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X-Ray Study on Phase Transitions of Ferroelectric Iron Iodine Boracite $Fe_3B_7O_{13}I$ at Low Temperatures

By

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The accurate lattice parameters of iron iodine boracite, $Fe_3B_7O_{13}I$, in the low-temperature range between -40 and -120 °C have been successfully determined using a special X-ray diffraction technique. In order to investigate the symmetry change occurring in this temperature range Weissenberg diagrams were also studied. It has been found that ferroelectric $Fe_3B_7O_{13}I$ exhibits two kinds of monoclinic C_s^2 and rhombohedral C_{3v}^6 phases, in addition to the well-known orthorhombic C_{2v}^{5} phase. The two kinds of monoclinic modifications, which are stable in the narrow temperature regions between the orthorhombic and rhombohedral phases, appear separately depending on history of temperature change of the crystal: one phase arises between -70 and -82 °C with decreasing temperature, the other between -55 and -68 °C with increasing temperature. They have almost similar crystal structures but possess slightly different lattice parameters, thermal expansion coefficients, and optical birefringences. The deviation of the axial angle β from 90° in the monoclinic phases is less than half a minute. The deviation of the rhombohedral axial angle γ is also extremely small, the difference from 60° is 48" at -120 °C. A simple model is proposed to explain the reason why the two monoclinic phases must bridge the orthorhombic and rhombohedral phases.

Die genauen Gitterparameter des Eisenjodborazits, Fe₃B₂O₁₃I, wurden im Tieftemperaturgebiet zwischen -40 und -120 °C mit einer speziellen Röntgenstrahltechnik erfolgreich bestimmt. Die Symmetrieänderung, die in diesem Temperaturgebiet auftritt, wurde mit Weissenbergdiagrammen untersucht. Es wurde gefunden, daß das ferroelektrische $Fe_3B_7O_{13}I$ zwei monokline Phasen C_8^2 und eine rhomboedrische Phase C_{3v}^6 einschließlich der bekannten rhombischen Phase zeigt. Die beiden monoklinen Phasen, die in dem engen Temperaturbereich zwischen der rhombischen und der rhomboedrischen Phase stabil sind, erscheinen einzeln; je nach dem Prozeß der Temperaturänderung erscheint eine Phase zwischen -70 und -82 °C unter Temperaturabnahme, die andere zwischen -55 und -68 °C bei Temperaturerhöhung. Sie besitzen ziemlich ähnliche Kristallsymmetrien, mit kleinen unterschiedlichen Gitterparametern, thermischen Ausdehnungskoeffizienten und Doppelbrechungskoeffizienten. Die Differenz des Achsenwinkels β von 90° in den monoklinen Phasen ist kleiner als eine halbe Minute. Die Abweichungen der rhomboedrischen Achsenwinkel γ sind ebenfalls gering, ihre Unterschiede von 60° betragen nur 48" bei -120 °C. Ein einfaches Modell wird vorgeschlagen, um die beiden monoklinen Phasen, die die rhombische und die rhomboedrische Phase überbrücken, zu erklären.

1. Introduction

Iron iodine boracite $Fe_3B_7O_{13}I$ (FIB) undergoes a phase transformation from a high-temperature (paraelectric) to a low-symmetry form at 72 °C, the space groups being cubic T_d^5 (F43c) and orthorhombic C_{2v}^5 (Pca) respectively [1]. The orthorhombic phase was found to be ferroelectric by an optical study of

domain reversal [2]. Although the spontaneous lattice strains in the ferroelectric orthorhombic phase are extremely small compared with those of other ferroelectric crystals, they have recently been determined by Kobayashi et al. [3] by using special X-ray diffraction techniques. Their X-ray work has also disclosed other phase transitions to occur at the low-temperature side. According to the work the nature of these transitions appeared to be unusual especially in the following two points: Firstly thermal hysteresis is apparently very large; a transition takes place at about -70 °C with decreasing temperature, and another transition at about -55 °C with increasing temperature. On this point Schmid and Trooster [4] had already made Mössbauer and optical studies and reported that the crystal transformed from the orthorhombic to a probably rhombohedral phase with an extremely large thermal hysteresis of about 50 °C. Secondly the pseudo-cubic cell edges in the orthorhombic modification happen to become equal at the transition points, that is to say, the unit cell of the orthorhombic phase becomes cubic by chance at the transition points. It can readily be supposed and has partly been discussed by Dvořák [5] and Kobayashi et al. [6, 7] that these peculiar characters of FIB might be closely related to its improper ferroelectric origin.

