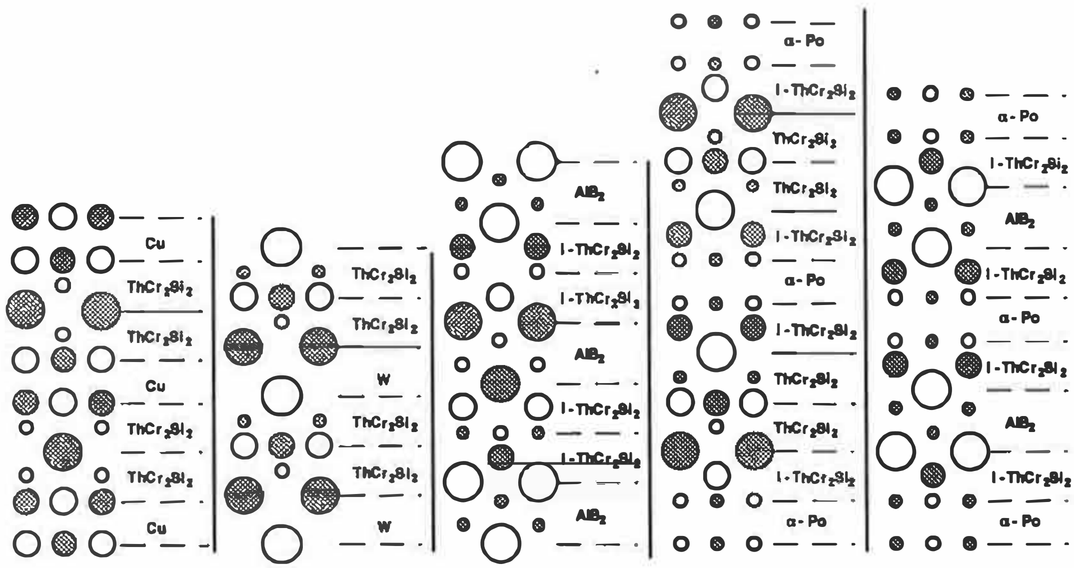
Empty and filled circles in Figure XI - 10 correspond to atoms which differ in half of a translation period perpendicular to the plane of projection. Thus if in a drawing of a slab the originally filled circles are empty and *vice versa* it simply means that this slab, as compared to the original one, is raised for half a translation period. In the ternary intergrowth structures presented in Figure XI - 11 the sites of the large circles are occupied by rare-earth elements (*R*), the medium circles by transition elements (*T*) and the small circles by the main group element silicon (*M*).

There are two kinds of complications as compared to the simpler case of intergrown Laves-type and $CaCu_5$-type slabs.

- Opposite interface planes of the ternary $ThCr_2Si_2$-type slab have not the same atom arrangement. One allows, for example, an intergrowth with a W-type slab and the other an intergrowth with a Cu-type slab. However, if a double slab is formed the external interfaces are identical. Depending which slab interface plane is used to form the double slab one has a $ThCr_2Si_2$-type double slab which can be intergrown on both sides with Cu-type slabs (example is $CeRe_4Si_2$) or W-type slabs, respectively (example is CeFeSi). A normal $ThCr_2Si_2$-type slab cannot be intergrown with an α-Po-type slab because there are no *M* atoms at the interface planes. However, an intergrowth is possible with an interchanged $ThCr_2Si_2$ slab, denoted by I - $ThCr_2Si_2$, which has the same composition, but where *T* and *M* elements have interchanged their sites (see $ScNi_2Si_3$ and $ScNiSi_3$).
- The parent structure, which serves to describe the atom arrangement of an intergrown segment, is not always found in the same ternary diagram. The parent structure will, however, have a relation to the structure observed at the same composition in the diagram. It might correspond to a high temperature modification, a high-pressure form or the structure of a homologue element or compound. For example, slabs consisting only of rare earth elements have an arrangement which corresponds to the W type, which is the structure of the high temperature modification of the rare earth elements. Slabs consisting only of main group elements have the atom arrangement of the α-Po type, which is the ultrahigh pressure structure of the ***5B*** elements. Slabs consisting of transition elements only are built as the Cu type.

The binary *RM* compounds (not shown in Figure XI - 9) are on the composition line between *R* and RM_2. Parent structures exist for *R* and RM_2. Thus a possibility for the structure of a *RM* compound is the linear intergrowth of W-type slabs with AlB_2-type slabs. This is exactly the CrB type, as can be verified by a closer study of Figure XI - 2. The CrB type is widely distributed with rare-earth monosilicides, germanides and gallides.

What has been demonstrated for CrB is equally valid for the five ternary intermetallic compounds of Figure XI - 9. Ternary compounds with a composition on the line between the compositions of two parent structures can be interpreted as an intergrowth of slabs of these two parent structures. $ScNiSi_3$ is located in a field between three parent structures and it can be interpreted as an intergrowth of slabs of these three parent structures. In Figure XI - 11 are presented drawings of these five intergrowth structures with the used slabs indicated on the right hand side of the drawings.

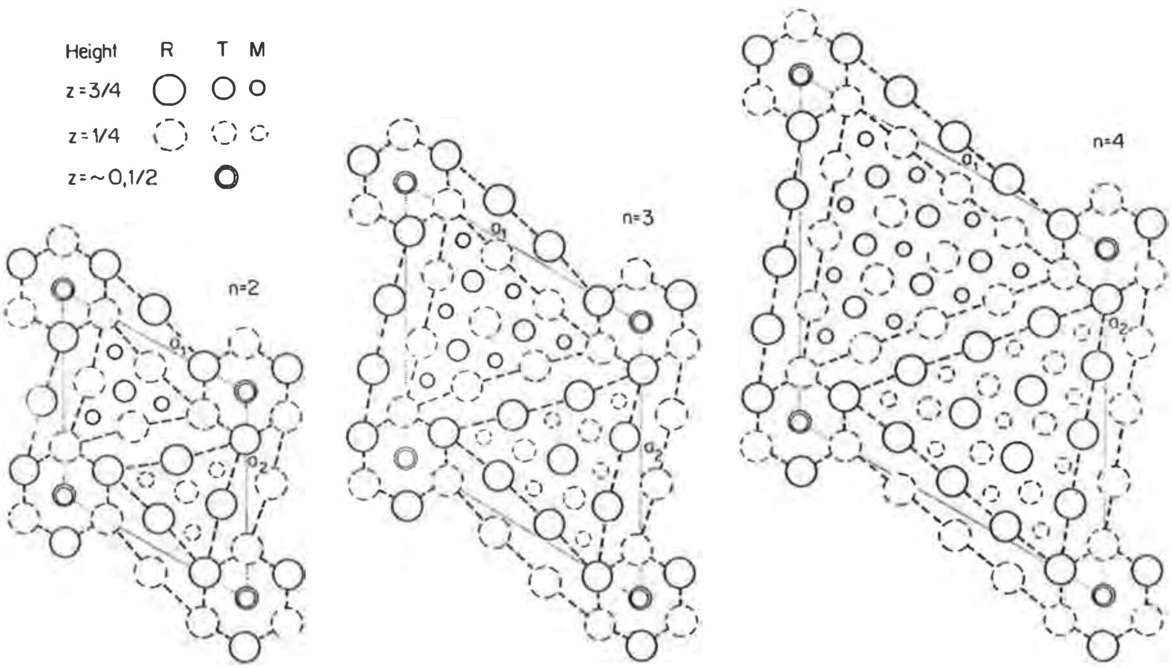


$CeRe_4Si_2$ CeFeSi $CeNiSi_2$ $ScNi_2Si_3$ $ScNiSi_3$

Figure XI - 11 : The linear intergrowth structures of $CeRe_4Si_2$, CeFeSi (PbClF antitype), $CeNiSi_2$, $ScNi_2Si_3$ and $ScNiSi_3$ and the slabs used for their construction.

Two-dimensional inhomogeneous structure series

In a two-dimensional inhomogeneous structure series we find intergrown columns of different diameters. We take as an example the $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ structure series. As seen in Figure XI - 12 this structure series is characterized by infinite triangular columns with (ternary) AlB_2 type, infinite hexagonal columns with NiAs type (at the origin of the hexagonal cells) and infinite rhombic columns with W type (inbetween the triangular columns). Within the structure series the diameter of the triangular column increases, expresses by the parameter *n* which corresponds to the number of joined trigonal prisms along one of the basal edges of the triangular columns. Due to the quadratic structure series formula the compositions of the members of this structure series are not on a straight line but on a curve, which can be seen in Figure XI - 13.



$Ce_6Ni_2Si_3$ $Ce_5Ni_2Si_3$ $Pr_{15}Ni_7Si_{10}$

Figure XI - 12 : The crystal structures of $Ce_6Ni_2Si_3$, $Ce_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$, members of the $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ structure series with $n = 2$, 3 and 4.

The particular order of the Ni and Si atoms on the prism center sites and, related with it, the composition of the ordered compounds can be derived by means of the **prism waist contact restriction rule.** [XI - 7] The Ni and Si atom ordering shown in Figure XI - 12 for $Pr_{15}Ni_7Si_{10}$ (originally published as $Pr_{15}Ni_4Si_{13}$) was derived by this rule and later verified experimentally. The composition published for $n = 2$ is $Ce_6Ni_2Si_3$, but Ce_2NiSi instead of $Ce_5Ni_2Si_3$ for $n = 3$. The here proposed changed composition and order of Si and Ni atoms should be tested.

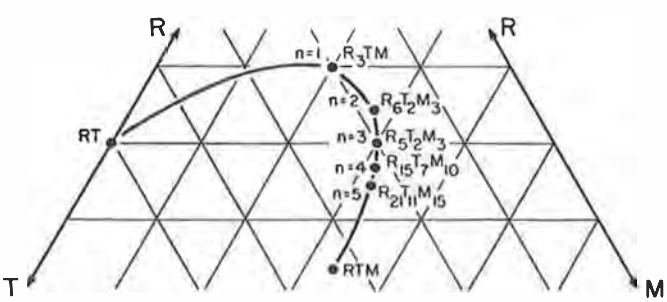


Figure XI - 13 : Composition curve for the $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ structure series in a R - T - M phase diagram.

XI - 7) The experimental prism waist contact restriction rule applies to ternary R - Ni - Si(Ge) compounds with Ni- and Si(Ge)- centred elongated trigonal prisms of R atoms. It refers to the waist contact of a Ni atom at the prism centre, i.e. the contact that this atom makes at bonding distance with another atom in the central plane perpendicular to the prism axis. The rule states that Ni - R and Ni - Ni waist contacts are to be excluded. This rule has been used successfully to predict the compositions for a perfect order of compounds for which a random distribution of prism-centre sites by Ni and Si(Ge) atoms has been reported. For details, see Parthé, E. & Hovestreydt, E. (1985). J.Less-Common Metals 110, 307 - 313.

APPENDIX A : UNIT CELL TRANSFORMATIONS

General transformation formulae

To elucidate geometrical relationships between structures which are not described with the same kind of unit cell it is useful to perform unit cell transformations.

We assume a unit cell characterized by the cell vectors **a**, **b**, **c** and having a volume V. The cell volume V can be calculated in a general way from the **Niggli matrix N** which contains as elements the scalar products of the cell vectors.

$$\mathbf{N} = \begin{pmatrix} \mathbf{a}\bullet\mathbf{a} & \mathbf{a}\bullet\mathbf{b} & \mathbf{a}\bullet\mathbf{c} \\ \mathbf{b}\bullet\mathbf{a} & \mathbf{b}\bullet\mathbf{b} & \mathbf{b}\bullet\mathbf{c} \\ \mathbf{c}\bullet\mathbf{a} & \mathbf{c}\bullet\mathbf{b} & \mathbf{c}\bullet\mathbf{c} \end{pmatrix} \qquad \text{(A - 1)}$$

The square root of the determinant of the Niggli matrix is equal to the unit cell volume, *i.e.*

$$V = |\mathbf{N}|^{1/2} \qquad \text{(A - 2)}$$

Example : Calculation of the volume of a monoclinic unit cell with $\beta \neq 90°$.

$$\mathbf{N} = \begin{pmatrix} a^2 & 0 & ac\cdot\cos\beta \\ 0 & b^2 & 0 \\ ac\cdot\cos\beta & 0 & c^2 \end{pmatrix} \qquad \text{thus} \quad V = abc\cdot\sin\beta \qquad \text{(A - 3)}$$

If the given unit cell has to be transformed to a new unit cell with the new cell vectors **a'**, **b'**, **c'** and having volume V', the following relations apply :

$$\begin{aligned} \mathbf{a}' &= s_{11}\mathbf{a} + s_{12}\mathbf{b} + s_{13}\mathbf{c} \\ \mathbf{b}' &= s_{21}\mathbf{a} + s_{22}\mathbf{b} + s_{23}\mathbf{c} \\ \mathbf{c}' &= s_{31}\mathbf{a} + s_{32}\mathbf{b} + s_{33}\mathbf{c} \end{aligned} \quad \text{or simply} \quad \begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{pmatrix} = \mathbf{S} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} \quad \text{with } \mathbf{S} = \begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{pmatrix} \qquad \text{(A - 4)}$$

The determinant of the transformation matrix **S** is equal to the quotient of the unit cell volumes.

$$V'/\,V = |\mathbf{S}| \qquad \text{(A - 5)}$$

Transformation of a triclinic cell into another triclinic cell (can be used for other systems as well)

$$\begin{aligned} \mathbf{a}'\bullet\mathbf{a}' = (a')^2 &= (s_{11}a)^2 + (s_{12}b)^2 + (s_{13}c)^2 + 2s_{11}s_{12}ab\cdot\cos\gamma + 2s_{11}s_{13}ac\cdot\cos\beta + 2s_{12}s_{13}bc\cdot\cos\alpha \\ \mathbf{b}'\bullet\mathbf{b}' = (b')^2 &= (s_{21}a)^2 + (s_{22}b)^2 + (s_{23}c)^2 + 2s_{21}s_{22}ab\cdot\cos\gamma + 2s_{21}s_{23}ac\cdot\cos\beta + 2s_{22}s_{23}bc\cdot\cos\alpha \\ \mathbf{c}'\bullet\mathbf{c}' = (c')^2 &= (s_{31}a)^2 + (s_{32}b)^2 + (s_{33}c)^2 + 2s_{31}s_{32}ab\cdot\cos\gamma + 2s_{31}s_{33}ac\cdot\cos\beta + 2s_{32}s_{33}bc\cdot\cos\alpha \end{aligned} \qquad \text{(A - 6)}$$

$$\begin{aligned} \cos\alpha' = {} & [s_{21}s_{31}a^2 + s_{22}s_{32}b^2 + s_{23}s_{33}c^2 + (s_{21}s_{32} + s_{22}s_{31})ab\cdot\cos\gamma + (s_{21}s_{33} + s_{23}s_{31})ac\cdot\cos\beta + \\ & + (s_{22}s_{33} + s_{23}s_{32})bc\cdot\cos\alpha] / (b'\cdot c') \\ \cos\beta' = {} & [s_{11}s_{31}a^2 + s_{12}s_{32}b^2 + s_{13}s_{33}c^2 + (s_{11}s_{32} + s_{12}s_{31})ab\cdot\cos\gamma + (s_{11}s_{33} + s_{13}s_{31})ac\cdot\cos\beta + \\ & + (s_{12}s_{33} + s_{13}s_{32})bc\cdot\cos\alpha] / (a'\cdot c') \\ \cos\gamma' = {} & [s_{11}s_{21}a^2 + s_{12}s_{22}b^2 + s_{13}s_{23}c^2 + (s_{11}s_{22} + s_{12}s_{21})ab\cdot\cos\gamma + (s_{11}s_{23} + s_{13}s_{21})ac\cdot\cos\beta + \\ & + (s_{12}s_{23} + s_{13}s_{22})bc\cdot\cos\alpha] / (a'\cdot b') \end{aligned} \qquad \text{(A - 7)}$$

To transform the positional atom coordinates one needs the inverse transformation matrix **T**.

$$\begin{aligned} \mathbf{a} &= t_{11}\mathbf{a}' + t_{12}\mathbf{b}' + t_{13}\mathbf{c}' \\ \mathbf{b} &= t_{21}\mathbf{a}' + t_{22}\mathbf{b}' + t_{23}\mathbf{c}' \\ \mathbf{c} &= t_{31}\mathbf{a}' + t_{32}\mathbf{b}' + t_{33}\mathbf{c}' \end{aligned} \quad \text{or simply} \quad \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} = \mathbf{T} \begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{pmatrix} \quad \text{with } \mathbf{T} = \begin{pmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{pmatrix} \qquad \text{(A - 8)}$$

In analogy to (A - 5) one finds that

$$V / V' = |\mathbf{T}| \qquad \text{(A - 9)}$$

The elements of **T** can be obtained as follows

$$\mathbf{T} = \begin{pmatrix} (s_{22}s_{33} - s_{23}s_{32}) / |\mathbf{S}| & (s_{13}s_{32} - s_{12}s_{33}) / |\mathbf{S}| & (s_{12}s_{23} - s_{13}s_{22}) / |\mathbf{S}| \\ (s_{23}s_{31} - s_{21}s_{33}) / |\mathbf{S}| & (s_{11}s_{33} - s_{13}s_{31}) / |\mathbf{S}| & (s_{13}s_{21} - s_{11}s_{23}) / |\mathbf{S}| \\ (s_{21}s_{32} - s_{22}s_{31}) / |\mathbf{S}| & (s_{12}s_{31} - s_{11}s_{32}) / |\mathbf{S}| & (s_{11}s_{22} - s_{12}s_{21}) / |\mathbf{S}| \end{pmatrix} \qquad \text{(A - 10)}$$

As final test serves the multiplication of **S** with **T** which must result in the unity matrix.

$$\mathbf{T} \bullet \mathbf{S} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \text{(A - 11)}$$

According to a formalism presented in Volume I of the 1952 edition of the International Tables for X - Ray Crystallography the transformation coefficients are placed into two complementary square matrices. The arrow originates from the cell (primed or unprimed) for which one wants to find new unit cell vectors or positional atom coordinates. The arrow points to the cell in which terms these parameters are expressed. For an exercise identify (A - 4) and (A - 8) in (A - 12).

