Table 2. *Face-centred cubic structures*

	Present method		Normal procedure	
Material	α	a_0 (kX.)	α	a_0 (kX.)
Co–Ni (31 wt. % Ni)	0·022	3·529(0)	0·022	3·529(5)
Co–Fe (7·9 wt. % Fe)	0·023	3·544(3)	0·023	3·544(5)
Cu–Al (4 wt. % Al)	0·016	3·631(2)	0·013	3·630(7)
Cu–Al (6 wt. % Al)	0·031	3·644(7)	0·031	3·642(2)
Pure silver	—	4·077(7)	—	4·0775*

* Accepted value.

become larger for increasing α, presumably because the accuracy of the method of locating the α_1 peak positions of the lines decreases with increasing α. Table 2 also gives a result of a_0 for pure silver, where it was found that the a' values lay on a good straight line, from which it was concluded that the faulting was negligible. The agreement between the value as found and the accepted value for pure silver is good.

6. Conclusions

For materials which it is difficult to strain-anneal satisfactorily, and where difficulties of grain size preclude the use of solid rod specimens in conventional powder cameras, the analytical method may be applied to deformed powders using a Geiger-counter diffractometer. Even in the unfavourable case of faulted face-centred cubic structures, lattice spacings may be obtained to $\pm 0{\cdot}001$ kX. for values of α up to 0·02, and for body-centred cubic structures the accuracy is considerably greater.

For more complex structures, complications from deformation faulting are improbable and, as for the close-packed hexagonal structures referred to above, the simple method should be applicable, provided that sufficient lines can be obtained which are not overlapped by other reflexions.

The time involved is of the order of three times that of the conventional method, and if allowance is made for the time of annealing, which in certain cases may not even then be satisfactory, it is clear that the above procedure is practicable.

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References

ANANTHARAMAN, T. R. & CHRISTIAN, J. W. (1953). *J. Appl. Phys.* **4**, 155.
CHRISTIAN, J. W. (1954). *Acta Cryst.* **7**, 415.
FRANK, F. C. & NICHOLAS, J. F. (1953). *Phil. Mag.* **44**, 213.
GEVERS, R. (1954). *Acta Cryst.* **7**, 337.
PATERSON, M. S. (1952). *J. Appl. Phys.* **23**, 805.
SUTTON, A. L. & HUME-ROTHERY, W. (1955). *Phil. Mag.* **46**, 1295.
WILSON, A. J. C. (1949). *X-Ray Optics*. London: Methuen.

Acta Cryst. (1958). **11**, 99

Electron-Optical Observations with Crystals of Antigorite*

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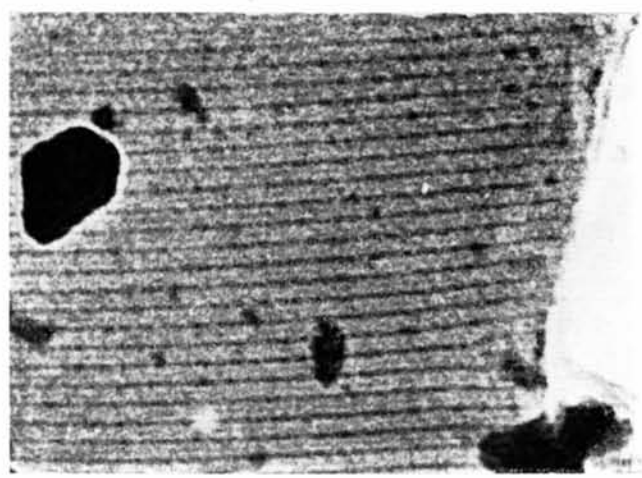
Electron-optical fringes are obtained from an antigorite (Yu Yen Stone) which agree in spacing and direction with the superlattice parameter $a = 100 \pm 10$ Å determined by electron diffraction. The nature of the superlattice is discussed.

In the course of a combined electron-diffraction (E.D.) and electron-microscope (E.M.) study of serpentine minerals (Zussman, Brindley & Comer, 1957, hereinafter labelled Z.B.C.), an unusual phenomenon was observed with a variety of antigorite from Manchuria called 'Yu Yen Stone', (U.S. National Museum, No. 94356). This material is massive in the hand specimen but finely ground powder yields single platy crystals suitable for E.D. and E.M. study. The phenomenon is illustrated in Fig. 1, which shows high-magnification

* Contribution No. 57-15, College of Mineral Industries.

(*a*)



(*b*)

Fig. 1. Electron-optical fringes obtained with Yu Yen Stone (antigorite) crystals. (*a*) Taken by J. J. Comer, (*b*) taken by H. Tochigi, Akashi Manufacturing Company, Tokyo.
Fringe separation 100 Å ± 10 Å.

electron micrographs of Yu Yen Stone crystals which are traversed by parallel straight evenly spaced fringes about 100 Å apart. The best fringes are obtained usually from crystals which appear in the electron microscope to be rather thin. The fringes are 'non-localized' and are visible with the same spacing and equally clearly at positions above and below the plane of the focused image.