On the other hand, it has been known [8] that some ferroelectric boracite crystals, e.g. Co–Cl- and Zn–Cl-boracites, exhibit a monoclinic phase. It seems, however, that detailed structural investigations have not yet been attempted for clarifying quantitatively the relation among the orthorhombic, monoclinic, and rhombohedral modifications of boracite crystals. From our previous experiment [3] it was inferred that the change of lattice parameters at the low– temperature transitions of FIB would be even smaller than that at the cubic– orthorhombic transition and so determination of it would be extremely difficult. However, in order to elucidate physical properties of boracite crystals which definitely reflect improper ferroelectricity, the accurate determination of the lattice parameters and exact knowledge of symmetry change in the low-temperature region are quite essential. Therefore, we have undertaken here X-ray studies on the lattice parameters and symmetry change of FIB at lower temperature region.

2. Experimental Results

The crystal structure of the orthorhombic C_{2v}^5 phase of FIB is based upon a very slightly deformed cubic lattice [3]. The other phases at lower temperatures can also be considered as modifications deformed from the cubic lattice. So we believe it convenient at the outset of the paper to survey the relation of crystallographic axes of the original cubic and the possible orthorhombic, monoclinic, and rhombohedral modifications. In what follows, subscripts c, o, m, r, and h will be attached to the crystallographic axes and indices when they are referred to cubic, orthorhombic, monoclinic, rhombohedral, and hexagonal cells, respectively. Two remarks must be made here: (i) All the crystal systems enumerated above can be conceived as special types of the monoclinic system having characteristic symmetry elements additively, and so the conventional crystallographic axes of each system can be represented by properly selected common monoclinic axes. (ii) The original cubic structure of this crystal is based upon a face-centered lattice. The face-centered lattice is destroyed, however, in the orthorhombic and monoclinic systems due to the loss of the triad axes, but restored again in the rhombohedral modification by the reformation of a triad axis.

The orthorhombic axes are related to the conventional cubic axes as follows [3]:

$$\boldsymbol{a}_{\mathrm{o}} = \frac{1}{2} \left(\boldsymbol{a}_{\mathrm{c}} + \boldsymbol{b}_{\mathrm{c}} \right), \qquad (1\,\mathrm{a})$$

$$\boldsymbol{b}_{\mathrm{o}} = rac{1}{2} \left(- \boldsymbol{a}_{\mathrm{e}} + \boldsymbol{b}_{\mathrm{c}}
ight),$$
 (1 b)

$$\boldsymbol{c}_{\mathrm{o}} = \boldsymbol{c}_{\mathrm{c}} \,. \tag{1 c}$$

This relation is schematically represented in Fig. 1a by $(001)_o$ (= $(001)_c$) and $(010)_o$ (= $(1\bar{1}0)_c$) projections. As described later, the systematic extinction of X-ray diffraction spectra indicates that the crystal contains $(010)_o$ glide planes at all temperatures with which we are concerned. Therefore the \boldsymbol{b}_o -axis remains always perpendicular to the $(010)_o$ plane. It then follows from the remark (i) that the crystallographic axes of FIB at all relevant temperatures could be expressed by the monoclinic \boldsymbol{a}_{m^-} , \boldsymbol{b}_{m^-} , and \boldsymbol{c}_m -axes of Fig. 1 c, where the \boldsymbol{b}_m -axis coincides with the \boldsymbol{b}_o -axis, the \boldsymbol{a}_m - and \boldsymbol{c}_m -axes correspond to the \boldsymbol{a}_o - and \boldsymbol{c}_o -axes in (1 a) to (1 c), and the interaxial angle β deviates from 90°. The orthorhombic cell, then, is a special monoclinic cell, where β is 90° as depicted in Fig. 1 b. The rhombohedral axes, \boldsymbol{a}_r , \boldsymbol{b}_r , and \boldsymbol{c}_r , can be expressed by the monoclinic axes, as shown in Fig. 1 d, only when the pseudo-cubic lattice becomes face-centered (remark (ii)):

$$\boldsymbol{a}_{\mathbf{r}} = \boldsymbol{a}_{\mathbf{m}}$$
, (2a)

$$b_{\rm r} = \frac{1}{2} (a_{\rm m} + b_{\rm m}) + \frac{1}{2} c_{\rm m} ,$$
 (2 b)

$$\boldsymbol{c}_{\mathrm{r}} = \frac{1}{2} \left(\boldsymbol{a}_{\mathrm{m}} - \boldsymbol{b}_{\mathrm{m}} \right) + \frac{1}{2} \boldsymbol{c}_{\mathrm{m}} \,.$$
 (2 c)

