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INTRODUCTION TO THE PROCEEDINGS OF THE 2ND INTERNATIONAL CONFERENCE ON MAGNETOELECTRIC INTERACTION PHENOMENA IN CRYSTALS, MEIPIC-2

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In the following text an attempt has been made to condense the main points of the MEIPIC-2 conference, to correlate certain results scattered over different contributions, to give some comments, suggestions for future work and a few historical reference points. Those contributions which have been less discussed, reflect simply the incompetence of the writer and not a ranking. The names in brackets without indication of the year represent authors of these Proceedings (see AUTHOR INDEX). The other references with numbers are given at the end of this Introduction. The subdivision in Sections 01. to 10. is a pragmatic one, implying many crossovers.

Keywords: Magnetoelectric effect (linear and higher order), piezomagnetoelectric effect, linear magneto-optic effect, piezomagnetic effect, magnetic symmetry, time parity violation, relativistic symmetries, crystal optics, quasimoving crystals, toroidal moments, nano-engineering, magnetoelectric spin chirality control, high magnetic fields (static and pulsed), magnetoelectric materials, domains (antiferromagnetic, ferromagnetic, ferroelectric, ferroelastic, chiral), magnetoelectric composites, elementary excitations, antiferromagnetic resonance, magneto-optics, Sagnac interferometer, magnetic quadrupole fields, magnetoelectric measurements, surface magnetoelectricity, crystal defects, magnetic ferroelectrics (ferromagnetic, antiferromagnetic magnetoelectric), "spin ferroelectricity," phase transitions, incommensurate phases, critical exponent.

01. LINEAR, HIGHER ORDER AND RELATED MAGNETOELECTRIC EFFECTS

Most magnetoelectric effects can be characterized by the presence of a corresponding term in a thermodynamic potential. Which one is applicable depends on the macroscopic crystal state and on the measuring conditions.

Considered here is the density of stored free enthalpy $g(E, H, T)$ which, for the situations we want to describe, can be written in the following way in SI-units[1,2]:

$$-g(E, H; T) = \cdots \kappa_i(T)E^i + \mu_i(T)H^i + 1/2\varepsilon_0\kappa_{ik}(T)E^iE^k + \alpha_{ik}(T)E^iH^k + 1/2\mu_0\mu_{ik}(T)H^iH^k + 1/2\beta_{ijk}(T)E^iH^jH^k + 1/2\gamma_{ijk}(T)H^iE^jE^k + \pi_{ijkl}(T)E^iH^j\sigma^{kl} + \cdots$$

In this expression $\kappa_i = P_i^s$ and $\mu_i = M_i^s$ are the spontaneous polarization and magnetization, κ_{ik} and μ_{ik} the electric and magnetic susceptibilities, ε_0 and μ_0 the permittivity and permeability of free space, respectively. The linear magnetoelectric effect is due to the coefficient α_{ik}, whereas β_{ijk}, γ_{ijk} and π_{ijkl} describe higher-order magnetoelectric effects. The first two ones have been introduced by Ascher[2] and the last one gives rise to the piezomagnetoelectric effect, first pointed out by Rado[3] and then worked out by Grimmer.[4] Additional terms of the density of stored free enthalpy can be found elsewhere.[5] In SI-units the above defined coefficients α_{ik}, β_{ijk}, γ_{ijk} and π_{ijkl} have the dimensions [s/m], [s/A], [s/V] and [(sm)/N] = [m^2/(V A)], respectively. The definition of α_{ik} in SI-units, which we adopt here (Rivera, Definitions . . .), has been given earlier[6] and has proved to be convenient for the experimentalist. It follows that α_{ik} (Gaussian units)† = $c\alpha_{ik}$ (SI units), with c being the free space velocity of light.

In other parts of the proceedings, the magnetoelectric effect is associated with the induction B instead of the magnetic field H as above. This is due to the fact that within the frame of Maxwell's equations, and in a relativistically covariant formulation, the linear magnetoelectric term appears together with the electric κ_{ik} and magnetic μ_{ik} ones as part of a relativistic covariant rank-four susceptibility tensor defining the constitutive equations which relate the antisymmetric rank-two tensor of the field strengths $(E, B) = F^{\mu\nu}$ to that of the electric and magnetic excitation fields $(D, H) = G^{\mu\nu}$ (See Post [9] and O'Dell[10]).

Let us here remark that such a covariant description of the magnetoelectric effect within the electrodynamics does not imply that one necessarily has a thermodynamically well defined state, even in a macroscopic approximation. If it is well defined, then thermodynamic conditions are imposed to the various terms of the general susceptibility tensor, as discussed, for example, in Landau-Lifshitz[11] and by Ascher.[1] In particular, as Ascher pointed out, precisely in the presence of a magnetoelectric effect the electric susceptibility at constant B differs from that at constant H. This is a situation one typically has to take into account when a macroscopic crystal state is characterized by a thermodynamic potential.

After these general remarks, let us consider in more detail the various magnetoelectric effects.

The Linear Magnetoelectric Effect (α_{ik} term)

After the prediction of the effect for Cr_2O_3 by Dzyaloshinskii[12] and its measurement by Astrov[13] and Folen, Rado and Stalder,[14] it was studied for many materials in the 1960s and '70s. It is allowed for 58 Shubnikov-Heesch point groups.

The tensor form of the linear magnetoelectric effect was first determined by Indenbom,[15] but with an incomplete list of point groups. Tables are also given in several textbooks[16–18] and in a review.[19] However, in all these tables the tensor form of orthorhombic groups with off-diagonal coefficients and that of some tetragonal groups is presented in an ill-defined, misleading way. Corrected tables with well-defined coordinates have been worked out (Rivera, Section 01.) based

†(N.B.: Here we do not follow Ascher's definition,[1] in which α_{ik} becomes dimensionless in SI-units and numerically equal to the value in Gaussian units. Let us also note that we use γ_{ijk} as notation for the coefficient of the third order term bilinear in E, at variance with Ascher[2] (using α_{ijk}), but in agreement with Rado.[7,8] This notation is recommended for avoiding confusion between the third rank tensor in matrix notation and α_{ik} of the linear effect).

on combining the tensors of the linear effect for low symmetries by means of the superposition principle.[10]

In a review in these proceedings (Siratori) some fields are put into relief in which the magnetoelectric effect has shown its importance in solid state sciences. For example the unique possibility offered by the ME effect to "pole" antiferromagnetic domains in simultaneous electric and magnetic fields, to measure their domain wall velocity, to determine their volume fractions or to distinguish them optically. All these possibilities are based on the apparent sign reversal (for a fixed measuring coordinate system) of the magnetoelectric coefficient for domains related by time reversal. The magnetoelectric lifting of the chiral degeneracy of screw spin structures is discussed, a precious complement for monitoring such chiral domains by polarized neutrons. The magnetoelectric effect is also shown to be a precious tool for studying defects. Two results are noteworthy: i) the symmetry of the ME signal reflects the symmetry of the defect and ii) the magnetoelectric effect of statistically distributed point defects appears to be amplified by the magnetic matrix (discussed for ferrimagnetic yttrium iron garnet). As concerns microscopic mechanisms of ME effects, apart from those discussed by Gehring (Section 03.), the electric field induced rotation of magnetization and change of anisotropy energy, as well as a so far unexplored magnetoelectric coupling mechanism in magnetic semiconductors are evoked.

At this conference several contributions on the measurements of the linear effect have been presented (for detail see Sections 01. and 05.):

Yttrium iron garnet (YIG) films (Krichevtsov *et al.*) and YIG single crystals (Takano *et al.*); in ferroelectric/weakly ferromagnetic $KNiPO_4$ single crystals (Lujan *et al.*); a very strong effect ($\alpha_{21} = 9.2 \times 10^{-3}$ Gaussian units) and a critical exponent of 0.334 for α_{12} are found in 'revisited' antiferromagnetic $LiCoPO_4$ (Rivera); searched, but not yet found in $BaNiF_4$ (Rivera *et al.*) and $K_3Fe_5F_{15}$ (Ishihara *et al.*); measured in static fields up to 20 T in the low field and spin flop phase of Cr_2O_3 (Wiegelmann *et al.*); measured in pulsed fields up to 28 T in $BiFeO_3$ (Popov *et al.*); measured in solid solution phases of the perovskite-orthoferrite system $BiFeO_3$-$REFeO_3$ with a spontaneous magnetic moment (Murashov); in Gd_2CuO_4 the linear effect is found below the Gd spin ordering temperature (Wiegelmann *et al.*), but where a very weak ferromagnetism is reported to survive.[20] This would explain the impossibility of obtaining superconductivity in this phase by doping; recently the linear effect has also been found in the homologous Sm_2CuO_4.[21]

Higher Order Magnetoelectric Effects

Beside the linear effects, the conference was also intended to deal with higher order magnetoelectric effects, of which we are interested in three types. The tensors of the first and second type had been elaborated by Ascher[2] and those of the third type, the piezomagnetoelectric effect, have been elaborated by Grimmer.[4]

First type (β_{ijk} *term*). This effect manifests itself as a magnetic susceptibility depending linearly on the applied electric field, as a magnetic field induced linear magnetoelectric effect or as an induced polarization depending bilinearly on the applied magnetic field. It is in the second form that Hou and Bloembergen measured it for the first time in 1965 on the non-centrosymmetric paramagnet $NiSO_4 \cdot 6H_2O$, calling it the 'paramagnetoelectric' effect.[22–24] As an induced polarization, bilinear in the applied magnetic field, often superposed by the linear effect, it was later measured at the University of Geneva in the ferroelectric magnetically ordered phase of boracites,[25–28] of $BaMnF_4$[29] and of perovskites.[30–32]

Measurements of the EHH effect on a few materials, discussed in more detail in Section 05., have been presented at this conference: $DyMn_2O_5$ (Tanaka *et al.*), $Cr_3B_7O_{13}Cl$ (Ye *et al.*), $KCoPO_4$ (Lujan *et al.*), $KNiPO_4$ (Lujan *et al.*) and $BaNiF_4$ (Rivera *et al.*, to appear later).

