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Further Electron Optical Observations on Crystals of Antigorite

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Fringe systems with appropriate spacings have now been observed in electron micrographs of crystals of antigorite varieties which have cell parameters $A \simeq 40$ Å and $A \simeq 19$ Å. Furthermore, contiguous regions of a single crystal of a fibrous antigorite show spacings of 19·1 and 16·8 Å respectively. Possible relationships between the variable spacings and crystal structure are discussed.

Introduction

In a previous paper (Brindley, Comer, Uyeda & Zussman, 1958) it was shown that sets of parallel fringes could be observed in electron micrographs of a variety of antigorite (Yu Yen Stone). These fringes, spaced at about 100 Å, agreed in spacing and direction with the superlattice parameter (A) derived from electron diffraction patterns from the same crystal. The exact nature of the (so-called) superlattice is not yet known but it is probably associated with a periodic corrugation or undulation of the sheet-like crystal structure similar to that postulated for antigorites with smaller A parameter (Onsager, 1952; Zussman, 1954; Kunze, 1956, 1957, 1958).

The purpose of this communication is to report the occurrence of similar fringes on micrographs of other varieties of antigorite. It will be shown that sets of fringes of different spacing can occur in the same crystal.

Experimental observations

Fringes and electron diffraction patterns were observed and recorded with a Siemens Elmiskop I operating at 80 kV. In most cases the electron diffraction pattern was first recorded, using the selected area microdiffraction method; the image at this stage was recorded at a low magnification to establish the orientation of the image of the crystal with respect to its diffraction pattern. The specimen was then removed from the instrument which was re-aligned for fine-focus condenser operation. Micrographs of the fringes were recorded at an instrumental magnification of 37,500. This magnification was determined from micrographs of the $(20\bar{1})$ planes of copper phthalocyanine (Menter, 1956).

(*a*) *Antigorite from Antigorio, Italy*

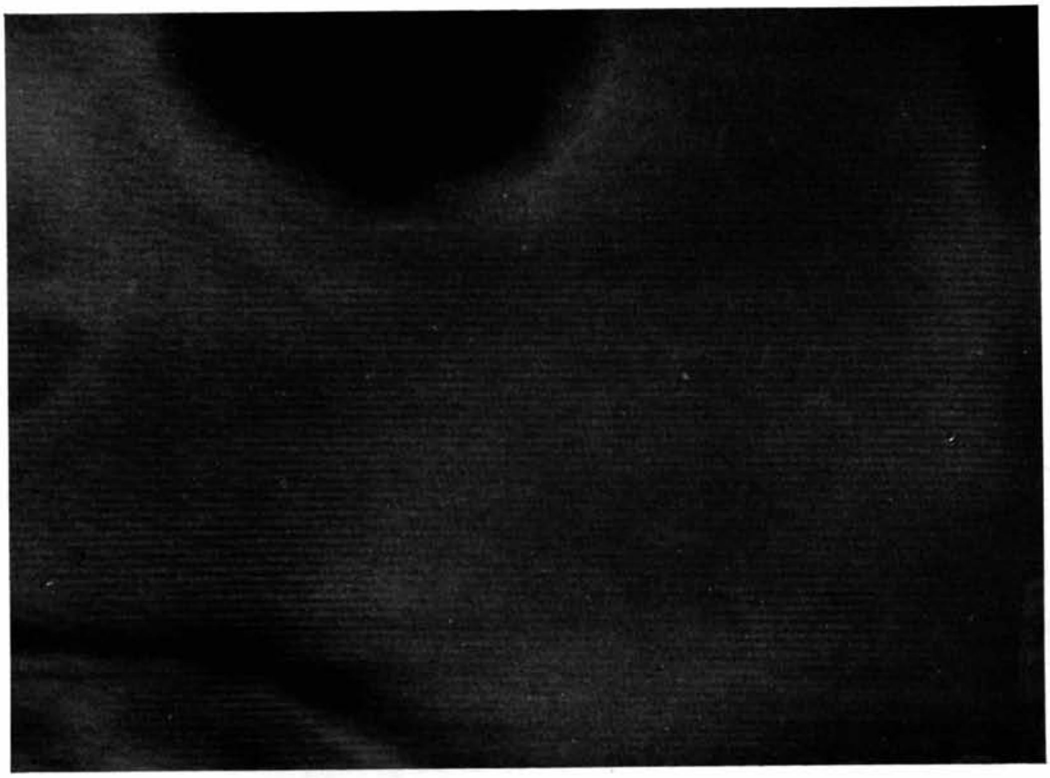
Diffraction patterns from most antigorites show a superlattice parameter in the range 35–45 Å but previously no electron-optical fringes could be obtained from such crystals (Brindley, Comer *et al.*, 1958). These fringes have now been observed in crystals of antigorite from Antigorio (Italy). Fig. 1 ((*a*) and (*b*)) shows a micrograph of part of such a crystal crossed by fringes with a spacing of 40 Å (±2 Å), together with a portion of the diffraction pattern from the same crystal. In the diffraction pattern, clusters of spots are in positions appropriate to a simple cell with approximate parameters $a = 5{\cdot}3$, $b = 9{\cdot}3$ Å. If the b spacing of the primary cell is assumed to be accurately 9·3 Å (the X-ray value) the separation of spots within clusters corresponds to a super cell in the a direction with parameter $A \simeq 40$ Å. It was confirmed that micrograph fringes were parallel to the b axis.

