References

BERTAUT, E. F. (1950). *Acta Cryst.* 3, 473–474.

BOVIN, J.-O., O'KEEFFE, M. & O'KEEFE, M. A. (1981). *Acta Cryst.* A37, 28–35.

HAHN, W. C. JR & MUAN, A. (1960). *Am. J. Sci.* 258, 66–78.

NIELSEN, K., SØTOFTE, I., THORUP, N. & NORRESTAM, R. (1978). *Acta Cryst.* A34, S171.

TAKÉUCHI, Y. (1978). *Recent Prog. Nat. Sci. Jpn,* 3, 153–181.

Electron Microscopy of Oxyborates.
III. On the Structure of Takéuchiite

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Abstract

The crystal structure of the new mineral takéuchiite, Me_3BO_5 (Me = Mg, Mn^{2+}, Mn^{3+}, Fe^{3+}, Ti^{4+}), has been derived by matching experimentally obtained high-resolution transmission electron microscope images with computed ones. The crystals are orthorhombic *Pnnm* or *Pnn2*, with $a = 27.50$ (1), $b = 12.614$ (2) and $c = 6.046$ (1) Å and $Z = 24$. The structure can be described as a periodic chemical twinning of the parent structure of pinakiolite, and is thus closely related to the other known chemical twins of pinakiolite, *viz* ludwigite and orthopinakiolite.

Introduction

The new mineral takéuchiite was found in a specimen from Långban mine, Sweden (Bovin & O'Keeffe, 1980). The specimen (Smithsonian Institute no. 138548) was labeled orthopinakiolite but was found, during a high-resolution electron transmission microscopy study of synthetic and natural oxyborates (Bovin, O'Keeffe & O'Keefe, 1981; Bovin & O'Keeffe, 1981), to contain only crystals of the new mineral imbedded in dolomite and calcite.

The group of mineral structures closely related to those of pinakiolite (Takéuchi, Watanabé & Ito, 1950; Moore & Araki, 1974) and hulsite (Yamnova, Simonov & Belov, 1975; Konnert, Applemen, Clark, Finger, Kato & Miura, 1976), comprise ludwigite (Takéuchi *et al.,* 1950), vonsenite (Takéuchi, 1956) and orthopinakiolite (Takéuchi, Haga, Kato & Miura, 1978). All these structures can be described as chemical twinnings (Andersson & Hyde, 1974) of the parent structure of pinakiolite (hulsite). Takéuchi (1978) predicted the existence of the new mineral, and by comparing the metal-atom occupancies in the structures of pinakiolite and orthopinakiolite he also suggested a model for the metal occupancies in the structure of the new mineral.

Using the Cowley–Moodie multislice formulation (Cowley & Moodie, 1957) it is possible to compute the electron microscope image to be expected from the structural model given by Takéuchi and to compare it with the experimentally obtained one. Thus it is possible to make a 'structure determination', not with the classical X-ray accuracy but accurately enough for determination of structure type and structural relations.

Structure model

The structural model used for takéuchiite can be derived by the structure building operation of chemical twinning on the unit-cell level (Andersson & Hyde, 1974).

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Just a brief summary will be given [for a more extensive description see Bovin *et al.* (1981)]. The twin plane is parallel to (201) [in the unit cell given by Moore & Araki (1974)] of the pinakiolite structure and the twin axis is perpendicular to that plane and runs through the center of a boron triangle. If the twin operation is carried out repeatedly, with a repeat of two octahedral

Table 1. *Positional parameters for the metal atoms in takéuchiite*, Me_3BO_5, *space group Pnnm*