As concerns microscopic mechanisms, a new type of resonant magnetoelectric effect of spin flip tunneling has been discussed, e.g. for Co^{++} doped SrO (Vikhnin). Since the off-centre Co^{++} (Fe^{++}, Ni^{++}, etc) ions in the oxyoctahedra of the NaCl-type lattice can be aligned in an electric field along cubic [111]-directions,[33] leading to the polar point group 3m1′, the EHH-effect should in principle become macroscopically measurable, provided the Co^{++} concentration is high enough. Magnetoelectric tunnelling effects of paramagnetic centres in piezoelectric quartz—measured by EPR—have also been reported (Brik). Also in this case it would be interesting, whether a sufficiently high concentration of these centres would give rise to a macroscopically measurable EHH-effect.

The EHH-effect is allowed in the 66 non-centrosymmetric Shubnikov point groups,[2] permitting also piezoelectricity, the linear electro-optic (Pockels) effect, second harmonic generation, etc. The effect does not necessarily require long range magnetic order! Its tensor form has the same internal symmetry as that of the piezoelectric effect [34] (see Tables by Grimmer, Section 02.).

Second type (γ_{ijk} *term*). This effect manifests itself either as an electric susceptibility depending linearly on an applied magnetic field[35] as an electric field induced linear magnetoelectric effect or as an induced magnetization depending bilinearly upon the applied electric field (similar to the inverse Faraday effect[36]). Just when preparing this conference it has been realized that the linear magneto-optic effect, first measured in 1976 by Kharchenko and co-workers,[37] can be considered as such a magnetic dc-field modulated electric susceptibility at optical frequency, an effect allowed in all 66 piezomagnetic groups, all of which necessitate crystals with magnetic long-range order. The effect may be useful for determining magnetic symmetry, as is the case for the linear magnetoelectric effect, although experimentally probably less convenient (Kharchenko).

In principle the HEE-term would also allow optical magnetic rectification,[38] an effect which does not seem to have been measured so far. Necessarily, second harmonic generation would be associated with the magnetic rectification.

The HEE-effect had been thoroughly studied at low frequencies on YIG by Mercier,[39] but there are no contributions at this conference on low frequency or quasistatic measurements of this effect.

A submillimeter spectroscopy study on the centrosymmetric orthoferrite $TmFeO_3$ has led to the conclusion that the HEE effect is proportional to the electrodipolar matrix element between quasidoublet states (Mukhin *et al.*). It would be interesting to study experimentally whether a more quantitative correspondence can be established between these microscopic findings and a macroscopic measurement of the magnetoelectric tensor component on the bulk.

The HEE-effect is allowed for the same 66 Shubnikov point groups which permit the piezomagnetic effect. These effects require structures with magnetic long-range order. For the tensor form see the tables by Grimmer (Section 02.).

Third Type (π_{ijkl} *term*). This effect, described by the piezomagnetoelectric coefficients π_{ijkl}, can manifest itself as an electric field induced piezomagnetic effect, as a magnetic field induced piezoelectric effect or as a stress induced linear magnetoelectric effect. First pointed out by Rado and searched in vain by him in chromium oxide in the latter configuration,[3] it was again attempted to be measured, this time in a piezoelectric oscillator configuration in the presence of a magnetic field, using an antiferromagnetic $LiCoPO_4$ crystal, permitting the linear magnetoelectric effect (Rivera and Schmid). The negative outcome of that experiment probably means that a material will have to be looked for, having simultaneously high mechanical compliance, high magnetic and high electric susceptibility, in analogy with simultaneous high electric and magnetic susceptibility, necessary for high coefficients of the linear magnetoelectric effect. These coefficients of linear effects are restricted by thermodynamic upper limits,[40–41] as will also be the case for the piezomagnetoelectric ones.

Even higher order terms can be imagined. So a fourth order magnetoelectric term, αE^2H^2, has been evoked in relation with magnetoelectric microwave effects (Smirnov), but no correspondence with macroscopic tensor components (same internal symmetry as that of the photoelastic tensor[34]) has been established.

Magnetic Field Induced Switching of Spontaneous Ferroelectric Polarization and Electric Field Induced Switching (Reorientation) of Spontaneous Magnetization

At this conference the (pulsed) magnetic field induced reversal of the spontaneous ferroelectric polarization in the paramagnetic phases of $Tb_2(MoO_4)_3$ and $TbGd(MoO_4)_3$ has been reported (Ponomarev *et al.*). It is remarkable that the coupling operates in the paramagnetic phase. However, the molybdate example is only a special case of a larger palette of possibilities offered by crystal symmetries. If we restrict ourselves to paramagnetic ferroelectrics, there exist 42 high temperature phase/low temperature ferroelectric phase point group pairs,[42] called "Species,"[43] for which in Aizu's nomenclature the low temperature ("ferroic") phase is both "fully ferroelectric" and "fully ferroelastic." This means that the spontaneous polarization vector is "fully" coupled to one of the possible ferroelastic domain states, its reorientation (special case: 180° reversal) causing necessarily a reorientation of the ferroelastic domain state and vice versa. Since the magnetostriction tensor and the magnetic susceptibility tensor are coupled to the second rank spontaneous deformation tensor, a magnetic field may drive a ferroelastic domain via magnetostriction and/or the anisotropy of magnetic susceptibility ("ferrobimagnetic" switching, i.e. a "secondary ferroic" effect[44,45]) to an energetically more favorable orientation state. Thus the "Magnetoelectric" phenomenon is due to the magnetic field induced switching of the spontaneous polarization and herewith it is a highly nonlinear effect, linked with hysteresis.

A similar effect, the 180°-reversal of the spontaneous polarization, induced by a 90°-rotation of a magnetic field, was demonstrated for the first time in the weakly ferromagnetic phase of $Ni_3B_7O_{13}I$.[46] The converse effect, i.e. the 90°-reorientation of the spontaneous magnetization, induced by the electric field induced 180°-reversal of the spontaneous polarization, has also been demonstrated on $Ni_3B_7O_{13}I$[46] for which initially the species $\bar{4}3mFm'm2'$ was assumed, whereas later[47] the species $\bar{4}3mFm'$ was established as the correct one.

02. SYMMETRY AND MODULATED STRUCTURES

Challenging New Perspectives

Two contributions are sources of inspiration when considering further developments based on the relation between magnetoelectricity and symmetry. The first one (by Dzyaloshinskii) is based on the fact that time parity violation in crystals is required for the linear magnetoelectric effect. The second one (by Janner) takes into account that magnetoelectricity is essentially a relativistic effect of a moving electromagnetic medium in the same sense as magnetism is that of moving electric charges.

Dzyaloshinskii considers the possible interplay in quantum systems between local and long-range order leading to spin and to orbital quantum liquids, respectively, and to systems with long-range order which has to be described by higher-order correlations because the lower-order ones vanish. He also discusses the possible detection of time parity violation at mesoscopic scale looking at optics in a scattering configuration and at the detectability of external magnetic fields in antiferromagnets.

Janner considers optics with a relativistic covariant formulation. First of all from a phenomenological point of view, by transforming the constitutive equations occurring in optics to inertial frames different from the laboratory one, in the case where this allows to simplify the equations. In deriving the corresponding conditions one gets at the same time a characterization of susceptibility tensors for media having non-trivial relativistic symmetries. As already considered by Ascher[1] one then obtains point group symmetries larger than those described by magnetic point groups (as discussed by Opechowski[48]). An attempt is also made to give a kind of microscopic foundation for those symmetries by means of a relativistic crystallography.

Tensors

Although the symmetries and the form of tensors describing magnetic, electric and toroidal properties are known for quite a while, the experimentalist may be misguided by a number of published tables, in which the relevant Cartesian coordinate system is often not univocally specified. There may be even more delicate situations, where different analogous properties, e.g. piezoelectricity and piezomagnetism, or linear electro-optic and linear magneto-optic effect are allowed for the same point group symmetry, where the corresponding tensors have same rank and even same internal symmetry, but different orientation in the crystal for a fixed coordinate system. With a view to clarifying these cases, very useful tables have been elaborated for the example of a third rank tensor symmetric in two indices, showing clearly how the tensor orientation differs for magnetic, electric and toroidal properties for a given point group (Grimmer). Future analogous elaboration of such well defined, "user-friendly" tables for other types of tensor would be very beneficial for experimentalists.

