Structural Transformations in Some Oxyborates Observed by High Resolution Transmission Electron Microscopy

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Well-ordered crystals of the magnesium manganese oxyborates ludwigite, orthopinakiolite, and takéuchiite were heated in air at temperatures of between 800 and 1200°C for periods of time varying from 2 hr at the higher temperature to 3 days at the lower temperature. At 1100°C and below neither takéuchiite nor orthopinakiolite reacted, but ludwigite transformed to takéuchiite at 1100°C, to orthopinakiolite at 900°C, and to pinakiolite at 800°C. At 1200°C takéuchiite transformed to ludwigite, orthopinakiolite transformed to takéuchiite, and ludwigite did not react. Mechanisms for these transformations are suggested. © 1991 Academic Press, Inc.

Introduction

A number of oxyborate minerals including ludwigite, orthopinakiolite, takéuchiite, and pinakiolite have the same idealized formula, M_3BO_5, where the metal ion M is usually a combination of Mg, Mn, and Fe. Structural studies on this series of compounds (*1–14*) have shown that they can be viewed as regularly twinned variants of pinakiolite. The phases differ from each other by having different twin plane separations.

Takéuchi (*15*) argued that the degree of twinning in these compounds was determined by the number of cation vacancies present. If this is the case, any process which tends to alter the ratio of cations to anions in a particular phase would tend to destabilize it with respect to another member of the series. The possibility of structural transformations involving two or more members of the pinakiolite family can therefore be envisaged.

To date only two studies have been published of such reactions. Diman and Nekrasov (*16*) reported on the transformation of synthetically prepared materials with the hulsite structure to compounds isostructural with ludwigite and vice versa. The reactions were found to depend upon temperature and oxygen partial pressure. Cooper and Tilley (*17*) observed the formation of orthopinakiolite from a synthetically produced ludwigite sample. In this study the ludwigite starting material was irradiated by the electron beam of a transmission electron microscope. The effect was attributed to the combined effect of the electron beam and sample heating in the vacuum of the electron microscope column.

These experiments did not lead to any broad conclusions regarding the mechanisms of the transformations or their reversibility. To clarify matters further we have

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studied several more transformations within the pinakiolite series, mainly by way of high resolution electron microscopy. These observations are presented in this paper together with mechanisms by which these transformations can come about.

Experimental

The starting materials for the reactions, synthetic ludwigite, takéuchiite, and orthopinakiolite, were prepared from appropriate quantities of MgO, Mn_3O_4, and B_2O_3 of "Specpure" quality supplied by Johnson Matthey Ltd. The boric oxide used was reported to have a water content of less than 200 ppm and was stored in a dessicator until used. Mn_3O_4 was prepared by heating MnO_2 powder in a Pt crucible at a temperature of 1000°C in air for 24 hr, followed by rapid quenching. The product was checked by weight loss measurements and powder X-ray diffraction. Appropriate quantities of these oxides were ground in an agate mortar, formed into pellets, sealed in platinum tubes, and heated at 1000°C for 7 days. After reaction the tubes were quenched in liquid nitrogen. Three preparations, $1.7MgO + 0.45Mn_3O_4 + 0.5B_2O_3$ ($M_{3.05}BO_5$); $1.3MgO + 0.55Mn_3O_4 + 0.5B_2O_3$ ($M_{2.95}BO_5$); and $0.9MgO + 0.65Mn_3O_4 + 0.5B_2O_3$ ($M_{2.85}BO_5$), gave rise to monophasic well crystalline samples of ludwigite, takéuchiite, and orthopinakiolite, respectively.

Structural transformations in the starting phases were induced by heating the samples in air at temperatures of 1200, 1100, 900, and 800°C for the times detailed in Table I. The weight changes which occurred were noted by weighing the samples before and after reaction using an analytical balance. The phases produced were identified by powder X-ray diffraction with a Guinier–Hägg focusing camera using strictly monochromatic $CrK\alpha_1$ radiation and KCl ($a_o = 0.62929$ nm) as an internal standard, and by transmission electron microscopy. For microscopy,

small quantities of the samples were crushed under n-butanol. A drop of the resulting suspension was placed on a holey carbon film and allowed to dry before examination in a JEOL 200CX transmission electron microscope fitted with a top entry goniometer stage and operated at 200 kV. Crystal fragments with thin edges projecting over holes in the support film were aligned so that the beam was parallel to the shortest unit cell axis. The resulting electron diffraction patterns and images were then recorded, usually at a direct magnification of 500,000×.

Results

Prior to heating, the starting materials were examined in the electron microscope. When crystal fragments were correctly aligned the three phases could be easily identified by the image contrast, which consisted of a rectangular pattern in the case of ludwigite and two recognizably different zigzag patterns in the cases of takéuchiite and orthopinakiolite. No significant defect microstructures were recorded at this stage of the investigation. The diffraction patterns of these pure materials, reproduced in Fig. 1, were sharp and showed no streaking.

The results of the heating experiments are summarized in Table I and described in the sections which follow. The weight gains and losses recorded in Table I have not been converted into compositions as the reactions were frequently incomplete.

Reaction at 1200°C for 2 hr. No reaction took place when the ludwigite was heated but structural transformations took place in takéuchiite and orthopinakiolite.

In the case of takéuchiite the reaction was accompanied by a weight decrease of 0.37 wt% and it was found that the sample had been partly converted to ludwigite. The electron diffraction pattern from a partially reacted takéuchiite crystal is shown in Fig. 2. The overall intensity distribution of this pattern can be simulated by the super-

TABLE I

REACTIONS OF SAMPLES HEATED IN AIR

Conditions	Reaction	Weight change
1200°C, 2hr	Orthopinakiolite → takéuchiite	−0.44 wt%
	Takéuchiite → ludwigite	−0.37 wt%
	Ludwigite; no change	
1100°C, 24 hr	Orthopinakiolite; no change	
	Takéuchiite; no change	
	Ludwigite → takéuchiite	+0.4 wt%
900°C, 17 hr	Orthopinakiolite; no change	
	Takéuchiite; no change	
	Ludwigite → orthopinakiolite	+1.15 wt%
800°C, 3 days	Orthopinakiolite; no change	
	Takéuchiite; no change	
	Ludwigite → pinakiolite	+1.94 wt%

position of the diffraction patterns from well-ordered takéuchiite and ludwigite crystals as can be judged by comparison with Fig. 1.

The electron microscope images associated with this partly transformed material revealed that the two structure types were intergrown as slabs in a coherent fashion, joined along boundaries which are parallel to the (100) planes of both structures. A typical example is shown in Fig. 3. Materials which had transformed by different amounts contained different ratios of the two phases. In general, these phase regions were well ordered apart from occasional planar defects due to localized irregularities in the twin repeat distance, also visible in Fig. 3. A fault was occasionally seen to have terminated within the crystal matrix. Two adjacent examples can be seen in the takéuchiite region of Fig. 3, separating a region of ludwigite from that of takéuchiite.