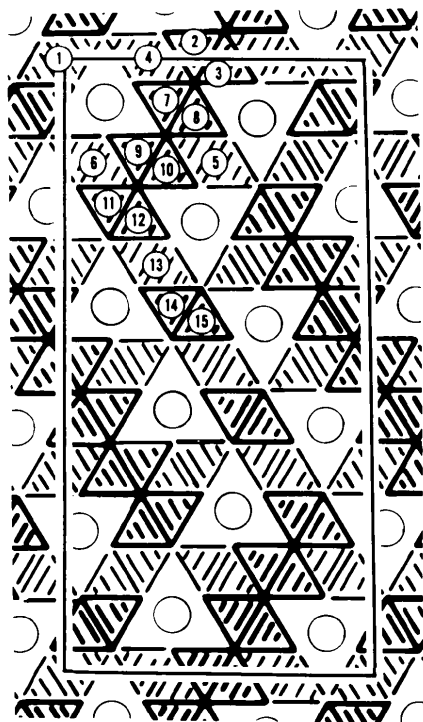| Atom Me	Position	x	y	z
Mn(1)	4(f)	0	0	0·248
Mn(2)	2(c)	0	$\frac{1}{2}$	0
Mn^{2+}(3)	2(d)	0	$\frac{1}{2}$	$\frac{1}{2}$
Mg(4)	8(h)	0·001	0·298	0·248
Mg(5)	8(h)	0·167	0·501	0·248
Mg(6)	8(h)	0·167	0·094	0·248
Mn(7)	4(g)	0·081	0·396	0
Mn^{2+}(8)	4(g)	0·081	0·396	$\frac{1}{2}$
Mn(9)	4(g)	0·167	0·298	0
Mn^{2+}(10)	4(g)	0·167	0·298	$\frac{1}{2}$
Mg(11)	4(g)	0·245	0·198	0
Mg(12)	4(g)	0·248	0·198	$\frac{1}{2}$
Mn(13)	8(h)	0·331	0·298	0·248
Mg(14)	4(g)	0·419	0·396	0
Mg(15)	4(g)	0·419	0·396	$\frac{1}{2}$

Fig. 1. The idealized structure of takéuchiite projected along **c** showing the coordination of metal-centered octahedra. The numbers in circles correspond to the metal atoms presented in Table 1. Large circles illustrate the positions of the boron atoms. **a** (27·50 Å) is vertical and **b** (12·614 Å) is horizontal.

layers, the ludwigite structure is obtained. A repeat of four octahedral layers generates the orthopinakiolite structure. The next possible twin repeat is every six octahedra and then the structure proposed for takéuchiite is generated. An idealized drawing of this structure projected along **c** is shown in Fig. 1. The metal atoms are each coordinated to six oxygen atoms in the form of more or less distorted octahedra which share corners and edges generating two types of wall. One wall, called an F wall by Takéuchi (1978), runs diagonally from the upper left corner of the unit cell through the center. The other kind of wall starts where the F wall ends and contains octahedra joined together in a zig-zag pattern passing through $\frac{1}{2}$,0,0 and 0,$\frac{1}{2}$,0. The boron atoms (big circles in Fig. 1) are coordinated to oxygen in the form of a planar triangle. The different metal-atom positions are numbered in Fig. 1 and correspond with the numbers given in parentheses in Table 1. X-ray diffraction data from single crystals show that possible space groups are *Pnnm* or *Pnn2*. We have chosen *Pnnm* for our calculations until a single-crystal X-ray crystal structure determination is finished. Takéuchi (1978) suggested that the positions 1 and 13 of the F wall should be occupied by Mn^{3+} (*cf.* Table 1). Octahedra 14, 15, 4, 5 and 6 are centered by Mg^{2+}. By comparison of the orthopinakiolite and pinakiolite structures with the present one, the positions of the centers of the octahedra of the zig-zag wall (octahedra 2, 3, 7, 8, 9 and 10) should be filled with Mn^{3+} and Mg^{2+}/Mn^{2+} alternating along **c**. We use full occupancy of Mn^{2+} and Mn^{3+} in these positions although in the cases of orthopinakiolite and pina-kiolite it was supposed that some of the Mg^{2+}/Mn^{2+} positions were only partly filled. However, crystals of pinakiolite, orthopinakiolite and takéuchiite are full of structural defects (Bovin *et al.*, 1981) which could lead to the partial occupancies obtained by refinement of X-ray data. The most difficult octahedra in which to decide the occupancy are 11 and 12 which belong to both the F wall and the zig-zag wall. Takéuchi suggests Mg^{2+} occupancy for both, but if the octahedra are chosen as members of the zig-zag wall they should be alternately occupied by Mg^{2+} and Mn^{3+}. We have tried both models. With one fourfold position of Mn^{3+} changed to Fe^{3+}, charge balance is obtained and the percentage of elements, 31·4% Mn, 4·5% Fe and 19·7% Mg, are close to the microprobe analysis (*cf.* Bovin & O'Keeffe, 1980). The occupancy suggested by Takéuchi is given in Table 1. It should be pointed out that some Mn in the table must be Mn^{2+} to balance the charge of the compound. In the image calculation, of course, the boron and the oxygen atoms are also included. Their coordinates are not tabulated but correspond to the large circles and the corners of the octahedra shown in Fig. 1. For atoms not on the mirror planes at $z = 0$ and $\frac{1}{2}$, we used the value $z = 0·248$ (by analogy with the structure of orthopinakiolite).