↓←		x	y	z
	↑→	**a**	**b**	**c**
x'	**a'**	s_{11}	s_{12}	s_{13}
y'	**b'**	s_{21}	s_{22}	s_{23}
z'	**c'**	s_{31}	s_{32}	s_{33}

↓←		x'	y'	z'
	↑→	**a'**	**b'**	**c'**
x	**a**	t_{11}	t_{12}	t_{13}
y	**b**	t_{21}	t_{22}	t_{23}
z	**c**	t_{31}	t_{32}	t_{33}

(A - 12)

Examples : $\mathbf{b}' = s_{21}\mathbf{a} + s_{22}\mathbf{b} + s_{23}\mathbf{c}$ $\quad y' = t_{12}x + t_{22}y + t_{32}z$ $\quad z = s_{13}x' + s_{23}y' + s_{33}z'$

The same matrices can be used to transform Miller indices *hkl* (direction of the arrows as for **a, b, c**), zone axes *u v w* and reciprocal lattice vectors **a*, b*, c*** (direction of the arrows as for *x, y, z*).

Determinant of a 3 x 3 matrix and multiplication of a matrix with a column vector or another matrix.

$$\begin{vmatrix} a & d & g \\ b & e & h \\ c & f & i \end{vmatrix} = aei + dhc + gbf - (ahf + dbi + gec) \qquad \begin{pmatrix} a & d & g \\ b & e & h \\ c & f & i \end{pmatrix} \bullet \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} a{\cdot}A + d{\cdot}B + g{\cdot}C \\ b{\cdot}A + e{\cdot}B + h{\cdot}C \\ c{\cdot}A + f{\cdot}B + i{\cdot}C \end{pmatrix}$$

$$\begin{pmatrix} a & d & g \\ b & e & h \\ c & f & i \end{pmatrix} \bullet \begin{pmatrix} A & B & C \\ D & E & F \\ G & H & I \end{pmatrix} = \begin{pmatrix} a{\cdot}A + d{\cdot}D + g{\cdot}G & a{\cdot}B + d{\cdot}E + g{\cdot}H & a{\cdot}C + d{\cdot}F + g{\cdot}I \\ b{\cdot}A + e{\cdot}D + h{\cdot}G & b{\cdot}B + e{\cdot}E + h{\cdot}H & b{\cdot}C + e{\cdot}F + h{\cdot}I \\ c{\cdot}A + f{\cdot}D + i{\cdot}G & c{\cdot}B + f{\cdot}E + i{\cdot}H & c{\cdot}C + f{\cdot}F + i{\cdot}I \end{pmatrix}$$

It is important to be aware, that for certain space groups the rotation or inversion of the coordinate system requires a translation component. [A - 1)] An example for space group *Imma* is found in Table I - 1 where it is shown that an interchange of the *a* and *b* axes of the KHg_2 structure requires an origin shift of the unit cell by $^1/_4\ ^3/_4\ ^3/_4$.

Transformations frequently used in crystal chemical studies

From the quotient of the unit cell volumes one can calculate the number of atoms contained in a new cell. This number should be used to check if one has found all the atoms when transforming unit cells. When using the transformation matrices to calculate the positional atom coordinates in a new cell one inserts as input the atom coordinates referred to the old cell. To obtain all the positional coordinates within the new cell it might be necessary - depending on the size and orientation of the new cell - to use as input also atom coordinates which are outside the original unit cell limits, *i.e.* $x, y, z \geq 1$ and/or < 0.

a) Rhombohedral cell (**r**) ⇔ Triple-hexagonal cell (**th**) with $V_{th} = 3V_r$

$x\,y\,z$ + [0 0 0]

$a_r = (a_{th}/3)\cdot[(c_{th}/a_{th})^2 + 3]^{1/2}$

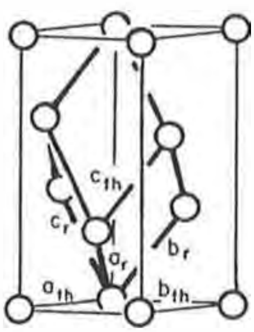
$\sin(\alpha/2) = 3/\{2\cdot[(c_{th}/a_{th})^2 + 3]^{1/2}\}$

$x\,y\,z$ + [0 0 0, $^1/_3\ ^2/_3\ ^2/_3$, $^2/_3\ ^1/_3\ ^1/_3$]

$a_{th} = 2a_r \sin(\alpha/2)$

$c_{th} = (3)^{1/2} a_r (1 + 2\cos\alpha)^{1/2}$

$c_{th}/a_{th} = [(3)^{1/2}\cdot(1 + 2\cos\alpha)^{1/2}] / [2\sin(\alpha/2)]$



$$\begin{array}{cc} & \mathbf{r} \\ \mathbf{th} & \begin{bmatrix} +1 & -1 & 0 \\ 0 & +1 & -1 \\ +1 & +1 & +1 \end{bmatrix} \end{array} \qquad \begin{array}{cc} & \mathbf{th} \\ \mathbf{r} & \begin{bmatrix} +^2/_3 & +^1/_3 & +^1/_3 \\ -^1/_3 & +^1/_3 & +^1/_3 \\ -^1/_3 & -^2/_3 & +^1/_3 \end{bmatrix} \end{array} \qquad \text{(A - 13)}$$

Figure A - 1 : Rhombohedral and its corresponding triple-hexagonal unit cell.

b) Cubic face-centred cell (cF) ⇔ Triple-hexagonal cell (**th**) with $V_{th} = ^3/_4\ V_{cF}$

$x\,y\,z$ + [0 0 0, 0 $^1/_2\ ^1/_2$, $^1/_2$ 0 $^1/_2$, $^1/_2\ ^1/_2$ 0]

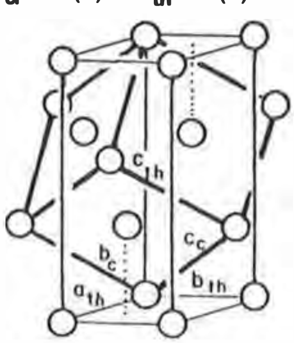
$a_{cF} = (2)^{1/2} a_{th} = (3)^{1/2} c_{th}/3$

$x\,y\,z$ + [0 0 0, $^1/_3\ ^2/_3\ ^2/_3$, $^2/_3\ ^1/_3\ ^1/_3$]

$a_{th} = (2)^{1/2} a_{cF}/2$

$c_{th} = (3)^{1/2} a_{cF}$

$c_{th}/a_{th} = (6)^{1/2} = 2.449$ $\qquad (\alpha_r = 60°)$



$$\begin{array}{cc} & \mathbf{cF} \\ \mathbf{th} & \begin{bmatrix} -^1/_2 & +^1/_2 & 0 \\ 0 & -^1/_2 & +^1/_2 \\ +1 & +1 & +1 \end{bmatrix} \end{array} \qquad \begin{array}{cc} & \mathbf{th} \\ \mathbf{cF} & \begin{bmatrix} -^4/_3 & -^2/_3 & +^1/_3 \\ +^2/_3 & -^2/_3 & +^1/_3 \\ +^2/_3 & +^4/_3 & +^1/_3 \end{bmatrix} \end{array} \qquad \text{(A - 14)}$$

Figure A - 2 : Face-centred cubic and its corresponding triple-hexagonal unit cell.

A - 1) For details see Table 6 in Parthé, E. & Gelato, L.M. (1984). Acta Cryst. ***A40****, 169 - 183.*

c) Cubic primitive cell **(cP)** ⇔ Triple-hexagonal cell **(th)** with $V_{th} = 3\ V_{cP}$

$x\,y\,z$ + [0 0 0]

$a_{cP} = (2)^{1/2}\, a_{th} / 2 = (3)^{1/2}\, c_{th} / 3$

$x\,y\,z$ + [0 0 0, 1/3 2/3 2/3, 2/3 1/3 1/3]

$a_{th} = (2)^{1/2}\, a_{cP}$

$c_{th} = (3)^{1/2}\, a_{cP}$

$c_{th} / a_{th} = (6)^{1/2} / 2 = 1.225 \qquad (\alpha_r = 90°)$

$$\begin{array}{cc} & \textbf{cP} \\ \textbf{th} & \begin{bmatrix} 0 & +1 & -1 \\ -1 & 0 & +1 \\ +1 & +1 & +1 \end{bmatrix} \end{array} \qquad \begin{array}{cc} & \textbf{th} \\ \textbf{cP} & \begin{bmatrix} -1/3 & -2/3 & +1/3 \\ +2/3 & +1/3 & +1/3 \\ -1/3 & +1/3 & +1/3 \end{bmatrix} \end{array} \qquad \text{(A - 15)}$$

d) Cubic body-centred cell **(cI)** ⇔ Triple-hexagonal cell **(th)** with $V_{th} = 3/2\ V_{cI}$

$x\,y\,z$ + [0 0 0, 1/2 1/2 1/2]

$a_{cI} = (2)^{1/2}\, a_{th} / 2 = 2\cdot(3)^{1/2}\, c_{th} / 3$

$x\,y\,z$ + [0 0 0, 1/3 2/3 2/3, 2/3 1/3 1/3]

$a_{th} = (2)^{1/2}\, a_{cI}$

$c_{th} = (3)^{1/2}\, a_{cI} / 2$

$c_{th} / a_{th} = (6)^{1/2} / 4 = 0.612 \quad (\alpha_r = 109.47°)$

$$\begin{array}{cc} & \textbf{cI} \\ \textbf{th} & \begin{bmatrix} 0 & +1 & -1 \\ -1 & 0 & +1 \\ +1/2 & +1/2 & +1/2 \end{bmatrix} \end{array} \qquad \begin{array}{cc} & \textbf{th} \\ \textbf{cI} & \begin{bmatrix} -1/3 & -2/3 & +2/3 \\ +2/3 & +1/3 & +2/3 \\ -1/3 & +1/3 & +2/3 \end{bmatrix} \end{array} \qquad \text{(A - 16)}$$

e) Hexagonal cell **(h)** ⇔ Orthohexagonal cell **(oh)** with $V_{oh} = 2\ V_h$

$x\,y\,z$ + [0 0 0]

$a_h \equiv b_h = (3)^{1/2}\, a_{oh} / 3 = b_{oh}$

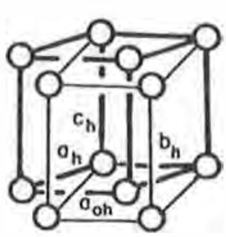
$c_h = c_{oh}$

$x\,y\,z$ + [0 0 0, 1/2 1/2 0]

$a_{oh} = (3)^{1/2}\, a_h$

$b_{oh} = a_h$

$c_{oh} = c_h$



$$\begin{array}{cc} & \textbf{h} \\ \textbf{oh} & \begin{bmatrix} +2 & +1 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & +1 \end{bmatrix} \end{array} \qquad \begin{array}{cc} & \textbf{oh} \\ \textbf{h} & \begin{bmatrix} +1/2 & -1/2 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & +1 \end{bmatrix} \end{array} \qquad \text{(A - 17)}$$

Figure A - 3 : Hexagonal and it's corresponding orthohexagonal unit cell.

⇒⇒⇒ Problem 14 in Appendix B

APPENDIX B : PROBLEMS IN INORGANIC STRUCTURAL CHEMISTRY

Solutions to these problems as well as comments can be found in the second part of Appendix B.

Problem 1 (Chapter I) : a) In the following list the stacking of the ZnS polytypes is denoted by Jagodzinski - Wyckoff stacking symbols. Write down the corresponding Zhdanov stacking symbols and calculate, using (I - 2b), the hexagonality of the polytypes.

Jagodzinski - Wyckoff	Zhdanov notation	hexagonality
h_2		
$(hc)_2$		
$(hc_2)_2$		
$[hc_5(hc)_3]_3$		
$hc_4hc_3hchc_2$		
$[hc_6hc_2hchc_3(hc_2)_2]_3$		
$hc_{16}hc_3hchc_2$		
$(hc_8)_2(hc_4)_2$		
c_3		

b) Find the *ABC* stacking sequence for polytype ZnS $14T$ with the Jagodzinski - Wyckoff stacking symbol $hc_4hc_3hchc_2$.

Problem 2 (Chapter IV) : Calculate the bond strength sums for the normal valence compound $Si_5P_6O_{25}$ with crystal chemical formula $Si_3^{[6o]}\,Si_2^{[4t]}\,P_6^{[4t]}\,O^{[2Si]}\,O_{24}^{[1Si,1P]}$ and find out if the PO_4 tetrahedra are distorted. The connectivity table of $Si_5P_6O_{25}$ has already been prepared here. For its construction the following crystal chemical formula has been used :

$$Si(i)^{[0,0,6,0,0]}\,Si(ii)_2^{[0,3,0,0,3]}\,Si(iii)_2^{[1,0,0,3,0]}\,P_6^{[0,1,1,1,1]}\,O(i)^{[0,0,2,0]}\,O(ii)_6^{[0,1,0,1]}\,O(iii)_6^{[1,0,0,1]}\,O(iv)_6^{[0,0,1,1]}\,O(v)_6^{[0,1,0,1]}$$

Connectivity table of $Si_5P_6O_{25}$:

	O(i)	6 O(ii)	6 O(iii)	6 O(iv)	6 O(v)	
Si(i)	-	-	6	-	-	
2 Si(ii)	-	6	-	-	6	
2 Si(iii)	2	-	-	6	-	
6 P	-	6	6	6	6	

Problem 3 (Chapter V) : For the following fourteen polychalcogenides the generalized 8 - *N* rule is applicable. Calculate VEC_A, AA, $^{[;0]}/_{[;1]}$ or $N'_{A/M}$ and formulate simple crystal chemical formulae. If $7 \geq VEC_A > 6$, *i.e.* $1 \leq AA < 2$ then (V - 9) (or the table on the inside cover) can be used to obtain $N'_{A/M}$ values. If $8 > VEC_A > 7$, *i.e.* $0 < AA < 1$ both isolated anions and anion dumb-bells are present and one has to use (V - 7) with $i = 0$ to obtain a value for $M_{[;0]} / M_{[;1]}$. The results for K_5Se_3 *LT* have already been filled in.

K_5Se_3 *LT*	KS	K_2S_3	NaS_2	K_2S_5	CsS_3	$CsTe_4$
$VEC_A = 7.67$ $AA = {}^1/_3$ $M_{[;0]}/M_{[;1]} = 2$ $K_5Se_2^{[;0]}Se^{[;1]}$ $K_{10}Se_4[Se_2]$	$VEC_A =$ $AA =$ $N'_{A/M} = 2$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$

Ba_2S_3	ZnS_2	BaS_3	BaS_4	$La^{3+}S_2$	$Th^{4+}{}_2S_5$	$Zr^{4+}Se_3$
$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$

Problem 4 (Chapter V) : Of the five ternary two-anion compounds, formed with Cd, an anion of group *5B* such as **P** or As, and a halogen element such as Cl or I, one is a normal valence compound and the four others polyanionic valence compounds. In the polyanionic valence compounds, bonds between halogen atoms can be excluded (the resulting neutral halogen dumb-bells would not be bonded to the remaining atoms of the compound). The experimental evidence [B - 1)] indicates that anion-anion bonds never occur between *5B* and *7B* elements but only between group *5B* elements. Considering this experimental rule construct simple crystal chemical formulae for the four polyanionic valence compounds. The data for the normal valence compound Cd_3AsCl_3 have already been filled in.

Cd_3AsCl_3	$Cd_4As_2I_3$	Cd_2AsCl_2	$Cd_7P_4Cl_6$	Cd_2As_3I
$VEC_A = 8$ $AA = 0$ $Cd_3\,As^{[;0]}\,Cl_3^{[;0]}$ Cd_3AsCl_3	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$	$VEC_A =$ $AA =$

B - 1) Rebbah, H. & Rebbah, A. (1994). J. Solid State Chem. 113, 1 - 8.

Problem 5 (Chapter V) : Find the compositions of binary polyanionic valence compounds C_mA_n with $1 \leq e_C \leq 4$, $4 \leq e_A \leq 7$ and $e_C < e_A$ which have an equal number of isolated anions and anion dumb-bells. Give your results in the form of numerical formulae where the elements are denoted by numerals which correspond to their number of valence electrons. Note that solutions for $e_A = 7$ are of no interest because this would mean that two thirds of the halogen atoms would be present as neutral dumb-bells without any bonding connection to the remaining atoms of the compound.

	m / n	e_A 4	5	6	7
e_C	1				-
	2				-
	3				-
	4	-			-

	formula	e_A 4	5	6	7
e_C	1				-
	2				-
	3				-
	4	-			-

Problem 6 (Chapter VI) : Which of the following equiatomic compounds could possibly crystallize with a tetrahedral structure ? Propose a simple possible crystal chemical formula.

	VEC	N_{NBO}	$N_{A/M}$	VEC_A	*AA*	*CC*	Crystal chemical formula
CdSb							
SCl							
BePo							
SiAs							
CF							
AsS							

Problem 7 (Chapter VI) : Formulate simple possible crystal chemical formulae for valence compounds of general composition CA_2 ($e_C \leq e_A$).

