

of enhancement are discernible, it may be concluded that a sublattice is present.

It may then be possible to obtain first the shape of the subcell, and from the relation (1) the absolute values of the subcell structure factors. Using these values, the distribution of the electron density within the subcell may be solved. This is a comparatively easy task, since the subcell will, in general, be very simple and contain only a few atoms as compared with the main cell. The solution of this step gives the phases (or signs) of  $F_H$ . On substituting these back into (1), phases of the structure factors of the main cell are then obtained.

The method described above is similar to a certain extent to the method of a heavy atom. Where the  $F_h^0$  are so small that only a few of the signs or phases of

the calculated  $F_h$  are incorrect, a Fourier synthesis of the main cell, using observed magnitudes of  $F_h$ , but calculated signs or phases, reveals not only the sublattice atoms, but also the rest of the atoms not belonging to the sublattice.

Further refinements may then be obtained, using the standard methods of structure analysis.

The above method has been successfully applied to trilaurenin, where the unit cell contains two subcell regions related by a centre of symmetry.

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## Barium Titanate Twinning at Low Temperatures

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The phase transitions of barium titanate ( $\text{BaTiO}_3$ ) single crystals have been investigated by means of X-rays from room temperature to  $-160^\circ\text{C}$ . Below the second transition at about  $0^\circ\text{C}$ ., crystals which were single at room temperature became highly twinned. Likewise, a complicated twinning occurred below the third transition at approximately  $-90^\circ\text{C}$ . The temperature variation of the axial parameters and of the unit-cell volume has been measured from X-ray diffraction photographs, and the symmetry and twinning arrangement of the low-temperature phases have been determined.

### 1. Introduction

The existence of three phase transitions in barium titanate ( $\text{BaTiO}_3$ ) has been established by optical observations, by X-rays, and from measurements of the dielectric constant. The nature of the first transition at approximately  $120^\circ\text{C}$ . was described (Megaw, 1947) from X-ray photographs of sintered material. Above this temperature  $\text{BaTiO}_3$  possesses the cubic symmetry of a typical perovskite-type structure. Below  $120^\circ\text{C}$ ., the symmetry becomes tetragonal with the development of polar properties along the tetrad axis of the unit cell. The structural change was shown to be discontinuous by Harwood, Popper & Rushman (1947) and by Kay (1948); this was also confirmed by the author.

The existence of two further transitions, near  $0^\circ\text{C}$ . and  $-90^\circ\text{C}$ . respectively, was first indicated by measurements of the dielectric constant (Wul, 1946; Roberts, 1947; Matthias & von Hippel, 1948; Merz, 1949). Optical observations on single crystals have

shown that the symmetry changes from tetragonal to orthorhombic at the second transition ( $0^\circ\text{C}$ .) and finally to trigonal below the third transition (Kay & Vousden, 1949; Forsbergh, 1949). Crystals of  $\text{BaTiO}_3$  have been studied by the author by X-ray methods down to liquid-air temperatures; the present paper describes the results obtained, and amplifies the conclusions already set out briefly in an earlier note (Rhodes, 1949). The account presented here describes experimental results, and offers interpretations, which are in harmony with those published by Kay & Vousden and by Forsbergh.

### 2. Apparatus

To obtain X-ray photographs of single crystals at low temperatures the camera, shown diagrammatically in Fig. 1, was designed for use with the Unicam goniometer. It consisted essentially of a thermally lagged, brass pot of outside radius 3 cm. and height 18 cm., provided with a 0.5 cm. slot for the passage of the X-rays. The film was contained in a light-tight, thermally insulated envelope, which fitted smoothly to the camera walls. By sliding the film vertically, a series of fifteen exposures could be made at different temperatures without reloading.