Experimental

Single crystals of the mineral were taken out of the dolomite/calcite bulk material and ground gently in acetone in an agate mortar. They were then deposited on a holey carbon film and transferred to a JEOL 100 B electron microscope operated at 100 kV. It was fairly difficult to find crystal flakes with edges thin enough, but a few good images were recorded with a standard point filament and an electron optical magnification of 500 000 to 800 000 ×. Correction of objective-lens astigmatism was carried out on the carbon support film by minimizing the contrast.
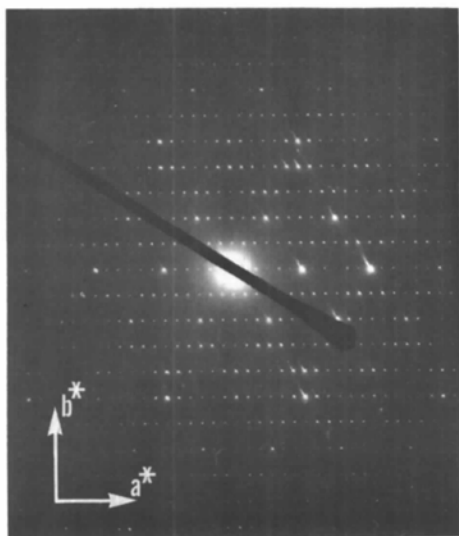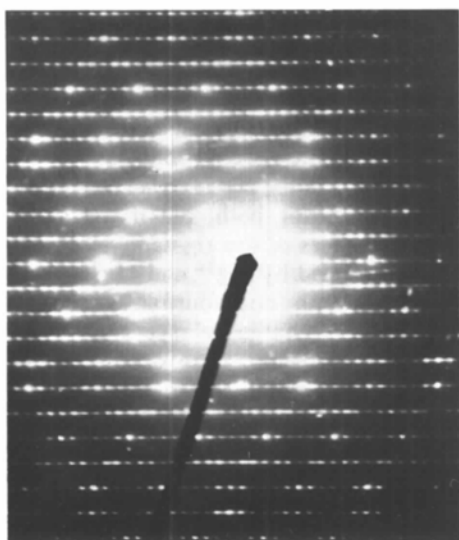
The image calculations were done using the multi-slice method (Goodman & Moodie, 1974; Cowley & Moodie, 1957) with a program developed (by MAO'K) from those of Fejes (1973), O'Keefe (1975) and Skarnulus (1976). Through-focus series of images were calculated from the structure parameters shown in Fig. 1 and for different crystal thicknesses: 30, 60, 90, 120 and 150 Å (slice thickness 3 Å which is equal to $c/2$). The best experimental image (Fig. 4) was obtained with a slight mistilt, the beam direction being $1\cdot3°$ from c, giving a diffraction pattern with the center of the Ewald sphere at $h = 7$ and $k = 7$. Parameters used in the calculation were: incident beam convergence $= 1\cdot2$ mrad, spherical aberration constant $C_s = 2\cdot2$ mm, focus spread due to chromatic aberration $= 150$ Å and aperture radius $= 0\cdot15$ Å^{-1} (Bovin et al., 1981).