"Userfriendly," corrected tables of the tensors of the linear magnetoelectric effect with well-defined coordinates have been worked out by Rivera (Section 01.).

'Hidden Magnetoelectric Symmetries'

Whereas magnetoelectricity in crystals was the main subject of the conference, a topic lying somewhat outside the main scope of the conference is an analysis of an emitter of electromagnetic radiation with isotropic intensity. The curiosity involved resides in the fact that the high symmetry of the radiation is linked to a hidden magnetoelectric symmetry of the emitted radiation (Matzner *et al.*). These findings may stimulate ideas by 'lateral thinking' in other fields of magnetoelectricity.

Magnetoelectric Effect and Symmetry Detection

So far the most important application of the magnetoelectric effect is that for the determination of magnetic point group symmetry of magnetically ordered phases. In order to avoid erroneous results, this requires, however, whenever possible, work on magnetic (and if present, also ferroelectric and/or ferroelastic) single domains (Schmid). Even if that condition is satisfied, unexpected phenomena may occur and utmost caution is necessary when interpreting results, for example:

i) *Non-detection of weak ferromagnetism by the magnetoelectric effect.* For $KNiPO_4$ neutron diffraction (Fischer *et al.*) and the measurable linear magnetoelectric effect tensor components indicate a collinear compensated antiferromagnetic with magnetic point group mm2, the symmetry of which does not allow weak ferromagnetism. Nonetheless, measurements with a SQUID-magnetometer clearly show weak ferromagnetism, proving herewith a lower symmetry (Lujan *et al.*). This teaches us the important lesson: neither the magnetoelectric effect alone, nor neutron diffraction alone are able to "see" magnetic symmetry reliably in a correct way. Therefore, as many cross-checks as possible by mutually independent methods should be performed.

ii) *"Weak ferromagnetism" and "weak ferroelectricity" in* $LiCoPO_4$? For $LiCoPO_4$, which has a structure different from that of $KNiPO_4$, analogous results as under item i) are obtained: again, neutron diffraction and measured magnetoelectric tensor components agree and show an antiferromagnetic point group (mmm'), however, a magnetoelectric butterfly hysteresis loop is obtained by means of a magnetic field alone. Such a loop is usually the signature of the presence of a spontaneous magnetic moment.[6,46,46a,46b] The magnetic domains are orientable upon cooling through the Néel temperature with a magnetic field alone. On the other hand, these antiferromagnetic domains can also be poled with an electric field alone upon cooling through T_N. Consequence: the material behaves both like a weak ferromagnet with a tiny magnetization and like a "weak ferroelectric" with a tiny polarization (mutually coupled magnetoelectrically), but both of which have so far not yet been observed by direct measurements (Rivera). Possibly we have here for the first time to do with a "spin ferroelectric," the domains of which appear to be identical with the "weakly ferromagnetic" ones due to magnetoelectric coupling, in contrast to the classical ionic-shift-type ferroelectrics. The important question arises: is the effect intrinsic or induced due to defects in the structure, for example due to growth sector related internal bias fields? More detailed work is required.

iii) *Electric field and interface induced symmetry changes.* The magnetoelectric effect can act in certain cases as a precious monitor for a change of symmetry, for example from centrosymmetric to non-centrosymmetric/polar in single crystals of yttrium iron garnet (YIG) due to the orientation of defects during electric field cooling. A similar decrease in symmetry of epitaxial layers of YIG on GGG (Kritchevtsov *et al.*) may be due to a layer/substrate interface, which can easily assume polar, hence non-centrosymmetric character in contrast to the undisturbed bulk crystals of YIG (see Garnets/Section 05.). A potential candidate is $Pb(Fe_{2/3}W_{1/3})O_3$ (Ye *et al.*), where the electric-field-induced ferroelectricity is supposed to lead to the linear ME effect. Likewise in the case of symmetry changes due to magnetic field-induced phase transitions the magnetoelectric effect also is a precious tool. Examples in these proceedings are: Cr_2O_3 (Wiegelmann *et al.*)[21] and $BiFeO_3$ (Popov *et al.*).

Incommensurate Toroidal Phase Transitions

Although the experimental demonstration of the existence of toroidal moments in crystals belongs still to "wishful thinking" (see item 04.), incommensurate toroidal phase transitions have already been imagined and the three- and two-dimensional representations of magnetic crystal point groups, according to which a toroidal moment transforms, and which admit a Lifshitz invariant, have been investigated. Independent invariants necessary for the description of a phase sequence initial ↔ incommensurate ↔ commensurate have been given (Sannikov).

Incommensurability and Linear Magnetoelectric Effect

A general theoretical treatment of the influence of incommensurability on the linear magnetoelectric effect is not yet at hand. So far we have two experimentally founded cases, where in incommensurate antiferromagnetic phases the linear magnetoelectric effect is not observable and seems to be cancelled due to the incommensurability of the phases. These examples are $BiFeO_3$[31] and $BaMnF_4$,[29] where only the EHH-type second order magnetoelectric effect is measurable, simulating herewith a paramagnetic non-centrosymmetric phase. In the framework of a review of the magnetoelectric anomalies of $BaMnF_4$ (Scott and Tilley), the attempt is made to explain the absence of the linear effect by means of a microscopic model.

One may also ask the more general question, what will happen if the incommensurate modulation in a magnetic structure is one-, two- or three-dimensional? Is it posssible in the two first cases that the linear magnetoelectric coefficients are cancelled only partially, so that the surviving ones may simulate a wrong magnetic point group? Intuitively one would be inclined to think that this is possible. If that is true, it means that the magnetic symmetry derived from the presence of certain magnetoelectric coefficients has absolutely to be complemented by an independent check for incommensurability.

In a study, possibly somewhat akin to the former questions, the "inhomogeneous magnetoeletric effect" in magnetically ordered dielectrics has been investigated theoretically (Stefanovskii), whereby the influence of macroscopic magnetic inhomogeneities, such as the effect of a cycloidal magnetic spiral structure ($CrBeO_4$), of a simple magnetic spiral structure ($TbAsO_4$) and of domain walls is understood.

For materials with coexisting magnetoelectric effect, piezoelectricity and piezomagnetism the corresponding point groups have been tabulated. It is also shown that the magnetoelectric effect influences the velocity and polarization of elastic waves in such crystals and that a new type of acoustic resonance can be foreseen due to the coexistence of the three effects (Lyubimov).

03. PHENOMENOLOGICAL AND MICROSCOPIC THEORY

Phenomenological Aspects

The macroscopic theoretical treatment of the magnetoelectric effect is based on the Landau-Dzyaloshinskii approach, in which symmetry and thermodynamic arguments are interwoven.

The chronological historical steps, which have led to this development, have been illustrated in detail, starting with the prediction of Curie[49] in 1894. Following the classification of magnetic structures based on the concept of magnetic groups, the Landau theory of phase transitions of magnetic crystals, with its specific phenomenological approach developed by Dzyaloshinskii, has been explicited (Tolédano).

An important point, when discussing the Landau expansion for a magnetic crystal is the relative importance of the relativistic interactions (spin-orbit, spin-spin) to the isotropic exchange interactions, the former one dominating close to T_c and the latter one far from T_c.

Whereas the concept of magnetic groups accounts well for the relativistic interactions, it neglects the symmetry of exchange forces. The concept of exchange symmetry group has therefore been introduced by Dzyaloshinskii in order to explain weak ferromagnetism and helimagnetism. Dominating relativistic and exchange forces are discussed for Cr_2O_3 and $Ni_3B_7O_{13}I$, respectively (Tolédano).

Microscopic Aspects

With a view to tailoring materials with high magnetoelectric coefficients, a good understanding of the microscopic mechanisms would be desirable. Up to now, however, only Cr_2O_3 is studied in more detail, together with very few other structures.

As explained in a tutorial overview (Gehring), the first microscopic theory goes back to Rado. He explained in a semiempirical way the temperature dependence of the magnetoelectric effect in Cr_2O_3 using a two ion model, Hornreich and Shtrikman[50] included antisymmetric (Dzyaloshinskii) exchange, changes in the g-factor and in the intrasublattice exchange. Yatom and Englman[51] made a thorough investigation on temperature dependence and de Alcantara Bonfirm and

Gehring[52] studied how the magnetoelectric effect is modified in a magnetic field strong enough to cant an antiferromagnet.

In the overview all terms appearing in the effective Hamiltonian for a magnetic crystal are considered, it is examined, how an applied electric field will modify each type of term, and under what circumstances the modification of the terms of the Hamiltonian can lead to an induced bulk magnetization. These terms are: Symmetric Exchange, Dipolar Interaction, Antisymmetric (Dzyaloshinskii) Exchange, Single Ion Anisotropy and Zeeman Energy. The experimental separation of these different contributions can in principle be tried by studying the temperature and magnetic field dependence of the magnetoelectric coefficient (Gehring).