	$e_A = 4$	$e_A = 5$	$e_A = 6$	$e_A = 7$
$e_C = 1$	$VEC = 3$ $VEC_A = 4.5$	$VEC = 3.67$ $VEC_A = 5.5$	$VEC = 4.33$ $VEC_A = 6.5$	$VEC = 5$ $VEC_A = 7.5$
$e_C = 2$	$VEC = 3.33$ $VEC_A = 5$	$VEC = 4$ $VEC_A = 6$	$VEC = 4.67$ $VEC_A = 7$	$VEC = 5.33$ $VEC_A = 8$
$e_C = 3$	$VEC = 3.67$ $VEC_A = 5.5$	$VEC = 4.33$ $VEC_A = 6.5$	$VEC = 5$ $VEC_A = 7.5$	$VEC = 5.67$ $VEC_A = 8.5$
$e_C = 4$	-	$VEC = 4.67$ $VEC_A = 7$	$VEC = 5.33$ $VEC_A = 8$	$VEC = 6$ $VEC_A = 9$
$e_C = 5$	-	-	$VEC = 5.67$ $VEC_A = 8.5$	$VEC = 6.33$ $VEC_A = 9.5$
$e_C = 6$	-	-	$VEC = 6$ $VEC_A = 9$	$VEC = 6.67$ $VEC_A = 10$

Problem 8 (Chapter VII) : Calculate the possible numerical formulae for ternary defect adamantane structure compounds with two kinds of cations where $e_C < e_{C^*} \leq 4$, $e_A \geq 5$ and where one of four cation sites is unoccupied. Using $C_{(3/4)nx}\, C^*_{(3/4)n(1-x)}\, \square_{(1/4)n}\, A_n$ as general composition calculate first possible solutions for $^x/_{(1-x)}$ and then insert the numerical formulae into the second table.

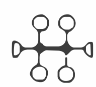
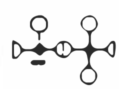
	$e_A = 5$			$e_A = 6$			$e_A = 7$		
$^x/_{(1-x)}$	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 4$	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 4$	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 4$
$e_C = 1$									
$e_C = 2$	-			-			-		
$e_C = 3$	-	-		-	-		-	-	

	$e_A = 6$			$e_A = 7$		
formulae	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 4$	$e_{C^*} = 2$	$e_{C^*} = 3$	$e_{C^*} = 4$
$e_C = 1$						
$e_C = 2$	-			-		
$e_C = 3$	-	-		-	-	

Problem 9 (Chapter VIII) : Find the most probable base tetrahedra which can be used to construct the anionic tetrahedron complexes of the following nine normal valence compounds. For simplicity denote the base tetrahedra by their codes [- - *TT*]. Which of these anionic tetrahedron complexes can be non-cyclic molecular ?

compound	complex	*VEC'*	*n / m'*	*TT*	$N(TT)_1 / N(TT)_2$	base tetrahedra
$Ag_{10}Si_3S_{11}$						
$K_5V^{5+}{}_3O_{10}$						
$Na_4Sc_2Ge_4O_{13}$						
$Sr_2P_6O_{17}$						
HoP_5O_{14}						
CaP_4O_{11}						
$Rb_6Si_{10}O_{23}$ *LT*						
$Na_3P_6N_{11}$						
$CaGa_6Te_{10}$						

Problem 10 (Chapter IX) : Determine the (anionic) tetrahedron complexes of the following (cation -) sulphur (selenium) - oxygen compounds. The most simple solution is found in all compounds with the exception of Se_2O_5 (for which the experimentally observed tetrahedron complex consisting of two different kinds of base tetrahedra has already been inserted in the following table). Note, that for SeO_2 exist two equally probable solutions due to the existence of two different base tetrahedra with the same *BEN* value. Find out where a non-cyclic molecular tetrahedron complex can occur and determine $N'_{A/M}$, *i.e.* the number of its atoms using (VIII - 6).

Compound	VEC_A	TT	$N'_{T/M}$	$N_{A\text{-}A}$, $C'C'$	BEN	$TT+N_{C'\text{-}C'}$	graph drawing of complex		VEC'	$N'_{A/M}$
	(VIII - 1)	(VIII - 7a)	(VII - 11)	(IX - 6 and 7)	(VIII - 8)	(IX - 24)	base tetrahedra in Figure IX - 2		(VIII - 3)	(VIII - 6)
KSO_4 persulphate										
K_2SO_4 sulphate										
$K_2S_2O_7$ pyrosulphate										
$K_2S_5O_{16}$ pentasulphate										
SO_3 trioxide										
KSO_3 dithionate										
Se_2O_5 pentoxide	$8^2/5$			$C'C' = 1$	$\boxed{21}$	2		not observed	6	-
					$\boxed{18} + \boxed{24}$ [102]			observed		
Na_2SO_3 sulphite										
$ZnSe_2O_5$ pyroselenite										
SeO_2 dioxide										
$NaSO_2$ dithionite										

Problem 11 (Chapter IX) : The four compounds $Ba_4Ga_2S_7$, $Li_2Cu^{2+}{}_3Se_4O_{14}$, $Cs_4Sn_2Te_7$ and $Na_2B_2Se_7$ with the same anion to central atom ratio $n / m' = 7/2$ have different anionic tetrahedron complexes. Find out which one of the five different tetrahedron complexes ① to ⑤, shown in Figure B - 1, should be assigned to which compound. Determine first what VEC_A value a compound must have to form one of the shown tetrahedron complexes and compare the results with the VEC_A values calculated for the compounds. Note, that for one of the compounds a drawing of its anionic tetrahedron complex is missing.

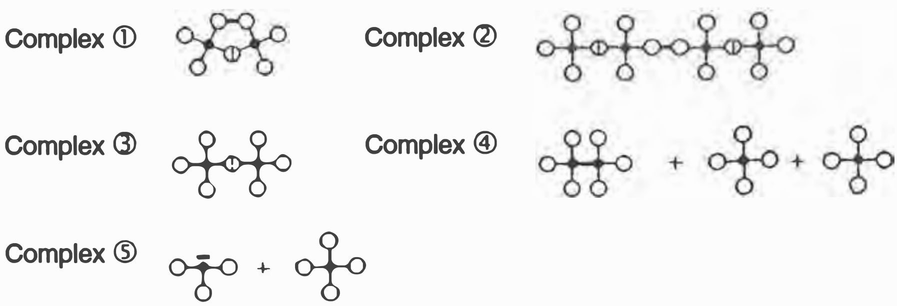


Figure B - 1 : Graph drawings of five different anionic tetrahedron complexes with $n / m' = 7/2$.

Calculations for shown complexes

	base tetrahedra	*BEN* values	<*BEN*>	VEC_A
①				
②				
③				
④				
⑤				

Calculations for listed compounds

	complex	VEC_A	N_{A-A}, $C'C'$	*BEN*
$Ba_4Ga_2S_7$				
$Li_2Cu^{2+}{}_3Se_4O_{14}$				
$Cs_4Sn_2Te_7$				
$Na_2B_2Se_7$				

Problem 12 (Chapter X) : Derive the equations for the three space filling curve branches of the cubic $Ca^{[8cb]}F_2^{[4t]}$ type (Figure IV - 2) and calculate the values of the two critical radius ratios ($\varepsilon = r_{Ca} / r_F$) where the branches intersect.

General equation for CaF_2 type $\phi =$

Ca - Ca contact, therefore $a_c =$ $\phi_{Ca\text{-}Ca} =$

Ca - F contact, therefore $a_c =$ $\phi_{Ca\text{-}F} =$

F - F contact, therefore $a_c =$ $\phi_{F\text{-}F} =$

Intersection of $\phi_{F\text{-}F}$ curve with $\phi_{Ca\text{-}F}$ curve at $\varepsilon =$

Intersection of $\phi_{Ca\text{-}Ca}$ curve with $\phi_{Ca\text{-}F}$ curve at $\varepsilon =$

Problem 13 (Chapter XI) : The four compounds Ce_3Co_8Si, $Dy_3Ni_7B_2$, $Ce_2Co_5B_2$ and $Ca_5Ni_{15}B_4$ are inside the composition field in Figure XI - 8 where structures with intergrown binary and/or ternary Laves-type and $CaCu_5$-type slabs are formed. Determine for each compound the most simple ratios of the four kinds of slabs : R_2T_4, R_2T_3M, RT_5 and RT_3M_2.

Problem 14 (Appendix A) : The NaCl structure is conventionally described with a face-centered cubic unit cell with length a_c having four formula units ($Z = 4$), *i.e.* 4 Na in 000 + [F] and 4 Cl in $^1/_2\ ^1/_2\ ^1/_2$ + [F] (where [F] = [0 0 0, 0 $^1/_2\ ^1/_2$, $^1/_2$ 0 $^1/_2$, $^1/_2\ ^1/_2$ 0]). The structure - by intentionally ignoring some of the symmetry elements inherent in this atom arrangement - can be described with a triple-hexagonal cell, a rhombohedral cell or a base-centered orthohexagonal cell. For these three unit cells find the number of formula units per unit cell (Z), the volume of the new cell (expressed in terms of V_c), the cell parameters (expressed in terms of a_c) and the new positional atom coordinates using (A - 14), (A - 13) and (A - 17), respectively. To shorten your list of new $x\ y\ z$ values make use of the Bravais lattice vectors [R] and [C], respectively.

Cubic cell	**Triple-hexagonal cell**	**Rhombohedral cell**	**Orthohexagonal cell**
$Z = 4$, $V_c = a_c^3$ a_c	$Z =$ $V_{th} =$ $a_{th} =$ $c_{th} =$	$Z =$ $V_r =$ $a_r =$ $\alpha_r =$	$Z =$ $V_{oh} =$ $a_{oh} =$ $b_{oh} =$ $c_{oh} =$
4 Na in 0 0 0 + [F]	Na in + [R]	Na in + [P]	Na in + [C]
4 Cl in $^1/_2\ ^1/_2\ ^1/_2$ + [F]	Cl in + [R]	Cl in + [P]	Cl in + [C]
[F] = [0 0 0, 0 $^1/_2\ ^1/_2$, $^1/_2$ 0 $^1/_2$, $^1/_2\ ^1/_2$ 0]	[R] = [0 0 0, $^1/_3\ ^2/_3\ ^2/_3$, $^2/_3\ ^1/_3\ ^1/_3$]	[P] = [0 0 0]	[C] = [0 0 0, $^1/_2\ ^1/_2$ 0]

Solutions to the problems

Problem 1a) : The Zhdanov notation and the hexagonality of ZnS polytypes.

Jagodzinski - Wyckoff	Zhdanov notation	hexagonality
h_2	1_2	$100 \cdot 1/1 = 100$
$(hc)_2$	2_2	$100 \cdot 1/2 = 50$
$(hc_2)_2$	3_2	$100 \cdot 1/3 = 33.3$
$[hc_5(hc)_3]_3$	$(6\ 2_3)_3$	$100 \cdot 4/12 = 33.3$
$hc_4hc_3hchc_2$	5 4 2 3	$100 \cdot 4/14 = 28.6$
$[hc_6hc_2hchc_3(hc_2)_2]_3$	$(7\ 3\ 2\ 4\ 3_2)_3$	$100 \cdot 6/22 = 27.3$
$hc_{16}hc_3hchc_2$	17 4 2 3	$100 \cdot 4/26 = 15.4$
$(hc_8)_2(hc_4)_2$	$9_2\ 5_2$	$100 \cdot 4/28 = 14.3$
c_3	∞_3	$100 \cdot 1/\infty = 0$

1b) : *ABCABCBACBCACB* (equally correct with letters *B* and *C* interchanged).

Problem 2 : Distortions of PO_4 tetrahedra in $Si_5P_6O_{25}$ ($Ge_5P_6O_{25}$ structure type).

Connectivity table extended with bond strength values (in *italics*) and their sums :

	O(i)	6 O(ii)	6 O(iii)	6 O(iv)	6 O(v)	
Si(i)	-	-	*6·4/6*	-	-	$\Sigma \equiv 4 = e_{Si}$
2 Si(ii)	-	*6·4/6*	-	-	*6·4/6*	$\Sigma \equiv 8 = 2e_{Si}$
2 Si(iii)	*2·4/4*	-	-	*6·4/4*	-	$\Sigma \equiv 8 = 2e_{Si}$
6 P	-	*6·5/4*	*6·5/4*	*6·5/4*	*6·5/4*	$\Sigma \equiv 30 = 6e_P$
	$\Sigma = 2$	$\Sigma = 11.5<12$	$\Sigma = 11.5<12$	$\Sigma = 13.5>12$	$\Sigma = 11.5<12$	
	$2 = 1(8-e_O)$	$12 = 6(8-e_O)$	$12 = 6(8-e_O)$	$12 = 6(8-e_O)$	$12 = 6(8-e_O)$	

According to the differences between calculated bond strength sums and the oxygen ion charges one can conclude that all PO_4 tetrahedra are distorted in the same way with one distance, *i.e.* $d_{P\text{-}O(iv)}$ being longer than the other three P - O distances.

In the following connectivity table the bond strength values have been substituted with bond valence values, calculated by O'Keeffe.[IV-3)] Using (IV - 8), $R_{Si\text{-}O} = 1.62$ Å and $R_{P\text{-}O} = 1.60$ Å he obtained for $d_{P\text{-}O(ii)}$, $d_{P\text{-}O(iii)}$, $d_{P\text{-}O(iv)}$ and $d_{P\text{-}O(v)}$ the values 1.50, 1.50, 1.60 and 1.50 Å, respectively. The experimentally determined distances in $Si_5P_6O_{25}$ are 1.52, 1.51, 1.58 and 1.50 Å, respectively.

Connectivity table extended with bond valence values (in **bold-face type**) and their sums :

	O(i)	6 O(ii)	6 O(iii)	6 O(iv)	6 O(v)	
Si(i)	-	-	**6·2/3**	-	-	$\Sigma \equiv 4$
2 Si(ii)	-	**6·2/3**	-	-	**6·2/3**	$\Sigma \equiv 8$
2 Si(iii)	**2·1**	-	-	**6·1**	-	$\Sigma \equiv 8$
6 P	-	**6·4/3**	**6·4/3**	**6·1**	**6·4/3**	$\Sigma \equiv 30$
	$\Sigma \equiv 2$	$\Sigma \equiv 12$	$\Sigma \equiv 12$	$\Sigma \equiv 12$	$\Sigma \equiv 12$	

Problem 3 : Crystal chemical formulae for binary polychalcogenides.

K_5Se_3 *LT*	KS	K_2S_3	NaS_2	K_2S_5	CsS_3	$CsTe_4$
$VEC_A = 7.67$	$VEC_A = 7.0$	$VEC_A = 6.67$	$VEC_A = 6.5$	$VEC_A = 6.4$	$VEC_A = 6.33$	$VEC_A = 6.25$
$AA = {}^1/_3$	$AA = 1$	$AA = {}^4/_3$	$AA = {}^3/_2$	$AA = {}^8/_5$	$AA = {}^5/_3$	$AA = {}^7/_4$
$M^{[;0]}/M^{[;1]} = 2$	$N'_{A/M} = 2$	$N'_{A/M} = 3$	$N'_{A/M} = 4$	$N'_{A/M} = 5$	$N'_{A/M} = 6$	$N'_{A/M} = 8$
$K_5Se_2^{[;0]}Se^{[;1]}$	$K_2\ \hat{2}\,[S_2]$	$K_2\ \hat{3}\,[S_3]$	$Na_2\ \hat{4}\,[S_4]$	$K_2\ \hat{5}\,[S_5]$	$Cs_2\ \hat{6}\,[S_6]$	$Cs_2\ \hat{8}\,[Te_6]$
$K_{10}Se_4[Se_2]$	$K_2[S_2]$	$K_2[S_3]$	$Na_2[S_4]$	$K_2[S_5]$	$Cs_2[S_6]$	$Cs_2[Te_8]$

Ba_2S_3	ZnS_2	BaS_3	BaS_4	$La^{3+}S_2$	$Th^{4+}{}_2S_5$	$Zr^{4+}Se_3$
$VEC_A = 7.33$	$VEC_A = 7.0$	$VEC_A = 6.67$	$VEC_A = 6.5$	$VEC_A = 7.5$	$VEC_A = 7.6$	$VEC_A = 7.33$
$AA = {}^2/_3$	$AA = 1$	$AA = {}^4/_3$	$AA = {}^3/_2$	$AA = {}^1/_2$	$AA = {}^2/_5$	$AA = {}^2/_3$
$M^{[;0]}/M^{[;1]} = {}^1/_2$	$N'_{A/M} = 2$	$N'_{A/M} = 3$	$N'_{A/M} = 4$	$M^{[;0]}/M^{[;1]} = 1$	$M^{[;0]}/M^{[;1]} = {}^3/_2$	$M^{[;0]}/M^{[;1]} = {}^1/_2$
$Ba_2S^{[;0]}S_2^{[;1]}$	$Zn\ \hat{2}\,[S_2]$	$Ba\ \hat{3}\,[S_3]$	$Ba\ \hat{4}\,[S_4]$	$LaS^{[;0]}S^{[;1]}$	$Th_2S_3^{[;0]}S_2^{[;1]}$	$ZrSe^{[;0]}Se_2^{[;1]}$
$Ba_2S[S_2]$	$Zn[S_2]$	$Ba[S_3]$	$Ba[S_4]$	$La_2S_2[S_2]$	$Th_2S_3[S_2]$	$ZrSe[Se_2]$

These crystal chemical formulae agree with the observed structural features.

Problem 4 : Crystal chemical formulae for ternary polyanionic halogen pnictides.