Electron microscope images

Most crystals were orientated so that the electron beam was parallel to c. A typical diffraction pattern recorded in this direction is shown in Fig. 2(a). In the space group Pnnm, reflections $h00$ with $h = 2n + 1$ and $0k0$ with $k = 2n + 1$ are forbidden, but appear due to multiple scattering in electron diffraction. 050, for example, is quite strong as can be seen in Fig. 2(a). Some patterns show a streaking along a^* [as can be seen in the heavily exposed diffraction pattern in Fig. 2(b)] due to structural defects (Bovin et al., 1981). However, takéuchiite crystals, without any doubt, represent a new phase with an ordered structure, as may be seen from Fig. 3 where more than 2000 Å of a perfect crystal is shown.

(a)

(b)

Fig. 2. (a) Electron diffraction pattern of a well-ordered takéuchiite crystal recorded with the electron beam parallel to c. Note the pseudo-hexagonal nature of the pattern. (b) Electron diffraction pattern from a takéuchiite crystal containing defects causing streaking along a^*.
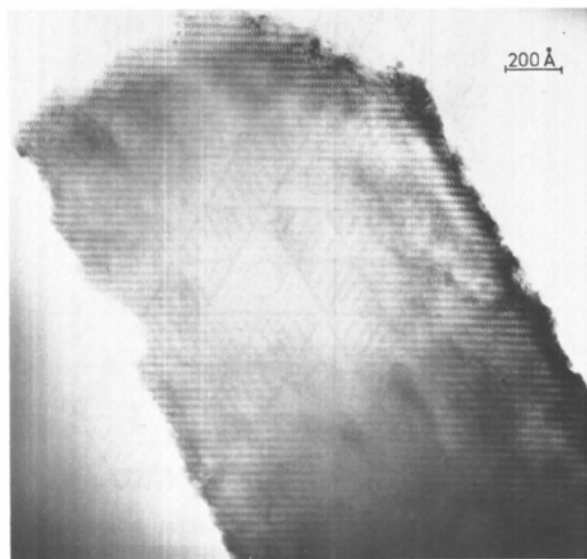

Fig. 3. Electron micrograph of a takéuchiite crystal. b is horizontal and a is vertical in the figure.

It was very difficult to find crystal edges thin enough to give an image directly interpretable with the crystal structure of Fig. 1. The best image recorded during the investigation is shown in Fig. 4. The corresponding electron diffraction pattern is shown in the lower right of the figure. The crystal is very thin at the edge, probably 20–40 Å, but becomes rapidly thicker. The crystal shows a few defects (marked with arrows) mainly caused by too-broad pinakiolite slabs between the chemical twinning planes (Bovin *et al.*, 1981).
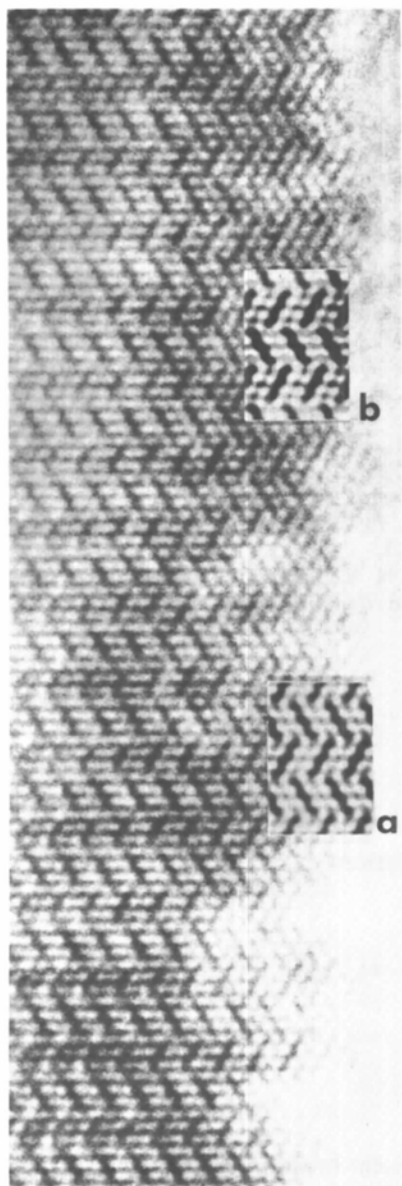