The fringes could also be observed by dark-field illumination. The illuminating system of the electron microscope was tilted so that the main beam fell beyond the edge of the objective aperture (of 50 microns diameter) and a low-order cluster of diffraction maxima was admitted by the aperture instead. As the dark-field image is formed by interference of beams of comparable intensity, the contrast of the fringe system is much enhanced (Fig. 2). This method has been used by Glossop & Pashley (1959) in the observation of periodic antiphase domain boundaries in copper–gold alloys.

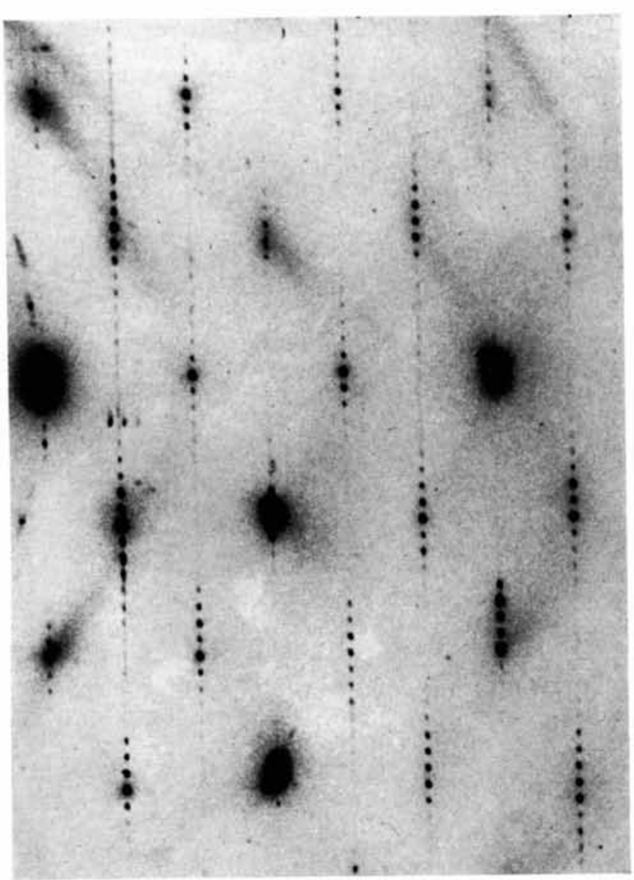
(*b*) *Picrolite*

Electron-diffraction patterns from most specimens of picrolite (a fibrous antigorite) exhibit an A parameter of approximately 40 Å. (As X-ray diffraction yields only fibre diagrams, selected area microdiffraction is the only method capable of providing single-crystal patterns.) Picrolite from Taberg (Sweden) however is unusual in having a much smaller superlattice cell with $A \simeq 18{\cdot}6$ Å.* Electron micrographs of this specimen show a clearly defined system of fringes (Fig. 3(*a*)), and electron diffraction from the

* See Zussman, Brindley & Comer, 1957, footnote on p. 150.



(*a*)



(*b*)

Fig. 1. (*a*) Antigorite (Antigorio). Electron micrograph of crystal showing fringes with spacing approx. 40 Å. (*b*) Antigorite (Antigorio). Part of electron diffraction pattern from crystal shown in 1(*a*).