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The actual 'cold chamber' is similar to that described by Ubbelohde & Woodward (1946). A copper tube (8), provided with a horizontal slot for the passage of the

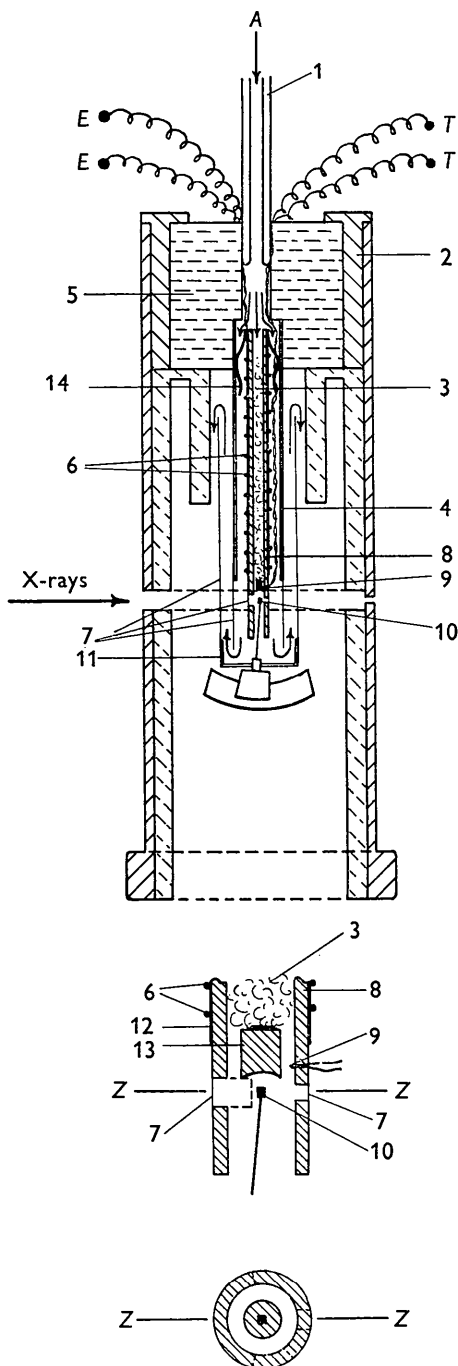


Fig. 1. Section through the low-temperature X-ray camera.

X-rays, surrounds the specimen (10). It is held centrally in position by spring clamps (14) within the glass tube (4) which, in turn, fits into a plastic block (5) forming the top of the camera. The cooling gas, obtained from the evaporation of liquid air by means of an immersion heater, enters the camera through Dewar

tubing in the direction of the arrow, *A*. The flow is conducted around the specimen by the cellophane baffles (7), as shown by the arrows in the diagram.

The horizontal slot, which extends through an angle of approximately  $60^\circ$  on either side of the incident X-ray beam, is shown in the enlarged view of the cold chamber in Fig. 1. Fine copper wool (3), inserted in the central tube, increases the heat exchange with the gas, and the copper plug (13) protects the specimen from the direct flow. At a steady rate of evaporation of the liquid air, the temperature of the cold chamber could be held constant to within  $\pm 0.1^\circ\text{C}$ . by manual control of the current through the heater (6) with an energy dissipation up to 3 W. A copper-constantan thermocouple (9) was used to measure the temperature. The principal limitation of the apparatus was that it restricted the investigations to an individual layer line.

### 3. Variation of axial parameters with temperature

Parameter values based on approximately 120 different exposures, made between room temperature and  $-160^\circ\text{C}$ ., have been plotted against temperature (Rhodes, 1949). Within the experimental accuracy, the points lie on smooth curves but they reveal a certain amount of scattering in the vicinity of the discontinuities at approximately  $0^\circ$  and  $-90^\circ\text{C}$ ., i.e. the second and third transitions respectively. (In the following analysis of the structural changes with temperature, the unit cell is considered from the point of view of a distortion from the cube. The axes of the unit cell are referred to as *a*, *b* and *c* at room temperature, *a'*, *b'* and *c'* between the second and third transitions, and *a''*, *b''* and *c''* below the third transition (see Figs. 3, 4). As subsequently explained, however, the true symmetry in the last two cases is orthorhombic and trigonal respectively.)

The average experimental values are summarized in Table 1; only the limiting values in the temperature ranges of the symmetry phases are given. There is a slight increase in the volume at the second transition, followed by a gradual decrease with temperature to the third transition. At this point, the volume decreases discontinuously, and, as the temperature is lowered still further, a very gradual shrinking of the cell continues to take place. The actual transition temperatures