Besides, the rhombohedral axes must satisfy the following conditions:



Fig. 1. Schematic representation of the reference crystallographic axes of a) cubic, b) orthorhombic, c) monoclinic, and d) rhombohedral phases of FIB (distortion exaggerated). It is shown that the crystallographic axes in every system can be represented by the common monoclinic axes a_m , b_m , and c_m





$$|\boldsymbol{a}_{\mathbf{r}}| = |\boldsymbol{b}_{\mathbf{r}}| = |\boldsymbol{c}_{\mathbf{r}}| = a_{\mathbf{m}}$$
(3a)

and

$$\boldsymbol{a}_{\mathrm{r}} \cdot \boldsymbol{b}_{\mathrm{r}} = \boldsymbol{b}_{\mathrm{r}} \cdot \boldsymbol{c}_{\mathrm{r}} = \boldsymbol{c}_{\mathrm{r}} \cdot \boldsymbol{a}_{\mathrm{r}} = a_{\mathrm{m}}^{2} \cos \gamma , \qquad (3 \,\mathrm{b})$$

where γ is an interaxial angle. In order that the crystal becomes rhombohedral, the above conditions (2a) to (3b) must be fulfilled for the a_{r} , b_{r} , and c_{r} -axes. As can be seen in Fig. 1d, the monoclinic lattice becomes body-centered when the equations (2a) to (2c) hold. Therefore, the following relation must be a necessary condition for the crystal to be rhombohedral:

$$h_{\rm m} + k_{\rm m} + l_{\rm m} = 2 n ,$$
 (4)

where n is an integer. From the conditions (3a) and (3b), it is easy to derive the relations

$$\beta = \cos^{-1} \left(\frac{a_{\rm m}^2 - b_{\rm m}^2}{a_{\rm m} c_{\rm m}} \right)$$
(5)

and

$$\gamma = \cos^{-1} \left(\frac{2 a_{\rm m}^2 - b_{\rm m}^2}{2 a_{\rm m}^2} \right). \tag{6}$$

Summarizing, if the X-ray reflections of a monoclinic modification follow an extinction rule (4) and, moreover, the observed β agrees with the calculated value given by (5), where any one of the parameters is measured independently of β , the modification must be rhombohedral. The relation between the pseudocubic axes and the rhombohedral axes are shown in Fig. 2.

2.1 Experimental method

As the crystal lattices of low-temperature modifications of FIB can be described in terms of general monoclinic lattices, our problem has been to measure the lattice parameters $a_{\rm m}$, $b_{\rm m}$, $c_{\rm m}$, and β of every low-temperature phase. We used a single-crystal X-ray diffractometer for determining reflection positions and a Weissenberg camera for examining symmetry elements. In these studies, two kinds of crystal specimens, S_1 and S_2 , were used. The specimen S_1 is a (101)_m plate crystal, and S_2 is a prism crystal with pinacoidal (101)_m planes. The crystal orientations of S_1 - and S_2 -specimens mounted in the two apparatuses are schematically depicted in Fig. 3a and b respectively. In both specimens, the (101)_m faces are electroded with gold and connected to X-Ray Study on Phase Transitions of Ferroelectric Fe₃B₇O₁₃I



Fig. 3. The sketch of the X-ray specimens of FIB on the goniometer heads of the diffractometer and Weissenberg camera. a) represents the crystal orientation of the specimen S_1 and b) that of the specimen S_2

a voltage source through fine iron needles and aluminium foils. Before beginning the measurements, the specimens were always subjected to field cooling from above the Curie point under an external electric field of 20 kV/cm. It was supposed that the present field cooling of the specimens would produce three orthorhombic domains with $[110]_0$, $[1\bar{1}0]_0$, and $[001]_0$ unique directions. Such a twinning mechanism was already observed in mineral boracite by Ito et al. [9]. We have confirmed it artificially in the present experiments. However, all the domains thus split were expected to coalesce to a single domain when the direction $[201]_m$ (= $[111]_e$) became a triad axis again at low temperature. Our experiments have also confirmed that this is really the case.