Fig. 2. Antigorite (Antigorio). Electron micrograph obtained with dark field illumination.

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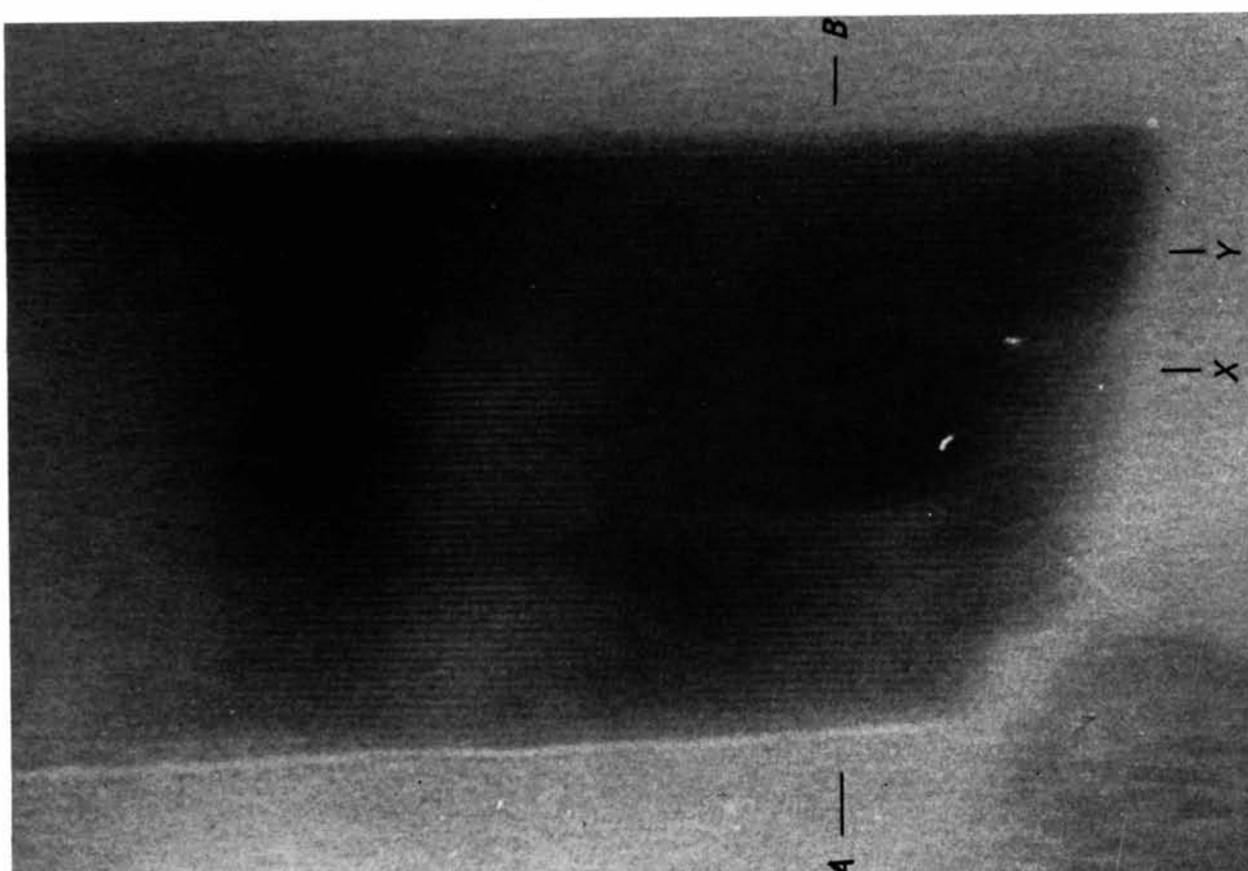
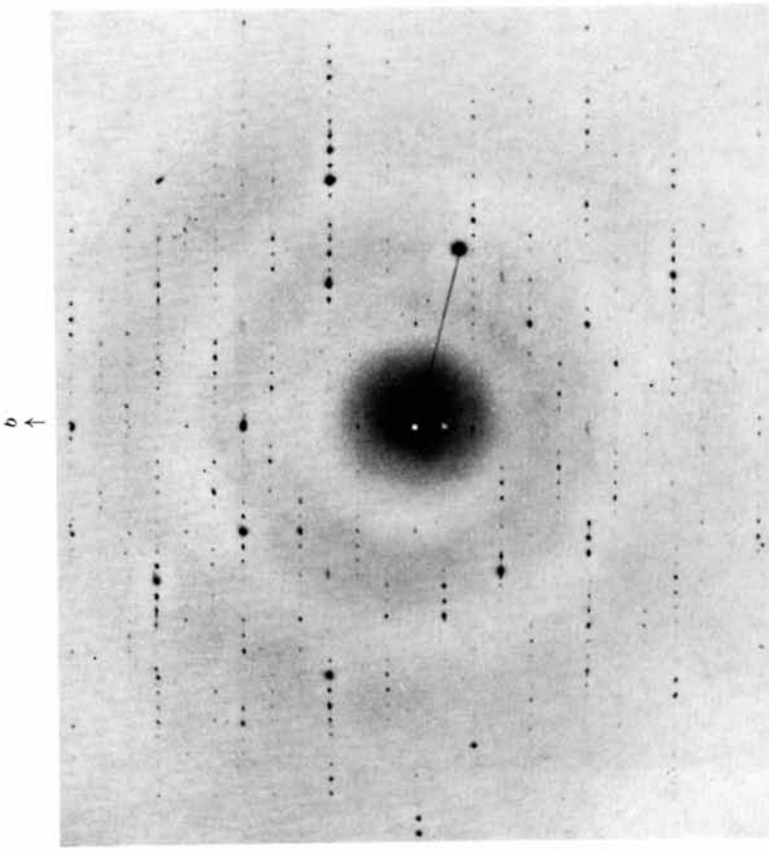