Table 1. Variation of parameters with temperature

Temp. ( $^\circ\text{C}$ .)	<i>a</i> ( $\text{\AA}$ .)	<i>b</i> ( $\text{\AA}$ .)	<i>c</i> ( $\text{\AA}$ .)	Volume ( $\text{\AA}^3$ )
+ 20	3.9920	3.9920	4.0361	64.317
+ 4	3.9910	3.9911	4.0357	64.282
Second transition occurs here				
+ 4	4.0185	3.9860	4.0162	64.319
- 99	4.0170	3.9750	4.0150	64.093
Third transition occurs here				
- 99	4.0015	4.0015	4.0020	64.079
- 160	3.9996	3.9996	3.9997	63.981

Accuracy of measurement below room temperature was  $\pm 0.0007\text{\AA}$ .

varied somewhat from one specimen to another. The transformation was completed in a fraction of a degree for very small crystals (0.1 mm.), but it extended over several degrees with larger specimens. In all cases, the shift in the X-ray reflexions, indicating a change in the lattice spacing, was discontinuous at the transitions. Both the symmetry phases, characteristic of higher and lower temperatures, were simultaneously present throughout the range of the transition; no reflexions corresponding to material with intermediate parameter values have been observed on any of the photographs. This is similar to our observations at the first transition where the structure changes abruptly from cubic to tetragonal symmetry, the two forms co-existing over

The diagrammatic table, shown in Fig. 2, summarizes the arrangement and character of the zero-layer-line reflexions obtained with the crystal oscillated about its three crystallographic axes in turn. The table is divided into two sections, according to whether the  $a$  ( $=b$ ) or the  $c$  axis of the tetragonal crystal was the rotation axis. The sections of the table headed by  $X$ ,  $Y$  and  $Z$  refer to the directions of the incident beam relative to the crystal; they are indicated by the large arrows of the subsequent diagrams (Figs. 3 and 4). The spot-multiplicities below the second and third transitions and the displacements in their reflecting angles  $\theta$ , relative to their room temperature values, appear opposite 0 and  $-100^\circ\text{C}$ . respectively.

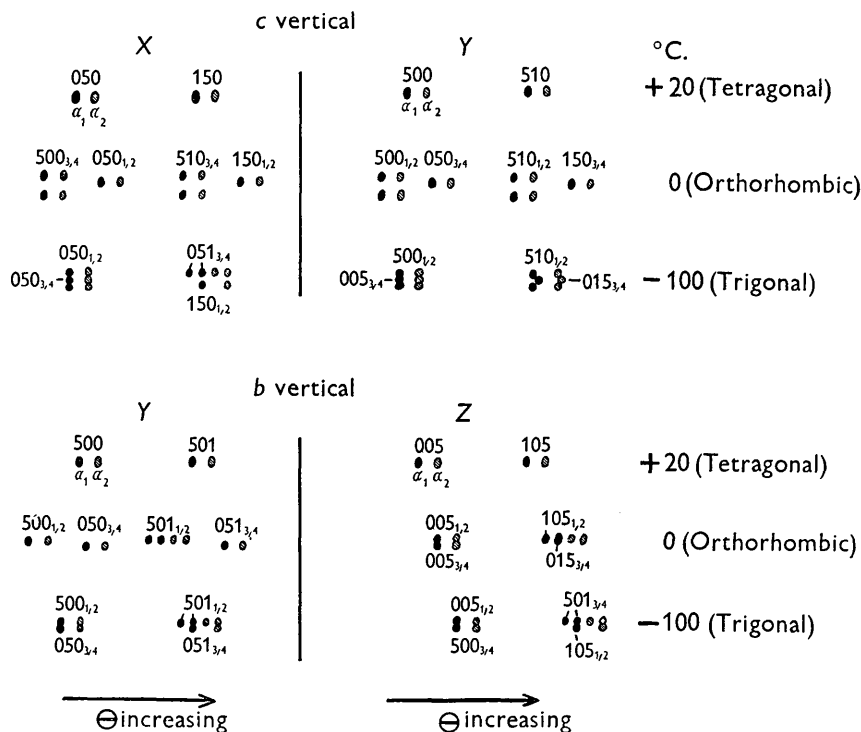


Fig. 2. Characteristic X-ray reflexions of the tetragonal, orthorhombic and trigonal symmetry phases.

a range of a few degrees of temperature (see also Harwood *et al.* 1947; Kay, 1948).