Fig. 5. High magnification of the crystal-edge image in Fig. 4 (**b** now horizontal in the figure). Calculated images are inserted at *a* and *b*. Image *a* is calculated with manganese in octahedron 11 (*cf.* Fig. 1) and with the electron beam parallel to **c** while image *b* is calculated with magnesium in octahedron 11 and with a mistilt given by the diffraction pattern in Fig. 4.

Image matching

It is difficult to estimate the thickness of the crystal and extent of underfocus exactly during the work in the microscope, therefore it is necessary to calculate several images varying those parameters. According to the theory, the best structure images should be recorded at an underfocus of ~ -1000 Å. In this case it was found that the best correspondence between the image in Fig. 4 and the calculated ones was obtained at an underfocus of -1050 Å. The image in Fig. 5 is a magnification of the crystal-edge image in Fig. 4. Two calculated images (*a*) and (*b*) are inserted for comparison. The image marked (*a*) is calculated with the octahedra marked 11 and 12 in Fig. 1 fully occupied with manganese and with the electron beam parallel to **c** and a crystal thickness of 90 Å. The black zig-zag bands correspond to the zig-zag octahedron wall in Fig. 1 and the white dots are the positions of the boron atoms. The calculated image has, in this case, higher symmetry than the experimental one because every second of the dark bridges between the black zig-zag walls is darker in the experimental image (as may be seen by looking at the image at a low angle in the **b** direction). At the end of each dark zig-zag band there is a gray 'tail' corresponding to the positions of the octahedra 11 and 12. In order to test the model of Takéuchi (1978) the occupancy of octahedron 11 was
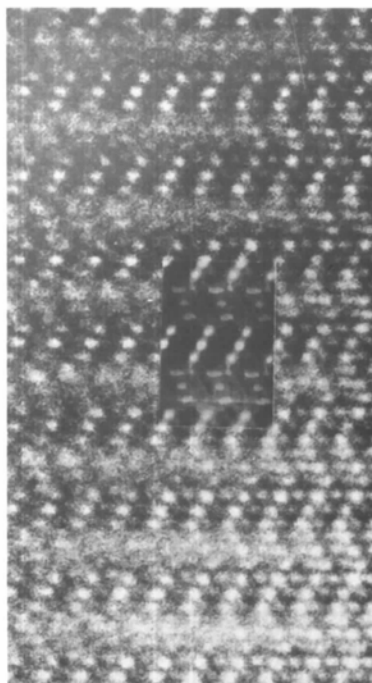