(a)



(b)

Fig. 3. (a) Picrolite (Taberg). Electron micrograph of crystal showing fringes. Fringe spacing between X–Y is 16·8 Å; elsewhere 19·1 Å. (b) Picrolite (Taberg). Electron diffraction pattern from crystal shown in Fig. 3(a).

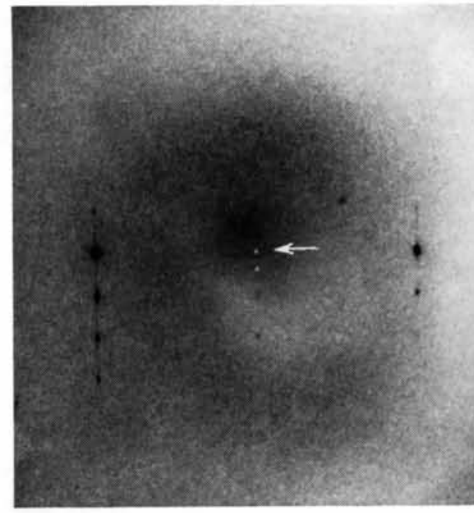


Fig. 4. Picrolite (Taberg). Central region of diffraction pattern shown in 3(b). Arrow indicates direct beam.

same crystal yields the pattern shown in Fig. 3(*b*). Measurement of fringe system and diffraction pattern gives $A \simeq 19$ Å in each case. It was again confirmed that the fringes were parallel to the *y* crystallographic direction.

In electron diffraction patterns from Yu Yen Stone and the Italian antigorite it is difficult to detect the zero-order satellites responsible for fringe formation. Their close proximity to the undiffracted beam results in almost complete obliteration by low-angle (inelastic) scattering. This difficulty is less acute with picrolite, due to greater separation between the central beam and the zero-order satellites. Using a 5 micron selector aperture and short exposure time, these satellites can just be observed (Fig. 4). In this figure two weak spots can be seen—one to the left and one to the right of the direct beam. (The direct beam, white due to photographic reversal, is marked by an arrow).