The reaction of orthopinakiolite to takéuchiite involved a weight loss of 0.44 wt%. The diffraction patterns from partly reacted crystals could be explained by assuming that they were the result of simultaneous diffraction from regions of orthopinakiolite and takéuchiite. The newly produced takéuchiite

was coherently intergrown with the orthopinakiolite matrix, with boundaries running parallel to the (100) planes of both phases. The orthopinakiolite was also found to contain isolated planar faults parallel to (100) planes during the early stages of the transformation. As the microstructures are similar in essence to those in Fig. 3, they are not shown.

Reaction at 1100°C for 24 hr. At this temperature the takéuchiite and orthopinakiolite did not react but ludwigite readily transformed to takéuchiite. This reaction was accompanied by an increase of 0.4 wt%.

Three distinct types of image were recorded from different crystals transformed by different amounts. Figure 4a shows a ludwigite crystal during the early part of the process, showing faults produced by the absence of some twin planes in the rectangular matrix characteristic of ludwigite. The faults usually extended all the way through the structure on planes perpendicular to the (100) direction. Whenever terminated defects were present they were always connected to adjacent missing twin planes by another type of defect perpendicular to the (010) direction, also revealed in Fig. 4a. Additionally, faults on (100) planes at different
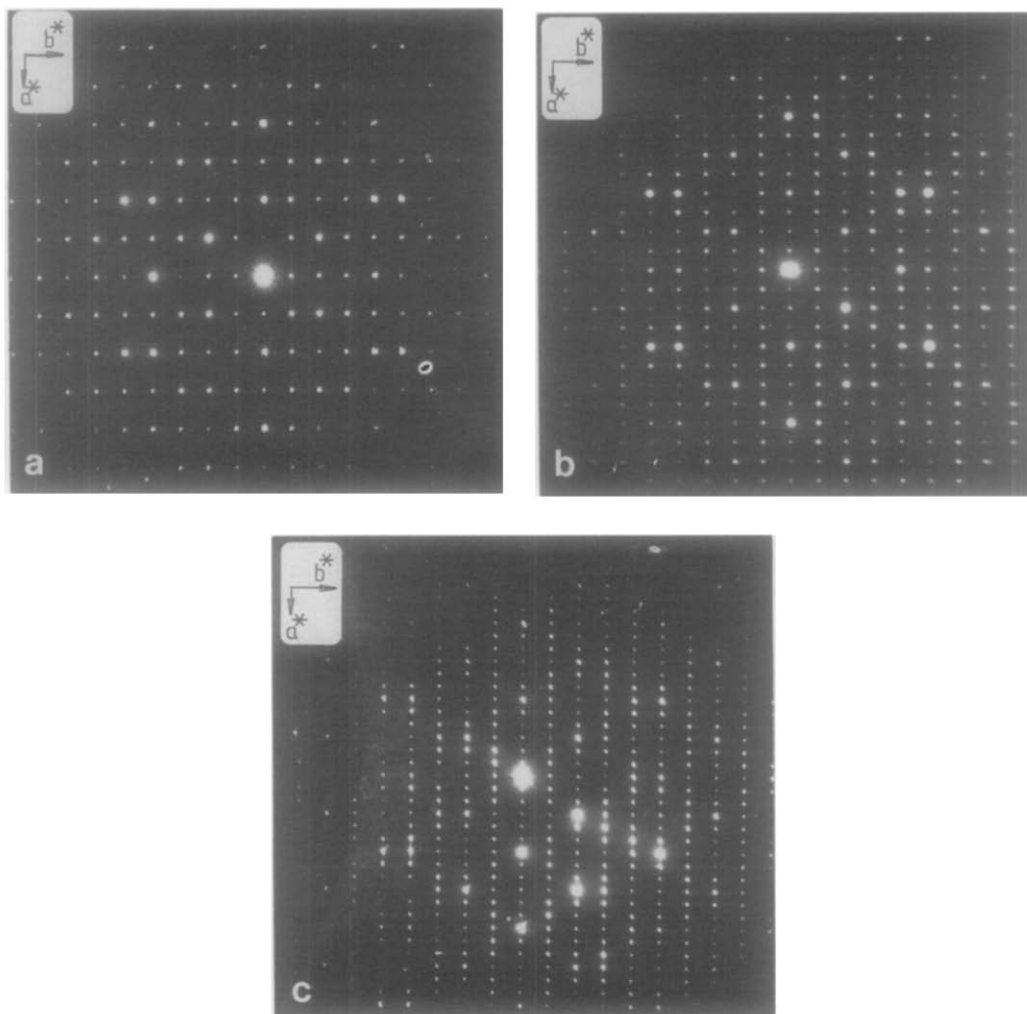
FIG. 1. Electron diffraction patterns of (a) ludwigite, (b) orthopinakiolite, and (c) takéuchiite, all projected down c^*.

levels were sometimes seen, connected by areas of diffuse contrast, such as seen in the region between the arrows in Fig. 4b. Crystal fragments observed at a later stage of the reaction sequence possessed highly disordered structures typified by the micrograph reproduced in Fig. 4c. All of the materials at this stage of the transformation had a twin plane density much lower than that of ludwigite and a zigzag contrast now predominated. The remaining twins were fairly randomly distributed on (100) planes. Crys-

tals of this type yielded diffraction patterns which were heavily streaked along the a^* direction. Finally, fragments which had transformed still further contained relatively large well-ordered regions of takéuchiite, marked T, with little remaining ludwigite, marked L, in Fig. 4d, usually separated by a region of disorder.

Reaction at 900°C for 17 hr. Crystals of takéuchiite and orthopinakiolite did not react at this temperature and only ludwigite showed signs of reaction. This transforma-
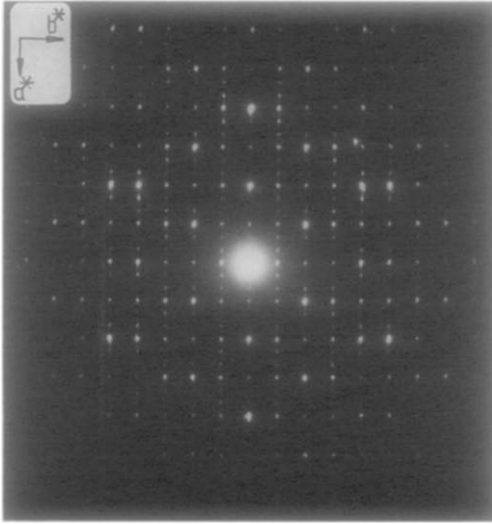
FIG. 2. Electron diffraction pattern from a crystal consisting of a coherent intergrowth of ludwigite and takéuchiite, projected down c^*.

tion was accompanied by a weight increase of approximately 1.15 wt.%.

