UNIVERSITÉ DE GENÈVE

Archive ouverte UNIGE
https://archive-ouverte.unige.ch

Article scientifique | Article | 1967

Published version | Open Access

This is the published version of the publication, made available in accordance with the publisher's policy.

Mössbauer effect and optical evidence for new phase transitions in Fe-Cl-, Fe-Br-, Fe-I-, Co-Cl- and Zn-Cl- boracite

Schmid, Hans; Trooster, J.M.

How to cite

SCHMID, Hans, TROOSTER, J.M. Mössbauer effect and optical evidence for new phase transitions in Fe-Cl-, Fe-Br-, Fe-I-, Co-Cl- and Zn-Cl- boracite. In: Solid state communications, 1967, vol. 5, n° 1, p. 31–35. doi: 10.1016/0038-1098(67)90041-5

This publication URL: https://archive-ouverte.unige.ch/unige:32924
Publication DOI: 10.1016/0038-1098(67)90041-5

© This document is protected by copyright. Please refer to copyright holder(s) for terms of use.

Solid State Communications, Vol. 5 pp. 31-35, 1967. Pergamon Press Ltd. Printed in Great Britain

MÖSSBAUER EFFECT AND OPTICAL EVIDENCE FOR NEW PHASE TRANSITIONS IN Fe-Cl-, Fe-Br-, Fe-I-, Co-Cl- and Zn-Cl- BORACITE

H. Schmid

Institute Battelle, Centre de recherche, 7, route de Drize, Genève, Switzerland

J. M. Trooster

Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, Netherlands

(Received 1 November 1966 by G. Busch)

Mössbauer measurements on Fe-Cl-, Fe-Br-, and Fe-I- boracite showed a new transition temperature which was recognized optically as a phase transition from orthorhombic to trigonal symmetry. The same type of transition was observed optically in Co-Cl- and Zn-Cl-boracite.

Introduction

MOST boracites, $Me_3 B_7 O_{13} X$, with Me = divalent metal and X = Cl, Br or I, are known to have a cubic (T_d^5) high temperature phase and an orthorhombic (C_{2v}^5) low temperature phase.[1] Ito and collaborators[2] have determined the structure of both phases of $Mg_3 B_7 O_{13} Cl$. Mg-Cl-,[3] Ni-Cl-,[4] Ni-Br-,[5] and Ni-I-[6 7] - boracites have been shown to be ferroelectric in the orthorhombic phase, and it is believed that this is the case for most other boracites.

Mössbauer measurements

We have made Mössbauer measurements on powder absorbers of Fe-Cl-, Fe-Br-, and Fe-I- boracites between 80 and 900°K. The optically determined[1] cubic-orthorhombic transition temperatures (T_1) of these compounds are : Fe-Cl, 607°K; Fe-Br, 499°K; and Fe-I, 345°K.

Three types of spectrum are observed in all three compounds. In Fig. 1 we give examples of those observed on $Fe_3 B_7 O_{13} Br$. The quantities derived from the spectra of $Fe_3 B_7 O_{13} Br$ are given in Fig. 2. Fe-Cl- and Fe-I- boracites gave similar results. In the high temperature, cubic, phase the spectra consist of one asymmetrical doublet. The splitting ($2\varepsilon_3$) and asymmetry of this doublet increase with temperature, and are larger the higher T_1 is.

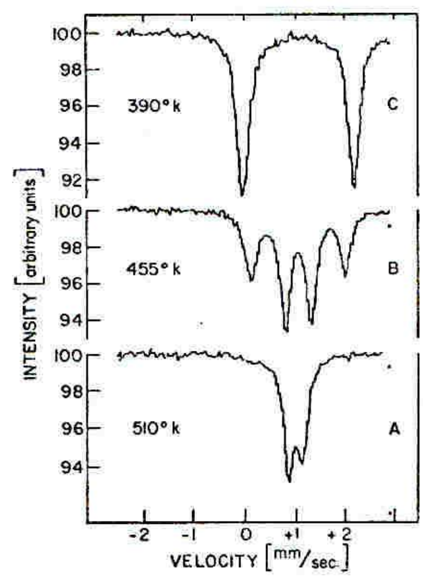

FIG. 1

Mössbauer spectra of $Fe_3 B_7 O_{13}$ Br in the cubic (A), orthorhombic (B), and trigonal (C) phase.