In the temperature range between -40 and -120 °C, the lattice parameters $a_{\rm m}$, $c_{\rm m}$, and β were determined by measuring the spacings of three $(h0l)_{\rm m}$ reflections issued from the specimens S₁, and the parameter $b_{\rm m}$ by a $(0k0)_{\rm m}$ reflection from the specimen S₂. The positions of the X-ray reflections were determined by the two-dimensional reciprocal-lattice method, which had successfully been applied to the measurement of lattice strains of the same crystal in the higher temperature range [3, 10]. Detailed account for that method was given elsewhere [11]. The temperature of the specimens was stabilized within the limit of +0.07 °C in the whole temperature range. In order to remove the main systematic errors, e.g., absorption of X-rays by the specimen and the eccentricity of the specimen position in the diffractometer, the Bradley-Jay extrapolation method was used at -95.0 and at -108.8 °C. Correction for refraction of X-rays to the crystal was also made by using the calculated refractive index of 0.999987 for CuK α radiation. As a result we could attain an accuracy of one part in 227000 in the determination of the lattice parameters in the low-temperature range.

2.2 Temperature dependence of lattice parameters

For the determination of lattice parameters $a_{\rm m}$, $c_{\rm m}$, and β we measured spacings of lattice planes $(800)_{\rm m}$, $(804)_{\rm m}$, and $(0\ 0\ 12)_{\rm m}$. Fig. 4 shows the temperature dependence of the spacings of these lattice planes. Lattice parameters $a_{\rm m}$, $c_{\rm m}$,





Fig. 4. The temperature dependence of lattice spacings of (800)m, (804)m, and (0 0 12)m reflections of FIB. The small circles represent the values measured with decreasing temperature, and the small triangles those with increasing temperature

Fig. 5. Thei lattice parameters $a_{\rm m}$, $c_{\rm m}$, and β of F1B as a function of temperature. "I" represents one monoclinic phase which appears with decreasing temperature, and "II" the other monoclinic one which arises with increasing temperature. Small circles on the β -line represent the calculated values by equation (5)

and β thus derived are represented in Fig. 5, as a function of temperature. When the crystal is cooled, the axial angle β stays exactly equal to 90° as far as -70 °C. Therefore the crystal is undoubtedly orthorhombic as has been reported [3]. However, it begins to change from a transition point of -70 °C, increasing linearly down to -82 °C, afterwards increasing less steeply. This fact implies that below -70 °C the crystal becomes monoclinic. The sudden change of the temperature dependence of β at -82 °C reveals that the crystal transforms from the monoclinic into another form, which we provisionally designate as the lowest-temperature phase. $a_{\rm m}$ - and $c_{\rm m}$ -parameters also display a similar character with regard to temperature. On the other hand, when the crystal is heated from the low-temperature end, the lowest-temperature phase survives up to -68 °C without recovering to the monoclinic phase at -82 °C. From -68 °C the three parameters begin to deviate from the previous branches and follow a different temperature dependence up to -55 °C, where they regain the original orthorhombic branches. In the temperature region between -68 and -55 °C, the crystal must also be monoclinic. It is very interesting that between the orthorhombic and the lowest-temperature phases the crystal exhibits two different monoclinic modifications whose appearance depends on the history of the temperature change; the one phase defined here as phase I appears only in a process of decreasing temperature from the orthorhombic phase, the other defined as phase II occurs only in a process of increasing temperature from the lowest-temperature phase.

The parameter $b_{\rm m}$ has been determined from the spacing of the $(080)_{\rm m}$ reflection of the S₂ specimen. The result is indicated in Fig. 6. It can be seen from Fig. 5 and 6 that $a_{\rm m}$ and $b_{\rm m}$ coincide with each other at -70 °C, viz. 8.6532 Å, as has already been mentioned. These changes of the lattice parameters $a_{\rm m}$,

Fig. 6. The lattice parameter b_m of FIB as a function of temperature. The small circles represent the value measured with decreasing temperature, and the small triangles those with increasing temperature



 $b_{\rm m}$, $c_{\rm m}$, and β at low-temperature phase transitions of FIB have been revealed to be extremely small as were suspected; they are even about one fifth smaller than those at the cubic-orthorhombic transition, and the deviation of the angle β from 90° is less than half a minute. The temperature dependence of the lattice volume is represented in Fig. 7 over a wide temperature range including the Curie point. It is interesting that low-temperature phase transitions are followed by far smaller volume change than that at the Curie point.