The diffraction patterns of the partly reacted crystals showed streaking and extra reflections along the a^* direction as shown in Fig. 5. Such patterns were interpreted as being superpositions of varying amounts of the ludwigite and orthopinakiolite diffraction patterns, as can be verified by comparison with the examples shown in Fig. 1, together with disorder. Electron microscopy showed that the reaction involved the loss of twin planes from the ludwigite crystals, but at this temperature the reaction was rather slow and did not reach completion. Structure images similar to that shown in Fig. 6 revealed that ludwigite crystals contained fairly high densities of defects on (100) planes. In addition, regions of orthopinakiolite were also formed, also containing defects consisting of irregularities in the twin plane spacing.
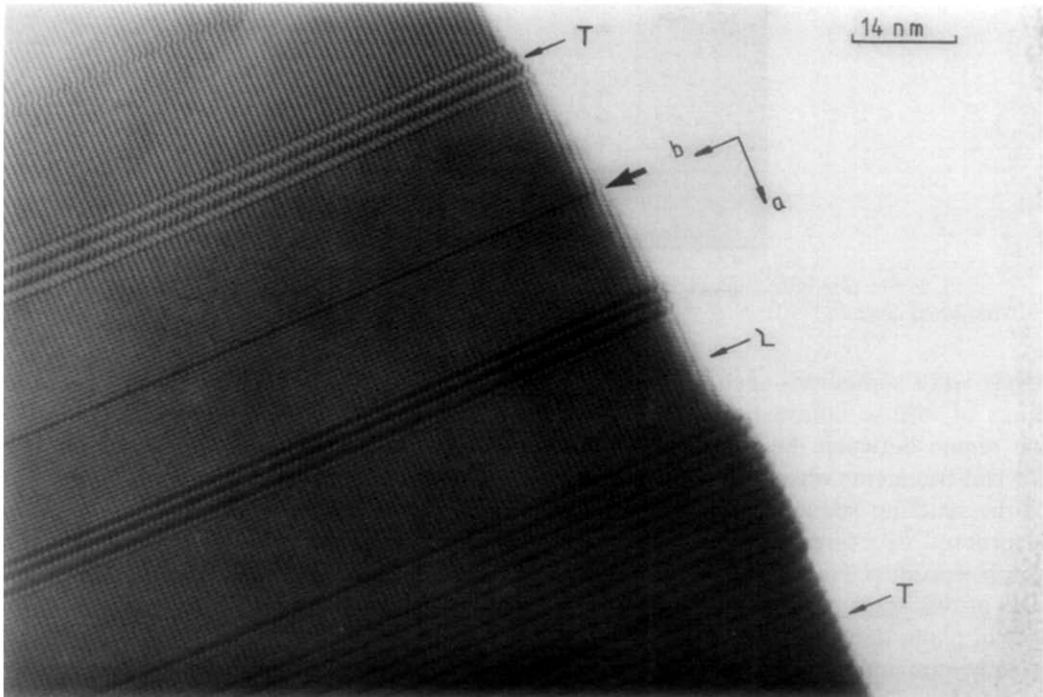

FIG. 3. Electron micrograph of a ludwigite–takéuchiite intergrowth produced by heating takéuchiite in air at 1200°C.
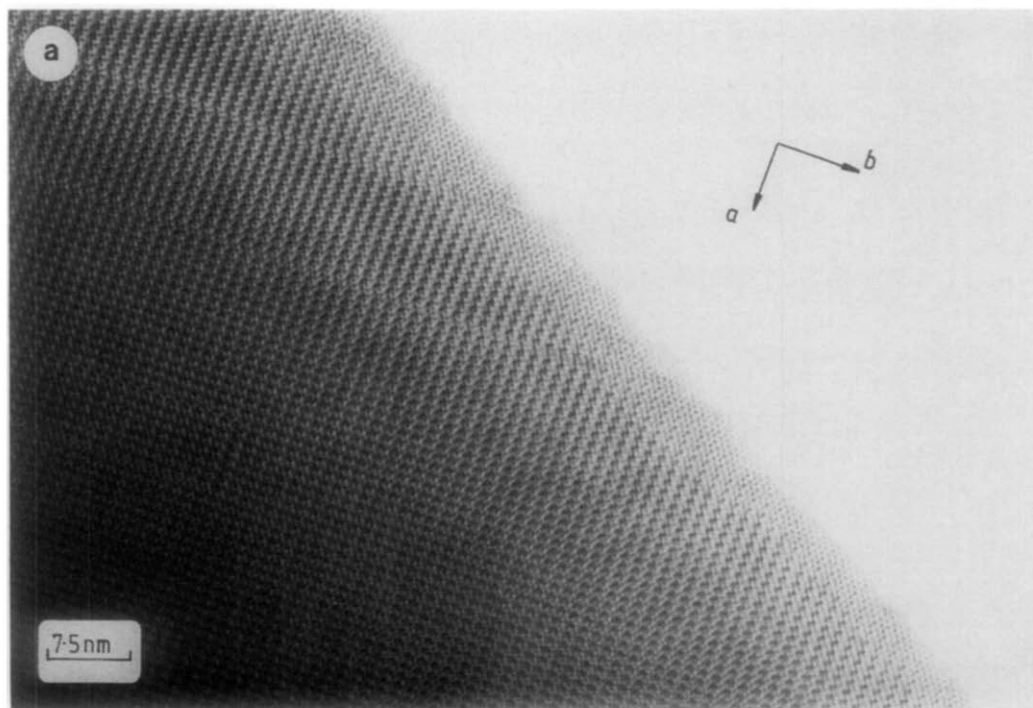
FIG. 4. A sequence of electron micrographs of faulted crystals formed by heating ludwigite in air at 1100°C. (a) Early stages of the reaction showing two types of fault at right angles to each other; (b) faults moving from one set of (100) planes to another, arrowed; (c) a highly disordered crystal formed at later stages of the reaction; (d) well-ordered takéuchiite separated from ludwigite by a disordered region.

Reaction at 800°C for 3 days. As at 900 and 1100°C the only material which underwent any change in structure was ludwigite. Material partially transformed to pinakiolite and small quantities of orthopinakiolite. At the same time a weight increase of approximately 1.94 wt% was observed.

Electron images revealed that the samples were disordered and defects which consisted of missing twin operations, lying on (100) planes, were seen. These often terminated within the crystal matrix. Other planar boundaries were also seen, sometimes connecting the (100) plane faults. At the earlier stages of reaction, small but well-defined areas of orthopinakiolite were observed together with irregularly shaped precipitates within the disordered ludwigite matrix.

These features are shown in Fig. 7. The lattice fringes observed in the larger precipitates are separated by a distance of 0.43 nm. This is close to the d_{100} spacing in MgO and the precipitates are tentatively interpreted as an (Mg,Mn)O rock salt phase. There did not seem to be any marked crystallographic or topotactic relationship between the matrix and the rock salt lattices.