For the special case of $TbPO_4$, which crystallizes in the tetragonal zircon type structure, the microscopic mechanism of the magnetoelectric effect is considered to be of the single ion type. Calculations in the mean-field approximation of the temperature dependence of the magnetoelectric tensor components are considered to agree satisfactorily with experiment (Kahle) (compare also Phosphates, Section 05.).

Surface Linear Magnetoelectric Effect (SLMEE)

At the surface of a (magnetic) crystal the structure and in certain cases also the symmetry are changing with respect to the bulk. This fact with its consequences on the magnetoelectric effect is treated theoretically (Chupis). It is shown for the case of exchange energy that its change close to the surface and its spatial inhomogeneity give rise to a surface polarization and to a SLMEE. Numerical estimates for the coefficient of the SLMEE give 10^{-2}, which is much higher than that of Cr_2O_3, but of the same order of magnitude as the highest magnetoelectric coefficients observed (cf. Section 05./Phosphates). The effect for a ferromagnetic film, a ferromagnetic/feroelectric film and a ferromagnetic film in contact with a ferroelectric one have been studied (for the latter type of composite layers cf. Rasing and Wierenga, Section 07.).

Long-range Spin Order of Non-orientable Type

Vitebsky and Lavrinenko discuss spin systems, closely related to those considered by Dzyaloshinskii, involving non-trivial relations between local and long-range order, and where one has to distinguish between time reversal symmetry at different length scales. Typical examples are one-spin disordered, two-spin glassy and three-spin ordered crystals as described by Chandra, Coleman and Ritchey.[53] Such a magnetic state, even if having a vanishing time-average of the spin moments at any point of the crystal, can have another magnetic symmetry than that of the corresponding paramagnetic state. A condition for allowing such peculiar ground states with non-orientable long-range order (like that one gets from a staggered local heliticity) is frustration. Also in those cases, symmetry considerations are important and the authors discuss possible relations between the symmetry group of the ordered phase G (O) (at zero temperature), of the frustrated one G (Fr), and of the high temperature paramagnetic state G (PM).

Most of the known magnetoelectric materials have not been studied on the level of microscopic theory. So there is a vast field of desirable collaboration between experimentalists and theoreticians for the future.

04. TOROIDAL MOMENTS

Toroidal Order

In analogy to the known 31 Shubnikov point groups permitting a spontaneous polarization (polar vector) and the 31 groups permitting a spontaneous magnetization (axial vector), Ascher[38] determined the 31 Shubnikov point groups, permitting a new type of vector, an "axio-polar" vector, changing sign both under space and time reversal and remaining invariant under the product of both. Physical examples are velocity, current density, etc. Ascher's hope was that this vector would describe the symmetry of the superconducting state, in conjunction with the postulation of superconducting domains. That guess has not led to a confirmation, but later Ginzburg, Gorbatsevich, Kopayev and Volkov[54] remarked that these same 31 point groups are also compatible with a spontaneous toroidal moment, all of which allow *a fortiori* (for symmetry reasons) the linear magnetoelectric effect. The triad of these three types of vector and their beautiful analogies had been thrown into relief by Ascher at the first international conference on magnetoelectricity.[55] We have a "magic" number of 9 Shubnikov groups, admitting all three vectors simultaneously. Materials with such symmetries do exist, for example the ferroelectric/ferromagnetic materials, but so far nobody has given an experimental evidence for the presence of a spontaneous toroidal moment density in any crystal.

We are lucky to have a theoretical review paper on toroidal order in crystals in these proceedings, essentially a microscopic approach (Gorbatsevich and Kopaev) as well as a related contribution on magnetoelectric effects in correlated electronic systems (Gorbatsevich, Krivitsky and Zaykov). In principle the occurrence of a spontaneous toroidal moment may be the consequence of both orbital and spin order. Since on the microscopic level a toroidal moment is connected with local spontaneous (nonsuperconductive) currents, the signature of magnetoelectrics with an orbital toroidal moment would be strong diamagnetism as expected to be found in 'superdiamagnets'[56] of non-superconductive nature. In the ferroelectric/ferromagnetic nickel iodine boracite, which has the required symmetry (below 61 K) for a spontaneous toroidal moment to occur, a very strong diamagnetic-like negative magnetization (with respect to an applied magnetic field) was reported and conjectured to be related to toroidal order.[57] Unfortunately that experiment could never be reproduced!

With the advent of the theory of anyons (particles obeying fractional statistics) for high-T_c superconductors, anyonic ferromagnet-like states, showing e.g. nonzero Faraday rotation, had been discussed[58] for the superconducting phase. Herewith Ascher's domain idea seemed to regain some revival. A hypothetical antiferromagnetic state of anyons with symmetries permitting the linear magnetoelectric effect was also argued.[59]

By taking relativistic symmetry breaking into account, an attempt has been made at interrelating anyonic states with toroidal moments in superconductors with magnetoelectric symmetry (Rubin).

Although the symmetry groups permitting toroidal order are known[38,55] (Grimmer), these different conjectures have not found an experimental confirmation so far. However, there remains the exciting challenge, to marry experiment with theory, for example to demonstrate the presence of a toroidal moment with a macroscopically measurable quantity.

"Nano-engineering"

It is also possible that the solution to the problem of toroidal moments will only come after the synthesis of an appropriate new material, by assembling building blocks permitting localized spontaneous currents with such ones guaranteeing magnetic order. It is not excluded that this may require organic or metal-organic structures rather than the classical inorganic ones.

A very tempting and promising alternative approach to the difficult task of uniting all the necessary building elements in a homogeneous single crystal structure lies probably in "nano-engineering." The recent progress in the production of superlattices by means of alternating epitaxial layers with a thickness control down to one atomic layer, and for example with the possibility of creating asymmetric, i.e. polar composition gradients in the growth direction, opens up a vast field of creating tailored artificial structures with suitable symmetry and property combinations. Magnetoelectric phenomena of such artificially made multiple quantum well structures (MQWS) with broken space and time reversal symmetry have been analysed theoretically (Gorbatsevich, Kapaev and Kopaev). The introduction of time reversal symmetry into such MQWSs is considered both for the application of an external magnetic field and the introduction of ferromagnetic building blocks. The magnetoelectric coefficient of such structures is predicted to exceed the bulk value, in some analogy to the drastically increased optical rectification coefficients obtained in artificial asymmetric quantum well structures of $GaAs/Al_xGa_{1-x}As$[60]. Even if high magnetoelectric coefficients should be obtained by using "nano-engineering," they will, however, never surpass the thermodynamic limits.[40,41]

Possibly "nano-engineering" of toroidal/magnetoelectric order may more rapidly lead to a solution than via the synthesis of a single crystal satisfying the multiple stringent requirements of building blocks and symmetry.

When symmetry allows in principle a certain physical effect, nature usually does not disappoint us. The effect or property will be found sooner or later, but we may have to fight for it.

05. MAGNETOELECTRIC MATERIALS

Synthesis, structural and magnetoelectric properties of representatives of about fifteen different crystal families have been treated in this conference. We shall try to illuminate some results:

Garnets. Since yttrium iron garnet (YIG) has the centrosymmetric prototype point group m3ml', one would expect that the ferromagnetic rhombohedral phase

3m′ would only allow the magnetoelectric effect with the HEE term. Astonishingly, however, after electric field cooling a linear effect is observed at low temperature, which was conjectured to be due to a magneto-structural phase transition around 125 K (Takano *et al.*). However, Mössbauer studies showed no evidence for such a transition, so that the hypothesis of a symmetry change due to frozen-in dipoles is more plausible (Komada *et al.*).

Even more astonishing and exciting is the observation that epitaxial thin films of magnetic garnets of different composition and on differently oriented GGG-substrates show a strong linear ME-effect even at room temperature, evidenced by a sensitive optical polarimetric method (Krichevtsov *et al.*).

In our opinion these findings merit great attention because they open up the possibility of tailoring materials and to create special, e.g. polar interfaces with a view to creating linear magnetoelectric properties in such ensembles. For example, there may be applications in the field of magnetoelectric "nano-engineering" (compare: Gorbatsevich, Kapaev and Kopaev).

Rare earth cuprates RE_2CuO_4. The family member Gd_2CuO_4, which curiously does not become superconducting by doping, has been shown to display the linear ME-effect below the antiferromagnetic ordering temperature (6.5 K) of the Gd-ion moments (Wiegelmann *et al.*). For the Nd_2CuO_4 member of that crystal family magnetoelectric microwave effects have been studied (Smirnov). Recently also Sm_2CuO_4 was found to be linearly magnetoelectric.[61]

Magnetite Fe_3O_4. When the search for ferroelectric ferromagnets was started more than 30 years ago, two strategies were at choice: to modify ferroelectrics, or to modify ferro(i)magnets. At that time it appeared terribly difficult to endow spinels with ferroelectric structural elements, so that the ferroelectrics finally became the starting point with a view to finding magnetically ordered ferroelectrics. The more surprising it was when magnetite was claimed to be ferroelectric below the Vervey temperature. On the basis of magnetoelectric measurements, but without simultaneous observation of the domain states, the conclusion is reached—in agreement with other authors—that magnetite is triclinic/polar below 35 K, and hence ferroelectricity is postulated (Miyamoto). In the writers opinion a convincing proof of ferroelectricity in magnetite has, however, not yet been given. More detailed studies on optically monitored single domains and on the possible microscopic mechanism of the onset of a spontaneous polarization are highly desirable in order to clarify the properties of that complex material.