Cd_3AsCl_3	$Cd_4As_2I_3$	Cd_2AsCl_2	$Cd_7P_4Cl_6$	Cd_2As_3I
$VEC_A = 8$	$VEC_A = 7.80$	$VEC_A = 7.67$	$VEC_A = 7.60$	$VEC_A = 6.5$
$AA = 0$	$AA = {}^1/5$	$AA = {}^1/3$	$AA = {}^2/5$	$AA = {}^3/2$
$Cd_3\ As^{[;0]}\ Cl_3^{[;0]}$	$Cd_4As^{[;0]}As^{[;1]}\ I_3^{[;0]}$	$Cd_2\ As^{[;1]}\ Cl_2^{[;0]}$	$Cd_7\ P_4^{[;1]}\ Cl_6^{[;0]}$	$Cd_2\ As_3^{[;2]}\ I^{[;0]}$
	$Cd_8\ As_2^{[;0]}\,[As_2^{[;1]}]\ I_6$	$Cd_4\,[As_2^{[;1]}]\ Cl_4$	$Cd_7\,[P_2^{[;1]}]_2\,Cl_6$	$Cd_2({}^1_\infty As_3^{[;2]})\ I$
$Cd_3\ As\ Cl_3$	$Cd_8\ As_2\,[As_2]\ I_6$	$Cd_4\,[As_2]\ Cl_4$	$Cd_7\,[P_2]_2\,Cl_6$	$Cd_2({}^1_\infty As_3)\ I$

These crystal chemical formulae agree with the observed structural features.

Problem 5 : Compounds with an equal number of isolated anions and anion dumb-bells.

An equal number of isolated anions $A^{[;0]}$ and anion dumb-bells $[A_2^{[;1]}]$ implies that the compound has a composition C_mA_n for which $AA = {}^2/3$ and, according to (V - 4), $VEC_A = {}^{22}/3$. From (IV - 2) one obtains

$$m/n = ({}^{22}/3 - e_A)/e_C \qquad \text{(B - 1)}$$

for which solutions are given below in the table on the left. To these solutions correspond the numerical formulae in the table on the right. Numerical formulae for which examples are known (Sr_5Si_3, Ba_2S_3, $Zr^{4+}Se_3$) have been framed.

	m/n	e_A = 4	5	6	7
e_C	1	$^{10}/9$ ...			

	formula	e_A = 4	5	6	7
e_C	1	$1_{10}4_3$	1_75_3	1_46_3	-
	2	$\boxed{2_54_3}$	2_75_6	$\boxed{2_26_3}$	-
	3	$3_{10}4_9$	3_75_9	3_46_9	-
	4	-	4_75_{12}	$\boxed{46_3}$	-

Problem 6 : Equiatomic tetrahedral structure compositions

	VEC	N_{NBO}	$N_{A/M}$	VEC_A	AA	CC	Crystal chemical formula
CdSb	3.5	-	-	7	1	0	$Cd\ Sb^{[;1]}$ No tetrahedral str.
SCl	6.5	5/2	4	13	0	5	$\hat{4}\,[\underline{S}_2^{[(1;1)n]}\,\underline{\underline{Cl}}_2^{[1]}]$
BePo	4	0	-	8	0	0	$Be^{[4t;]}\ Po^{[4t;]}$
SiAs	4.5	1/2	-	9	0	1	$Si^{[(3;1)t]}\ \underline{As}^{[3n;]}$
CF	5.5	3/2	-	11	0	3	$C^{[(1;3)t]}\ \underline{\underline{F}}^{[1]}$ or $\underline{C}^{[(2;1)n]}\ \underline{F}^{[2n;]}$
AsS	5.5	3/2	-	11	0	3	$\underline{As}^{[(2;1)n]}\ \underline{S}^{[2n;]}$ or $As^{[(1;3)t]}\ \underline{\underline{S}}^{[1]}$

Problem 7 : Crystal chemical formulae of valence compounds with general composition CA_2. To the right and below the upper double-line border the formation of tetrahedral structures is possible in principle ($VEC \geq 4$). Below the lower double-line border one finds non-cyclic molecular tetrahedral structures ($VEC > 6$).

	$e_A = 4$	$e_A = 5$	$e_A = 6$	$e_A = 7$
$e_C = 1$	$VEC = 3$ $VEC_A = 4.5$ $C\ A^{[;3]}A^{[;4]}$?	$VEC = 3.67$ $VEC_A = 5.5$ $C\ A^{[;2]}A^{[;3]}$ CuP_2	$VEC = 4.33$ $VEC_A = 6.5$ $C_2\ \hat{4}\,[A_4]$ NaS_2	$VEC = 5$ $VEC_A = 7.5$ $C_2\ A_2[A_2]$ Not possible 1)
$e_C = 2$	$VEC = 3.33$ $VEC_A = 5$ $C\ A_2^{[;3]}$ $CaSi_2$	$VEC = 4$ $VEC_A = 6$ $C\ A_2^{[;2]}$ ZnP_2	$VEC = 4.67$ $VEC_A = 7$ $C\,[A_2]$ BaS_2	$VEC = 5.33$ $VEC_A = 8$ $C^{[;0]}\ A_2^{[;0]}$ BeF_2
$e_C = 3$	$VEC = 3.67$ $VEC_A = 5.5$ $C\ A^{[;2]}A^{[;3]}$?	$VEC = 4.33$ $VEC_A = 6.5$ $C_2\ \hat{4}\,[A_4]$ $LaAs_2$	$VEC = 5$ $VEC_A = 7.5$ $C_2\ A_2[A_2]$ LaS_2	$VEC = 5.67$ $VEC_A = 8.5$ $C^{[;1]}\ A_2$?
$e_C = 4$	-	$VEC = 4.67$ $VEC_A = 7$ $C\,[A_2]$ ($GeAs_2$) 2)	$VEC = 5.33$ $VEC_A = 8$ $C^{[;0]}\ A_2^{[;0]}$ SiO_2	$VEC = 6$ $VEC_A = 9$ $C^{[;2]}A_2$ or $\underline{C}^{[;0]}A_2$ SiI_2 3)
$e_C = 5$	-	-	$VEC = 5.67$ $VEC_A = 6.5$ $C^{[;1]}\ A_2$ (PO_2) 4)	$VEC = 6.33$ $VEC_A = 9.5$ $[\underline{C}_2^{[;1]}\ A_4]$ PI_2
$e_C = 6$	-	-	$VEC = 6$ $VEC_A = 9$ $C^{[;2]}A_2$ or $\underline{C}^{[;0]}A_2$ SeO_2 5)	$VEC = 6.67$ $VEC_A = 10$ $[\underline{C}^{[;0]}\ A_2]$ SCl_2

1) The crystal chemical formula indicates that half of the halogens would be present in the form of neutral dumb-bells.
2) The crystal chemical formula of the observed structure is $Ge\ As^{[;0]}\ {}^{1}_{\infty}\,As^{[;2]}$ *(see Figure V - 4).*
3) Observed crystal structure corresponds to the first crystal chemical formula.
4) The crystal chemical formula of the observed structure is $\bullet[P_2^{[4;0]}\ \underline{P}_2^{[3;0]}\ O_8]$.
5) Observed crystal structure corresponds to the second crystal chemical formula.

Problem 8 : Compositions of ternary defect adamantane structures with $u/n = 1/4$.
The general composition of these compounds is $C_{(3/4)nx}\ C^{*}_{(3/4)n(1-x)}\ \square_{(1/4)n}\ A_n$. These compounds are normal valence compounds, thus

$$(3/4)\cdot x\cdot e_C + (3/4)\cdot(1 - x)\cdot e_{C^*} = 8 - e_A \qquad \text{(B - 2)}$$

This equation can be used to derive an expression for the ratio $^{x}/_{(1-x)}$:

$$^{x}/_{(1-x)} \; = \; [3e_{C'} \; - \; 4\cdot(8 - e_A)] \; / \; [4\cdot(8 - e_A) \; - \; 3e_C]. \qquad \text{(B - 3)}$$

Solutions of $^{x}/_{(1-x)}$ for different values of e_C, $e_{C'}$ and e_A are given below in the upper table. To these solutions correspond the numerical formulae in the lower table. Numerical formulae for which examples are known ($AgIn_5Se_8$, $CdAl_2S_4$, Hg_2SnSe_4, β-Ag_2HgI_4) have been framed.

	$e_A = 5$			$e_A = 6$			$e_A = 7$		
$^{x}/_{(1-x)}$	$e_{C'} = 2$	$e_{C'} = 3$	$e_{C'} = 4$	$e_{C'} = 2$	$e_{C'} = 3$	$e_{C'} = 4$	$e_{C'} = 2$	$e_{C'} = 3$	$e_{C'} = 4$
$e_C = 1$	< 0	< 0	0	< 0	$^1/_5$	$^4/_5$	$^2/_1$	$^5/_1$	$^8/_1$
$e_C = 2$	-	< 0	0	-	$^1/_2$	$^4/_2$	-	< 0	< 0
$e_C = 3$	-	-	0	-	-	< 0	-	-	< 0

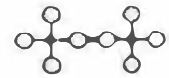
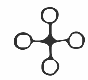
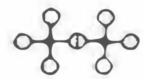
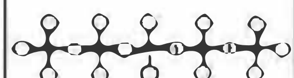
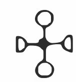
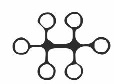
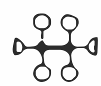
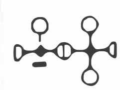
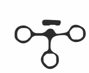
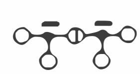
	$e_A = 6$			$e_A = 7$		
formulae	$e_{C'} = 2$	$e_{C'} = 3$	$e_{C'} = 4$	$e_{C'} = 2$	$e_{C'} = 3$	$e_{C'} = 4$
$e_C = 1$	-	$\boxed{1\,3_5\square_2 6_8}$	$1_4 4_5\square_3 6_{12}$	$\boxed{1_2 2\square 7_4}$	$1_5 3\square_2 7_8$	$1_8 4\square_3 7_{12}$
$e_C = 2$	-	$\boxed{2\,3_2\square 6_4}$	$\boxed{2_2 4\square 6_4}$	-	-	-
$e_C = 3$	-	-	-	-	-	-

Problem 9 : Base tetrahedra for anionic complexes of normal valence compounds.

To obtain the *TT* values one applies (VIII - 7a) for the first seven compounds, but (VIII - 7b) for the last two. If *TT* is not an integer one uses (VIII - 10b). The first three anionic tetrahedron complexes are molecular because *VEC '* > 6 (equation (VIII - 6)). The anionic tetrahedron complex of the first compound should consist of one isolated tetrahedron and one double tetrahedron (<*TT*> = $^2/_3$). For the anionic complexes of the second and third compound we expect from (VIII - 11) finite chains of three and four corner-linked tetrahedra, respectively. For all compounds mentioned there is an agreement between expected and experimentally observed structural features.

compound	complex	*VEC '*	*n / m '*	*TT*	$N(TT)_1 / N(TT)_2$	base tetrahedra
$Ag_{10}Si_3S_{11}$	$(Si_3S_{11})^{10-}$	$6\,^2/_7$	$3\,^2/_3$	$^2/_3$	$N(TT{=}0)/N(TT{=}1) = {}^1/_2$	1 x [- - 0] + 2 x [- - 1]
$K_5V^{5+}{}_3O_{10}$	$(V^{5+}{}_3O_{10})^{5-}$	$6\,^2/_{13}$	$3\,^1/_3$	$1\,^1/_3$	$N(TT{=}1)/N(TT{=}2) = {}^2/_1$	2 x [- - 1] + 1 x [- - 2]
$Na_4Sc_2Ge_4O_{13}$	$(Ge_4O_{13})^{10-}$	$6\,^2/_{17}$	$3\,^1/_4$	$1\,^1/_2$	$N(TT{=}1)/N(TT{=}2) = {}^1/_1$	1 x [- - 1] + 1 x [- - 2]
$Sr_2P_6O_{17}$	$(P_6O_{17})^{4-}$	< 6	$2\,^5/_6$	$2\,^1/_3$	$N(TT{=}2)/N(TT{=}3) = {}^2/_1$	2 x [- - 2] + 1 x [- - 3]
HoP_5O_{14}	$(P_5O_{14})^{3-}$	< 6	$2\,^4/_5$	$2\,^2/_5$	$N(TT{=}2)/N(TT{=}3) = {}^3/_2$	3 x [- - 2] + 2 x [- - 3]
CaP_4O_{11}	$(P_4O_{11})^{2-}$	< 6	$2\,^3/_4$	$2\,^1/_2$	$N(TT{=}2)/N(TT{=}3) = {}^1/_1$	1 x [- - 2] + 1 x [- - 3]
$Rb_6Si_{10}O_{23}$ *LT*	$(Si_{10}O_{23})^{6-}$	< 6	$2\,^3/_{10}$	$3\,^2/_5$	$N(TT{=}3)/N(TT{=}4) = {}^3/_2$	3 x [- - 3] + 2 x [- - 4]
$Na_3P_6N_{11}$	$(P_6N_{11})^{3-}$	< 6	$1\,^5/_6$	5		[- - 5]
$CaGa_6Te_{10}$	$(Ga_3Te_5)^{1-}$	< 6	$1\,^2/_3$	6		[- - 6]

Problem 10 : Tetrahedron complexes in (cation -) sulphur (selenium) - oxygen compounds.

Compound	VEC_A	TT	$N'_{T/M}$	N_{A-A}, $C'C'$	BEN	TT+$N_{C'-C}$	graph drawing of complex	VEC'	$N'_{A/M}$
	(VIII - 1)	(VIII -	(VIII -	(IX - 6 and 7)	(VIII - 8)	(IX - 24)	base tetrahedra in Figure IX - 2	(VIII - 3)	(VIII - 6)
KSO_4 persulphate	$7^3/_4$			$N_{A-A} = 1$	$\boxed{31}$	0		$6^1/_5$	10
K_2SO_4 sulphate	8	0	1	0	$\boxed{32}$	0		$6^2/_5$	5
$K_2S_2O_7$ pyrosulphate	8	1	2	0	$\boxed{26}$	1		$6^2/_9$	9
$K_2S_5O_{16}$ pentasulphate	8	$^8/_5$	5	0	3 x $\boxed{24}$ + + 2 x $\boxed{28}$	$^8/_5$		$6^2/_{21}$	21
SO_3 trioxide	8	2	∞	0	$\boxed{24}$	2		6	-
KSO_3 dithionate	$8^1/_3$			$C'C' = 1$	$\boxed{25}$	1		$6^1/_4$	8
Se_2O_5 pentoxide	$8^2/_5$			$C'C' = 1$	$\boxed{21}$	2	 not observed	6	-
					$\boxed{18}$ + $\boxed{24}$ [1 0 2]		 observed		
Na_2SO_3 sulphite	$8^2/_3$			$C'C' = 2$	$\boxed{26}$	0		$6^1/_2$	4
$ZnSe_2O_5$ pyroselenite	$8^4/_5$			$C'C' = 2$	$\boxed{22}$	1		$6^2/_7$	7
SeO_2 dioxide	9			$C'C' = 2$	$\boxed{18}$ [1 0 2]	2	 observed	6	-
					$\boxed{18}$ [0 2 0]		 not observed		
$NaSO_2$ dithionite	$9^1/_2$			$C'C' = 3$	$\boxed{19}$	1		$6^1/_3$	6

Problem 11 : Anionic tetrahedron complexes for compounds with $n / m' = {}^{7}/_{2}$.
$Ba_4Ga_2S_7$, $Li_2Cu^{2+}{}_3Se_4O_{14}$ and $Cs_4Sn_2Te_7$ have anionic tetrahedron complexes ③, ⑤ and ①, respectively. The drawing for the anionic tetrahedron complex of $Na_2B_2Se_7$ is missing. According to BEN = 25 one expects that its complex is built up of [- 3 1] base tetrahedra in full agreement with the experimentally determined crystal structure. The anionic tetrahedron complex is in construction similar to complex ①, but with each of the four endstanding anions also participating on one Se - Se bond.

Calculations for shown complexes

	base tetrahedra	*BEN* values	<*BEN*>	VEC_A
①	[- 1 1]	$\boxed{27}$	27	$^{54}/_{7}$
②	[- - 1] + [- 1 1]	$\boxed{27}$ + $\boxed{26}$	$27^{1}/_{2}$	$^{55}/_{7}$
③	[- - 1]	$\boxed{28}$	28	$^{56}/_{7}$
④	[0 1 0] + [- - 0]	$\boxed{25}$ + $\boxed{32}$	$28^{1}/_{2}$	$^{57}/_{7}$
⑤	[1 0 0] + [- - 0]	$\boxed{26}$ + $\boxed{32}$	29	$^{58}/_{7}$

Calculations for listed compounds

	complex	VEC_A	$N_{A\text{-}A}$, $C'C'$	*BEN*
$Ba_4Ga_2S_7$	$(Ga_2S_7)^{8-}$	$^{56}/_{7}$	0	$\boxed{28}$
$Li_2Cu^{2+}{}_3Se_4O_{14}$	$(Se_2O_7)^{4-}$	$^{58}/_{7}$	$C'C' = 1$	$\boxed{28}$
$Cs_4Sn_2Te_7$	$(Sn_2Te_7)^{4-}$	$^{54}/_{7}$	$N_{A\text{-}A} = 1$	$\boxed{27}$
$Na_2B_2Se_7$	$(B_2Se_7)^{2-}$	$^{50}/_{7}$	$N_{A\text{-}A} = 3$	$\boxed{25}$

Problem 12 : Space filling curves for the $Ca^{[8cb]}F_2^{[4t]}$ type.