A remarkable feature of the fringe system in the picrolite crystal shown in Fig. 3(*a*) is that the spacing is not everywhere the same. Fringes in the region $X-Y$ are more closely spaced than those elsewhere. In Fig. 5 the positions of the fringes along the normal $A-B$ (as measured by a travelling microscope) have been plotted against fringe number. The spacing, which is given by the slope of the graph, changes abruptly at fringe number 8, from 19·1 to 16·8 Å, and back again to 19·1 Å at fringe number 18. The probable error in the above values, derived from the scatter of points about the straight lines in Fig. 5,

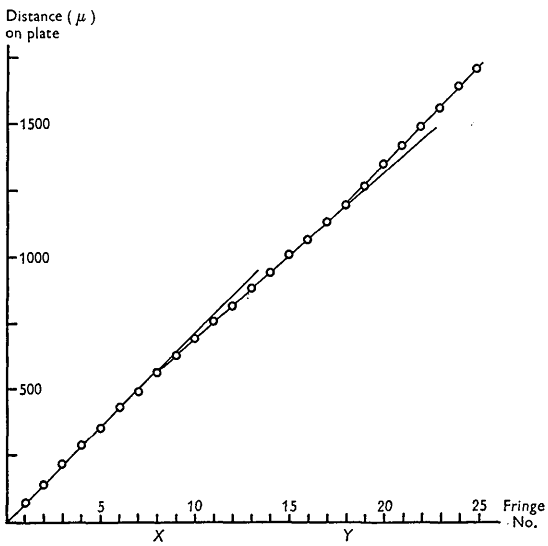


Fig. 5. Positions of successive fringes as measured along $A-B$ in micrograph 3(*a*) (Magnification of original plate × 37,500).

is ±0·2 Å, and the difference in the two spacings is thus 2·3±0·3 Å. Uncertainty of the magnification factor may introduce a systematic error of up to 10%. The fringes were not visible in all parts of the crystal so that it was not possible to determine whether or not the different spacings were maintained throughout its length.

The corresponding diffraction pattern (Fig. 3(*b*)) does not show two values for the *A* parameter but, in some parts of the pattern, streaks pass through the spots in the *A* direction, indicating some irregularity parallel to the *A* axis. Some very faint additional spots close to the main spots and colinear with them are also discernible on the original diffraction pattern.

Discussion

These experimental observations agree with previous work in pointing to considerable variability in the superlattice periodicity in crystals of antigorite. Variations were initially discovered between specimens from different localities, then in different crystals from a single specimen, and now in different regions of a single crystal. Electron diffraction and direct imaging by electron microscopy show that quantitatively the variability is of two kinds.

First, the spacings so far observed fall into three definite ranges:

Superlattice spacing	Occurrence
16– 19 Å	Picrolite (Taberg)
35– 45 Å	Antigorite (Antigorio); other antigorites and picrolites; some crystals of Yu Yen Stone
80–110 Å	Antigorite (Yu Yen Stone)

It will be interesting to see if the small spacing observed in picrolite can be explained on the basis of the 'alternating wave' structure put forward by Kunze (1956, 1957, 1958).

Secondly, within the above ranges certain values of *A* are 'preferred'; these preferred values are separated by intervals of approximately $\frac{1}{2}a$ (= 2·6 Å).

The models already suggested for the antigorite structure imply that the longer parameter (*A*) is controlled by the number of half-cell ($\frac{1}{2}a$) units which occur between the periodic irregularities responsible for the super cell (Kunze, 1957); the recent observations clearly support this theory. Variability in this number can apparently occur even in one crystal as in the case of picrolite (Taberg) where two fringe systems differing in spacing by approximately $\frac{1}{2}a$ have been observed adjoining one another.

One of the possible configurations which could be responsible for the two fringe spacings observed is illustrated in Fig. 6, which shows the Si–O network only. The cells to the left of the line marked *P* would give a fringe spacing of approximately $7 \times 2{\cdot}65$ Å = 18·6 Å and those to the right $6 \times 2{\cdot}65$ Å = 15·9 Å. (The true cell to the right of *P* has $A = 12 \times 2{\cdot}65$ Å, but since the network is centred, odd orders of *h*00 reflections will be missing and the fringe spacing will be halved.) In antigorite from Mikonui (Kunze, 1958) discontinuities in the structure occur through inver-