In the orthorhombic phase, two doublets are observed. The intensity ratio of the two pairs

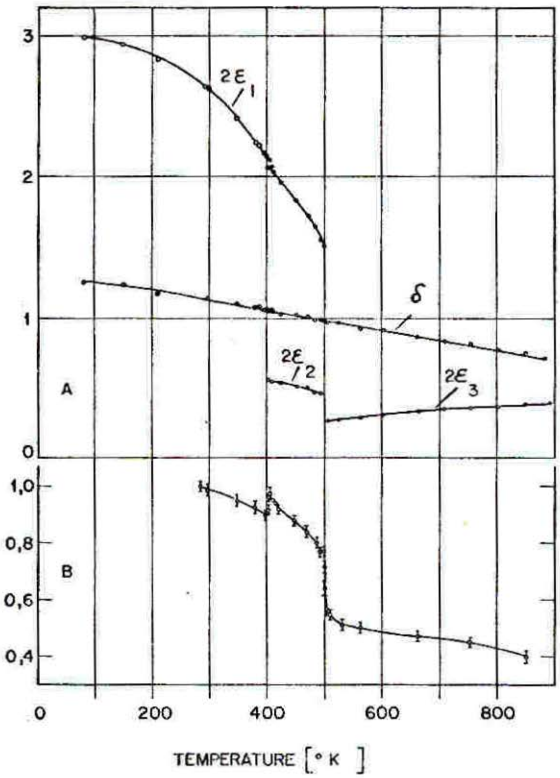

FIG. 2

A. Quadrupole splitting and isomer shift of Mössbauer spectra of $Fe_3 B_7 O_{13} Br$ versus temperature.

B. Area under absorption-curve as a function of temperature.

is 1.65 ± 0.10, assuming equal widths for the four lines. When the temperature is lowered, a second transition (T_2) takes place : the inner pair disappears, and the intensity of the doublet increases correspondingly. There is a small discontinuity in the splitting ($2\epsilon_1$) of this pair. The spectra of Fe-I-boracite in the vicinity of T_2 deviate from those of Fe-Br- and Fe-Cl- boracites : the transition takes place gradually over a range of ~ 25° K, and in the transition region the splitting of the inner pair increases rapidly. There is also a large hysteresis (~ 20°K). The values of $2\epsilon_1$ at 80°K are : Fe-Cl, (3.00 ± 0.01) mm/sec; Fe-Br, (2.99 ± 0.01) mm/sec; Fe-I, (2.79 ± 0.01) mm/sec.

Within accuracy (0.01 mm/sec) the isomer shift, δ, is continuous at T_1 and T_2. Above 250°K, δ decreases linearly with the temperature: $\Delta\delta/\Delta T$ = (0.072 ± 0.001) mm/sec 100° K.

At 300° K, the values of δ, relative to metallic iron, are: Fe-Cl, (1.14 ± 0.01) mm/sec; Fe-Br, (1.14 ± 0.01) mm/sec; Fe-I, (1.12 ± 0.01) mm/sec.

The area under the absorption curve was measured between 300° and 900° K. At $T = T_1$ a sudden decrease in area is observed. The fractional change is larger the higher T_1 is. The slight increase in absorption area at T_2, visible in Fig. 2b, was not observed on the thinner absorber of Fe-Cl- boracite and is probably due to saturation effects. [8]

Experiments at lower temperatures and on iron doped Ni-boracites are in progress.

Optical studies

Platelets (20 to 200 μ thick) were cut from a couple of boracites parallel to the cubic {100}, {110} and {111} faces, and the twinning configurations were observed as a function of temperatures between crossed polarizers (down to 80°K).