Hausmannite $CuCr_2O_4$. With a view to clarifying the low temperature magnetic symmetry, in literature indicated to be orthorhombic ferromagnetic and polar (hence potentially ferroelectric and magnetoelectric), single crystals of $CuCr_2O_4$ were synthesized by high temperature solution growth. An X-ray structure refinement was realized and confirmed, however, centrosymmetric tetragonal symmetry at room temperature (Ye *et al.*).

Rare earth ferrites $REFe_2O_4$. In polycrystalline ferrimagnetic $ErFe_2O_4$, a member of the large $REFe_2O_4$ family, a magnetoelectric response has been found. Its origin may reside in point defects or charge ordering due to the mixed valency (Fe^{2+}/Fe^{3+}) situation (Ikeda *et al.*). With a view to obtaining better understanding, a comparative study on other mixed valency compounds of iron would therefore seem rewarding.

Rare earth manganese (III, IV) oxides $REMn_2O_5$ form a large, little investigated crystal family. The representatives with RE = Eu, Gd, Tb, Dy and Y have been reviewed (Kohn) and show the common feature of a Néel temperature of about 40–45 K, due to Mn spin ordering and one or two phase transitions at lower temperatures. The special case of $DyMn_2O_5$ is discussed separately (Tanaka *et al.*). Only a second order magnetoelectric effect of EHH type has been observed below the Néel point with sign reversal of the signal upon change of sign of the electric cooling field. This seems to show ferroelectricity, but if that is true, it is astonishing that no linear effect is found, in particular since neutron diffraction shows magnetic order. Thus the EHH effect simulates paramagnetic phases (m1′ or mm21′). Therefore one should ask the question whether this behavior might be due to incommensurate phases, in which the linear magnetoelectric effect may be cancelled as is the case in $BiFeO_3$ (Popov *et al.*) and $BaMnF_4$ (Scott and Tilley). More detailed work is therefore necessary.

Rare earth molybdates $RE_2(MoO_4)_3$. In the "fully ferroelectric"/"fully ferroelastic" (in Aizu's nomenclature[43]) rare earth molybdates $Tb_2(MoO_4)_3$ and $TbGd(MoO_4)_3$ a symmetry and magnetostriction conditioned magnetic field induced 180°-degree reversal of spontaneous polarization has been demonstrated above the Néel temperature, giving rise to a "giant magnetoelectric effect" with nonlinear (hysteresis) character (Ponomarev *et al.*). This phenomenom is akin to the magnetic field induced reversal of spontaneous polarization and its reverse effect in fully coupled ferromagnetic/ferroelectric/ferroelastic nickel iodine boracite[46] (cf. also item 01.).

Perovskites. A breakthrough in magnetoelectric perovskites has been achieved by replacing bismuth in $BiFeO_3$ partially by rare earth elements, i.e. by creating $BiFeO_3$ (perovskite)-$REFeO_3$ (orthoferrite) solid solutions with different, concentration dependent structures. One of them (with Dy) is reported to be even polar ($Pna2_1$) and ferromagnetic above room temperature, with a linear ME effect and corresponding ME butterfly loop (at 77 K) (Murashov), the signature of a ferro(i)magnetic magnetoelectric. By the explanation of the crystal optics of the ferroelastic domains of the orthorhombic phases (Rabe *et al.*), the route has been opened for more quantitative magnetoelectric and related measurements on optically controlled single domains.

Thirty-five years after the announcement of Smolenskii and Ioffe[62] of $Pb(Fe_{2/3}W_{1/3})O_3$ as 'the first ferroelectric antiferromagnet', it has now been shown on single crystals and with simultaneous polarized light control that the material is in reality non-ferroelectric at zero electric field, but that a ferroelectric phase can be induced by an electric field and rendered metastable at low temperatures (Ye *et al.*), similar to the behavior of $Pb(Mg_{1/3}Nb_{2/3})O_3$.[63] In this induced ferroelectric phase a magnetoelectric effect, at least the one quadratic in the magnetic field, is expected to be measurable. The perovskite $Pb(Fe_{1/2}Nb_{1/2})O_3$, also synthesized first by Smolenskii and Ioffe,[62] is in fact ferroelectric and apparently weakly ferromagnetic[64] and linearly magnetoelectric below 9 K.[65] Some complementary magnetic susceptibility and EPR data of that compound have been presented at this meeting (Maryanowska and Pietrzak).

In a Review paper (Venevtsev and Gagulin) references of many more potential magnetic perovskite type ferroelectrics and antiferroelectrics, as well as of materials with other structure types, can be found. Since most of those potential magnetoelectrics are known in polycrystalline form only, there is offered a vast field with challenge for crystal growers, before serious magnetoelectric work can be started.

Boracites. In the fully coupled ferromagnetic/ferroelectric/ferroelastic boracite family the EHH-type magnetoelectric effect was measured in $Cr_3B_7O_{13}Cl$, but the linear one remains at the limit of detectability (Ye *et al.*). A second magnetic phase transition has been discovered, using a special dynamic method (Rivera, item 01.). For $Co_3B_7O_{13}Br$ it has been shown by powder neutron diffraction (Schobinger-Papamantellos *et al.*) that in the magnetoelectric ferroelectric/ferromagnetic phase the magnetic ordering occurs in a two step process, probably caused by complex frustration phenomena as also found for $Ni_3B_7O_{13}Br$.[66]

Phosphates. On single crystals of $LiCoPO_4$ with antiferromagnetic point group mmm′, already studied many years ago,[67] high accuracy measurements of the linear ME effect coefficients by means of the quasistatic $(ME)_H$-technique gave a particularly large value for α_{21} at 4 K: α_{21} (4 K) $= 0.92 \times 10^{-2}$ (Rivera), of the same order of magnitude as the one reported at this conference for epitaxial layers of YIG (Krichevtsov *et al.*) and as the one of $TbPO_4$ ($\alpha^{max} = 1.1 \times 10^{-2}$),[68] which was considered up to now as the largest known coefficient of the linear magnetoelectric effect (for $TbPO_4$ compare also Kahle, Section 03.). Thus it is encouraging that the presence of rare earth elements in crystals is not a necessary condition for high magnetoelectric coefficients!

A second curiosity of $LiCoPO_4$ worthwhile mentioning is the easy ‘poling’ of the antiferromagnetic domains by means of a magnetic field alone upon cooling through T_N and a magnetoelectric butterfly loop between T_N and T_N-1 K with a maximum field of 10 kOe (Rivera) and down to 4 K with higher fields.[69] Such a butterfly loop, which is known to be the signature of a spontaneous magnetic moment,[6,46] would indicate here a weakly ferromagnetic behavior. It is not clear so far whether this effect is intrinsic and allowed for the collinear antiferromagnetic structure, or generated by extrinsic origin (defects, stress, internal electric bias field, etc.). Thus it would be worthwhile to investigate more carefully the concept of magnetoelectric annealing[70,71] and that of the "coercive product" $(E_iH_j)_c$ as an analogon of the ferromagnetic (or ferroelectric) coercive field.

A third strong point in Rivera's work on $LiCoPO_4$ is the accurate magnetoelectric measurement of a critical exponent of 0.334 for one of the coefficients, with an excellent fit both close to the Néel point and extending far to lower temperatures. Perfect agreement between quasistatic and dynamic techniques is achieved.

Weakly ferromagnetic and pyroelectric orthorhombic single crystals of $KNiPO_4$ have been grown and studied magnetoelectrically (Lujan *et al.*; see Section 02.).

Hexagonal single crystals of $KCoPO_4$ are found to be pyroelectric and metastable, showing down to liquid He-temperature the EHH magnetoelectric effect only. Upon heating, $KCoPO_4$ transforms irreversibly into a stable state, having a sequence of three phases (Lujan *et al.*).

Fluorides. A detailed review of the properties of the antiferromagnetic/ferroelectric $BaMnF_4$ has been given (Scott and Tilley). A remarkable feature of this compound is the cancelling of the linear magnetoelectric effect due to the incommensurate structure and the monitoring of the spin flop by means of the EHH effect. On single crystals of the homologous, but apparently commensurate $BaNiF_4$, the spin-flop has also been monitored,[72] but the linear ME effect has escaped detection up to now.

In the weakly ferromagnetic/ferroelastic, mixed Fe^{2+}/Fe^{3+} valency transparent fluoride $K_3Fe_5F_{15}$ with tungsten bronze type structure, predicted to be ferroelectric, both the ferroelectricity and the linear ME-effect were searched but not found up to now (Ishihara).