2.3 Phase transitions

From the measurements of the lattice parameters of FIB in the temperature range between -45 and -120 °C, we have disclosed three crystal modifications to appear, viz., monoclinic phases I and II and the lowest-temperature phase. In order to investigate symmetry elements contained in these phases, we took Weissenberg photographs of the two specimens S_1 and S_2 at 25 °C (orthorhombic phase), -75 °C (phase I), and -90 °C (the lowest-temperature phase) in consecutively cooling, and subsequently at -75 °C (the lowest-temperature phase) and -65 °C (phase II) in continuously heating.

In the first place, we examined $(h0l)_{\rm m}$, $(h1l)_{\rm m}$, $(h2l)_{\rm m}$, and $(h3l)_{\rm m}$ Weissenberg diagrams of the S₁ specimen. There were no spectrum absences for non-equatorial $(hkl)_{\rm m}$ reflections with h and l odd. However, the reflections were present only with even values of h among equatorial $(h0l)_{\rm m}$ reflections at all the abovementioned temperatures. This fact indicates that the $(010)_{\rm m}$ glide planes $(\frac{1}{2}a_0$ component), which have existed in the cubic phase, survive down to the



Fig. 7. The temperature change of the lattice volume of FIB

lowest-temperature phase. The existence of the $(010)_{\rm m}$ glide planes proves that the $\boldsymbol{b}_{\rm m}$ -axis is always perpendicular to $\boldsymbol{a}_{\rm m}$ - and $\boldsymbol{c}_{\rm m}$ -axes. This is the decisive evidence that both phases I and II are truly monoclinic and the lowest-temperature phase can be expressed in terms of monoclinic axes.

We paid special attention to $(h0l)_{\rm m}$ and $(h2l)_{\rm m}$ reflections with odd values of $h_{
m m}+ar{k_{
m m}}+ar{l_{
m m}},$ because they could provide important informations concerning crystal systems of the low-temperature modifications. It is easily understandable for the reason of (4) that they all must be absent in the cubic phase. Several reflections, such as $(801)_m$, $(803)_m$, $(821)_m$, and $(823)_m$, however, became discernible in the orthorhombic phase, but with weak intensities, owing to the loss of the triad axes. It is very important to note that these reflections became weaker in their intensities, but still persisted in phases I and II. They completely disappeared again in the lowest-temperature phase. Thus the condition (4) has been found to be satisfied in the lowest-temperature phase, but not in phases I and II. It follows that the lowest-temperature phase has the possibility of being rhombohedral, but phases I and II have not. We have checked whether the relation (5) holds or not in the lowest-temperature phase. The result is shown in Fig. 5; the circles indicate the β -values calculated by using the observed $a_{\rm m}$, $b_{\rm m}$, and $c_{\rm m}$. Here it must be stressed that the measurements of $(a_{\rm m}, c_{\rm m}, \beta)$ pairs and $b_{\rm m}$ were performed independently. The agreement is excellent. Therefore, it can be concluded that the lowest-temperature phase must be rhombohedral. It is necessary to repeat that phases I and II are not rhombohedral but purely monoclinic.

After having changed the crystal orientation of the specimen S_1 by the application of a sufficiently high voltage of opposite polarity, we could take $(0kl)_m$ Weissenberg diagrams at the same temperatures. In both cubic and orthorhombic phases, all the reflections with l odd were missing. This indicates the existence of $(100)_m$ glide planes $(\frac{1}{2}c_0 \text{ component})$ in these phases. In phases I and II and in the rhombohedral phases, however, a few spectra violating the above extinction rule, e.g., $(0\ 1\ 11)_m$ and $(0\ 3\ 11)_m$, were present although their intensities were weak. Meanwhile, the possibility of the \boldsymbol{b}_m -axis being a diad axis must be excluded by the condition that the crystal is ferroelectric and so noncentrosymmetrical in the present temperature range. Thus we can determine that the space groups of the phases I and II must be C_s^2 (Pa).