The thermal hysteresis was much more pronounced at the second and third than at the first transition. Depending on the rate of the temperature variation, this 'freezing-in' of the structure sometimes extended over quite wide intervals. With rapid reheating through the second transition the low-temperature structure persisted to approximately  $+15^\circ\text{C}$ . before the reversion to tetragonal symmetry took place. The third transition did not occur until approximately  $-100^\circ\text{C}$ . on cooling some specimens and at  $-80^\circ\text{C}$ . on reheating. The X-ray reflexions, characteristic of the single-domain, tetragonal crystal, were always reproduced at room temperature, even after numerous cooling cycles.

The mean thermal expansion coefficients  $\alpha_a$ ,  $\alpha_b$  and  $\alpha_c$  of the respective axes of the unit cells were calculated from the slopes of the parameter-temperature curves. These are given in Table 2. Apart from the  $b'$  axis of the orthorhombic phase, it can be seen that the unit-cell parameters vary very little with temperature within the ranges in question. (Near the actual transitions, of course, there are more pronounced changes in the dimensions of the cells.)

Table 2. Thermal expansion coefficients

Temp. range (°C.)	$\alpha_a \times 10^6$ (per °C.)	$\alpha_b \times 10^6$ (per °C.)	$\alpha_c \times 10^6$ (per °C.)
+20 to +4	15.7	15.7	6.2
+4 to -99	4.9	28.4	-0.9
-99 to -160	7.8	7.8	8.2

#### 4. The orthorhombic phase

Below the second transition, the X-ray spots either remained single or became doubled along the layer line in oscillation photographs about the  $b$  axis of the original crystal. In both cases abrupt changes took place in their  $\theta$  values. These alternative effects were sometimes produced with successive coolings of the same crystal but, in the majority of experiments, both the single and doubled spots occurred on the same film. Similar changes were observed in the  $a$ -oscillation photographs.

The (500) reflexions were recorded as single spots on the films and, in order to investigate their possible duplex nature, a series of exposures was made at small angular intervals of 3–6 min. of arc through the reflecting position of the crystal. It was found that these spots actually represent the superposition of the reflexions from two twinned individuals with a difference of 24 min. of arc between their reflecting angles. No doubling of the (005) reflexions was observed by this method.

##### (a) *The structural interpretation*

The X-ray evidence can only be interpreted as a breaking down of the single tetragonal crystal into a multi-domain, mosaic structure, composed of sub-crystallites of lower symmetry. The parameter changes which take place below the second transition are (i) a contraction in the  $c$ -axial direction, (ii) contraction or expansion along either  $a$  or  $b$ , and (iii) a slight change from  $90^\circ$  of the inter-axial angle between  $a$  and  $c$ . Actually, however, since two of the axes are equal, within the experimental accuracy (Rhodes, 1949) the true symmetry is orthorhombic, i.e. the lattice should be referred to the axes which form the diagonals of the monoclinic (010) face with an inter-axial angle of  $90^\circ$  (Megaw, 1946). (Note that the angle  $\beta = 90^\circ$ , referred to in the original communication (Rhodes, 1949), indicates this angle between the orthorhombic  $a$  and  $c$  axes.) For purposes of description, however, it is more convenient to use the monoclinic cell.

The arrangement of the crystallites, relative to the original pseudo-cubic framework, is shown diagrammatically in Fig. 3. Four separate orientations of the unit cells have been distinguished according to their directions of shear with respect to the original axes. These have been labelled as 1, 2, 3 and 4 in the accompanying drawing with axes  $a'$ ,  $b'$  and  $c'$ . The  $a' = c'$  axes and the included angle  $\beta$  ( $90^\circ 12'$ ) remained practically constant with temperature between the second and third transitions. The  $b'$  axis, normal to the  $a'c'$  plane, appeared to be the only variable in the monoclinic cell. The small arrows, shown within the unit cells in the diagram, indicate the positions of the optic or polar axes as determined from microscope observations and d.c. field measurements.

From the arrangement of the unit cells shown in Fig. 3, it is evident that when the crystal is oscillated

about its  $b$  axis, with the incident beam in the direction of the arrow  $Y$ , the unit cells with orientation (1, 2) will contribute reflexions which are doubled along the layer line, i.e. (501) is composed of four spots corresponding to the  $CuK\alpha_1$  and the  $CuK\alpha_2$  pairs. On the same exposure the crystallites with orientation (3, 4) produce the (051)  $\alpha_1\alpha_2$  doublet at a higher  $\theta$  value.