Orthoferrites. The magneto- and electrodipolar excitations of Tm^{3+} have been studied in $TmFeO_3$ by means of submillimeter spectroscopy. The electrodipolar rare earth modes of $TmFeO_3$ were theoretically found to contribute substantially to the quasistatic permittivity and to the magnetoelectric effect of HEE-type (Mukhin *et al.*).

Orthoferrites play also an important role as components in high temperature magnetoelectric solid solutions with the perovskite $BiFeO_3$ (Murashov).

Molecular-Based Magnets. Since 1986 a new kind of molecular materials is being developed, which exhibits a spontaneous magnetization or antiferromagnetism up to relatively high critical temperatures. In a tutorial talk Olivier Kahn has presented recent progress[73–76] (these proceedings do not contain a corresponding article) and in particular the strategy of designing heterobimetallic molecular lattices in a way that there is no compensation of the local spin moments. In a recent overview on organic ferromagnets,[77] the ambitious programme of chemists is outlined, with a view to designing and synthesizing new classes of magnetic materials using the techniques of molecular organic chemistry.

These new materials offer a variety of centrosymmetric and noncentrosymmetric ferromagnetic and antiferromagnetic structures, hence a fascinating and rich field for magnetoelectric and related studies out of the beaten track.

Composites—Theory. It has been shown that the effective coefficient of the linear magnetoelectric effect of a composite, made of two isotropic magnetoelectric materials, can be determined exactly if the properties of the pure components, the effective dielectric constant, and the magnetic permeability of the composite are known. The problem is shown to be a special case of relations existing between general, linear response coefficients of composite systems (Milgrom and Shtrikman).

In one of the studies a two-phase composite, consisting of a piezoelectric (ferroelectric, non-piezomagnetic) phase and a piezomagnetic (ferromagnetic, non-piezoelectric) phase has been analysed both for laminated and fibrous ensembles with a view to obtaining a linear magnetoelectric response. It has been shown that the figures of merit depend on the individual coefficients of the constituents and on the connectivity pattern (Getman).

Composites—Experiment. On the experimental side some microwave properties of ferrimagnetic yttrium-iron garnet/ferroelectric PZT composites have been studied with a view to creating ultra-high-frequency devices of magnetic type by means of a "resonance magnetoelectric effect" under electric field control (electric field shift of ferromagnetic resonance line) (Bichurin and Petrov). More work will certainly be required in order to test the potential technological usefulness.

PZT/Ferrite composites have also been synthesized and an optimum composition determined. The unavoidable strong piezoelectric response of such devices has to be taken into account if devices have to be designed. Interdiffusion problems during preparation have to be mastered (Lopatin *et al.*).

Generally speaking, there remains the question to what extent composites with such a "two-phase-magnetoelectric effect" will really have a technological future. It is felt highly desirable that the sum of all theoretical and experimental information presented at this conference, together with former and recent work[78,79] found in literature, should be used to perform—under the critical eye of an applications engineer—an in-depth-analysis of the entire field of magnetoelectric composites.

06. MAGNETOELECTRICALLY MONITORED PHENOMENA

Magnetic Field Induced Phase Transitions and Related Phase Diagrams

The recently established availability of static magnetic fields up to 30 tesla and that of pulsed fields up to the same order of magnitude opens up a large field for applying the magnetoelectric effect for studies of magnetic field induced phase transitions and temperature/magnetic field phase diagrams. Many materials studied about twenty or thirty years ago gain herewith renewed interest. Because magnetic structure determination by neutron diffraction in very high magnetic fields cannot be performed up to now, the symmetry information obtained from the magnetoelectric effect in high fields is invaluable. The experimental possibilities in high static fields (up to 30 T), offered by the High Magnetic Field Laboratory, Max-Planck Institut Für Festkörperforschung/CNRS, Grenoble, have been presented by Jansen. However, his contribution does not appear in these proceedings.

As an example let us mention the monitoring of the destruction of the antiferromagnetic cycloidal spin structure of the ferroelectric perovskite $BiFeO_3$ by observing the appearance of the linear magnetoelectric effect in the high magnetic field induced phase, using pulsed fields (Popov *et al.*), whereas it appears to be cancelled in the incommensurate one in the field free state, simulating paramagnetism (cf. Scott and Tilley).

Although Cr_2O_3 is probably the best studied magnetoelectric material, it has still not revealed all its secrets. Thus the magnetoelectric study of its spin-flop transition in static fields up to 20 tesla along three crystallographic directions (Wiegelmann *et al.* and Reference 21) has brought insight by delimiting the symmetry of the induced spin-flop phase to only two possible magnetic point groups. Whereas in the first publications on Cr_2O_3 the values of the magnetoelectric coefficient were strongly scattering, very reliable values have now been obtained.

These investigations will stimulate in turn magnetization and other physical measurements at high fields of these induced phases. Since neutron diffraction studies are, however, often unable to end up with the magnetic point or space group, the usefulness of the magnetoelectric effect as a precious auxilliary tool has insistently to be stressed.

As pointed out elsewhere for rare earth molybdates (Ponomarev *et al.*), high magnetic fields enable also the switching of ferroelectric/ferroelastic or simple ferroelastic magnetic phases ("secondary ferroic switching"[44,45]). Here we have another vast realm for the application of high magnetic fields. Magnetic (ferroelectric, ferroelastic) domain switchings can be assimilated to first order phase transitions with the magnetic (electric, stress) field as intensive constraint.

Chirality Control of Helimagnets

Following the demonstration for $ZnCr_2S_4$ of chirality control in a helimagnet in the presence of an electric field[80] and the theoretical symmetry analysis showing that an electric field applied in the basal plane of a stacked triangular antiferromagnet breaks chiral degeneracy associated with a frustration induced 120° spin structure (Plumer *et al.*), experiments on the stacked triangular antiferromagnet $CsMnBr_3$ were performed in the presence of an electric field (Visser *et al.*). By testing a potential change in domain population by a polarisation analysis of the neutron Bragg scattering and by the determination of the change of critical exponent with increasing electric field, the conclusion was reached that the electric field probably induces a first order transition rather than lifting the chiral degeneracy. In spite of these negative results, it is enjoyable that such kinds of experiment, exploiting magnetoelectric couplings, start to become used for complementing magnetic structure determinations by neutrons (see also Wiegelmann *et al.*).

Under the heading of this section would also fit the magnetoelectric monitoring of the antiferromagnetic and ferromagnetic domain state. This topic is discussed under item 08.

07. OPTICAL PROPERTIES

At variance with the first international conference on magnetoelectrics in 1973,[81] an important part of the Ascona meeting was intentionally dedicated to optical properties.

Light Propagation

In the centre of interest stood the light propagation in magnetoelectric media and the associated non-reciprocal phenomena. There is a noteworthy particularity that non-reciprocal effects in magnetoelectrics may occur in the absence of magnetic moment and only the loss of the time reversal operation is required (Pisarev). Possible new phenomena, conditioned by the magnetoelectric state, have been discussed, such as non-reciprocal gyrotropic birefringence, the rotation of the optical indicatrix, the non-reciprocal reflexion and the electric field induced non-reciprocal rotation. So far Cr_2O_3 is the only material which has been studied more thoroughly. The electric field induced non-reciprocal rotation versus temperature has now very properly been measured and there is also quite a strong experimental evidence for the long-searched for gyrotropic birefringence by the observation of a tilting of the optical indicatrix in opposite directions for two types of antiferromagnetic domain (Pisarev). Also the non-reciprocal rotation of the reflected light and of the reflexion circular dichroism versus temperature have been demonstrated very clearly (Pisarev).

Electric Current Induced Non-reciprocal Rotation

The literature on some unusual electromagneto-optical phenomena has also been reviewed by Pisarev. Among those effects the non-reciprocal rotation induced by electric current in tellurium[82] seems particularly noteworthy. Tellurium has the non-centrosymmetrical Shubnikov point group 321′, which allows reciprocal rotation along the ternary axis, however, the current induced rotation along the 3-fold axis (parallel to the inducing current) is non-reciprocal and linearly proportional to the current. One is strongly tempted to consider this result as the first example of the "kinetomagnetic effect," formulated by Ascher at the first conference on magnetoelectrics.[55] This predicted effect is analogous to the linear magnetoelectric effect and is also allowed in 58 Shubnikov-Heesch groups. It is noteworthy that some of them are magnetic groups and some are even grey ones. The group 321′ of Te is one of them. The tensor has only diagonal coefficients $\zeta_{11} = \zeta_{22}$, ζ_{33}. The experiment corresponded only to the latter coefficient and the induced non-reciprocal rotation should be associated with an induced magnetization. It would be worthwhile trying to measure optically the orthogonal effect, corresponding to the coefficient $\zeta_{11} = \zeta_{22}$. In that case the non-reciprocal rotation would be superposed on birefringence, i.e. an experimental challenge for the Sagnac interferometer (Dodge *et al.*), permitting to separate non-reciprocal rotation from reciprocal optical properties or for the high accuracy universal polarimeter "HAUP,"[83,84] which allows to separate reciprocal and non-reciprocal rotation from birefringence, in principle. The detection of the converse effect, a magnetic field induced current (collinear with the field!), would be challenging. Maybe it can give rise to an induced toroidal moment.