In order to ensure our conclusions on symmetries of the crystal, we further took Weissenberg photographs of the specimen S_2 from the zero to four levels at 80 °C and at the above-mentioned temperatures. The Weissenberg diagrams of the cubic phase directly demonstrated the presence of one of the triad axes. The diagrams of the orthorhombic phase and the phases I and II manifested the disappearance of the triad axis, and were smeared by a number of reflections issued from twinned components. In the rhombohedral phase, however, it was clear from the diagrams of any level that the triad axis came into being again. Fig. 8 represents an $(hk2)_h$ Weissenberg diagram at -90 °C, where the size of the spots is set approximately proportional to the diffraction intensities observed in the photograph. Here the hexagonal cell is represented by the rhombohedral lattice as

$$oldsymbol{a}_{\mathrm{h}} = oldsymbol{a}_{\mathrm{r}} - oldsymbol{b}_{\mathrm{r}}$$
 , (7 a)

$$oldsymbol{b}_{\mathrm{h}} = oldsymbol{b}_{\mathrm{r}} - oldsymbol{c}_{\mathrm{r}}$$
 , (7 b)

$$\boldsymbol{c}_{\mathrm{h}} = \boldsymbol{a}_{\mathrm{r}} + \boldsymbol{b}_{\mathrm{r}} + \boldsymbol{c}_{\mathrm{r}} \,.$$
 (7 c)





Fig. 8. The reciprocal-net plane $(hk_2)_h$ of the rhombohedral phase of FIB. The size of spots in the net is made approximately proportional to the intensities of reflections observed

Fig. 9. The axial angle γ of the rhombohedral phase of FIB as a function of temperature. The dashed line corresponds to γ of the phase which survives when the crystal is heated from the low-temperature side

Considering that the $(010)_{\rm m}$ glide planes still remain in this phase, the space group of this phase is completely consistent with C_{3v}^6 (R3c), which Schmid [12] and Ascher [13] have ever suggested.

We derived the rhombohedral axial angles γ , which are shown in Fig. 9 as a function of temperature. The difference of these angles from 60° is extremely small, e.g., 48'' even at -120 °C. It is interesting, however, that the rhombohedral cell is compressed along the polar triad axis. Recently Hilti (cf. [12]) measured the rhombohedral lattice parameters of Fe–Cl, Fe–Br, and Zn–Cl boracites at 25 °C by means of Jagodzinski and de Wolff diagrams. The γ 's of these materials are larger by about one order of magnitude than that of FIB. The lattice parameters and their thermal expansion coefficients of FIB are summarized in Tables 1 and 2 respectively.

3. Discussion

In the present experiments we have concluded that ferroelectric FIB contains two monoclinic C_s^2 and a rhombohedral C_{3v}^6 phases at low temperatures. The fact that the two different monoclinic phases arise depending on the history of the temperature change is of particular interest, and so further study seems hopeful. Here we will make a brief discussion on these phases.

In order to know whether any structural difference exists between the two monoclinic phases, we investigated Weissenberg photographs of the respective phases. However, it was difficult to find any perceptible difference in the reflection intensities within the sensitivity of visual inspection. Then we made optical observation about the interference colour of a $(101)_{o}$ -plate specimen of about 0.97 mm thickness, which was put between crossed polaroids. When

Table 1	parameters of Fe-I-boracite
	Lattice

In the first column, the values without asterisks correspond to decreasing temperature

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-	ig tempe
	increasin
	5
	asterisks
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	while

rhombohedral cell	ý)°00′22″)°00′28″)°00′34″
	a_{T} (Å)	$egin{array}{c} 8.65496 \pm 0.00004 & 60 \ 8.65453 \pm 0.00004 & 60 \ 8.65399 \pm 0.00004 & 60 \ \end{array}$
monoclinic cell	β	90°00'00'' 90°00'17'' 90°00'13'' 90°00'27'' 90°00'33''
	$c_{ m m}$ (Å)	$egin{array}{cccccccccccccccccccccccccccccccccccc$
	$b_{ m m}$ (Å)	$\begin{array}{c} 8.65268 \pm 0.00004 \\ 8.65495 \pm 0.00004 \\ 8.65430 \pm 0.00004 \\ 8.65547 \pm 0.00004 \\ 8.65538 \pm 0.00004 \\ 8.65528 \pm 0.00004 \\ 8.65528 \pm 0.00004 \end{array}$
	a _m (Å)	$\begin{array}{c} 8.65411 \pm 0.00004 \\ 8.65508 \pm 0.00004 \\ 8.65392 \pm 0.00004 \\ 8.65496 \pm 0.00004 \\ 8.65453 \pm 0.00004 \\ 8.65399 \pm 0.00004 \\ 8.65399 \pm 0.00004 \end{array}$
temper-	ature (°C)	