General equation for CaF_2 type	$\phi = [4 \cdot (4\pi / 3) \cdot (r_{Ca}{}^3 + 2\, r_F{}^3)] / a_c{}^3$
Ca - Ca contact, therefore $a_c = 2 \cdot (2)^{1/2} \cdot r_{Ca}$	$\phi_{Ca\text{-}Ca} = [\pi / (3 \cdot (2)^{1/2})] \cdot [(\varepsilon^3 + 2) / \varepsilon^3)]$
Ca - F contact, therefore $a_c = 4 \cdot (r_{Ca} + r_F) / (3)^{1/2}$	$\phi_{Ca\text{-}F} = [(3)^{1/2}\, \pi / 4] \cdot [(\varepsilon^3 + 2) / (\varepsilon + 1)^3)]$
F - F contact, therefore $a_c = 4\, r_F$	$\phi_{F\text{-}F} = [\pi / 12] \cdot [\varepsilon^3 + 2]$

Intersection of $\phi_{F\text{-}F}$ curve with $\phi_{Ca\text{-}F}$ curve at $\varepsilon = (3)^{1/2} - 1 = 0.732$
Intersection of $\phi_{Ca\text{-}Ca}$ curve with $\phi_{Ca\text{-}F}$ curve at $\varepsilon = 2 + (6)^{1/2} = 4.449$

Problem 13 : Intergrown slabs in Ce_3Co_8Si, $Dy_3Ni_7B_2$, $Ce_2Co_5B_2$ and $Ca_5Ni_{15}B_4$.

For a compound of composition $R_r\, T_t\, M_m$ the ratio of L, the number of (binary and/or ternary) Laves-type slabs $R_2(T,M)_4$, to C, the number of (binary and/or ternary) $CaCu_5$-type slabs $R(T,M)_5$, can be calculated from the known $r / (t + m)$ ratio with

$$L / C = \{5\, [r / (t + m)] - 1\} \;/\; \{2 - 4\; [r / (t + m)]\,\} \qquad \text{(B - 4)}$$

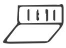
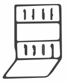
If one wants to distinguish also between binary and ternary slabs one can write :

$$R_r\, T_t\, M_m \;=\; x\, L{\cdot}(R_2T_4) + (1\text{-}x)\; L{\cdot}(R_2T_3M) + y\; C{\cdot}(RT_5) + (1\text{-}y)\; C{\cdot}(RT_3M_2) \qquad \text{(B - 5)}$$

For each compound is known the value of the ratio m / t which may be expressed by

$$m / t \;=\; [(1\text{-}x)\; L \;+\; (2\text{-}2y)\; C] \;/\; [4x\, L \;+\; (3\text{-}3x)\; L \;+\; 5y\, C \;+\; (3\text{-}3y)\; C] \qquad \text{(B - 6)}$$

Using (B - 4) it is possible to derive a linear relation between x and y for each compound (fifth column of the following table). For each relation exist different solutions depending on the chosen x and y values. Of interest is a solution with the minimum number of slabs. From the calculated L / C values one concludes that all four compounds contain in the most simple case only one Laves-type slab. Thus only solutions of the linear equations with x = 0 or x = 1 are of interest. Solutions of the linear equations with these two x values are presented in columns 6 and 7. Those in the last column require in one unit cell twice the number of slabs as compared to the solutions in the last but one column. We expect thus for these compounds an intergrowth of binary and/or ternary Laves- and $CaCu_5$-type slabs as presented schematically in the sixth column.

	$r / (t+m)$	L / C	m / t	x - y relation	solutions with the mininum number of slabs		solutions with more slabs
Ce_3Co_8Si	$^3/_9$	1 : 1	$^1/_8$	$2 = x + 2y$	$x = 0,\ y = 1$		$x = 1,\ y = {}^1/_2$
$Dy_3Ni_7B_2$	$^3/_9$	1 : 1	$^2/_7$	$1 = x + 2y$	$x = 1,\ y = 0$		$x = 0,\ y = {}^1/_2$
$Ce_2Co_5B_2$	$^2/_7$	1 : 2	$^2/_5$	$1 = x + 4y$	$x = 1,\ y = 0$		$x = 0,\ y = {}^1/_4$
$Ca_5Ni_{15}B_4$	$^5/_{19}$	1 : 3	$^4/_{15}$	$3 = x + 6y$	$x = 1,\ y = {}^1/_3$		$x = 0,\ y = {}^1/_2$

The experimentally observed crystal structures agree with these predictions on the number and kind of slabs. It is, however, not possible to predict whether successive (binary and/or ternary) Laves-type slabs are rotated as in $MgZn_2$ or are not rotated as in $MgCu_2$. All four compounds have, as seen in Figure B - 2, a stacking of Laves-type slabs as in $MgZn_2$.

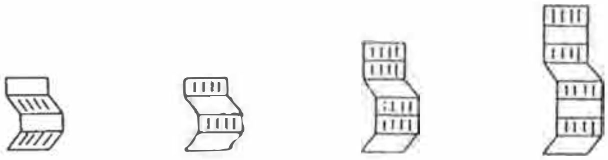


Figure B - 2 : Schematic drawings of the observed crystal structures of Ce_3Co_8Si, $Dy_3Ni_7B_2$, $Ce_2Co_5B_2$ and $Ca_5Ni_{15}B_4$, characterized by an intergrowth of (binary and/or ternary) Laves- and $CaCu_5$-type slabs. The meaning of the rectangles and parallelograms is the same as in Figure XI - 8.

Problem 14 : The NaCl structure described with four different unit cells.

Cubic cell	**Triple-hexagonal cell**	**Rhombohedral cell**	**Orthohexagonal cell**
$Z = 4,\ V_c = a_c^3$ a_c	$Z = 3,\ V_{th} = {}^3/_4\ V_c$ $a_{th} = (2)^{1/2}\ a_c / 2$ $c_{th} = (3)^{1/2}\ a_c$	$Z = 1,\ V_r = {}^1/_4\ V_c$ $a_r = (2)^{1/2}\ a_c / 2$ $\alpha_r = 60°$	$Z = 6,\ V_{oh} = {}^3/_2\ V_c$ $a_{oh} = (6)^{1/2}\ a_c / 2$ $b_{oh} = (2)^{1/2}\ a_c / 2$ $c_{oh} = (3)^{1/2}\ a_c$
4 Na in 0 0 0 + [F]	3 Na in 0 0 0 + [R]	1 Na in 0 0 0 + [P]	6 Na in 0 0 0, $^1/_6$ $^1/_2$ $^2/_3$, $^1/_3$ 0 $^1/_3$ + [C]
4 Cl in $^1/_2$ $^1/_2$ $^1/_2$ + [F]	3 Cl in 0 0 $^1/_2$ + [R]	1 Cl in $^1/_2$ $^1/_2$ $^1/_2$ + [P]	6 Cl in 0 0 $^1/_2$, $^1/_6$ $^1/_2$ $^1/_6$, $^1/_3$ 0 $^5/_6$ + [C]

APPENDIX C : PC PROGRAM "VEC" TO DEDUCE POSSIBLE STRUCTURAL FEATURES

Purpose and structure of program

"VEC" is a personal computer program to deduce possible structural features of inorganic valence compounds from the chemical composition. It is based on considerations developed in this book for normal, polyanionic or polycationic valence compounds, for normal and defect tetrahedral and adamantane structures and structures with anionic tetrahedron complexes. Together they constitute about one fifth of all known inorganic compounds.

The general characteristics of this program can be summarized as follows :

- The "VEC" program is simple to use. One has only to type-in the chemical formula. There is no need to remember all the notations used in the book.
- The results are obtained in a fraction of a second.
- The conclusions are in text form and/or in the form of schematic drawings. The parameters used in the book are listed as well.
- The output can be seen on the screen but it is also recorded on the file `VEC.OUT`.

This program is the result of a collaboration between Dr. Karin Cenzual and the author. In a pocket in the cover of this book can be found a floppy disk which contains the "VEC" program (together with a database of data sets representative of structure types). Technical details and installation are discussed in Appendix D.

The "VEC" program consists of three subprograms which we shall label : `Input`, `Crystal chemical parameters` and `Simple structure proposal` in agreement with the heading on the corresponding output screens.

1) The `Input` subprogram produces on the screen from the typed-in chemical formula a table of the elements in the compound where
   - default values are attributed to the elements for the number of contributing valence electrons
   - a proposal is made concerning the roles which the elements play in the compound, *i.e.* as cations (*C*), central atoms (*C'*) or anions (*A*).

   The program user has to check these attributions which he can modify if he so desires.
2) The `Crystal chemical parameters` subprogram uses the (modified) data of the `Input` screen to calculate different (average) crystal chemical parameters such as $<VEC_A>$, $<VEC>$ or $<VEC'>$ or $<BEN>$ which appear on the screen in form of a list.
3) The `Simple structure proposal` subprogram evaluates the crystal chemical parameters and writes a possible simple crystal chemical formula **under the assumption that the generalized 8 - *N* rule is applicable and under the assumption that all or the specified atoms are *sp*^{3} hybridized**. For a structure with an anionic tetrahedron complex a schematic graph drawing of the possible base tetrahedron(a) involved will be seen on the screen. In the latter case

the user is asked by the computer if he would like to see further (more complicated and less probable) combinations of base tetrahedra. A positive response leads to a new screen with the heading : `Further possible combination of base tetrahedra` where new graph drawings are presented. The procedure can be repeated up to the point where no more new combinations are found which respect the criteria defined by the program.

The program is written in FORTRAN and only ASCII characters appear on the screen. This means that many of the special print features used in the text for the notation of crystal chemical parameters and formulae cannot be reproduced on the screen in the same way. For example, italics, bold-faced characters, superscripts and subscripts are all transformed on the screen to normal-print (lower and upper-case) characters of same size and all are on the base line. Since it is impossible to underline a character on the screen a lone-electron pair in the crystal chemical formula will now be presented differently, *i.e.* by a colon (:) before the element symbol. For technical reasons the single prime (') is replaced by a double prime ("). On the `Crystal chemical parameters` screen a brief explanation of the parameters has been added to avoid possible misinterpretations.

Input of chemical formula and attribution of the valence electron numbers

Activate the program by typing `VEC`. Upon request, a chemical formula is to be entered from the keyboard. Inorganic compounds containing at least one non-metal element (group ***3B - 8B*** in the Periodic Table of Elements), but not simultaneously C and H, are accepted as input. The following conditions must be respected :

- Upper- and lower-case characters have to be used as customary for the symbols of the chemical elements.
- Integer or decimal numbers can be used, but no fractions.
- Not more than 10 chemical elements. The order of the elements is irrelevant. Spaces, parentheses and brackets are ignored by the program.
- $(OH)^-$ or $(NH_4)^+$ groups are recognized as univalent negative or positive elemental units, respectively, if they are inserted as OH and NH4.
- Free text (including *e.g.* solvent molecules) may be added after a comma.
- Atoms of the same chemical element which are expected to play a different role in the structural analysis, *i.e.* cation, central atom, anion (see below), must be separated in the input formula.

Input examples :

```
NH4Al2Br7    Na3[P3O8],14H2O    K2(PO3OH)    Cu11.5Zn23Ga7.5Ge8As16Se30Br4
```

The program makes a preliminary analysis of the chemical formula. On the screen is shown a line for each element with the (stoichiometry) number, *i.e.* how often it appears in the formula of the compound (copied from the input), the presumed role of the element in the structure as cation, central atom and anion (attributed by default), the number of contributing valence electrons (attributed by default) and the electronegativity value of the element. The top screen in Table C - 1 is an example with default values for the contributing electrons and for the role of the elements. On entering a digit corresponding to the number of the line, the user has the possibility to modify the number of contributing valence electrons and/or the role that the element should play in the structure. After each modification an updated table appears on the screen which can be further modified by the same procedure.

For the majority of the non-metals, as well as for alkaline, alkaline-earth, most rare-earth and a few transition elements, the number of contributing valence electrons can be attributed by default without difficulties. However, for elements which commonly adopt different oxidation states, the program will ask for the number of valence electrons to be considered. Positive integer and decimal numbers are accepted, fractions are not. The help option (question mark) will list common valences for the chemical element under consideration, starting from the most frequently observed.

TABLE C - 1 : UNMODIFIED AND TWO MODIFIED INPUT SCREENS FOR AL_2SiO_5. THE SECOND AND THE THIRD INPUT SCREEN LEAD TO OUTPUTS WHICH CORRESPOND TO TWO KNOWN MODIFICATIONS OF AL_2SiO_5.

```
Input for Al2SiO5, Default values for electrons and role of the elements
line nbr.   element     role  nbr.valence el.  electroneg.
------------------------------------------------------------------------
1     2.     Al          C"        3.              1.5
2     1.     Si          C"        4.              1.8
3     5.     O           A         6.              3.5

Input for AlAlSiO5,  sillimanite modification
line nbr.   element     role  nbr.valence el.  electroneg.
------------------------------------------------------------------------
1     1.     Al          C         3.              1.5
2     1.     Al          C"        3.              1.5
3     1.     Si          C"        4.              1.8
4     5.     O           A         6.              3.5

Input for Al2SiO4O,  kyanite modification
line nbr.   element     role  nbr.valence el.  electroneg.
------------------------------------------------------------------------
1     2.     Al          C         3.              1.5
2     1.     Si          C"        4.              1.8
3     4.     O           A         6.              3.5
4     1.     O           Y         6.              3.5
```

For a comment on the corresponding outputs see page C - 153.

Attribution of the role of an element and the different compound categories

Based on the positions of the different elements of a compound in the periodic table, their relative electronegativity, their tendency to form sp^3 hybridization together with the number of available valence electrons, a role will be attributed to each element. At the default stage only three different roles are foreseen : cation *C*, central atom *C'* and anion *A* which are written in the program as `C`, `C"` and `A`, respectively.

`C` Cation **without sp^3 hybridization** which in the ionic bonding state is assumed to transfer to the other atoms part or, in particular if a `C"` atom is present, the total number of valence electrons defined on the input screen.

`C"` Central atom **in sp^3 hybridization**, bonded to `A` atoms and possibly to other `C"` atoms.

`A` Anion which completes its electron octet, eventually also by forming covalent bonds with other `A` atoms. If `C"` atoms are present, each `A` atom must have a covalent bond to a `C"` atom.

In order to define their most probable role they play in the structure, the chemical elements have, based on experimental evidence, been classified into three classes :

(1) sp^3 hybridization presumed :	group ***3B - 8B*** elements but not Sn^{2+}, Pb^{2+}, Tl^+
(2) sp^3 hybridization possible :	Li, Be, Na, Mg, V^{5+}, Cr^{6+}, Fe, Cu^+, Zn, Ag, Cd, Hg
(3) sp^3 hybridization not probable :	All group ***A*** and ***T*** elements except those mentioned under class 2. A sp^3 hybridization is also unlikely for Tl^+, Sn^{2+} and Pb^{2+}.

The elements in the chemical formula are first grouped by the program according to their class, and, within each class, ordered according to decreasing electronegativity. The total number of valence electrons of the compound is then distributed among the elements, first all electrons are given to only one element and then progressively distributed over more and more elements, starting from the most electronegative element of class 1. The first element (the most electronegative element of class 1) is always considered as A. The following elements are considered as :

A	if the above defined valence electron sum ≥ 8 <u>or</u> if the difference in electronegativity with other anions is none
C"	if the element is expected to form a *sp*³ hybridization (class 1 or 2) <u>and</u> the valence electron number per atom ≥ 4 <u>and</u> the difference in electronegativity with A ≤ 2 for non-metals, ≤ 1 for metals
C	if none of the conditions listed above are fulfilled.

All anions in compounds with a tetrahedron complex are assumed to be bonded to at least one C" atom. However, this may not be true for part of them. The introduction of a fourth role, Y, makes it possible to subdivide the anions into two subcategories. The Y anions are assumed to be purely ionic and will in valence compounds not be taken into consideration for possible anion - anion bonds. For compounds with a tetrahedron complex, Y anions do not form bonds with the C" or/and A atoms.

Y Anion which completes its electron octet. It has no covalent bonds to C" atoms or other A atoms.

The program user can influence the calculation of the crystal chemical parameters as well as the structure proposals derived from these values by relabelling C" atoms as C atoms or vice versa and/or by denoting some of the A atoms as Y atoms.

As example serve the two modified `Input` screens for Al_2SiO_5, shown in the middle and lower half of Table C - 1. The values which will appear on the `Crystal chemical parameters` screen will be different and consequently also the base tetrahedron graphs on the `Simple structure proposal` screen which correspond to kyanite and sillimanite, respectively (see page VIII - 74). Note, that in the typed-in chemical formula the chemical elements of same kind, which play a **different role** in the structure, must be **separated** (Al atoms in sillimanite and O atoms in kyanite).

According to the different possible combinations of the element roles the compounds are subdivided into seven categories listed in Table C - 2.

TABLE C - 2 : THE SEVEN CATEGORIES OF COMPOUNDS ACCORDING TO THE ROLE OF THE PARTICIPATING ELEMENTS.

General valence compounds (without C" element, *sp*³ hybridization is not considered)		
Category **A1**	C - A -	General valence compound C_mA_n
Category **A2**	C - A Y	General valence compound $C_mA_nY_{n''}$ with isolated $Y^{(8-e_Y)-}$ anions
Category **A3**	- - A -	Element which obeys the Hume-Rothery 8 - *N* rule (degenerated case)
Compounds with a tetrahedron complex (with *sp*³ hybridized C" element)		
Category **B1**	- C" A -	Tetrahedral structure compound $C''_{m''}A_n$ with a neutral tetrahedron complex
Category **B2**	C C" A -	Compound $C_mC''_{m''}A_n$ with a charged tetrahedron complex $(C''_{m''}A_n)^{(m\cdot e_C)-}$
Category **B3**	C C" A Y	Compound $C_mC''_{m''}A_nY_{n''}$ with a charged complex $(C''_{m''}A_n)^{[m\cdot e_C - n''\cdot(8-e_Y)]-}$ and isolated $Y^{(8-e_Y)-}$ anions which are neither bonded to C" nor to A
Category **B4**	C C" - -	Compound $C_mC''_{m''}$ with a degenerated charged complex $(C''_{m''})^{(m\cdot e_C)-}$

There are two main categories of compounds labelled as **A** and **B** which differ in the following way :

- Category **A** compounds containing at least one `A` but no `C"` element are considered only as possible general valence compounds and are investigated for the presence of homonuclear bonds using the generalized 8 - *N* rule. The type of hybridization of the atoms does not enter in consideration. The only key parameter calculated is `<VEC/A>`. No graph drawings will be seen on the third screen.
- Category **B** compounds containing at least one `C"` element will be tested with the generalized 8 - *N* rule but also with the tetrahedral structure equation for the presence of non-bonding orbitals. Two key parameters are evaluated : `<VEC/A>` and `<VEC>` or `<VEC">`. In the `Simple structure proposal` screen will normally appear graph drawings of base tetrahedra.