At later stages in the transformation the crystal fragments consisted of extensive areas of pinakiolite, which contained a few random widely spaced twin planes, often separated by several hundred nanometers. Crystal fragments containing intergrowths of pinakiolite together with small regions of orthopinakiolite and remnants of ludwigite were also occasionally observed.
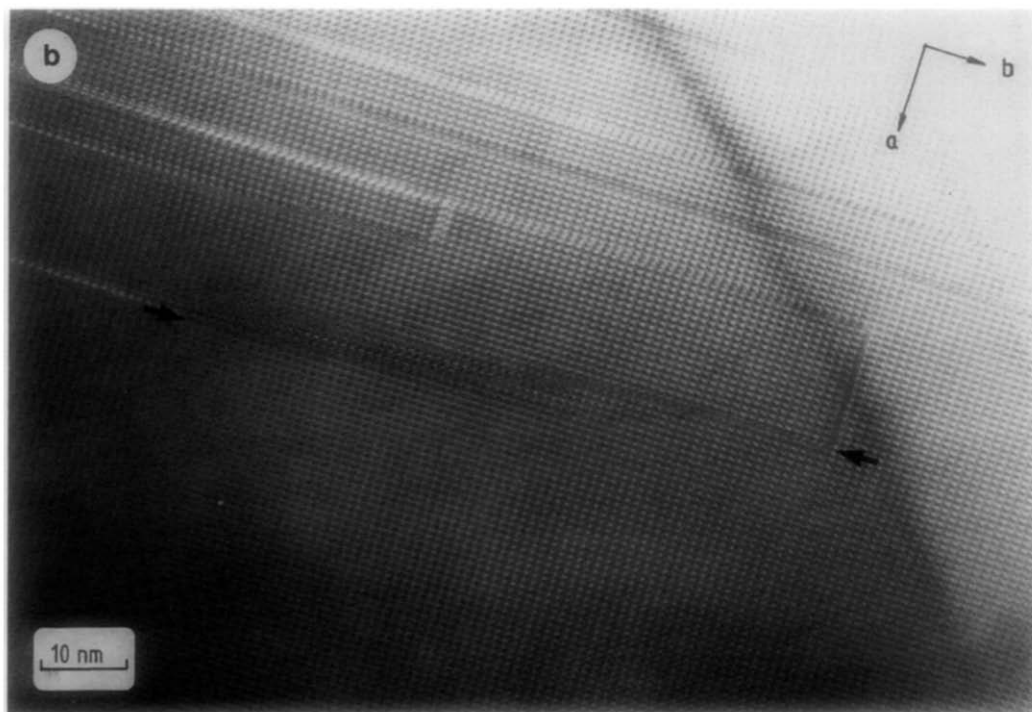
FIG. 4—*Continued*

The electron diffraction patterns from these materials reflected the complexity of the microstructures observed and confirmed the interpretations given. At earlier stages of the reaction the diffraction patterns resembled ludwigite patterns, but with heavy streaking parallel to a^*. At later stages these patterns also contained prominent maxima midway between successive ludwigite spots which were due to the simultaneous diffraction from the intergrown orthopinakiolite material. Eventually the patterns resembled those expected from pinakiolite more and more.

Discussion

The results showed that at 1200°C takéuchiite and orthopinakiolite lost weight to produce ludwigite or takéuchiite. At the other temperatures investigated ludwigite gained weight to form takéuchiite at 1100°C and orthopinakiolite or pinakiolite at lower temperatures. We presume, in the absence of other evidence, that the weight changes are solely due to oxygen loss or gain. In this paper we intend to concentrate upon the mechanism of the transformations taking place. The phase relations in the Mg–Mn–B–O system which have a bearing on the reactions will be considered in a forthcoming publication.

Mechanisms of transformation. During their investigations into the defect structures found in the pinakiolite family of oxyborate minerals, Bovin *et al.*(5) often observed intergrowths of pinakiolite and ludwigite. As a consequence of this, they described a mechanism for the transformation of pinakiolite to ludwigite, even though they did not observe such a reaction. This mechanism involved an ordered slip pro-
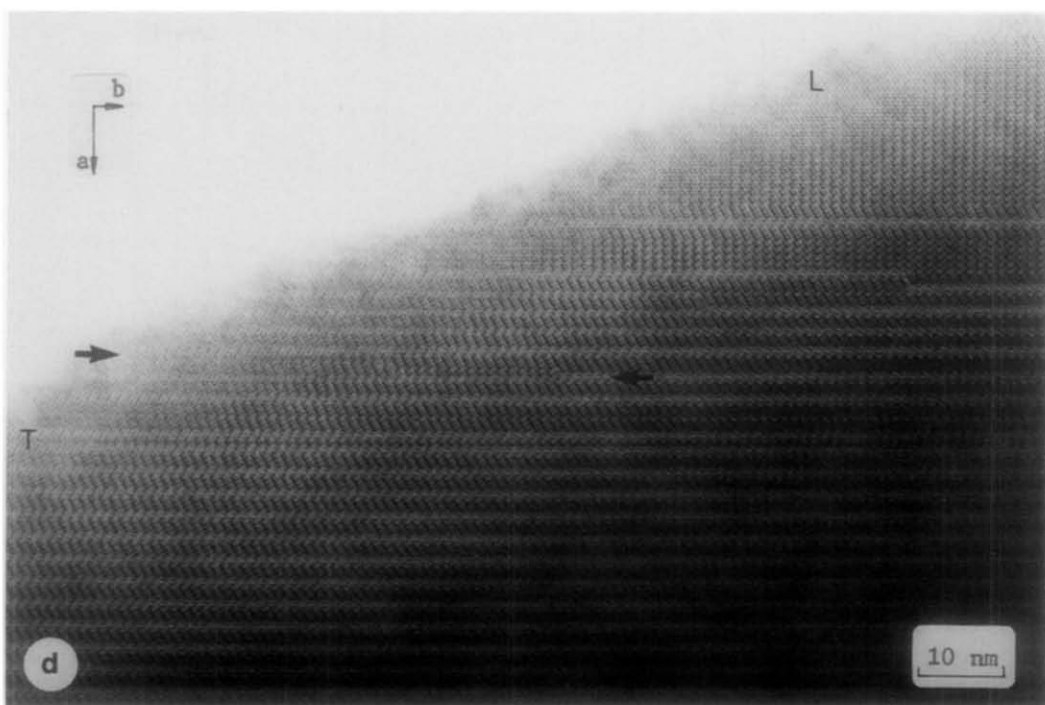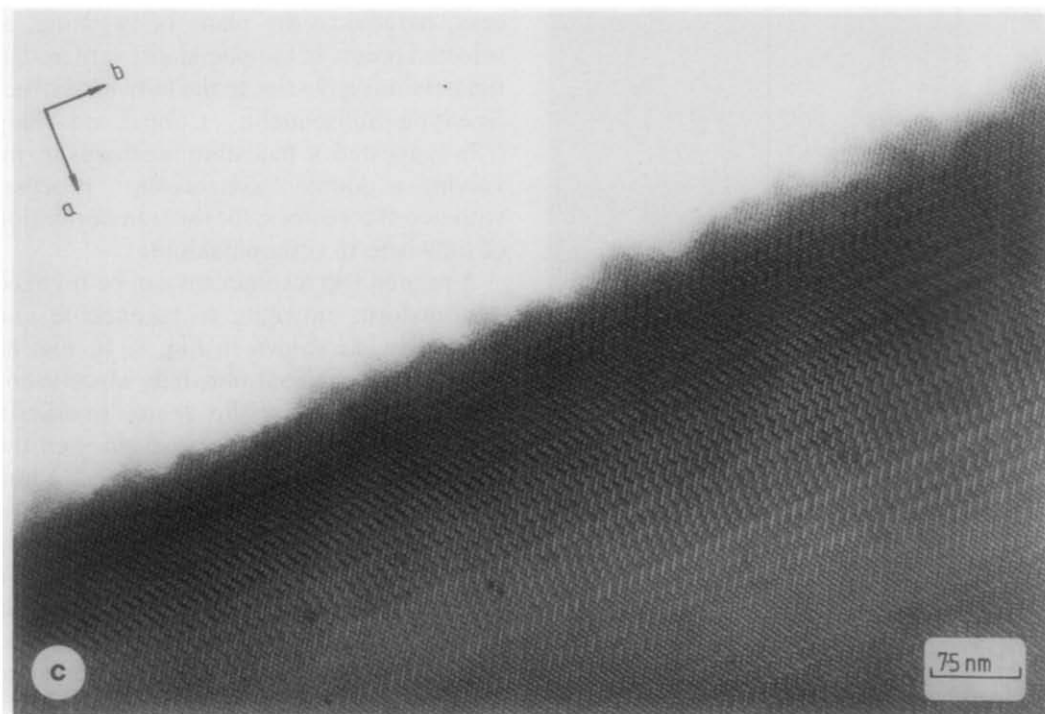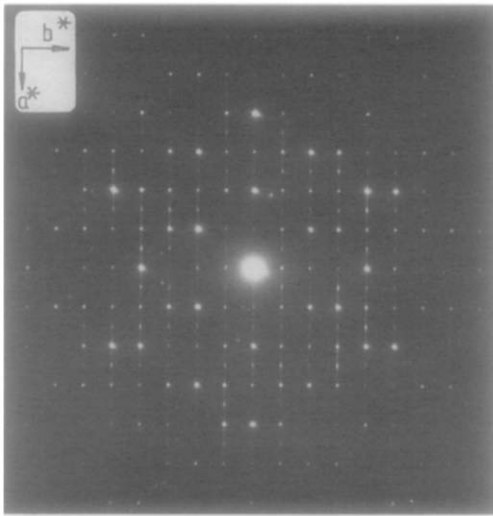
FIG. 4—*Continued*