the specimen was cooled, the phase transition at -70 °C was realized as nucleation and subsequent sidewise-expansion of the new phase I domains, which immediately prevailed over the whole specimen. The interference colour for phase I was slightly different from that of the orthorhombic phase. The transition at -82 °C was accomplished in the similar way by the nucleation and expansion of the dark rhombohedral domains. When the specimen was heated from the rhombohedral phase, the phase transitions were characterized by the reverse sequence of the domain behaviour. It is, however, noteworthy that the interference colours of the intermediate phases I and II were slightly different.

On the other hand, it took at least half an hour for collecting X-ray diffraction intensity data necessary for mapping out a two-dimensional intensity distribution of anyone reflection (see, e.g., Fig. 3 in [3]). Therefore, it is certain that the intermediate phases I and II are the equilibrium states bridging the orthorhombic and rhombohedral phases. Further, if they were not homogeneous phases but a mixture of the extreme phases even in the submicroscopic level, the present X-ray diffraction method would disclose the coexistence of both extreme phases [14]. However, we have had no experimental evidence for the coexistence at all. Thus it must be said that the two intermediate phases corto characteristic monoclinic respond modifications which have similar crystal structures but different lattice parameters, different thermal expansion coefficients, and different birefringences. It must be noted that the change of the interference colour is reversible if the temperature change of the specimen is reversed within the temperature region of each monoclinic phase.

Here we try to demonstrate the reason why the intermediate monoclinic phases must appear in narrow temperature ranges, by using iodine ions which

Table 2

Thermal-expansion coefficients of Fe–I-boracite

temper- ature (°C)	thermal-expansion coefficients				avatoma
	α _{am} (×10 ⁻⁶)	$lpha_{b_{ m m}}$ ($ imes 10^{-6}$)	$\alpha_{c_{\rm m}}$ ($ imes 10^{-6}$)	$lpha_eta$ ($ imes 10^{-6}$)	systems
-55	5.4	-2.5	2.9	Ó	orthorhombic
-65*	-16.2	-24.3	-1.8	-5.3	monoclinic
-75	-17.9	-22.5	-7.3	-8.3	monoclinic
-75*	5.8	1.2	2.0	-1.9	rhombohedral
-85	5.8	1.2	2.0	-1.9	rhombohedral
-95	5.8	1.2	2.0	-1.9	rhombohedral

In the first column, the values without asterisks correspond to decreasing temperature, while those with asterisks to increasing temperature.

occupy the highest symmetric positions. A schematic representation of the four crystal structures (cubic, orthorhombic, monoclinic, and rhombohedral) projected on $(001)_0$ and $(010)_0$ planes is given in Fig. 10. Two iodine atoms, which are located in special positions in the cubic phase, shift in the a_{0} - and c_{o} -directions in the orthorhombic phase. They are, however, interrelated by $(100)_{o}$ glide planes; each atom is displaced along the a_{o} -axis with the same magnitude but in opposite sense. In the final rhombohedral phase, their displacements should be the same and parallel to a triad axis. Therefore the transition from the orthorhombic to the rhombohedral phases necessitates the sudden rotation of one of the iodine ions, and so must overcome a considerable potential barrier. It can be conceived that the monoclinic phases have structures where gradual and consequently easy rotations of iodine ions are permitted with the change of temperature. Then the transition from the orthorhombic to the rhombohedral phases or the reverse one would be greatly facilitated by the appearance of these intermediate states. If the monoclinic phases could not be realized, the transitions would become extremely sluggish. It must be considered that thanks to the monoclinic phases the true thermal hysteresis has been



Fig. 10. The schematic representation of the four crystal structures of FIB projected on $(001)_0$ and $(010)_0$ planes. White and hatched circles represent iodine ions (displacements greatly exaggerated)

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reduced only to a temperature range of two degrees (-70 to -68 °C). A more detailed investigation of the origin of the intermediate monoclinic phases of FIB seems interesting.

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