No distinction will be made between different chemical elements with the same role. It may be noted that a binary compound may be entered for an analysis of the possible anion - anion bonds as :

- C_mA_n (neither one is sp^3 hybrized, category **A1**),
- $C_mC"_{m'}$ (only `C"` is sp^3 hybrized, category **B4** with `A` - `A` bonds labelled here `C"` - `C"`)
- $C"_{m'}A_n$ (both elements adopt sp^3 hybridization, category **B1**).

The kinds of crystal chemical parameters calculated depend on the chosen category for the combination of element roles as `C`, `C"`, `A` and `Y`. In the following we shall present commented examples for five of the seven categories of Tables C - 2 together with a summary of the equations used for the calculations. Each equation will be labelled in two ways, *i.e.* by a running index number (preceded by the letter C) in the order the equation appears in Appendix C and, secondly, by the number the equation is marked in the main text. This will permit the reader to go back to the text and inform himself on the background of each equation.

Crystal chemical parameters and structure proposals for compounds of category A

The key parameter for compounds of category **A** is `<VEC/A>` which is calculated for the three subcategories as follows :

For **A1** $\langle VEC/A \rangle = (m \cdot e_C + n \cdot e_A) / n$ for C_mA_n (C - 1_1) ≡ (IV - 2)

For **A2** $\langle VEC/A \rangle = [m \cdot e_C + n \cdot e_A - n" \cdot (8 - e_Y)] / n$ for $C_mA_nY_{n"}$ (C - 1_2)

For **A3** $\langle VEC/A \rangle = e_A$ for A (C - 1_3)

In compounds of category **A1** and **A2** the average number of homonuclear bonds (and/or lone-pair electrons on the cation) is determined with the generalized 8 - *N* rule :

$$\langle VEC/A \rangle = 8 + \langle CC \rangle / (n/m) - \langle AA \rangle \quad \text{for } C_mA_n \text{ and } C_mA_nY_n \qquad \text{(C - 2)} \equiv \text{(V - 3)}$$

On the `Crystal chemical parameters` screen is found the label of the kind of valence compound (according to the value calculated for `<VEC/A>`), the `<VEC/A>` and the `<AA>` or `<CC>` value, respectively. The last two parameters are calculated using

$$\langle AA \rangle = 8 - \langle VEC/A \rangle \quad \text{for } C_mA_n \text{ and } C_mA_nY_n \qquad \text{(C - 3)} \equiv \text{(V - 4)}$$

and

$$\langle CC \rangle = (n/m) \cdot (\langle VEC/A \rangle - 8) \quad \text{for } C_mA_n \text{ and } C_mA_nY_n \qquad \text{(C - 4)} \equiv \text{(V - 12)}$$

On the `Simple structure proposal` screen can be seen a crystal chemical formula where homonuclear bonds are distributed in agreement with the obtained `<AA>` or `<CC>` value. However, in the trivial case of a normal valence compound alone the remark `Single anions` is found.

For **polyanionic valence compounds** the values for `<AA>` obtained with (C - 3) are interpreted on the `Simple structure proposal` screen as follows :

If <AA> = 0	⇒	single anions
If 0 < <AA> < 1	⇒	single anions and anion dumb-bells
If <AA> = 1	⇒	anion dumb-bells
If 1 < <AA> < 2	⇒	finite non-cyclic anion chains
If <AA> = 2	⇒	infinite anion chains or rings.

For an average of less than one homonuclear bond per anion, the ratio of single anions and anion dumb-bells is calculated by means of an equation derived from (V - 7) with $i = 0$:

$$N[;0] \,/\, (\tfrac{1}{2} \cdot N[,1]) \;=\; 2 \cdot [(1 \,/\, \langle AA \rangle) - 1] \qquad \text{(C - 5)}$$

If the number of homonuclear bonds per anion is between 1 and 2, the average number of atoms per non-cyclic unit is calculated using

$$N'_{A/M} \;=\; 2 \,/\, (2 - \langle AA \rangle) \qquad \text{(C - 6)} \equiv \text{(V - 9a)}$$

For fractional values of $N'_{A/M}$ is proposed a ratio of anion chains, the lengths of which differ by 1 atom. The results appear on the last line of the `Simple structure proposal` screen in verbatim form.

For **polycationic valence compounds** it is important to recall that <CC> calculated with (C - 4) corresponds to the sum of the C - C bonds per cation ($N_{C\text{-}C}$) plus the sum of the electrons which remain in lone-electron pairs on the cations. Using the parameter $N_{lep/C}$, the average number of lone-electron pairs on the cation, the parameter *<CC>* can be expressed in analogy to (IX - 4) by

$$\langle CC \rangle \;=\; 2\, N_{lep/C} \;+\; N_{C\text{-}C} \qquad \text{(C - 7)}$$

For the simple structure proposal it is assumed that the highest possible integer number of electrons remains in lone-electron pairs on the cation. This means in more detail :

If 0 < <CC> < 1	then $N_{lep/C} = 0$, $0 < N_{C\text{-}C} < 1$	⇒	single cation and cation dumb-bell
If <CC> = 1	then $N_{lep/C} = 0$ and $N_{C\text{-}C} = 1$	⇒	cation dumb-bell
If 1 < <CC> < 2	then $N_{lep/C} = 0$, $1 < N_{C\text{-}C} < 2$	⇒	finite cation chain with an average of $N'_{A/M}$ atoms per non-cyclic unit, where $N'_{A/M} = 2 / (2 - \langle CC \rangle)$
If <CC> = 2	then $N_{lep/C} = 1$ and $N_{C\text{-}C} = 0$	⇒	single cation with one lone-electron pair
If <CC> = 3	then $N_{lep/C} = 1$ and $N_{C\text{-}C} = 1$	⇒	cation dumb-bell with one lone-electron pair / cation
If <CC> = $2n$	then $N_{lep/C} = n$ and $N_{C\text{-}C} = 0$	⇒	single cation with n lone-electron pairs / cation
If <CC> = $2n+1$	then $N_{lep/C} = n$ and $N_{C\text{-}C} = 1$	⇒	cation dumb-bell with n lone-electron pairs / cation

The $N_{lep/C}$, $N_{C\text{-}C}$ and $N'_{A/M}$ values do not appear on the screen. The results are indicated in the crystal chemical formula (colons represent lone-electron pairs) and are also expressed on the screen by short phrases similar to those shown to the right of the arrows.

The number of lone-electron pairs on the cations may be larger than calculated if at the input the electrons used for the lone-electron pairs on the cations are already substracted, as for example by specifying that the cations <u>Tl</u>$^{+}$ or <u>Sn</u>$^{2+}$ provide only one or two electrons, respectively.

The program does not consider the rare case of a mixed polyanionic - polycationic valence compound. Depending on whether the <VEC/A> value is calculated to be smaller or larger than eight the compound is treated by the program as normal polyanionic or polycationic valence compound, respectively. The <AA> or <CC> values seen on the screen are therefore smaller than those derived from the observed crystal structure. Correct <AA> or <CC> values can be obtained if one subtracts at the input the electrons used for the extra C - C or A - A bonds, respectively. A demonstration of this procedure is given on page V - 40 for the "polyanionic" valence compound $Hg_9P_5I_6$ where Hg - Hg dumb-bells are observed in addition to the homonuclear P - P bonds.

Category A1 `C - A -` General valence compound C_mA_n

In Tables C - 3a and 3b are presented as examples the screens for a polyanionic (<VEC/A> < 8, <AA> > 0) and a polycationic valence compound (<VEC/A> > 8, <CC> > 0).

TABLE C - 3A : SCREENS FOR THE POLYANIONIC VALENCE COMPOUND $CA_{14}SI_{19}$.

```
Input for Ca14Si19
line  nbr.   element     role  nbr.valence el.  electroneg.
---------------------------------------------------------------------------
1      14.     Ca          C          2.               1.0
2      19.     Si          A          4.               1.8

Crystal chemical parameters for Ca14Si19
---------------------------------------------------------------------------
Polyanionic valence compound.
                           Average number of :
<VEC/A>   =  5.474         valence electrons per A
<AA>      =  2.526 (48/19) anion-anion bonds per A

Simple structure proposal for Ca14Si19
---------------------------------------------------------------------------
   Crystal chem. formula  C14 A10[;3] A9[;2]
```

$Ca_{14}Si_{19}$: Currao, A., Wengert, S., Nesper, R., Curda, J. & Hillebrecht, H. (1996). Z. anorg. allg. Chem. ***622****, 501 - 508.*

TABLE C - 3B : SCREENS FOR THE POLYCATIONIC VALENCE COMPOUND SN.

```
Input for SN
line  nbr.   element     role  nbr.valence el.  electroneg.
---------------------------------------------------------------------------
1      1.      S           C          6.               2.5
2      1.      N           A          5.               3.0

Crystal chemical parameters for SN
---------------------------------------------------------------------------
Polycationic valence compound.
                           Average number of :
<VEC/A>   = 11.000         valence electrons per A
<CC>      =  3.000         C-C bonds or non-bonding electrons on C

Simple structure proposal for SN
---------------------------------------------------------------------------
   Crystal chem. formula  :C[;1] A
   Cation dumb-bells.
   1 lone-electron pair(s) per cation.
```

In SN the S atom is by default a cation. This is different for realgar AsS, shown in Figure V - 8.

Category A2 `C - A Y` General valence compound $C_mA_nY_{n''}$ with isolated $Y^{(8 - e_Y)-}$ anions

The extra Y anions take up valence electrons from the valence electron pool to complete their octets and thus become separate structural units which do not enter in the calculation of <VEC/A>.
Examples for category **A2** are the ternary halogen pnictides treated in Problem 4 of Appendix B. In Table C - 4 are presented the screens for polyanionic $Cd_4As_2I_3$. The I atoms remain isolated, not forming any bonds with the As anions which themselves are (partially) linked by homonuclear bonds.

TABLE C - 4: SCREENS FOR THE POLYANIONIC VALENCE COMPOUND $CD_4AS_2I_3$ WITH EXTRA Y ANIONS.

```
Input for Cd4As2I3
line  nbr.   element     role  nbr.valence el.  electroneg.
---------------------------------------------------------------------------
1      4.      Cd          C          2.               1.7
2      2.      As          A          5.               2.0
3      3.      I           Y          7.               2.5
```

```
Crystal chemical parameters for Cd4As2I3
--------------------------------------------------------------------------
Polyanionic valence compound.
Anions Y are not considered for calculation of anion-anion bonds.
                          Average number of :
<VEC/A>   =  7.500        valence electrons per A
<AA>      =   .500 ( 1/2 ) anion-anion bonds per A

Simple structure proposal for Cd4As2I3
--------------------------------------------------------------------------
   Crystal chem. formula  C4 A[;1] A[;0] Y3[;0]
   2 single anion(s) for 1 anion dumb-bell(s).
```

Category A3 `- - A -` Element which obeys the Hume-Rothery 8 - *N* rule

---

For completeness is mentioned this trivial case of a degenerate polyanionic valence compound without cations, *i.e.* an element which obeys the Hume-Rothery 8 - *N* rule (see III - 19 and V - 37).

Crystal chemical parameters and structure proposals for compounds of category B

The two key parameters for compounds of category **B** are <VEC/A> and <VEC> or <VEC">. They are calculated by the program as follows :

For **B1** $\mathtt{<VEC/A>} = (m''\cdot e_{C''} + n\cdot e_A)/n$ for $C''_{m''}A_n$ (C - 8$_1$) ≡ (IV - 2)

For **B2** $\mathtt{<VEC/A>} = (m\cdot e_C + m''\cdot e_{C''} + n\cdot e_A)/n$ for $C_mC''_{m''}A_n$ (C - 8$_2$) ≡ (VIII - 1)

For **B3** $\mathtt{<VEC/A>} = [m\cdot e_C + m''\cdot e_{C''} + n\cdot e_A - n''\cdot(8 - e_Y)]/n$ for $C_mC''_{m''}A_nY_{n''}$ (C - 8$_3$)

For **B4** <VEC/A> is not defined (no A atoms) for $C_mC''_{m''}$

and

For **B1** $\mathtt{<VEC>} = (m''\cdot e_{C''} + n\cdot e_A)/(m'' + n)$ for $C''_{m''}A_n$ (C - 9$_1$) ≡ (VI - 2)

For **B2** $\mathtt{<VEC">} = (m\cdot e_C + m''\cdot e_{C''} + n\cdot e_A)/(m'' + n)$ for $C_mC''_{m''}A_n$ (C - 9$_2$) ≡ (VIII - 3)

For **B3** $\mathtt{<VEC">} = [m\cdot e_C + m''\cdot e_{C''} + n\cdot e_A - n''\cdot(8 - e_Y)]/(m''+n)$ for $C_mC''_{m''}A_nY_{n''}$ (C - 9$_3$)

For **B4** $\mathtt{<VEC">} = (m\cdot e_C + m''\cdot e_{C''})/m''$ for $C_mC''_{m''}$ (C - 9$_4$)

Parameters derived from the first key parameter <VEC/A> which appear on the `Crystal chemical parameters` screen are :

<AA> : average number of anion - anion bonds per anion (only when <VEC/A> < 8), calculated with (C - 3). The parameter <AA> is not defined for a compound of category **B4**.

<N(A-A)> : average number of anion - anion bonds per tetrahedron (only when <VEC/A> < 8), derived from <AA> according to

$$\mathtt{<N(A-A)>} = \mathtt{<AA>}\cdot\mathtt{<n/m">} \qquad (C - 10) \equiv (IX - 2)$$

<C"C"> : average number of C" - C" bonds per C" atom and/or the average number of valence electrons per C" atom which rest inactively with the C" atom in lone-electron pairs (only when <VEC/A> > 8), calculated for $C''_{m''}A_n$, $C_mC''_{m''}A_n$ and $C_mC''_{m''}A_nY_{n''}$ with

$$\mathtt{<C"C">} = \mathtt{<n/m">}\cdot(\mathtt{<VEC/A>} - 8) \qquad (C - 11) \equiv (IX - 7)$$

<C"C"> has for a compound of category **B4** the same value as <VEC">.

Screen parameters derived from the second key parameter <VEC> (or <VEC">) are :

<N(NBO)> (or <N"(NBO)>) : average number of non-bonding orbitals per atom of the neutral (or charged) tetrahedron complex, obtained with

<N(NBO)> = <VEC> - 4 for $C"_{m'}A_n$ (C - 12_1) ≡ (VI - 4)

or <N"(NBO)> = <VEC"> - 4 for $C_mC"_{m'}A_n$, $C_mC"_{m'}A_nY_{n'}$, $C_mC"_{m'}$ (C - 12_2) ≡ (VIII - 5)

<N(A/M)> (or <N"(A/M)>) : average number of atoms per non-cyclic unit of the neutral (or charged) tetrahedron complex [applicable only if <N(NBO)> (or <N"(NBO)>) > 2], calculated with

<N(A/M)> = 2 / [<VEC> - 6] (C - 13_1) ≡ (VI - 10)

or <N"(A/M)> = 2 / [<VEC"> - 6] (C - 13_2) ≡ (VIII - 6)

<TT> : average number of C"-A-C" links per tetrahedron, calculated for normal and polyanionic valence compounds from the *n / m"* ratio with (VIII -7a), (VIII - 7b) and (VIII - 7c), respectively. In the case of polycationic valence compounds with tetrahedron complexes is the calculation of <TT> more complicated. The program computes the limiting values <TTmin> and <TTmax>.

<TTmin> : average number of C"-A-C" links per tetrahedron for a maximum number of C"-C" bonds and a minimum number of lone-electron pairs on the C" atoms.

<TTmax> : average number of C"-A-C" links per tetrahedron for a minimum number of C"-C" bonds and a maximum number of lone-electron pairs on the C" atoms.

The <TTmin> and <TTmax>. values can be obtained using (IX - 21) and (IX - 23) by inserting $N_{C'-C'}$ = <C"C"> and $N_{C'-C'}$ = 0, respectively. There exist limiting conditions such as that <TT> cannot have negative values or that the sum of the number of C" and A neighbours of a C" atom and the number of lone-electron pairs attached to it cannot exceed four. This can lead in certain cases to the result that there is a smaller or even no difference between <TTmin> and <TTmax>. One example is $Li_2Cu^{2+}{}_3Se_4O_{14}$ (Figures IX - 6 and 7).

<BEN> : average number of valence electrons per neutral or charged base tetrahedron, calculated with

<BEN> = <VEC/A> · <n/m"> (C - 14) ≡ (VIII - 8)

For a compound of category **B4** the value of the parameter <BEN> is equal to <VEC">.