FIG. 5. Electron diffraction pattern from a crystal consisting of a coherent intergrowth of ludwigite and orthopinakiolite formed by heating a ludwigite crystal at 900°C.

cess, parallel to the plane of twinning, at selected points in the pinakiolite lattice. Ultimately this gave rise to the ludwigite structure type. Subsequently, Cooper and Tilley (17) suggested a plausible mechanism, involving a double "synchroslip" process, with two slip vectors, for the transformation of ludwigite to orthopinakiolite.

A related slip mechanism can be invoked to transform ludwigite to takéuchiite and vice versa, as shown in Fig. 8. In Fig. 8a the slightly idealized ludwigite structure is shown along with a slip vector (marked). If the slip operation is performed then the structure given in Fig. 8b is produced. A unit jump of Mg or Mn cations into neighboring octahedral sites, indicated by the arrows on Fig. 8b, results in the structure shown in Fig. 8c. This diagram represents a lamella of takéuchiite within a ludwigite matrix. Repetition of this slip process at equivalent
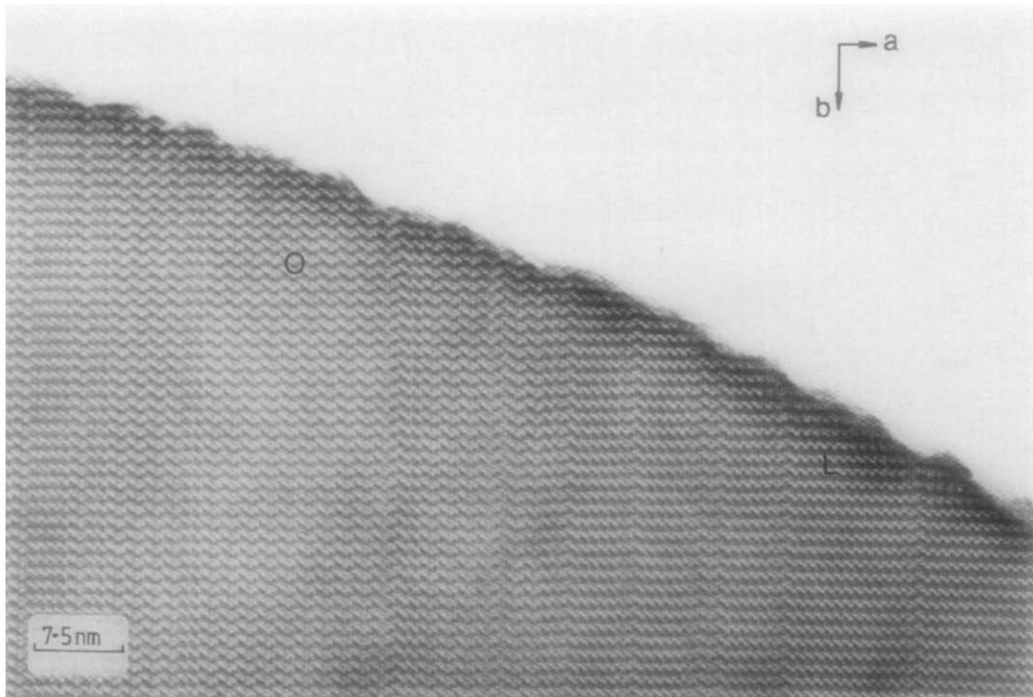

FIG. 6. Electron micrograph of a crystal of ludwigite heated at 900°C, containing ludwigite (L) and orthopinakiolite (O). The ludwigite structure contains a large number of faults due to missing twin planes.
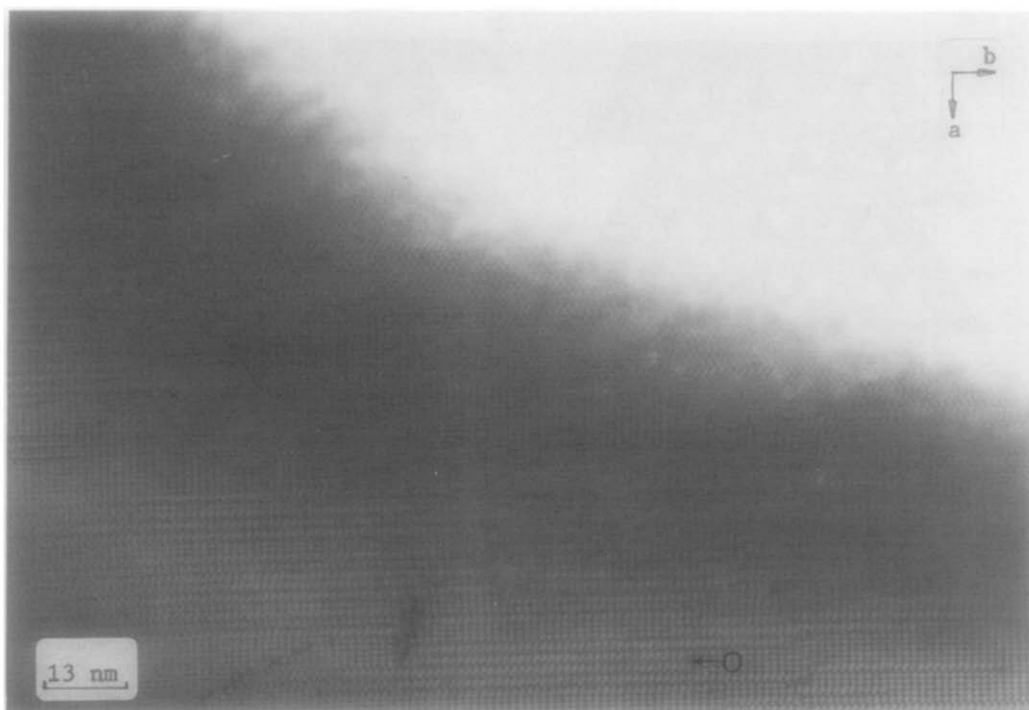
FIG. 7. Electron micrograph of a ludwigite crystal heated at 800°C transforming to pinakiolite. Small areas of orthopinakiolite can be seen, along with a large number of fault planes and some irregularly shaped precipitates.