Another current effect, the non-reciprocal reflection of light from a current-carrying superconductor, has been treated phenomenologically, based on symmetry properties of the reflexion polarization matrix (Gridnev). This problem is of interest in connection with theories of 'unconventional' superconductivity, for which broken time reversal symmetry might occur due to an expected spontaneous magnetic moment. With a view to overcoming the experimental problem of distinguishing between the effects originating from the current and those of the magnetic field, generated by the current, the use of thin films is proposed for which the magnetic field effect on the reflexion can be made negligibly small.

The propagation of electromagnetic waves in magnetoelectric crystals has theoretically been treated by using the discrete dipole approach (van Gisbergen *et al.*). Only small differences are found with the classical continuum approach. A direct link between the microscopic quantities and the crystal optical properties can be established.

Linear Magneto-Optic Effect

The linear magneto-optic effect, analogous to the linear electro-optic effect (Pockels effect), has been measured for the first time in 1976 by Kharchenko *et al.*[37] on $CoCO_3$ and by Dillon *et al.*[85] on $Dy_3Al_5O_{12}$, followed by detailed studies by Kharchenko's group in Kharkov. The effect can be shown to be due to the magnetoelectric term $H_iE_jE_k$ of the thermodynamic potential. That is why a review had been solicited for these proceedings (Kharchenko). It is allowed in the 66 Shubnikov-Heesch groups permitting piezomagnetism, as well as its reverse effect, linear magnetostriction. Linear magnetostriction was probably measured for the first time on single crystals of nickel by Masiyama in 1928 (see Ascher[86]). Therefore a review of the materials on which the piezomagnetic effect has been measured, appeared timely (Borovik-Romanov). It shows that there is great paucity of data, as also holds true for the linear magneto-optic effect. Among the cited 66 groups we find all the 31 groups permitting ferromagnetism. Thus, for measuring the linear magnetooptic effect on ferro(i)magnetics (no example known), there remains the challenge for experimentalists, to separate induced from spontaneous non-reciprocal optical properties, both in transmission and reflection! (cf.: Dodge *et al.*).

A subject to some extent akin to the former one—for some materials which allow the linear magnetoelectric effect—concerns the intensity of Raman light scattering by exchange magnons, which is theoretically shown to exceed by far the intensity related to the acoustic magnons for magnetic structures, the sublattice moments of which are noncollinear in the exchange approximation (Pashkevich *et al.*).

A propos Raman effect, additional Stokes and anti-Stokes lines due to the linear magnetoelectric effect, have been predicted,[87] but no experimental evidence is available so far.

Surface and Interface Phenomena

Surface phenomena represent a new subject having made inroads at this conference. For example magnetic field induced second harmonic generation has been shown to be a new and promising tool to probe surface and interface magnetic properties (e.g. on multilayers of magnetic and nonmagnetic materials). At interfaces between ferromagnetic and ferroelectric materials magnetoelectric effects are also expected to appear (Rasing and Wierenga). In this context the induction of the linear magnetoelectric effect in YIG layers on GGG substrate (Kitchevtsov *et al.*), probably an interface effect decreasing the symmetry, is worthwhile mentioning as well as the theoretical paper on the "surface linear magnetoelectric effect" (Chupis, Section 02.).

Quadrupole Effects

A theory has been presented in the electric quadrupole-magnetic dipole approximation of various birefringences in non-absorbing, antiferromagnetic crystals of the uniaxial and cubic system. A test for this multipole theory would be the observation of birefringence in cubic classes when propagation is parallel to an edge (Graham and Raab, I). Such a birefringence being expected to be very small, its measurement represents a challenge for the experimentalist.

With a view to the smallness of the quadrupole effects, a warning seems, however, appropriate and allowed at this place: real crystals are always imperfect and parasitic birefringence of different origin may hide the real effects looked for. The most spectacular optical anomalies are probably those due to sectorial growth (growth pyramids), a phenomenon discovered by Sir David Brewster in 1815, much studied thereafter in the last century, but nearly forgotten in the 20th century.[88] For example linear birefringence of this type in cubic boracites has erroneously been attributed to quadrupole contributions.[89] A source of error may for example also come from birefringence, irreversibly induced by polishing in initially rather perfect isotropic cubic crystals.[90]

Another challenge for experimentalists consists in the verification of a presented theory of a reflexion experiment for determining magnetoelectric properties of cubic antiferromagnets at optical frequencies (Graham and Raab, II).

The ascoustic diffraction of light in magnetoelectric antiferromagnets with tetragonal easy plane anisotropy has been treated theoretically (Turov). Also the influence of the linear magnetoelectric effect on the acoustic and acousto-optic properties has been considered theoretically for some uniaxial antiferromagnetic magnetoelectrics (Cr_2O_3, trirutile structures), as well as the effect on the antiferromagnetic resonance (Turov). In order to evaluate the practical importance of these effects, more quantitative estimates of their order of magnitude would be highly desirable.

08. DOMAINS AND DOMAIN WALLS

In the field of domains and domain walls the majority of the contributions were theoretical in nature, in particular as concerns the properties of the walls themselves. These different predictions are hoped to appeal to the imagination and skill of future experimentalists.

For non-ferroelastic magnetoelectric twin laws (domain pairs) the form of some important material property tensors (e.g. for piezomagnetism), and the sign of the components of which are different in the two non-ferroelastic magnetoelectric domain states for a fixed coordinate system, have been analysed group-theoretically (Litvin *et al.*). This information may be useful when the direct detection of the magnetoelectric tensor components is difficult, for example in the case of too high electric conductivity of the material. The authors show for a domain pair with a particular magnetoelectric point group that the sign of all tensor components changes upon switching the domain for a fixed measuring coordinate system. They do not dare to say, however, that this will always be the case for non-ferroelastic magnetoelectric domain pairs, independently of the particular point group permitting the magnetoelectric effect. There does not seem to be any experimental counter example.

In several papers the dynamic behavior of domain walls has been analysed: In a model of a ferroelectric/antiferromagnetic phase the domain walls are found to behave like discommensurations in incommensurate crystal phases, showing a magnetoelectric coupling of the domain wall motion in the electric and the magnetic subsystem (Janssen). Ferroelectric domain walls of ferromagnets, oscillating in an electric field are found to lead to resonance excitation of spin waves (Manzhos), and localized excitations and domain walls in hexagonal antiferromagnetic ferroelectrics ($RMnO_3$, where R = rare earth or Y) have been analysed (Soboleva). The electric field induced drift motion and velocity of magnetic domain walls have been analysed for the case of the symmetry of an orthorhombic, magnetoelectric, ferroelectric/ferromagnetic Ni-Cl boracite (Sukstanskii and Grasimchuk).

Experimentally the electric field induced magnetic domain wall motion has elegantly been demonstrated magnetoelectrically on garnets using optical techniques (Selitsky *et al.*).

The crystal optics of the ferroelastic domain structure of orthorhombic $Bi_{1-x}La_xFeO_3$ has been studied and elucidated experimentally by polarized light microscopy, a must with a view to reliable magnetoelectric measurements on single domains (Rabe *et al.*; cf. also: Murashov).

By simple etching (often ignored by physicists, because too simple an approach!) the pyroelectric, magnetoelectric weak ferromagnet $KNiPO_4$ was found to be composed of 180°-ferroelectric domains! (Lujan *et al.*).

In short review of complex ferroic magnetoelectrics, in particular of materials being simultaneously ferroelectric, ferroelastic and (anti)ferromagnetic, it has been shown that the complexity rises with increasing number of equivalent domain states, which may climb up to 96 for the case of triclinic, ferroelectric, magnetic perovskite or spinel. In order to avoid misleading artefacts and herewith useless publications due to uncontrolled domain states, experimentalists are exhorted to work with single crystals and to perform physical measurements in conjunction with polarized light microscopical studies on optically controlled single domain states, or at least on well-defined multi-domain arrangements (Schmid).

X-ray and Neutron Topography

The usefulness of the techniques of X-ray and neutron topography has been put into relief as a complementary approach for studying structural and magnetic domains, as well as phase coexistence in (magnetoelectric) antiferromagnetic crystals (Schlenker and Baruchel). A limitation of these methods is due to the requirement of relatively large, good quality crystals.

09. EXCITATIONS

When looking at the physics of the macroscopic mechanical, electric, magnetic and optical properties, we have always the common feature of the propagation of waves through the periodic lattice and the attribution of particles or quasiparticles to these waves (phonons, magnons, electrons, excitons, polaritons, etc.). By excitations we understand all these different kinds of wave and particles. In case of disturbance by the limiting surfaces or disruption of coupling between different lattice cells, we may also have surface modes and localized excitations (single ion spectra, local vibrations, etc.), respectively. With the advent of magnetoelectric interactions, in particular theoreticians, but also a few experimentalists became 'excited' and started to look what kinds of effect on excitations might be expected to be found due to magnetoelectric coupling.