E.D. patterns of many antigorite specimens, including Yu Yen Stone, have been studied previously (Z.B.C.). They show 'layer' lines corresponding to a spacing $b \simeq 9{\cdot}2$ Å, and along the layer lines are closely spaced spots corresponding to an a parameter between 33 and 45 Å, depending on the particular specimen of antigorite. Fig. 2 shows an enlargement of part of a

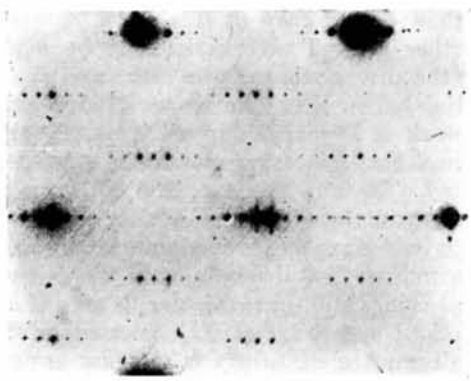


Fig. 2. Part of an electron-diffraction diagram of an antigorite crystal from Antigorio, Italy, showing closely spaced diffractions parallel to the a axis.

typical antigorite diffraction pattern with $a = 38{\cdot}5$ Å, $b = 9{\cdot}2$ Å, and the closely spaced spots are seen to run almost continuously across the diagram. Fig. 3 shows a similar enlargement of part of a diagram obtained

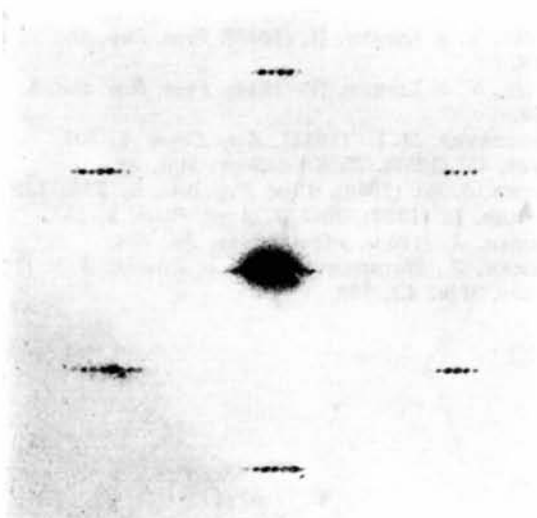


Fig. 3. Part of an electron-diffraction diagram of Yu Yen Stone antigorite showing an a parameter of about 100 Å.

with the Yu Yen Stone antigorite. The b parameters obtained from Figs. 2 and 3 are practically identical, but the closely spaced spots in Fig. 3 tend to be restricted to clusters and correspond to an a parameter of about 100 Å. The strong reflections in Fig. 2 and the clusters in Fig. 3 correspond to a repeat distance of about 5·3 Å parallel to a. From this and other evidence (see Z.B.C.) the antigorite structure is considered to be a hexagonal sheet type with

$$a = 5{\cdot}3 \text{ Å}, \quad b = 9{\cdot}2 \text{ Å}, \quad b/a = \sqrt{3},$$

which is modulated by a superstructure along a which gives rise to the closely spaced spots in the E.D. diagrams. The close agreement between the superlattice parameter and the spacing of the electron-optical fringes raises many interesting questions.

Experimental data

For observation and measurement of the fringe systems instrumental magnifications of approximately 19,000× were used in most cases, followed by a further 12× photographic magnification. The electron microscope was calibrated by use of a carbon replica of a grating having 15,000 lines in.$^{-1}$. The total separation of as many consecutive fringes as possible was measured to obtain the fringe spacing for each specimen. Table 1 lists a number of these spacings, the average

Table 1. *Electron-optical fringe spacings for Yu Yen Stone antigorite*

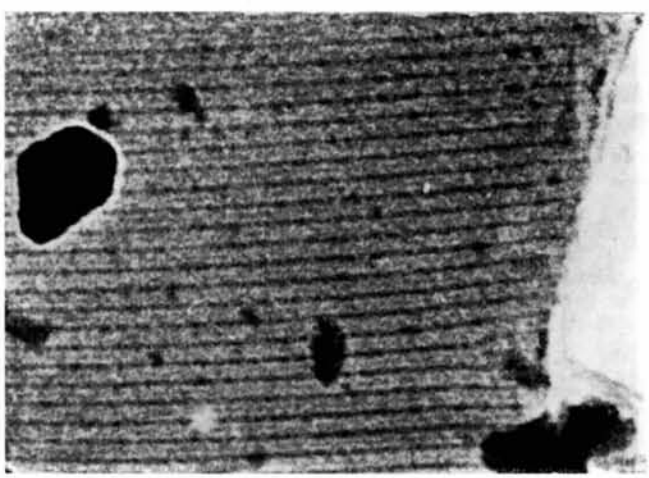
Fringes counted	Average spacing (Å)	Fringes counted	Average spacing (Å)
22	104	4	105
8	97	13	97
13	104	20	102
15	99	6	114
7	92	5	106

of which is 102±5 Å. Electron-diffraction diagrams were calibrated with respect to ring patterns of MgO and an average value of the a parameter was obtained, namely 103±5 Å.