Beside the well-known cubic-orthorhombic transition, [1] we found a new kind of phase change in the Fe-Cl-, Fe-Br-, Fe-I-, Co-Cl-, and Zn-Cl- boracites (see Table 1). For Fe-Cl boracite we obtained evidence for trigonal (optically negative) symmetry by conoscopic means on a single domain of a $\{111\}_{cub}$ - cut sample. For the Fe-Br-and Fe-I- boracites, only orthoscopic evidence for trigonal symmetry was obtainable: occurrence of domains with 54° 44' - extinction on $\{110\}_{cub}$-cuts. The new transition in Co-C and Zn-Cl-boracites seems to be of the same type. According to Ascher's selection rules, [9] the space group of the trigonal phase which was found to be polar by etching with hydrochloric acid, should be C_{3v}^6, provided the transition is associated with no change of unit cell with reference to the cell of the cubic phase T_d^5. X-ray work on the trigonal and orthorhombic phases of the iron boracites is in progress.

The trigonal phase is characterized by an extremely fine lamellar structure (twinning plane is $\{100\}_{cub}$ thickness of lamellars often ≪1 μ, which sets on or disappears rather abruptly by changing the temperature. There is little or no thermal hysteresis in the case of the Fe-Cl-, Fe-Br-, Co-Cl-, and Zn-Cl-boracites. Fe-I-boracite, however, displays a considerable amount of thermal hysteresis of about 50 degrees and shows the coexistence of both phases within about 15 to 20 degrees. This behavious is also shown by the Mössbauer measurements (Table 1).

TABLE 1

Orthorhombic-trigonal transition temperatures of some boracites

Compound	Evidence by: Mössbauer effect	Evidence by: Polarizing microscope
$Fe_3B_7O_{13}Cl$	$520 \pm 2^{\circ}K$	$523^{\circ} \pm 1^{\circ}K$
$Fe_3B_7O_{13}Br$	↑ $405 \pm 1^{\circ}K$ ↓ $402 \pm 1^{\circ}K$	$402^{\circ} \pm 1^{\circ}K$
$Fe_3B_7O_{13}I$	↓ $\sim185^{\circ}K$ beginning ↑ $\sim215^{\circ}K$ end	↓ $\sim175^{\circ}K$ beginning ↑ $\sim220^{\circ}K$ end ↓ $\sim150^{\circ}K$ end ↑ $\sim207^{\circ}K$ beginning
$Co_3B_7O_{13}Cl$	not measured	$457^{\circ} \pm 1^{\circ}K$
$Zn_3B_7O_{13}Cl$	not measured	↓ $466 \pm 2^{\circ}K$ ↑ $471 \pm 2^{\circ}K$

Remark : For the following boracites, no trigonal phase was found optically above $80^{\circ}K$: Mg-Cl, Co-Br, Co-I, Ni-Cl, Ni-Br, Cd-Cl, Cd-Br, Chambersite [(10)] (a nearly pure Mn-Cl-boracite).

We have measured the birefringence versus temperature of the Fe-Cl-, Fe-Br-, and Fe-I-boracites along the 45° - extinction directions of $\{100\}_{cub}$ -cuts. Fe-Cl- and Fe-Br- boracites clearly show the orthorhombic-trigonal transition because of a discontinuity in the 45°-birefringence ($n_{\gamma} - n_{\alpha}'$ trigonal ↔ $n_{\gamma} - n_{\beta}$ orthorhombic). The optical indicatrix of the orthorhombic Fe-boracites is positive, but the optic axes lie in $\{110\}_{cub}$, and the polar axis with n_{α} along < 001 > cub, the acute bisetrix along <110>. This contrasts with Mg-, Mn-, and Ni-boracites, Fe-I-boracite lies no discontinuity in the 45° birefringence; this is probably accidental. Therefore we could determine its hysteresis phenomena only by observing the jump of orthorhombic domains with parallel extinction to trigonal ones with 45° - extinction (with lamellas) and vice versa (Fig. 3 and Table 1).

Discussion

We assume that the structure of all boracites is essentially the same and use the data from Ito et al.[2] In the cubic phase, the metal ion is located in an elongated octahedron, formed by two halogen ions on the long axis and four nearly