If the macro-crystal is now rotated through an angle of  $90^\circ$  about its  $b$  axis so that the X-rays are in the direction of the arrow  $Z$ , the diffraction spots from the cells in the (1, 2) and (3, 4) orientations are almost superimposed. The (105)<sub>1,2</sub> and the (015)<sub>3,4</sub> reflexions have slightly different  $\theta$  values from each other. This results in a group of four spots with different intensities between the corresponding pairs of  $\alpha_1\alpha_2$  doublets. The very small separation between the layer lines, corresponding, respectively, to the two orientations of unit cells, indicates that there is an angular tilt between them of a few minutes of arc. The actual size of this angle could not be measured because of the difficulty of accurate crystal setting at the low temperatures.

In the reciprocal-lattice net for the  $b$ -axis oscillation photographs, discussed above, the  $c^*$  axes of the cell orientations 1 and 2 are common, but their respective  $a^*$  axes are inclined to each other at an angle of approximately  $24'$ . The cell orientations 3 and 4 are coincident in this reciprocal projection. The distance of a reciprocal-lattice point from the origin is represented by the co-ordinate  $\xi$  which is directly proportional to the film distance for the zero-layer-line spots ( $\zeta = 0$ ). It is evident, therefore, that the (501) and the (50 $\bar{1}$ ) reflexions will be separated on the film. The (051) spots from the unit cells 3 and 4 have the same reflecting angle for both and they will be recorded on the film as a single doublet at a higher  $\theta$  value. Photographs, taken with the macro-crystal oscillated about its  $a$  axis, produced similar combinations of diffraction spots. With the crystal oscillated about its  $c$  axis the doubling of the reflexions occurred perpendicular to the layer line, as illustrated in Fig. 2.

As noted previously, sometimes only single pairs of spots occurred when the specimen was cooled below the second transition. This evidence indicates that unit cells of either orientations (1, 2) or (3, 4) may exist. In the first instance an oscillation about the  $a$  axis would produce only  $\alpha_1\alpha_2$  doublets, i.e. either (105) or (051). In the second case the pairs of spots (015) or (051) would be recorded by oscillation about the  $b$  axis.

It has therefore been possible to explain all the diffraction spots obtained on the zero-layer-line photographs in terms of the postulated orientations of the unit cells shown in Fig. 3.

##### (b) *Twinning*

The pairs of subcrystallites illustrated in Fig. 3, with either the cell orientation (1, 2) or (3, 4), have been assumed to extend throughout the mosaic crystal by repeated twinning on the (001) monoclinic planes.

Either or both of these cell orientations may develop in the crystal below the second transition, depending on the condition of minimum strain and distortion of the macro-crystal boundaries.

The true symmetry cell has been shown previously to be orthorhombic; this is consistent with the microscope evidence of the position of the optic axis, which has been observed to coincide with the diagonal of the  $a'c'$  face of the monoclinic unit cell. Either inclined or parallel optical extinction is obtained in both the  $ac$  and  $bc$  crystal faces, depending on which twin arrangement predominates. The extinction in the  $ab$  face remains parallel to the crystal edges in both cases.

When the crystal was oscillated about its  $c$  axis, however, there was a pronounced doubling perpendicular to the layer line. From this X-ray evidence the actual structure would appear to be very much like that above this transition, that is, it is composed of twinned sub-units or crystallites having definite orientations with reference to the original pseudo-cubic framework (Fig. 4). Here also there appear to be four different arrangements of the unit cells. These have been labelled 1, 2, 3 and 4 in the diagram, with lattice parameters  $a''=b''=c''\sim 4\cdot000$  A. at  $-100^\circ$  C. The slight doubling of the reflexions perpendicular to the layer line of the  $b$ -oscillation photographs (Fig. 2) indicates that there