In the first sentence on the `Crystal chemical parameters` screen is given a description of the structure as normal, polyanionic or polycationic valence compound depending on the value of the first key parameter <VEC/A>. Further, there is found a phrase that a tetrahedron complex is considered, provided the following condition is satisfied :

4 - 4 <n/m"> ≤ [<n/m"> · (<VEC/A> - 8)] ≤ 8 - 2 <n/m"> and 0 ≤ <n/m"> ≤ 4 (C - 15)

This range where a tetrahedron complex can occur is larger as the one shown in Figure IX - 2 and Table VIII - 2, because in the program are considered 152 theoretically possible kinds of base tetrahedra where equipartition is respected (see below).

On the `Simple structure proposal` screen one finds a possible crystal chemical formula and a graph drawing of the base tetrahedron(a) which may be used for the construction of the anionic tetrahedron complex.

For the derivation of the crystal chemical formula the following considerations are made :
For normal and polyanionic valence compounds each C" atom is bonded to four A atoms forming a tetrahedron. For polycationic compounds the number of anions bonded to C" depends on the relative partition of the electrons used for homonuclear C" - C" bonds and the electrons in lone-electron pairs on C". Whenever $N_{C"-C"}$ and N_{lep} are within the permitted limits (as defined by <TTmin> and <TTmax>) a number of electrons corresponding to the maximum even integer lower than or equal to <C"C"> is placed into lone-electron pairs, the remaining electrons into C" - C" bonds. The number of

anion - central atom bonds is distributed among the anions so that the numbers of neighbours do not differ by more than one (equipartition principle). For polyanionic valence compounds the number of homonuclear bonds are distributed so that the number of anion-anion bonds for the different atoms do not differ by more than unity. Homonuclear bonds are added first to the anions with less *A - C"* bonds.

For the derivation of the base tetrahedron(a) of a structure with a tetrahedron complex the following considerations are made :
Only base tetrahedra are considered which obey an extended equipartition principle, *i.e.* the number of bonded neighbours (anions or C" atoms) of the A atoms do not differ by more than unity. The program will search for a possible combination involving a **minimum** number of base tetrahedra. Based on the value of <n/m"> and <C"C"> or <N(A-A)> per tetrahedron, a systematic scan is undertaken, searching first for solutions with one single base tetrahedron and then for solutions combining two base tetrahedra. In the large majority of cases one single base tetrahedron corresponds to a particular combination of <n/m"> and <C"C"> or <N(A-A)> per tetrahedron. However, at eight points in the extended base tetrahedron gallery used by the program occur base tetrahedron pairs (four of them shown in Figure IX - 2). They have the following codes : [102] ⇔ [020], [103] ⇔ [021], [106] ⇔ [022], [112] ⇔ [030], [116] ⇔ [031], [202] ⇔ [120], [206] ⇔ [121], [108] ⇔ [023]. Whenever a solution with a single base tetrahedron is possible, the base tetrahedron on the left hand side of each pair is used for the derivation of the crystal chemical formula. A combination of two base tetrahedra, for which *TT* differs by unity, will be proposed for normal valence compounds with <n/m"> < 2. For valence compounds where anions are unshared and/or are shared between two tetrahedra a graph table corresponding to Figure IX - 2 is scanned, starting with horizontal lines (constant value of <C"C"> or <N(A-A)>), then vertical lines (constant n/m" ratio) and then diagonal lines with different slopes. The method of finding base tetrahedron pairs and the lever rule used to find their proportion are summarized on pages IX - 85. No base tetrahedron combinations are presented if the solution would require more than two base tetrahedra. Due to the different selection criteria for the formulation of a crystal chemical formula and for the choice of the minimum possible number of base tetrahedra, the base tetrahedra presented on the screen may not always correspond to the crystal chemical formula.
The program makes a special distinction between different kinds of central atoms which plays a role for the structural analysis of polycationic valence compounds. The C" atoms are divided by the program in two subcategories, *i.e.* those which may carry lone-electron pairs (non-metallic elements) and those where lone-electron pairs are not expected. If there are present two kinds of central atoms of the first subcategory the program will consider as first answer only solutions without C" - C" bonds. If central atoms of both subcategories are present the program will provide solutions where the percentage of base tetrahedra without lone-electron pairs and without C" - C" bonds is equal or higher as the ratio of the number of central atoms of the second subcategory to the total number of central atoms. As example serve the screens for $Ca_3Co^{[4t]}\underline{Se_4}^{[3n]}O_{12}$ presented in Table C - 6d.

There might exist different geometrical possibilities of combining base tetrahedra which result in the same average <BEN> and <n/m"> values. Answering with Y(es) to the program request if you want to see Further possible combinations of base tetrahedra a new screen with such a title will appear showing graphs of other possible base tetrahedron combinations. The above mentioned constraints concerning the choice of possible base tetrahedra are now removed. It you want to find other base tetrahedron combinations in addition to those proposed on the screen by the program one can refer to the base tetrahedron gallery in Figure IX - 2. To plot a compound point on the $(n\,/\,m')\cdot(VEC_A - 8)$ versus $n\,/\,m'$ grid one can conveniently use the <C"C"> or <N(A-A)> and <n/m"> parameters listed on the `Crystal chemical parameters` screen. The procedure to be used to find the base tetrahedron pairs in Figure IX - 2 is described on page IX - 85. Note, that not all these geometrical solutions are equally probable from a crystal chemical point of view.

In the graph drawings of the base tetrahedra an unshared anion is represented on the screen by a grouping of 13 `A` characters assembled in form of a (deformed) filled circle and a central atom by a similar arrangement of 13 `C` and `"` characters. The `C" - A` links are shown by `----` and `I` characters arranged in a row or a column, respectively. The symbol `X` is used to represent lone-electron pairs, homonuclear `C" - C"` and `A - A` bonds and indicates also the separation line in anions which are shared with one, two or three other tetrahedra. Anions shared between two tetrahedra have the (approximate) shape of half-circles, those shared between three tetrahedra a triangular shape and those shared between four the shape of a square (or rectangle). Each drawing on the screen is identified by its `<BEN>` number in the rectangular line box to the upper right and its base tetrahedron code within square brackets on the lower right.

Category B1 [- C" A -] Tetrahedral structure compound $C''_m A_n$ with a neutral tetrahedron complex

In tetrahedral structure compounds all atoms are sp^3 hybridized. In the program the composition is denoted, differently from the text in chapters VI and VII, as $C''_m A_n$, *i.e.* the `C` atoms carry a double prime. In this way the program recognizes that these atoms are central atoms of a (neutral) tetrahedron complex. For compounds of category **B1** the program makes an extra test whether or not the valence electron rules for an adamantane structure are satisfied, *i.e.*

$$4 \le \langle VEC \rangle \le 4.923 \quad \text{and} \quad \langle VEC/A \rangle = 8 \qquad (C - 16) \equiv (VII - 7)$$

and a corresponding remark is made. In the particular case of a defect adamantane structure the percentage of unoccupied `C"` sites in ZnS will be calculated and indicated on the screen.
The screens for a defect adamantane structure compound (`<VEC/A>` = 8) are shown in Table C - 5a. Here is presented for demonstration purposes also the optional fourth screen with the title `Further possible combination of base tetrahedra` where are found graphs of other possible base tetrahedra. In Table C - 5b are shown the screens for a polycationic defect tetrahedral structure compound and in Table C - 5c the screens for a polyanionic valence compound for which in a test calculation a defect tetrahedral structure is assumed.

TABLE C - 5A : SCREENS FOR THE DEFECT ADAMANTANE STRUCTURE COMPOUND $AgIn_5Se_8$.

```
Input for AgIn5Se8
line  nbr.   element     role  nbr.valence el.  electroneg.
---------------------------------------------------------------------
1      1.     Ag          C"        1.              1.9
2      5.     In          C"        3.              1.7
3      8.     Se          A         6.              2.4

Crystal chemical parameters for AgIn5Se8
---------------------------------------------------------------------
Normal valence compound.
Defect tetrahedral structure compound.
Neutral tetrahedron complex considered with <n/m"> =  1.333.
                                Average number of :
<VEC/A>   =  8.000              valence electrons per A
<VEC>     =  4.571              valence electrons per atom
<N(NBO)> =   .571 ( 4/7 )  non-bonding orbitals per atom
<TT>      =  8.000              C"-A-C" links per tetrahedron
<BEN>     = 10.667              val. electrons per neutral (base) tetrahedron
```

```
Simple structure proposal for AgIn5Se8
--------------------------------------------------------------------------
   Crystal chem. formula  C"[4;0] C"5[4;0] :A8[3;0]
   One kind of base tetrahedron [- - 8].
   Defect adamantane structure with 1/4 voids on cation sites of ZnS.

                         X               ..........
                       XAAAX             . 10 2/3 .
                     XAAAAAAAX           ..........
                         I
              X          I          X
           XAAA         C"C         AAAX
        XAAAAAAA ----- C"C"C"C ----- AAAAAAX
           XAAA         C"C         AAAX
              X          I          X
                         I
                     XAAAAAAAX
                       XAAAX
                         X               [ - - 8]

Further possible combination of base tetrahedra for AgIn5Se8
--------------------------------------------------------------------------
   Two kinds of base tetrahedron  1 [- - 7] +  2 [- - 9].
   Defect adamantane structure with 1/4 voids on cation sites of ZnS.

   One                                   ......
                      XXXXXXX            . 12 .
                        AAA              ......
                         I
              X          I          X
           XAAA         C"C         AAAX
        XAAAAAAA ----- C"C"C"C ----- AAAAAAX
           XAAA         C"C         AAAX
              X          I          X
                         I
                     XAAAAAAAX
                       XAAAX
                         X               [ - - 7]

   for two
                         X               ......
                       XAAAX             . 10 .
                     XAAAAAAAX           ......
                         I
              X          I
           XAAA         C"C         XXXXXX
        XAAAAAAA ----- C"C"C"C ----- AAAAAX
           XAAA         C"C         XXXXXX
              X          I
                         I
                     XAAAAAAAX
                       XAAAX
                         X               [ - - 9]
```

The structure of $AgIn_5Se_8$ can be constructed with the single base tetrahedron on the third screen.

TABLE C - 5B : SCREENS FOR THE POLYCATIONIC DEFECT TETRAHEDRAL STRUCTURE COMPOUND Si_2Te_3.

```
Input for Si2Te3
line  nbr.   element     role  nbr.valence el.  electroneg.
--------------------------------------------------------------------------
1      2.     Si          C"         4.               1.8
2      3.     Te          A          6.               2.1

Crystal chemical parameters for Si2Te3
--------------------------------------------------------------------------
Polycationic valence compound.
Defect tetrahedral structure compound.
Neutral tetrahedron complex considered with <n/m"> =  1.500.
                              Average number of :
<VEC/A>   =  8.667            valence electrons per A
<C"C">    =  1.000            C"-C" bonds or non-bonding electrons on C"
<VEC>     =  5.200            valence electrons per atom
<N(NBO)> =  1.200 ( 6/5 ) non-bonding orbitals per atom
<TTmin>   =  3.000            C"-A-C" links per tetrahedron for 1.000 C"-C"
```

```
                                bond(s) and no lone-electron pair on C"
<TTmax>    =  5.000             C"-A-C" links per tetrahedron for no C"-C"
                                bond and  .500 lone-electron pair(s) on C"
<BEN>      = 13.000             val. electrons per neutral (base) tetrahedron

Simple structure proposal for Si2Te3
------------------------------------------------------------------------
   Crystal chem. formula  C"2[3;1] ::A3[2;0]
   One kind of base tetrahedron [0 1 3].
                                             ......
                                             . 13 .
                           X                 ......
                           X
             XA           C"C            AX
             XAAA ----- C"C"C"C ----- AAAX
             XA           C"C            AX
                           I
                           I
                          AAA
                        XXXXXXX          [0 1 3]
```

The proposed base tetrahedron agrees with the experimental data (see Figure VI - 5).

TABLE C - 5C : SCREENS FOR POLYANIONIC ZnS_2 ASSUMING A DEFECT TETRAHEDRAL STRUCTURE .

```
Input for ZnS2
line nbr.   element     role  nbr.valence el.  electroneg.
------------------------------------------------------------------------
1      2.      Zn         C"        2.               1.6
2      7.      S          A         6.               2.5

Crystal chemical parameters for ZnS2
------------------------------------------------------------------------
Polyanionic valence compound.
Defect tetrahedral structure compound.
Neutral tetrahedron complex considered with <n/m">  =  2.000.
                                Average number of :
<VEC/A>    =  7.000             valence electrons per A
<AA>       =  1.000             anion-anion bonds per A
<N(A-A)> =  2.000               anion-anion bonds per tetrahedron
<VEC>      =  4.667             valence electrons per atom
<N(NBO)> =   .667 ( 2/3 )       non-bonding orbitals per atom
<TT>       =  4.000             C"-A-C" links per tetrahedron
<BEN>      = 14.000             val. electrons per neutral (base) tetrahedron

Simple structure proposal for ZnS2
------------------------------------------------------------------------
   Crystal chem. formula  C"[4;0] :A2[2;1]
   One kind of base tetrahedron [- 2 4].
                                             ......
                        XXXXXXX XXXX         . 14 .
                          AAA                ......
                           I
                           I
             XA           C"C            AX
             XAAA ----- C"C"C"C ----- AAAX
             XA           C"C            AX
                           I              X
                           I              X
                          AAA
                   XXXX XXXXXXX
                                          [- 2 4]
```

The base tetrahedron graph with *BEN* = 14, code [- 2 4] and $n / m'' = 2$ cannot be found in the simplified base tetrahedron gallery in Table VIII - 2 and Figure IX - 2. Each of the anions is shared between two tetrahedra and each anion extends one anion - anion bond to another tetrahedron. This means, however, that each of these anion - anion bonds, shared between two tetrahedra, counts only as half a bond per anion. Thus `<N(A-A)> = 2`.

The assumption of Table C - 5c that both Zn and S are sp^3 hybridized is not verified. ZnS_2 crystallizes in the pyrite $Fe^{[6o]}S_2^{[(3;1)t]}$ type where only the anions are sp^3 hybridized. The base tetrahedron shown in Table C - 5c is used for the construction of a complex in the ternary compound $KGa^{[4t]}\underline{Sb_2}^{[2;1]}$. This result is not unexpected because $(35_2)^{1-}$ is isoelectronic with $(26_2)^{\pm 0}$.

Category B2 $\boxed{C \;\; C" \;\; A \;\; -}$ Compound $C_mC"_{m"}A_n$ with a charged tetrahedron complex $(C"_{m"}A_n)^{(m \cdot e_C)-}$

In a compound with a charged anionic tetrahedron complex the number of valence electrons, defined in the input screen, of the cations C outside the complex are **all** added to the electron pool. The parameters which refer alone to the atoms of the **charged** complex (not to all the atoms of the compound) carry a double prime, *i.e.* <VEC">, <N"(NBO)> and <N"(A/M)>.

In Tables C - 6 are presented five screen examples of normal, polycationic and polyanionic valence compounds with anionic tetrahedron complexes. Of the three examples for polycationic compounds the first (Table C - 6b) presents a not yet described complex consisting of an isolated ψ - tetrahedron and a corner-linked ψ - tetrahedron pair. The second (Table C - 6c) has as solution a pair of base tetrahedra with same <BEN> and <n/m"> value and the third (Table C - 6d) has two kinds of C" atoms, one being a metal and the second a main-group element.

TABLE C - 6A: SCREENS FOR THE NORMAL VALENCE COMPOUND $NaBa_3Nd_3Si_6O_{20}$ WITH TETRAHEDRON COMPLEX.

```
Input for NaBa3Nd3Si6O20
line nbr.    element      role  nbr.valence el.  electroneg.
------------------------------------------------------------------------
1      3.      Ba          C         2.               .9
2      3.      Nd          C         3.              1.2
3      1.      Na          C         1.               .9
4      6.      Si          C"        4.              1.8
5     20.      O           A         6.              3.5

Crystal chemical parameters for NaBa3Nd3Si6O20
------------------------------------------------------------------------
Normal valence compound.
Anionic tetrahedron complex considered with <n/m">  =  3.333.
Cations C are not included in the complex.
                               Average number of :
<VEC/A>    =  8.000            valence electrons per A
<VEC">     =  6.154            val. electrons per atom in charged complex
<N"(NBO)>=  2.154 (28/13)  non-bonding orb. per atom in charged complex
<N"(A/M)>= 13.000   .        atoms per non-cyclic charged complex
<TT>       =  1.333 ( 4/3 )  C"-A-C" links per tetrahedron
<BEN>      = 26.667            val. electrons per charged (base) tetrahedron

Simple structure proposal for NaBa3Nd3Si6O20
------------------------------------------------------------------------
   Crystal chem. formula  C7 C"6[4;0] A4[2;0] A16[1;0]
   Non-cyclic units containing  3 tetrahedra.
   Two kinds of base tetrahedron  2 [- - 1] +  1 [- - 2].
   Finite chains of corner-linked C"A4 tetrahedra.

   Two
                          AAA              ......
                        AAAAAAA            . 28 .
                          AAA              ......
                           I
                           I
            AAA           C"C            AX
          AAAAAAA ----- C"C"C"C ----- AAAX
            AAA           C"C            AX
                           I
                           I
                          AAA
                        AAAAAAA
                          AAA              [- - 1]
```

```
   for one
                        AAA              ......
                      AAAAAAA            . 24 .
                        AAA              ......
                         I
                         I
            XA          C"C           AX
            XAAA -----  C"C"C"C ----- AAAX
            XA          C"C           AX
                         I
                         I
                        AAA
                      AAAAAAA
                        AAA              [- - 2]
```

The proposed solution for the anionic tetrahedron complex in $NaBa_3Nd_3Si_6O_{20}$ is a finite non-cyclic chain of three corner-linked tetrahedra. As seen in Figure VIII - 8 the tetrahedron complex in $NaBa_3Nd_3Si_6O_{20}$ consists of two kinds of finite chains with two and four tetrahedra, respectively. However, for this more complicated solution the average values of the crystal chemical parameters agree with the calculated values given in Table C - 6a. The simple finite three-tetrahedron chain is found as anionic tetrahedron complex in isoelectronic $Na_2Ca_3Si_3O_{10}$, $Na_5P_3O_{10}$ II and $K_2Cr_3O_{10}$.