The diffraction and electron-optical measurements were obtained in many cases for the same crystals so that the identity of the spacings and the fact that the fringes ran in a direction normal to the a^* axis of the diffraction diagram were established beyond any doubt. However, it was not always possible to make both measurements on the same crystal, and many examples were found in which one type of observation could be made more clearly than the other.

Correlation of the fringe separation with the lattice parameter a was established by taking E.M. and E.D. patterns for the same crystal, without movement of the specimen holder in the instrument. At the high magnification required to see the fringes, there is some optical rotation of the image. Micrographs were recorded, therefore, at low and high magnifications in

(*a*)



(*b*)

Fig. 1. Electron-optical fringes obtained with Yu Yen Stone (antigorite) crystals. (*a*) Taken by J. J. Comer, (*b*) taken by H. Tochigi, Akashi Manufacturing Company, Tokyo.
Fringe separation 100 Å $\pm$ 10 Å.

addition to the diffraction diagrams. The results showed without any uncertainty that the optical fringes run normal to the *a* crystallographic axis, and therefore that there is a true physical relation between the two sets of observations.

Some Yu Yen crystals give a smaller *a* parameter of about 42 Å, which is more nearly in accordance with data obtained for many other antigorites. Clearly defined optical fringes have not been obtained so far with antigorites having *a* parameters in the range 33–45 Å, and the reason for this is not yet clear.

Comparison with results by Menter (1956)

The fringe systems obtained with Yu Yen Stone appear to be similar to those observed by Menter (1956), using copper and platinum phthalocyanines; the latter fringes were attributed to interference between the direct beam and a very strong first-order diffraction from planes of high scattering power arising from the arrangement of the platinum atoms.

A similar explanation cannot be put forward in the case of Yu Yen Stone since the atoms involved, Si, Mg and O, are of similar scattering power and are distributed more or less uniformly across the large unit cell of the structure.

Other points of difference are that for Pt phthalocyanine an interplanar spacing of 11·97 Å is involved and in consequence the diffracted beams lie at considerably greater angles with respect to the direct beam, so that no more than one or perhaps two orders of diffraction can contribute to the interference pattern, owing to the apertures of the microscope. In any case, aberrations would be expected to distort the correct phase relations for higher-order diffractions. For Yu Yen Stone the first few orders subtend only very small angles so that phase relationships may be preserved and several orders contribute to the formation of sharp fringes. Such low-order spectra are too close to the direct beam to be observed directly in the E.D. patterns. However, since similar spectra are observed at each of the nodes of the reciprocal lattice corresponding to the small $5{\cdot}3 \times 9{\cdot}2$ Å pseudo-cell, their occurrence in the region of the zero node is to be expected.

Discussion

An explanation for the production of the fringes must be sought in the superlattice of the antigorite structure. A corrugated or undulating structure has been suggested by Onsager (1952) and considered in more detail by Zussman (1954) and Kunze (1956). A 'rectified wave' structure is feasible if a modified structure is assumed at the cusps joining successive half-waves. An 'alternating wave' structure is feasible if the structural half-waves are inverted with respect to one another with the necessary structural adjustments where the half-waves join one another. Zussman found it impossible on the basis of X-ray data to distinguish between these possibilities, although he considered the rectified wave 'to be structurally more plausible'. It is conceivable that both kinds of superlattice exist and that the rectified waveform has the shorter *a* parameter (33–45 Å) and the alternating wave the longer *a* parameter, ($\simeq$ 100 Å). This is a matter of conjecture rather than of certainty at this stage.

A further general observation can be made concerning the distribution of the diffracted spots from the modulated lattice. Hargreaves (1951), extending earlier work of Daniel & Lipson (1943, 1944), shows that when the scattering power in a structure is modulated, 'the amplitude of the satellites is thus independent of the order of the main reflection', but when the lattice spacing is modulated, 'the amplitude of the satellites thus depends upon the order of the main reflection, and, in particular, is zero if h [order of reflection] is zero'. The E.D. patterns of Yu Yen Stone fall much more nearly in the first group where the scattering factor is modulated.

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References

Daniel, V. & Lipson, H. (1943). *Proc. Roy. Soc.* A, **181**, 368.
Daniel, V. & Lipson, H. (1944). *Proc. Roy. Soc.* A, **182**, 378.
Hargreaves, M. E. (1951). *Acta Cryst.* **4**, 301.
Kunze, G. (1956). *Z. Kristallogr.* **108**, 82.
Menter, J. W. (1956). *Proc. Roy. Soc.* A, **236**, 119.
Onsager, L. (1952). *Brit. J. Appl. Phys.* **3**, 281.
Zussman, J. (1954). *Miner. Mag.* **30**, 498.
Zussman, J., Brindley, G. W. & Comer, J. J. (1957). *Amer. Min.* **42**, 133.