positions in the surrounding regions of ludwigite would produce wider lamellae of takéuchiite. Ultimately this could then bring about the complete transformation of ludwigite to takéuchiite. Furthermore, following the diagram sequence in the reverse direction gives rise to a slip mechanism by which takéuchiite can convert to ludwigite, as was observed at 1200°C.

The propagation of a slab of ludwigite into takéuchiite can also be envisaged in terms of a diffusion process, as illustrated in Fig. 9. In Fig. 9a the probable geometries of a terminated ludwigite lamella in a takéuchiite matrix are seen. The arrows in this diagram indicate the diffusion steps that must take place in order to produce the structure given in Fig. 9b. The sequence of arrows given in Fig. 9b produces the structure shown in Fig. 9c. This succession of steps leads to the extension of the ludwigite lamella into the

takéuchiite matrix from the left to the right. Further structural rearrangements, of this type, on neighboring levels to either side of the ludwigite lamella, would therefore lead to the gradual transformation of takéuchiite to ludwigite. Once more, it is clear that the reverse operation would bring about the transformation of ludwigite to takéuchiite.

Evidence for mechanisms. A single slip process such as that proposed for the ludwigite to takéuchiite transformation would result in the displacement of the lattice on one side of the slip plane relative to the matrix on the other. Consequently, it should be possible to distinguish if such a displacement had occurred by reference to the appropriate electron micrographs. The absence of such a displacement would constitute evidence for the diffusion mechanism.
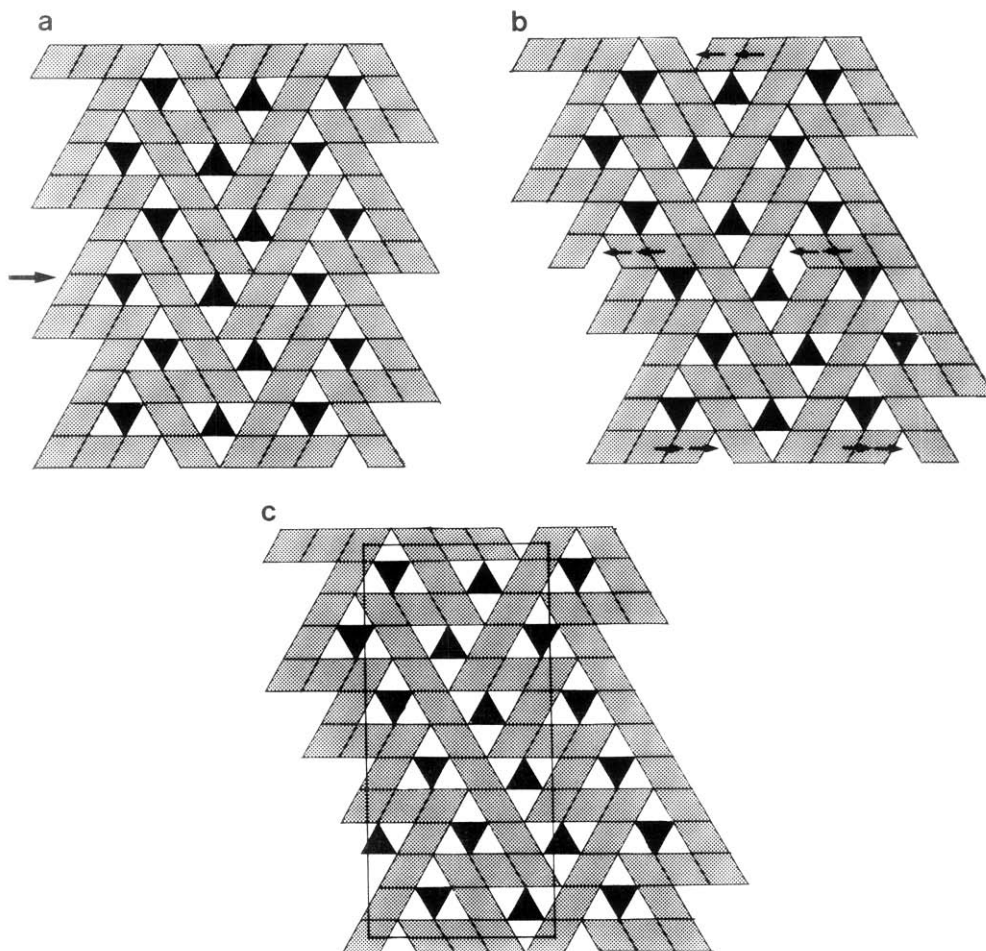
In actual fact, such lattice displacements

FIG. 8. Idealized drawings showing a possible slip mechanism for the transformation of ludwigite to takéuchiite.

can be seen across the planar defects produced in crystals during the takéuchiite to ludwigite transformation which took place at 1200°C and shown in Fig. 3. A very clear example, best seen when the figure is viewed at grazing incidence, is arrowed. Similarly, in the sequence of micrographs of the reverse transformation, that of ludwigite to takéuchiite, which took place at 1100°C, the same displacements can be recognized, especially in Fig. 4a. These observations indicate that a slip transformation process has occurred.