Fig. 6. High magnification of a thicker part of the crystal in Fig. 4 with a calculated image inserted. The image is calculated as (*b*) in Fig. 5 but with an underfocus of -1250 Å and a crystal thickness of 150 Å.
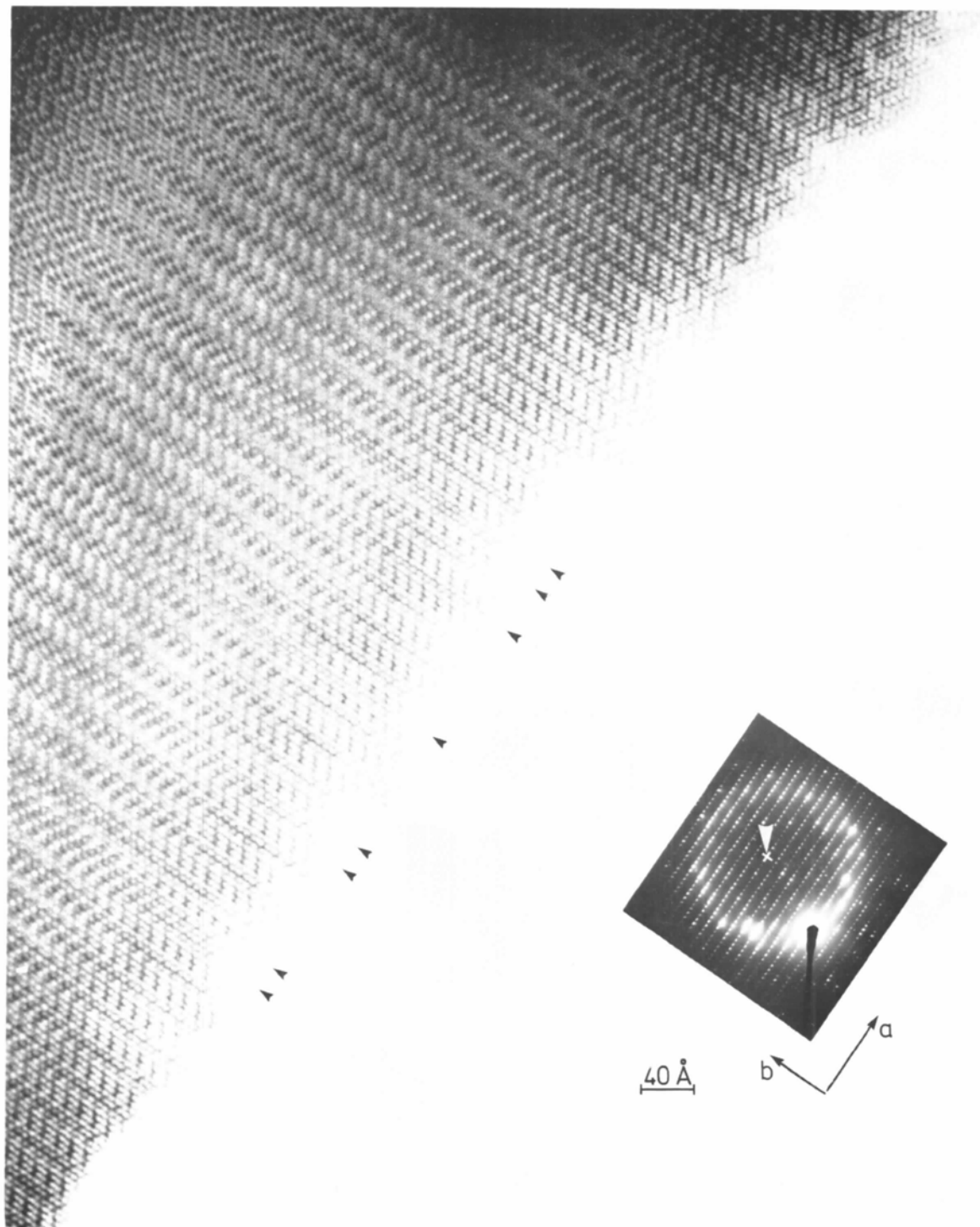
Fig. 4. Electron micrograph of a thin-edged takéuchiite crystal projected approximately along **c**. The deviation from the **c** direction is illustrated by the inserted electron diffraction pattern for which the center of the Ewald sphere is at 770. Defects in the crystals are marked with arrows and become easily observed if the reader looks at the image at a small angle to the paper.