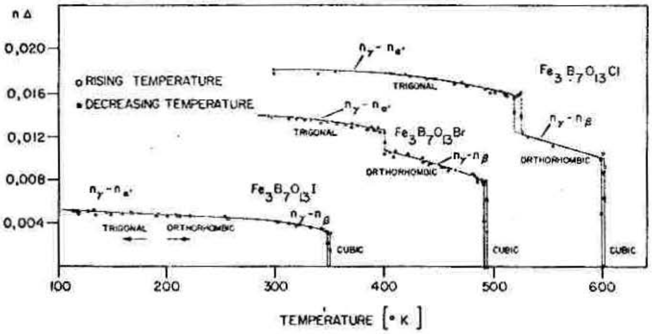

FIG. 3

Spontaneous birefringence of iron boracites versus temperature (along the 45° - extinction directions of { 100 } - cuts)

coplanar oxygen ions. In $Mg_3 B_7 O_{13}$ Cl, the distances within the octahedron are: Mg-Cl, 3.02 Å and Mg-O, 2.04 Å. The structure of the orthorhombic phase differs only in the position of metal and halogen ions. The metal ion-shifted along a < 100 > direction - occupies a strongly asymmetrical position (point symmetry 1) within the octahedron which is deformed by a shift of the halogen ions along < 111 > directions. Two types of metal envirenment can be discerned. In type 1, the two halogen ions are shifted along < 111 > and < $\bar{1}\bar{1}1$ > resp; this is the case for 1/3 of all metal ions. In type 2 (2/3 of the metal ions), both halogen ions are shifted in the same direction, which is either < 111 > or < $\bar{1}\bar{1}1$ >. Though the intensity ratio of the two quadrupole pairs observed in the orthorhombic phase is smaller than 2, the smallest splitting ($2\,\varepsilon_2$) is probably due to iron-ions of type 2. The disappearance of this pair in the trigonal phase then means that the metal and halogen ions shift in such a manner that all metals have an environment of type 1. The asymmetry of the doublet in the cubic phase points to a large anisotropy in the vibration amplitude in this phase,[11] which is not surprising in view of the large difference in metal-halogen and metal-oxygen distances, observed in Mg-Cl-boracite. In the orthorhombic phase, the iron-ion is trapped in a more isotropic potential : the vibration-amplitude along the X-Fe-X axis is reduced, resulting in the observed increase in absorption intensity, and a less pronounced asymmetry. From the measurements it follows that the vibration anisotropy is largest for the Cl-compound. As the lattice constant of the iron-boracites varies by less than one percent for the different halogens, the larger anisotropy is probably due to the smaller ionic radius of the Cl -ion.

Conclusion

Except for the intensity ratio of the two quadrupole pairs in the orthorhombic phase, the Mossbauer spectra can be explained on the basis of the structure determination of Ito et al. The new trigonal phase is probably also formed by displacement of the halogen and metal ions, and may be common to most boracites.

Acknowledgement - We wish to thank Prof. A. Janner, Nijmegen, for suggesting the Mössbauer measurements; Dr. R.M. Honea, Boulder, for providing Chambersite crystals; Dr. E. Ascher, Battelle-Geneva for valuable comments; and H. Tippman, Battelle-Geneva for preparing crystals, samples, and making the birefringence measurements.

References

1. SCHMID H., J. Phys. Chem. Solids 26, 973, (1965).

2. ITO T., MORIMOTO N. and SADANAGA R., Acta Cryst. 4,

3. LE CORRE Y., J. Phys. Radium 18, 629 (1957).

4. ASCHER E., SCHMID H. and TAR D., Solid State Comm. 2, 45, (1964).

5. SCHMID H., to appear

6. ASCHER E., RIEDER H., SCHMID H. and STOSSEL H., J. Appl. Phys. 37, 1404 (1966).

7. SCHMID H., Proceedings of the Symposium on Crystal Growth. Moscow, July 1966, to appear.

8. LANG G., Nucl. Instr. and Math. 24, 425 (1963).

9. ASCHER E., Physics Letters 20, 352, (1966).

10. HONEA R.M. and BECK F.R., Am. Mineralogist 45, 665, (1962).

11. GOLDANSKII V.I., MAKAROV E.F. and KHRAPOV V.V., Phys. Letters 3, 344, (1963).

Mittels Mössbauereffektmessungen wurde in den Fe-Cl-, Fe-Br- und Fe-I- Boraciten eine neue Umwandlungstemperatur gefunden und auf polarisationsoptischem Wege als orthorhombisch ⟷ trigonaler Übergang erkannt. Die gleiche Umwandlungsart wurde optisch im Co-Cl und Zn-Cl- Boracit gefunden.