TABLE C - 6B : SCREENS FOR POLYCATIONIC $FeSe_3O_7(OH)$ WITH ANIONIC TETRAHEDRON COMPLEX.

```
Input for FeSe3O7(OH)
line nbr.   element     role  nbr.valence el.  electroneg.
------------------------------------------------------------------------
1     1.      Fe         C          3.             1.8
2     3.      Se         C"         6.             2.4
3     7.      O          A          6.             3.5
4     1.      OH         A          7.             3.5
Crystal chemical parameters for FeSe3O7(OH)
------------------------------------------------------------------------
Polycationic valence compound.
Anionic tetrahedron complex considered with <n/m"> =  2.667.
Cations C are not included in the complex.
                                  Average number of :
<VEC/A>    =  8.750               valence electrons per A
<C"C">     =  2.000               C"-C" bonds or non-bonding electrons on C"
<VEC">     =  6.364               val. electrons per atom in charged complex
<N"(NBO)>=  2.364 (26/11)  non-bonding orb. per atom in charged complex
<N"(A/M)>=  5.500               atoms per non-cyclic charged complex
<TTmin>    =    .000              C"-A-C" links per tetrahedron for  .667 C"-C"
                                  bond(s) and  .667 lone-electron pair on C"
<TTmax>    =    .667  ( 2/3 )  C"-A-C" links per tetrahedron for no C"-C"
                                  bond and 1.000 lone-electron pair(s) on C"
<BEN>      = 23.333               val. electrons per charged (base) tetrahedron

Simple structure proposal for FeSe3O7(OH)
------------------------------------------------------------------------
   Crystal chem. formula  C C"3[3;0] A[2;0] A7[1;0]
   1 single tetrahedra(on) for  1 unit(s) with two tetrahedra.
   Two kinds of base tetrahedron  1 [1 0 0] +  2 [1 0 1].
   Single C"A3 psi-tetrahedra and pairs of corner-linked psi-tetrahedra.

   One
                                        ......
                                        . 26 .
                                        ......
                      XXXXXXX
           AAA          C"C           AAA
         AAAAAAA -----  C"C"C"C ----- AAAAAAA
           AAA          C"C           AAA
                         I
                         I
                        AAA
                      AAAAAAA
                        AAA             [1 0 0]
```

```
   for two                                   ......
                                             . 22 .
                                             ......
                           XXXXXXX
          AAA               C"C              AX
        AAAAAAA -----    C"C"C"C -----    AAAX
          AAA               C"C              AX
                             I
                             I
                            AAA
                          AAAAAAA
                            AAA            [1 0 1]
```

$FeSe_3O_7(OH)$: Muilu, H. & Valkonen, J. (1987). Acta Chem. Scand. ***A41****, 183 - 189. Same program output for $Ca_2Se_3O_8$: Giester, G. & Lengauer, C.L. to be published.*

TABLE C - 6C : SCREENS FOR THE POLYCATIONIC VALENCE COMPOUND $CsPO_2$. AQUA.

```
Input for CsPO2, aqua
line  nbr.   element      role  nbr.valence el.  electroneg.
------------------------------------------------------------------
1      1.      Cs          C        1.               .7
2      1.      P           C"       5.              2.1
3      2.      O           A        6.              3.5

Crystal chemical parameters for CsPO2, aqua
------------------------------------------------------------------
Polycationic valence compound.
Anionic tetrahedron complex considered with <n/m"> =  2.000.
Cations C are not included in the complex.
                          Average number of :
<VEC/A>   =  9.000        valence electrons per A
<C"C">    =  2.000        C"-C" bonds or non-bonding electrons on C"
<VEC">    =  6.000        val. electrons per atom in charged complex
<N"(NBO)>=   2.000        non-bonding orb. per atom in charged complex
<TTmin>   =   .000        C"-A-C" links per tetrahedron for 2.000 C"-C"
                          bond(s) and no lone-electron pair on C"
<TTmax>   =  2.000        C"-A-C" links per tetrahedron for no C"-C"
                          bond and 1.000 lone-electron pair(s) on C"
<BEN>     = 18.000        val. electrons per charged (base) tetrahedron

Simple structure proposal for CsPO2, aqua
------------------------------------------------------------------
   Crystal chem. formula  C C"[3;0] A[2;0] A[1;0]
   Infinite tetrahedron chains or rings.
   One kind of base tetrahedron [1 0 2]/[0 2 0].
   Crystal chem. formula corresponds to the former.

                                        ......
                                        . 18 .
                                        ......                    X
                XXXXXXX                                           X
    XA           C"C            AX              AAA              C"C
    XAAA -----  C"C"C"C -----  AAAX    or     AAAAAAA -----    C"C"C"C XXXX
    XA           C"C            AX              AAA              C"C
                  I                                               I
                  I                                               I
                 AAA                                             AAA
               AAAAAAA                                         AAAAAAA
                 AAA       [1 0 2]              [0 2 0]          AAA
```

For BEN = 18 exist two base tetrahedra which are equally probable. The tetrahedron complex in $CsP^{[2;2]}O_2 \cdot$ aqua is constructed of [0 2 0] base tetrahedra, but in isoelectronic $KAs^{[3;0]}Se_2$ of [1 0 2] tetrahedra.

TABLE C - 6D : SCREENS FOR POLYCATIONIC $Ca_3CoSe_4O_{12}$ WITH ANIONIC TETRAHEDRON COMPLEX.

```
Input for Ca3CoSe4O12
line  nbr.   element      role  nbr.valence el.  electroneg.
------------------------------------------------------------------
1      3.      Ca          C        2.              1.0
2      1.      Co          C"       2.              1.8
3      4.      Se          C"       6.              2.4
4     12.      O           A        6.              3.5
```

```
Crystal chemical parameters for Ca3CoSe4O12
---------------------------------------------------------------------------
Polycationic valence compound.
Anionic tetrahedron complex considered with <n/m"> =  2.400.
Cations C are not included in the complex.
                                  Average number of :
<VEC/A>   =  8.667                valence electrons per A
<C"C">    =  1.600 ( 8/5 ) C"-C" bonds or non-bonding electrons on C"
<VEC">    =  6.118                val. electrons per atom in charged complex
<N"(NBO)>=  2.118 (36/17) non-bonding orb. per atom in charged complex
<N"(A/M)>= 17.000                 Atoms per non-cyclic charged complex
<TTmin>   =   .000                C"-A-C" links per tetrahedron for 1.600 C"-C"
                                  bond(s) and no lone-electron pair on C"
<TTmax>   =  1.600 ( 8/5 ) C"-A-C" links per tetrahedron for no C"-C"
                                  bond and  .800 lone-electron pair(s) on C"
<BEN>     = 20.800                val. electrons per charged (base) tetrahedron

Simple structure proposal for Ca3CoSe4O12
---------------------------------------------------------------------------
   Crystal chem. formula  C3 C"[4;0] C"4[3;0] A4[2;0] A8[1;0]
   Two kinds of base tetrahedron  1 [- - 4] +  4 [1 0 1].

   One
                                XXXXXXX       ......
                                  AAA         . 16 .
                                   I          ......
                                   I
                XA                C"C           AX
                XAAA -----  C"C"C"C ----- AAAX
                XA                C"C           AX
                                   I
                                   I
                                  AAA
                                XXXXXXX       [- - 4]

   for four
                                              ......
                                              . 22 .
                                              ......
                                XXXXXXX
              AAA                 C"C           AX
           AAAAAAA -----  C"C"C"C ----- AAAX
              AAA                 C"C           AX
                                   I
                                   I
                                  AAA
                                AAAAAAA
                                  AAA         [1 0 1]
```

$Ca_3CoSe_4O_{12}$: Wildner, M. (1996). J. Solid State Chem. ***124****, 143 - 150.*

TABLE C - 6E : SCREENS FOR POLYANIONIC Na_3SiSe_4 WITH ANIONIC TETRAHEDRON COMPLEX.

```
Input for Na3SiSe4
line  nbr.   element     role  nbr.valence el.  electroneg.
---------------------------------------------------------------------------
1      3.      Na          C         1.              .9
2      1.      Si          C"        4.             1.8
3      4.      Se          A         6.             2.4

Crystal chemical parameters for Na3SiSe4
---------------------------------------------------------------------------
Polyanionic valence compound.
Anionic tetrahedron complex considered with <n/m"> =  4.000.
Cations C are not included in the complex.
                                  Average number of :
<VEC/A>   =  7.750                valence electrons per A
<AA>      =   .250 ( 1/4 ) anion-anion bonds per A
<N(A-A)> =  1.000                 anion-anion bonds per tetrahedron
<VEC">    =  6.200                val. electrons per atom in charged complex
<N"(NBO)>=  2.200 (11/5 ) non-bonding orb. per atom in charged complex
<N"(A/M)>= 10.000                 atoms per non-cyclic charged complex
<TT>      =   .000                C"-A-C" links per tetrahedron
<BEN>     = 31.000                val. electrons per charged (base) tetrahedron
```

```
Simple structure proposal for Na3SiSe4
--------------------------------------------------------------------------
   Crystal chem. formula  C3 C"[4;0] A[1;1] A3[1;0]
   Single units containing two tetrahedra.
   One kind of base tetrahedron [- 1 0].
   Units of two C"A4 tetrahedra linked by a A-A bond.
                                X             ......
                                X             . 31 .
                               AAA            ......
                             AAAAAAA
                               AAA
                                I
                                I
              AAA              C"C            AAA
            AAAAAAA ----- C"C"C"C ----- AAAAAAA
              AAA              C"C            AAA
                                I
                                I
                               AAA
                             AAAAAAA
                               AAA            [~ 1 0]
```

A molecular anionic tetrahedron complex consisting of ten atoms and constructed of two such base tetrahedra linked by a homonuclear Se - Se bond is found in the structure of Na_3SiSe_4.

Category B3 $\boxed{\texttt{C C" A Y}}$ Compound $C_mC"_{m"}A_nY_{n"}$ with a charged complex $(C"_{m"}A_n)^{[m \cdot e_C - n" \cdot (8 - e_Y)]-}$ and isolated $Y^{(8 - e_Y)-}$ anions which are neither bonded to C" nor to A

As in category **A2** the extra Y anions take up electrons from the valence electron pool to complete their octets and thus become separate structural units. For the calculation of <VEC/A> and <VEC"> the program uses (C - 8_3) and (C - 9_3), respectively. As example are presented in Table C - 7 the screens for epidote. To obtain this result the default values in the input screen had to be modified as shown.

TABLE C - 7 : SCREENS FOR THE NORMAL VALENCE COMPOUND EPIDOTE $Ca_2Al_2Fe(OH)Si_3O_{12}$.

Input for Ca2Al2FeO(OH)Si3O11, epidote

line	nbr.	element	role	nbr.valence el.	electroneg.
1	2.	Ca	C	2.	1.0
2	1.	Fe	C	3.	1.8
3	2.	Al	C	3.	1.5
4	3.	Si	C"	4.	1.8
5	11.	O	A	6.	3.5
6	1.	O	Y	6.	3.5
7	1.	OH	Y	7.	3.5

```
Crystal chemical parameters for Ca2Al2FeO(OH)Si3O11,  epidote
--------------------------------------------------------------------------
Normal valence compound.
Anionic tetrahedron complex considered with <n/m">  =  3.667.
Cations C and anions Y are not included in the complex.
                               Average number of :
<VEC/A>    =  8.000            valence electrons per A
<VEC">     =  6.286            val. electrons per atom in charged complex
<N"(NBO)>=  2.286 (16/7 )  non-bonding orb. per atom in charged complex
<N"(A/M)>=  7.000            atoms per non-cyclic charged complex
<TT>       =   .667 ( 2/3 )  C"-A-C" links per tetrahedron
<BEN>      = 29.333            val. electrons per charged (base) tetrahedron

Simple structure proposal for Ca2Al2FeO(OH)Si3O11,  epidote
--------------------------------------------------------------------------
   Crystal chem. formula  C5 C"3[4;0] A[2;0] A10[1;0] Y2[0;0]
   1 single tetrahedra(on) for  1 unit(s) with two tetrahedra.
   Two kinds of base tetrahedron  1 [- - 0] +  2 [- - 1].
   Single C"A4 tetrahedra and pairs of corner-linked tetrahedra.
```

```
One
                       AAA               ......
                     AAAAAAA             . 32 .
                       AAA               ......
                        I
                        I
       AAA             C"C             AAA
     AAAAAAA ----- C"C"C"C ----- AAAAAAA
       AAA             C"C             AAA
                        I
                        I
                       AAA
                     AAAAAAA
                       AAA               [- - 0]

for two
                       AAA               ......
                     AAAAAAA             . 28 .
                       AAA               ......
                        I
                        I
       AAA             C"C             AX
     AAAAAAA ----- C"C"C"C ----- AAAX
       AAA             C"C             AX
                        I
                        I
                       AAA
                     AAAAAAA
                       AAA               [- - 1]
```

Category B4 | C C" - - | Compound $C_mC"_{m"}$ with a charged degenerated complex $(C"_{m"})^{(m\cdot e_C)-}$

For completeness there is mentioned category **B4** where the anion partial structure of a polyanionic valence compound is analyzed under the assumption that the anions (here labelled C" atoms) are sp^3 hybridized. Only the five degenerated base tetrahedra with $n/m" = 0$ on the left edge of Figure IX - 2 can occur. For this degenerated case only the key parameter <VEC">, as defined by (C - 9_4), is meaningful, which is here equal in numerical value to <BEN> and <C"C">. Since there are no A anions present , the parameter <TT> has no meaning and is left out from the list of crystal chemical parameters. By considering a compound of category **A1** as belonging to **B4** one obtains an equivalent result but in addition also graphs of the degenerated base tetrahedra.

As a demonstration how the program can be used to test different hypothetical structure models we shall comment the outputs of different possible inputs for Al_2SiO_5 given in Table C - 1.

- The first (unmodified) input screen in Table C - 1 corresponds to a defect tetrahedral structure with crystal chemical formula $Al_2^{[4t]}Si^{[4t]}O_5$ where according to (II - 1) the five O atoms together extend twelve bonds, *i.e.* some of the anions would have three tetrahedral bonds which seems unlikely for a silicate.
- If in the first input all Al atoms change function from C" to C the anionic tetrahedron complex would have composition $[Si^{[4t]}O_5]^{6-}$. However, on the Crystal chemical parameters screen appears now a message that a tetrahedron complex cannot form when <n/m"> > 4.
- If only half of the Al atoms change function from C" to C (second input screen) then the anionic tetrahedron complex has composition $(Al^{[4t]}Si^{[4t]}O_5)^{3-}$. With the base tetrahedron shown on the screen one can construct the anionic tetrahedron complex found in sillimanite.
- In the model corresponding to the third input screen the Al atoms and one of the five O atoms do not participate on the tetrahedron complex which has formula $[Si^{[4t]}O_4]^{4-}$. The isolated tetrahedron presented on the screen is the anionic tetrahedron complex in kyanite.

APPENDIX D : DATABASE CONTAINING DATA SETS REPRESENTATIVE FOR STRUCTURE TYPES

To enable the reader to verify the crystal chemical features which have been predicted for various compounds in this book there has been included a database labelled "STYP" containing complete data sets representative of 386 structure types discussed here. The data sets contain the structure type formula and name, space group, Wyckoff sequence, Pearson code, standardized positional atom coordinates, literature references as well as remarks on possible errors, changes of space group due to overlooked symmetry elements, crystal chemical parameters, structural features and a reference to the page(s) in the book where the type is discussed. The data sets can be adressed with the type number, the type formula, the mineral name and the Strukturbericht notation. The type number, surrounded by square brackets, can be looked-up in the Structure Formula Index on pages 159 ff. Help screens with an explanation of other search options (chemical elements, colloquial name, *e.t.c.*) are obtained by typing `?1`. Help screens for the explanation of the used codes can be accessed by typing `?2`. The output is on the screen and also on the file `STYP.OUT`.

Technical Data and Installation

The database "STYP" is found together with the PC program "VEC", treated in Appendix C, on a floppy disk 3.5" HD in a pocket in the cover of this book. The database and the PC program occupy $1^1/2$ MB hard disk space. The program runs on a PC using MS-DOS 6.xx. A 386 processor or higher is required.

To install database and program insert the disk and type `INSTALL` from the floppy disk drive unit. The program will ask for the disk drive unit where you want the data base and the program to be installed (A, B, C, D, E or F, a single letter and make no carriage return). The directory `EISC` (after the first letters of the four key words in the title of this book) will be created on this unit. The complete installation procedure takes less than 1 minute for a 486 processor.

Upon entering the command `STYP` or `VEC` from the appropriate `EISC` directory the title screen for the "STYP" database or the "VEC" program, respectively, will appear. A carriage return leads to a menu which gives further instructions how to proceed.

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STRUCTURE FORMULA INDEX

Structure formulae printed with heavy type indicate that the formula (also name) of this compound is used as structure type label for the corresponding atom arrangement. Structure formulae printed with normal characters are followed by the structure type forrmula or name (bold faced characters within parentheses). The structure type formula or name is left out if the compound has different structure modifications and no reference is made to a particular one.
A type number, surrounded by square brackets, is added to each type in the structure formula index table. Data sets representative for structure types can be found in a database on a floppy disk in a pocket in the hard cover of this book with this type number. For technical details see Appendix D. If there are listed more than one number this means that there exist different structure modifications of the compound for which all the data are given in the database.

SUBJECT INDEX

PARAMETER INDEX

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