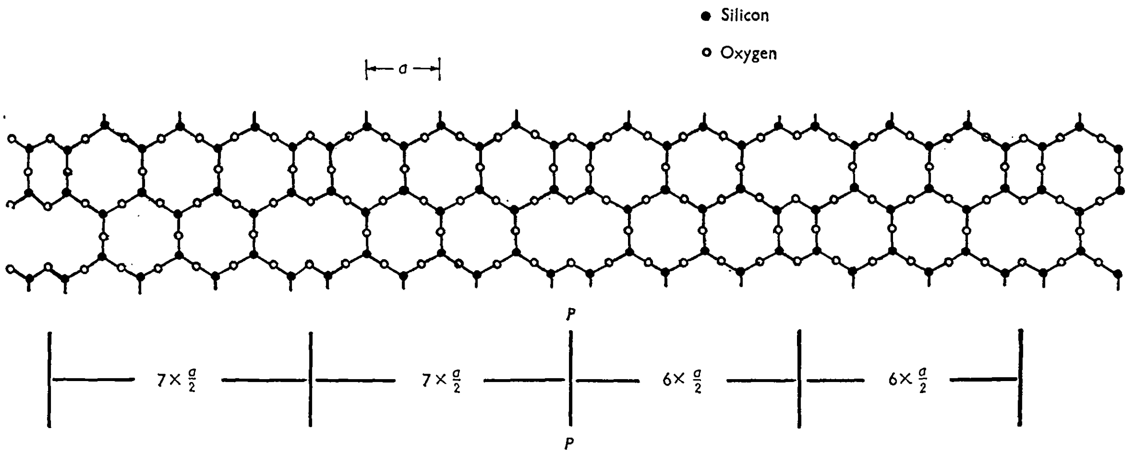


Fig. 6. A possible configuration of the Si–O layer which would produce fringe systems differing by $\frac{1}{2}a$.

sions of the sheet, and half of the inversions are associated with the occurrence of four- and eight-membered rings of tetrahedra. In the picrolite examined, curvature and inversion of the fundamental layers may or may not take place, since it is conceivable that regular sequences of six-, four- and eight-membered rings could suffice to produce the super-cell. Alternatively a model could be devised containing only six-membered rings in which sheet inversions alone produce a true cell of $6 \times 2{\cdot}65$ Å to the right of *P*. Allowing for experimental errors the two fringe spacings measured could correspond to either 7 and 6 times or 8 and 7 times 2·65 Å. The electron diffraction patterns from picrolite suggest that the former pair of values is more likely to be correct.

With decreasing super-cell parameter, as in picrolite compared with antigorite, the small cell with $a \simeq 5{\cdot}3$ Å loses its significance in the structure. This is reflected in the less obvious clustering of spots in the electron diffraction pattern.

Uyeda, Masuda, Tochigi, Ito & Yotsumoto (1958) have suggested the use of antigorite (Yu Yen Stone) superlattice fringes as a standard for magnification calibration in electron microscopy. Even if electron diffraction is used to check the spacing, the possibility of the occurrence of more than one spacing in the image still exists, so that a calibration method which uses antigorite must be applied with caution.

Note added in proof: — Hashimoto and Yotsumoto (1959) have recently reported the occurrence of a spacing anomaly in electron microscope images of certain lattices, explicable by the dynamical theory of electron diffraction in terms of a bending or a thickening of the crystal. We have not yet considered in detail if the variable spacing in images of picrolite could be explained in this way but the magnitude of the effect in picrolite (about 12 %) is much greater than that observed by Hashimoto and Yotsumoto in copper phthalocyanine.

References

Brindley, G. W., Comer, J. J., Uyeda, R. & Zussman, J. (1958). *Acta Cryst.* **11**, 99.

Glossop, A. B. & Pashley, D. W. (1959). *Proc. Roy. Soc.* A. (In press).

Hashimoto, H. & Yotsumoto, H. (1959). *Nature*, Lond. **183**, 1001.

Kunze, G. (1956). *Z. Kristallogr.* **108**, 82.

Kunze, G. (1957). *Fortschr. d. Mineralogie*, **35**, 46.

Kunze, G. (1958). *Z. Kristallogr.* **110**, 282.

Menter, J. W. (1956). *Proc. Roy. Soc.* A, **236**, 119.

Onsager, L. (1952). *Brit. J. Appl. Phys.* **3**, 281.

Uyeda, R., Masuda, T., Tochigi, H., Ito, K. & Yotsumoto, H. (1958). *J. Phys. Soc. Japan*, **13**, 461.

Zussman, J. (1954). *Miner. Mag.* **30**, 498.

Zussman, J., Brindley, G. W. & Comer, J. J. (1957). *Amer. Min.* **42**, 133.