changed from Mn^{2+} to Mg (as given in Table 1). Image (b) in Fig. 5 was then calculated with the beam slightly mistilted according to the diffraction pattern in Fig. 4. The image obtained has a lower symmetry and closely resembles the experimental one. The tail of the dark zig-zag band of octahedra corresponding to positions 11 and 12 is not so dark in this case, but it is impossible to judge from the image which occupancy is the best for octahedron 11. It was possible to match the experimental image of a thicker part of the crystal with an image calculated with an underfocus of -1250 Å and a crystal thickness of 150 Å as can be seen in Fig. 6. Thus it can be concluded that the structural model given in Table 1 is essentially correct, even if some doubt may remain about the cation ordering at certain positions.

Conclusions

This work shows that it is possible to test models of an unknown and complex structure by comparing experimentally obtained electron micrographs with calculated ones. It is of course first necessary to find intuitively a plausible model but this model can be changed by trial and error to give at least an approximate structure which can be very useful as a starting model for a classical X-ray structure determination. It should be of especially good help for compounds like takéuchiite with two long and one short axes.

References

ANDERSSON, S. & HYDE, B. (1974). *J. Solid State Chem.* **9**, 92–101.
BOVIN, J.-O. & O'KEEFFE, M. (1980). *Am. Mineral.* In the press.
BOVIN, J.-O. & O'KEEFFE, M. (1981). *Acta Cryst.* A**37**, 35–42.
BOVIN, J.-O., O'KEEFFE, M. & O'KEEFE, M. A. (1981). *Acta Cryst.* A**37**, 28–35.
COWLEY, J. M. & MOODIE, A. F. (1957). *Acta Cryst.* **10**, 609–619.
FEJES, P. L. (1973). Thesis, Arizona State Univ.
GOODMAN, P. & MOODIE, A. F. (1974). *Acta Cryst.* A**30**, 280–290.
KONNERT, J. A., APPLEMEN, D. E., CLARK, J. R., FINGER, L. W., KATO, T. & MIURA, Y. (1976). *Am. Mineral.* **61**, 116–122.
MOORE, P. B. & ARAKI, T. (1974). *Am. Mineral.* **59**, 985–1004.
O'KEEFE, M. A. (1975). Thesis, Univ. of Melbourne.
SKARNULUS, A. D. (1976). Thesis, Arizona State Univ.
TAKÉUCHI, Y. (1956). *Mineral. J.* **2**, No. 1, 19–26.
TAKÉUCHI, Y. (1978). *Recent Prog. Nat. Sci. Jpn*, **3**, 153–181.
TAKÉUCHI, Y., KAGA, N., KATO, T. & MIURA, Y. (1978). *Can. Mineral.* **16**, 475–485.
TAKÉUCHI, Y., WATANABÉ, T. & ITO, T. (1950). *Acta Cryst.* **3**, 98–107.
YAMNOVA, N. Y., SIMONOV, M. A. & BELOV, N. V. (1975). *Sov. Phys. Crystallogr.* **20**, 156–159.

Self-Crystallizing Molecular Models.
VI. Geometrical Supplement

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Abstract

Magnetic molecular models for simulation of crystal structures are supplemented by calculations based on geometrical idealization of the molecules. An answer is given to the question why solid nitrogen and acetylene present polymorphism whereas carbon dioxide does not. The different crystal structures of SiF_4, CF_4 and SiI_4 and those of UF_6, UCl_6 and WCl_6 are discussed.

Introduction

The molecular models with magnetic multipoles reported in this series of papers (Kihara, 1963, 1966, 1970, 1975; Kihara & Sakai, 1978) were invented for the purpose of explaining the crystal structures of nonpolar molecules.

If the molecules do not possess any appreciable electric multipoles, the crystal structures are governed