Spin Waves

A theoretical analysis of spin waves in crystals with linear magnetoelectric interactions, but without spontaneous polarization, has been realized (Barnas). The spin wave frequency is found to depend linearly on the applied electric field. The frequency of surface modes is also found to depend on the magnetoelectric parameters and the linear magnetoelectric interaction can induce coupling between spin waves and other excitations (phonons, collective electron excitations). The different effects are considered to be small and hence will be difficult to observe. The linear dependence of spin wave frequency on the electric field waves, however, observed experimentally.[91] The resonance excitation of spin waves,[92] for example induced by the low frequency oscillations of ferroelectric domain walls[93] may be an additional possibility.

The shift of the antiferromagnetic resonance (AFMR) line due to an applied electric field has been called a "magnetoelectric resonance effect" (Bichurin). Both theoretical and experimental investigations of the effect for antiferromagnetic Cr_2O_3 (shift linear in the electric field) and weakly ferromagnetic $FeBO_3$ (shift quadratic in the electric field) have been reported. It is noteworthy that the linear shift of magnetoelectric Cr_2O_3 is consistent with Barnas' prediction, whereas the $FeBO_3$, which does not allow the linear magnetoelectric effect, the shift is found to be quadratic in the electric field.

Magneto- and Electrodipolar Excitations

On the centrosymmetric orthorhombic rare-earth(RE) orthoferrite $TmFeO_3$, submillimeter spectroscopy of the magneto- and electrodipolar excitations within the Tm^{3+} ion ground multiplet was performed. Due to electro- and magnetodipolar transitions inside a ground state RE-ion multiplet, a contribution of the RE-subsystem to the magnetoelectric susceptibility should be expected. A quadratic in the electric field magnetoelectric effect (HEE type) is found to be proportional to the electrodipolar matrix element between quasidoublet states. However, since $TmFeO_3$ is centrosymmetric, only the HEE-effect is allowed. Therefore more interesting would be $TbFeO_3$ and $TbAlO_3$, in which a transition to a non-centrosymmetric phase occurs, permitting the linear and EHH-type magnetoelectric effects in principle (Mukhin *et al.*).

On the antiferromagnetic Nd_2CuO_4, which belongs to a large family of high-T_c superconductors, magnetoelectric microwave effects were studied. A quadratic influence of the electric field on the microwave magnetic susceptibility and the AFMR spectrum was found below 10 K, where the magnetic Nd subsystem has high polarization, as well as the excitation of a spin precession by the microwave field in the AFMR mode (Smirnov). It would be interesting to compare these microscopic findings with a potential bulk magnetoelectric effect in this crystal, as found already in the homologous compositions Gd_2CuO_4 (Wiegelmann *et al.*) and Sm_2CuO_4.[6]

The compound Nd_2CuO_4 has also been the subject of a theoretical study of the two-magnon absorption of light, caused by the linear magnetoelectric effect of exchange nature (Blinkin and Pashkevich).

Magnetoelectric Superlattice

For the sample of a hypothetical two-component magnetoelectric superlattice, consisting of alternating layers of magnetoelectric Cr_2O_3 and diamagnetic Al_2O_3, the dispersion equations describing the propagation of polaritons (mixed states of spin waves and photons) have been obtained (Borisov *et al.*). Numerical simulations and ideas about the practical realization of such a superlattice would be of great interest.

Orbital Magnetic Moments

Stimulated by the recent observation of a strong magnetostrictive interaction in $Tb_2(MoO_4)_3$, due to the "non-frozen" orbital momentum of the Tb^{3+} ion, the spectrum and charactger of elementary excitations has been studied theoretically for a uniaxial ferroelectric ferromagnet with a magnetic moment of orbital nature, and for the cases with parallel and mutually perpendicular orientation of the equilibrium electric and magnetic dipole moment. High frequency oscillations of the magnetic moment with change of its magnitude and precession of the electric polarization vector are predicted (Chupis).

Potential Coupling between Phonon Polaritons and Magnon Polaritons

Coupling of light to electric dipole excitations (here phonons) leads to phonon polaritons and coupling to magnetic dipole excitations (magnons) to magnetic polaritons. In the past these two types of wave have been studied separately, because of occurrence in different frequency ranges. The former ones were investigated in polar, non-magnetic crystals and the latter ones in media without polar bonds between the constituent elements. Magnetoelectric coupling offers a new kind of interaction between phonon polaritons and magnon polaritons. In this context a theoretical analysis was performed on the influence of magnetoelectric coupling on surface polaritons, forming in ionic magnetically ordered crystals. By using a simplified model with scalar dielectric, magnetic and magnetoelectric coefficients, it was found that the magnetoelectric coupling leads to a degeneration of the two TE and TM waves to a single wave with mixed polarization (Dimitriev *et al.*). It is of course evident that the practical realization of such a system requires that the resonances of the magnetic and electric subsystems are situated in the same frequency range, a condition, probably very difficult to put into practice in a crystal.

Considering quite generally the results both by theory and experiment in the field of 'excitations,' it is probably allowed to have some feeling of frustration, because it becomes evident that a long way is still to go with a view to relating the different results to the macroscopically measurable magnetoelectric tensorial properties.

10. MEASURING TECHNIQUES

Magnetic Field Induced Charge Measurements

These proceedings contain a few papers on measuring techniques for the magnetoelectric effects. One of them deals in more detail with the quasistatic magnetic field induced charge measurement technique, which has turned out as straightforward, necessitating no calibration and permitting high sensitivity, qualities at variance with an earlier, unjustified discrediting description of the charge collection technique, which was initially considered inferior to the dynamic methods.[10] In fact, both methods should always be used in a complementary fashion in order to eliminate possible artefacts (Rivera).

SQUID-Magnetometer

The method for measuring the magnetoelectric effect by detecting the electric field induced magnetization, initiated by Astrov,[4,94] seems to become less and less used because of the necessity of calibration, which may be a source of error. This is probably one of the reasons why authors often give unfortunately merely arbitrary units for the magnetoelectric coefficient. However, if using a SQUID-magnetometer with its high sensitivity, as described in these proceedings (Kita), the method may possibly find a revival in appropriate cases.

An interesting challenge for the SQUID magnetometer is the detection of external magnetic fields of magnetoelectric antiferromagnets due to a non-zero quadrupole magnetic moment (Dzyaloshinskii). The symmetry requirements for a quadrupole magnetic moment to exist are the same as those permitting the magnetoelectric effect.[95] Recently the measurement of the quadrupole magnetic field of Cr_2O_3 has been reported[96]; however, some doubts about the experimental results have arisen, in particular the observed equality of the radial and tangential components of the quadrupole field looks surprising.[97] These results call for additional measurements.

Sagnac Interferometer

During the search for evidence for loss of time reversal symmetry in high-T_c superconductors, predicted by the anyon theory, the problem was attacked worldwide, using different optical detection techniques, among which the Sagnac interferometer seemed to be the champion. It has the particular advantage of being only sensitive to effects due to broken time reversal symmetry, such as Faraday rotation and magnetooptic Kerr effect, but not to reciprocal properties such as ordinary birefringence for example (Dodge *et al.*). When we generate magnetoelectrically a very weak electric field induced magnetization, we have a similar situation for the experimentalist. Therefore a detailed description of the capabilities of the Sagnac-interferometer has been sollicited for this conference.

High Accuracy Universal Polarimeter (HAUP)

The high accuracy universal polarimeter, the so-called "HAUP," has been developed by Kobayashi.[83,84] One of its diverse faculties is the possibility of separating gyration from linear birefringence. Up to now it has in particular been used for that purpose, but not yet for magneto-optic problems. Whereas it is relatively easy to measure the magnetoelectrically generated Faraday effect or polar Kerr effect along an optical axis of a crystal, as demonstrated with a classical polarimeter for Cr_2O_3 (Pisarev), the measurement of both effects in case of superposition with birefringence or bireflectance is less trivial. For many point groups this can be foreseen. The HAUP may be helpful in solving such problems. The possibilities offered by HAUP have been presented by Kremers. His contribution, however, does not appear in these proceedings.

CONCLUSIONS

This "Introduction" contains in fact a number of conclusions, questions and suggestions that we do not want to repeat.

So far the magnetoelectric effect finds two important applications in solid state sciences:

i) for the study of magnetic phases and phase transitions of insulating magnetic crystals and

ii) for determining their magnetic symmetry as a complementary tool for neutron diffraction. For magnetic symmetry studies of magnetic phases in very high magnetic fields this tool becomes even of primary importance since neutron diffraction in very high magnetic fields cannot be performed up to now.

As the reader of the proceedings will remark, the field of magnetoelectrics is a very rich and fascinating one, requiring broad interdisciplinary competences and hence the interaction of diverse specialists. We hope that the preceding comments, although rather incomplete and patchwork, may stimulate theoreticians, experimentalists and newcomers to the field, but also trigger new collaborations and friendships.

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