A disadvantage of the slip operation is that it would tend to generate a highly strained and distorted region at the end of the advancing slip plane front. This problem appears to be resolved, at least in ludwigite fragments at the early stage of the transformation to takéuchiite, as shown in Figs 4a and 4b, by connecting any terminated (100) planar defects to similar faults by another type of fault lying on (010) planes. Presumably, these additional fault planes could lower the strain energy below that which would be present in an elastically distorted
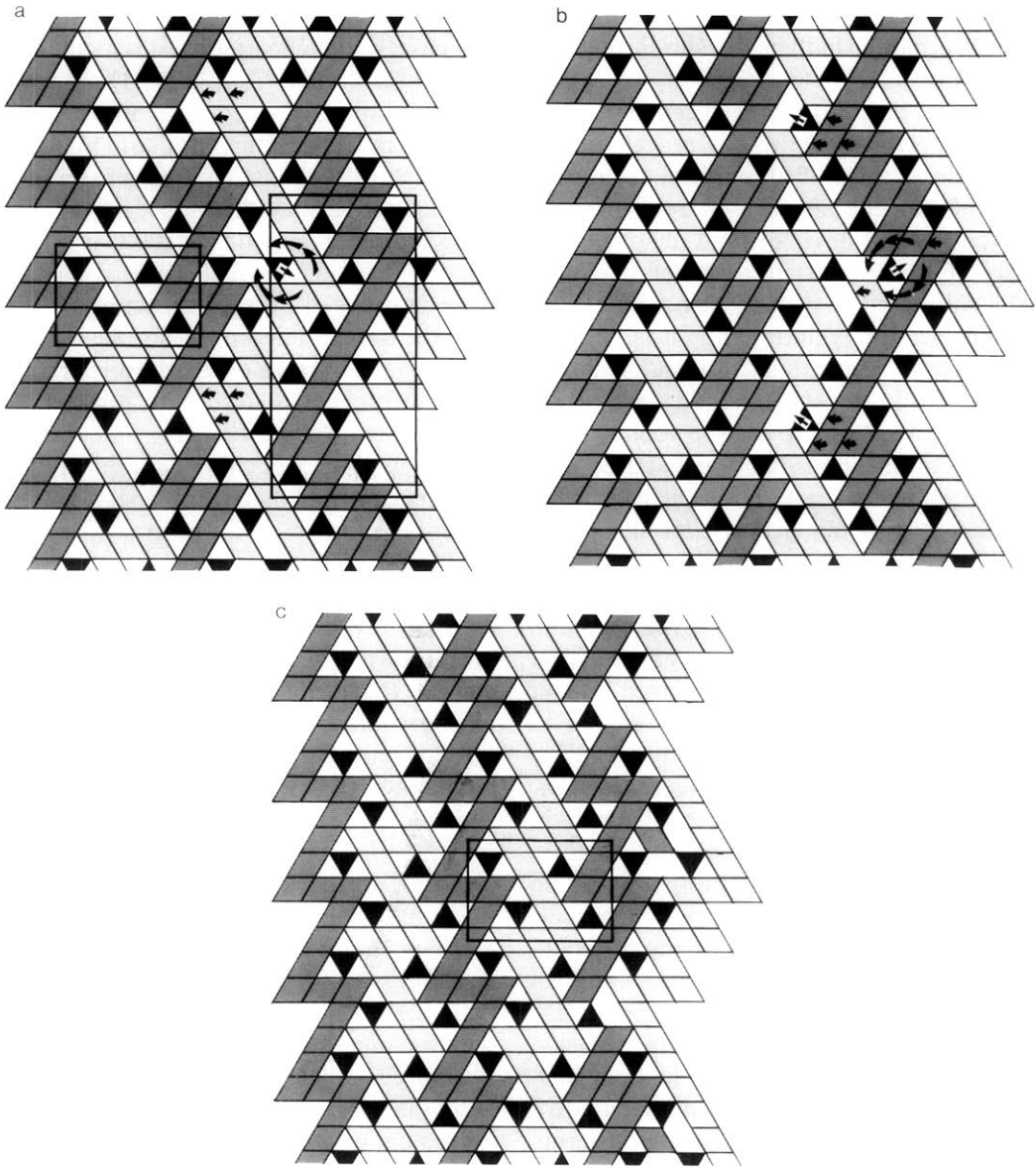
FIG. 9. Idealized drawings showing a mechanism by which an intergrown lamella of ludwigite can extend through a takéuchiite crystal via diffusion. In (a) and (b) the ludwigite extends to the left by way of the arrowed cation jumps to produce the structure in (c).

region at the end of a single slip plane front. In such instances the faults lying perpendicular to the slip planes can be considered to be analogous to edge dislocations in metallic materials. This is because they lie perpendicular to the slip plane and also denote the line of demarkation between the slipped and the unslipped portions of the lattice. As with metals, the gradual movement of such a dislocation type of fault is likely to present

a much smaller energy barrier to the slip process than instantaneous slip through an entire crystal.

In Fig. 4a a lattice displacement of approximately half the a-axis repeat can be seen across these (010) defects, suggesting that this defect is also caused by a slip of the lattice on one side of the fault relative to the other. Furthermore, the width of the defect is slightly greater than the b repeat of ludwigite. From this information it is possible to construct a model of these faults, shown in Fig. 10. In Fig. 10a, the ludwigite structure is shown along with a slip vector. If the slip operation is performed so that the points of attachment of the zigzag chains are all shifted by two octahedral edge distances, then the faulted structure in Fig. 10b is generated. The geometry of the fault produced by this process would then agree with that which is observed in the micrographs. That is, the ludwigite lattice is displaced by half the a-axis repeat, on one side relative to the other, and the fault is slightly greater in width than the ludwigite b-axis dimension.

The generation of the open channels in Fig. 10b is not very likely since the structure would tend to collapse. Furthermore, no contrast indicative of such empty tunnels was seen on any of the micrographs examined. More probably the channels are filled with atoms that diffuse from the surrounding ludwigite matrix. For example, the inclusion of one extra MO_6 octahedron and one BO_3 triangle in each channel would give rise to a structure similar to that in Fig. 10c. Alternatively the channels could remain partially filled and allow the diffusion of atoms either into or out of the transforming regions.

In the electron micrographs which show the transformation of ludwigite to orthopinakiolite, Figs. 6 and 7, no displacements can be observed with certainty. However, this transformation requires a double synchroslip process which would not result in such a displacement. Hence the absence of a displacement cannot be taken as proof of the operation of a diffusion mechanism in this case, and the matter must remain open.

Transformation ordering. During the transformation of one phase into another not only must the number of twin planes be altered but they must also be separated by the required regular intervals. The takéuchiite to ludwigite reaction at 1200°C in air was the only reaction in which extra twin planes were introduced into the structure. In this case the transformation process seemed not to involve any stages of great disorder. Only one slip process is needed to produce the required twin plane density, and the evidence suggests that this occurred midway between the existing twin planes. Such an event is reasonable as a central position is likely to minimize interactions between the new twin plane and the existing neighboring twin planes, and such interactions have been shown to be important in other twinned phases (*18*). If this is the case, ordered ludwigite would be produced with no further rearrangements needed.

The reverse of this process, in which ludwigite loses twin planes to form takéuchiite or orthopinakiolite, seems to be a far more disordered process. Initial removal seems to be more or less at random so that the mechanism of transformation to ordered structures involves two steps, removal of twin planes and a subsequent reordering of the remaining twin planes into the new structure.