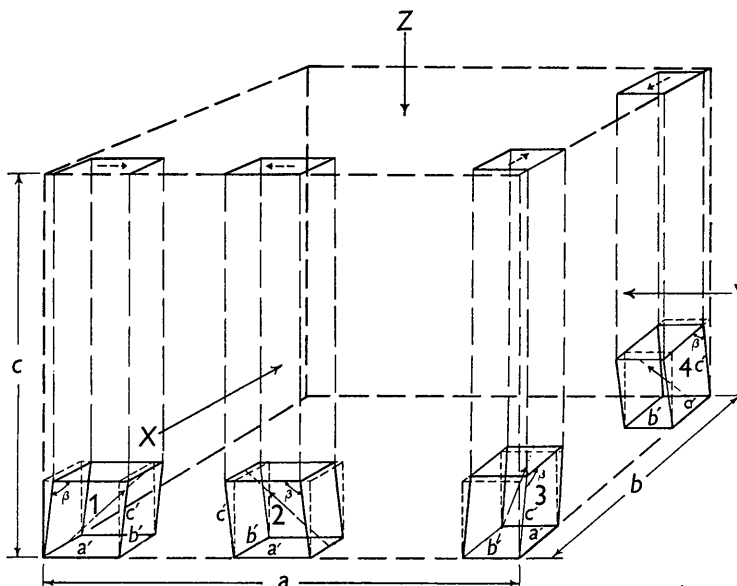


Fig. 3. Orientation of the unit cells of the orthorhombic phase within the cubic framework.

The complicated manner in which the subcrystallites, composing the mosaic crystal, fit together without any visible signs of physical rupture has not been completely established. The two types of twins are extended in the  $c$  direction of the macro-crystal in a zigzag manner by repeated twinning on their  $a'b'$  planes. The junctions between these groups are probably composed of distorted cells forming the dark boundary lines observed on examination in the microscope. These four possible arrangements always occur in such a way that the (001) plane and both the  $a$  and  $b$  axial directions of the original framework are retained.

### 5. The trigonal phase

With either the  $a$  or the  $b$  axis of the original pseudo-cubic crystal as the oscillation axis, the (501)-type diffraction spots became split along the zero layer line, in every case of cooling below approximately  $-90^\circ$  C. (see Fig. 2). The (500)-type reflexions, on the other hand, did not show any horizontal doubling for reasons similar to those which apply in the orthorhombic case.

is a small angular tilt between the orientations of the twins of types (1, 2) and (3, 4) respectively.

Although small differences were observed between corresponding reflexions from different crystals and from successive coolings of the same crystal, the spots were recorded essentially as shown opposite the temperature  $-100^\circ$  C. in Fig. 2. Since the three axes of the unit cell are equal, reflexions of the type  $(h0l)_{1,2}$  are superimposed on those of type  $(0kl)_{3,4}$ , thus making their interpretation difficult. Optical investigations of crystals, at temperatures below the third transition, have shown that the projection of the optic axis on the crystal face under observation lies at an angle of approximately  $45^\circ$  to the edges when viewed along each of the three cubic directions. This can only be interpreted if the optic axis is in the [111] direction of the unit cell. From these facts we are able to postulate that the true symmetry is trigonal, corresponding to a slight distortion along the cube body diagonal.

The possible twinning arrangement of the four types of trigonal units, within the parent framework, is shown

in Fig. 4. The small arrows in the diagram indicate the orientations and probable directions of polarity of the optic (polar) axes.

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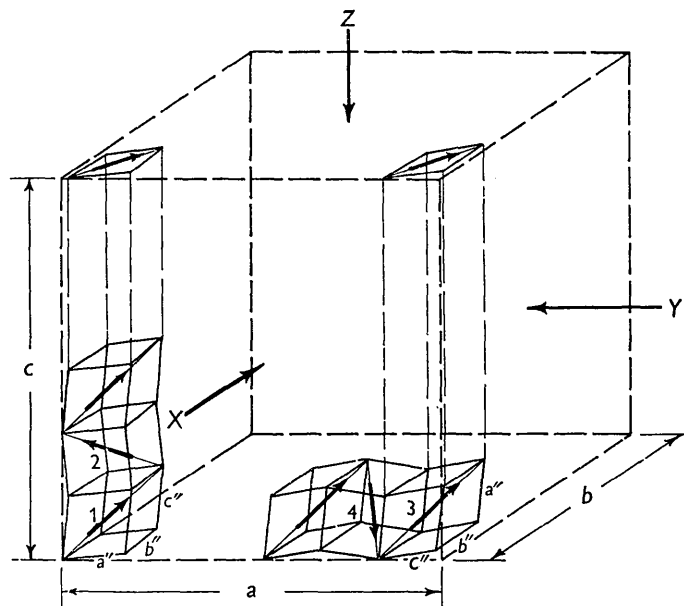


Fig. 4. Twinning of the trigonal phase.

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