A plausible mechanism for sideways movement or climb which could lead to the ordering of the twin planes in disordered crystals of the type shown in Figs. 4 and 6 is given in Fig. 11. In this diagram, the twinned pinakiolite structure in Fig. 11a undergoes a slip to produce the structure shown in Fig. 11b from that in Fig. 11a. A unit jump of cations into the neighboring octahedral sites indicated by the arrows on Fig. 11b results in the structure shown in Fig. 11c. This structure is the same as that in Fig. 11a except that the twin plane has moved two octa-
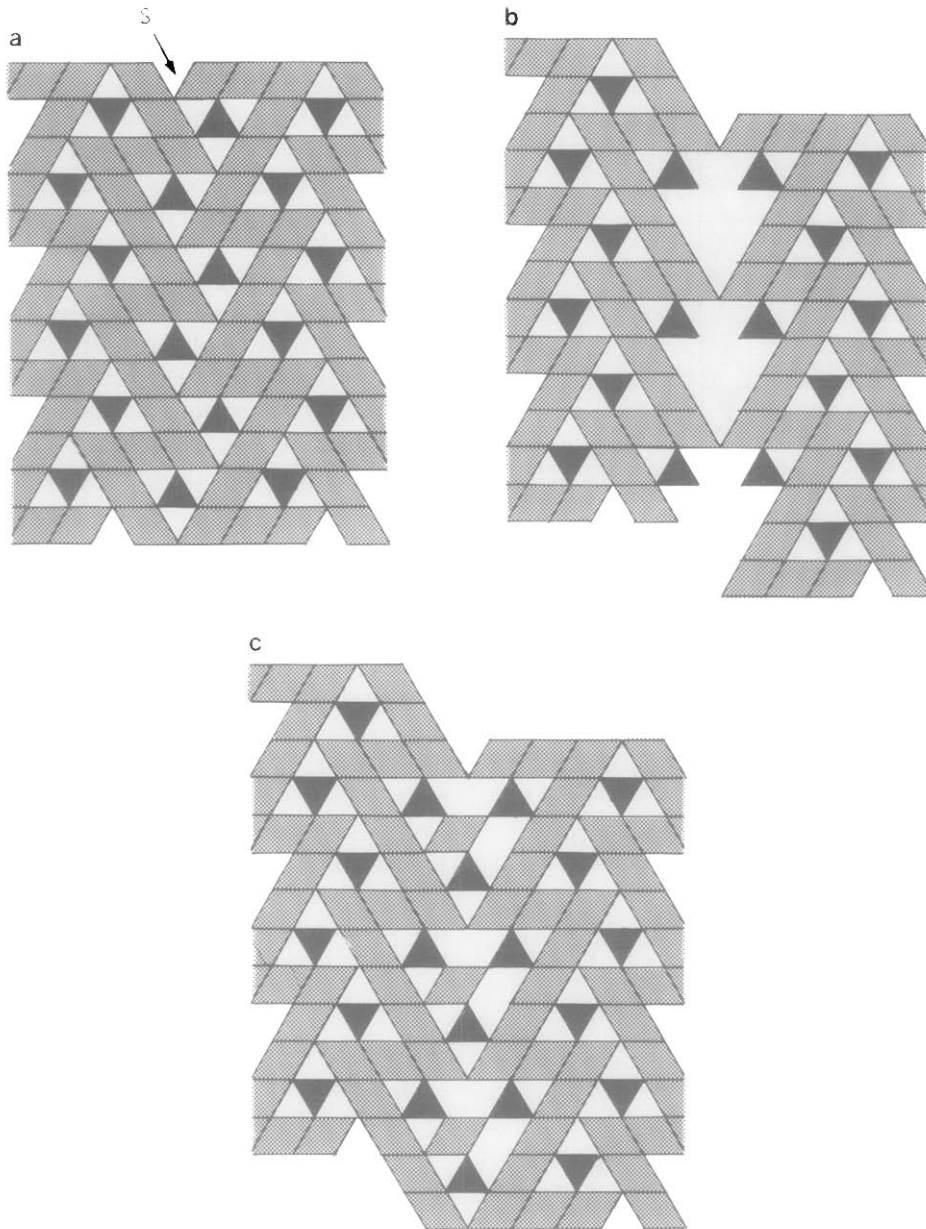
FIG. 10. Idealized drawings of the ludwigite structure showing a mechanism for the generation of the faults seen in Fig. 4a which lie perpendicular to the twin planes. The operation of the slip vector in (a) generates the structure shown in (b). A way in which the tunnels so generated can be filled is shown in (c).
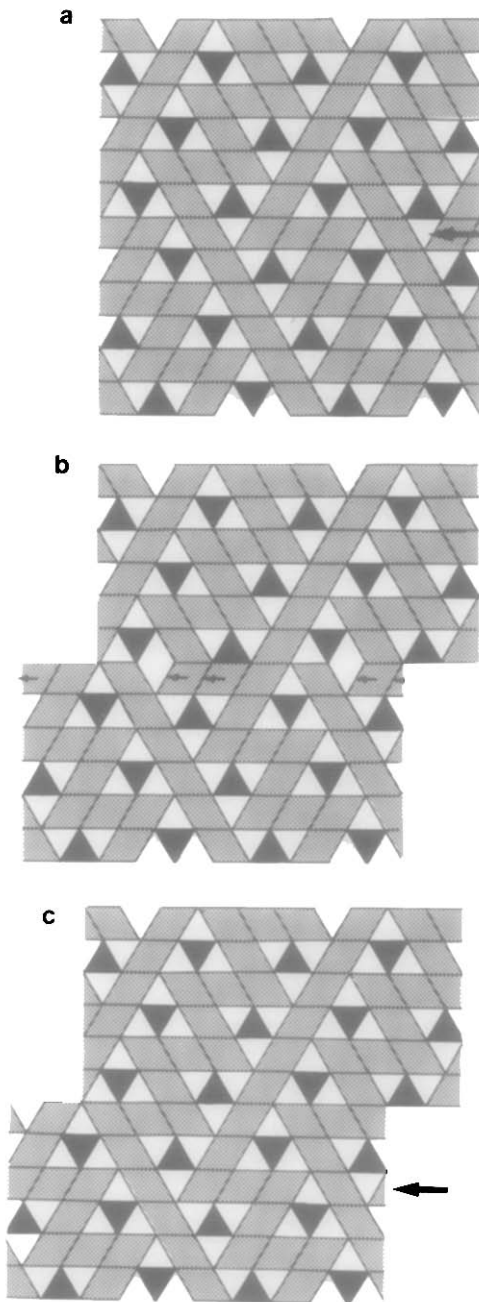
FIG. 11. Idealized drawings showing a mechanism by which twin planes may climb in pinakiolite. The operation of the arrowed slip vector in (a) produces the structure shown in (b). When followed by the arrowed cation jumps, the structure shown in (c) is generated. This diagram is similar to (a) but now the twin plane is two octahedral layers lower.

hedral layers down through the crystal. Similar climb mechanisms can be drawn for the other phases in this system.

Evidence to support the existence of a climb process is to be found in Figs. 4c and 4d. In Fig. 4d the arrows pick out a region where a twin plane appears to be moving from one level to another. Gradual extension of the twin plane on one level at the expense of the counterpart on the next level would lead to twin plane climb. Repetition of this process would eliminate disorder by eventually transporting the mismatch between differing regions to the surface or by combination with a defect of the opposite sense.

Conclusions. The experimental evidence presented in this paper suggests that the transformation reactions between these phases consist of two stages. The first involves a slip mechanism by which the twin plane density is altered. The second is a climb process by which disordered twin planes order. Different reaction rates for the two processes would explain the variation in microstructures observed at different temperatures and heating times. The relationship between the compositional changes involved and the phase relations in this system will be considered in a future publication.

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