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Twinning in the superlattice structure of CuSe, synthetic klockmannite.

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Electron diffraction data have been obtained showing evidence of the hexagonal superlattice structure of CuSe, and confirming an earlier theory of twinning in this structure.

The crystal structure of klockmannite, both in the natural and synthetic forms, has been studied in some detail by Earley (1949) and Berry (1954), who established that it was substantially isomorphous with covellite, CuS, although some indication of a twelvefold superlattice was suggested. The space group was stated to be hexagonal $P6_3/mmc$, with $a = 3{\cdot}94$ and $c = 17{\cdot}25$ Å. Taylor & Underwood (1960) attempted a more detailed analysis of the superlattice structure, and proposed a model in which the hexagonal superlattice had a unit cell with $a_{\text{sup}} = \sqrt{13}\,a$, and in which a and a_{sup} had different directions. They further proposed that twinning in the superlattice structure on (1120) planes produces spots in reciprocal space which appear to lie on a reciprocal lattice with $a^*_{\text{sup}} = a^*/13$, and that the early workers incorrectly observed this relationship as $a^*_{\text{sup}} = a^*/12$.

The structure of this material is being studied in this department by X-ray diffraction and electron microscopy. The detailed structure of the superlattice has not yet been elucidated, but preliminary electron diffraction results have been obtained which confirm directly the hypothesis of Taylor & Underwood. Using the technique of selected-area diffraction, patterns have been obtained from a single twin component which clearly show the superlattice reflexions postulated by these workers.

Specimen

Synthetic CuSe was obtained commercially from Koch Light Laboratories Ltd., Colnbrook, Bucks., England, who prepared it by dry fusion of the powdered elements in quartz tubes. The resulting black mass was crushed, and the thin fracture edges formed in this process were used as the specimens for electron diffraction. Two mounting techniques were tried: (*a*) sprinkling the powder on a glass slide, tapping off the large grains, and coating the residue with carbon, followed by stripping and mounting on grids; (*b*) simply sprinkling the powder on grids previously given a very thin coating of vacuum grease to improve adhesion of the particles. Method (*a*) produced smaller particles, but for some reason not yet understood gave almost no indication of the CuSe superlattice structure. Also, particles were extremely prone to decomposition in the electron beam, giving off selenium vapour. Method (*b*) gave fewer thin edges, but less tendency to decomposition and much more evidence of the CuSe superlattice.

The specimens were examined in an A.E.I. EM6G microscope.

Results

Figs. 1–3 show some of the diffraction patterns obtained. Fig. 1 shows the pattern from the twinned structure. The strong lattice reflexions indicate that the orientation is near [0001]. Several other patterns were obtained of inclined sections of the reciprocal lattice *e.g.* $[31\bar{4}\bar{1}]$, $[12\bar{3}\bar{1}]$, which show that if the specimen is tilted away from the [0001] direction, the superlattice reflexions do not disappear as expected, but the distribution in the plane of the section simply elongates perpendicular to the tilt axis. This indicates that there is pronounced streaking of the superlattice reflexions along the [0001] direction. It appears, therefore, that while the lattice is ordered along the c axis, the superlattice is disordered in this direction. This conclusion is confirmed by X-ray data (S. F. Darlow, unpublished).

Fig. 2 shows a pattern obtained from a single twin component. The superlattice reflexions are as predicted by Taylor & Underwood; the relationship $a^* = \sqrt{13}\,a^*_{\text{sup}}$ and the different orientations of the lattice and superlattice are apparent. The diffraction pattern is not in focus: many attempts have been made to obtain further patterns of this type with a view to improving the quality, but it has not proved possible so far, using present techniques, to repeat this pattern. Fig. 3 shows a similar example, although in this case both twin orientations are present, but with one orientation predominating.

References

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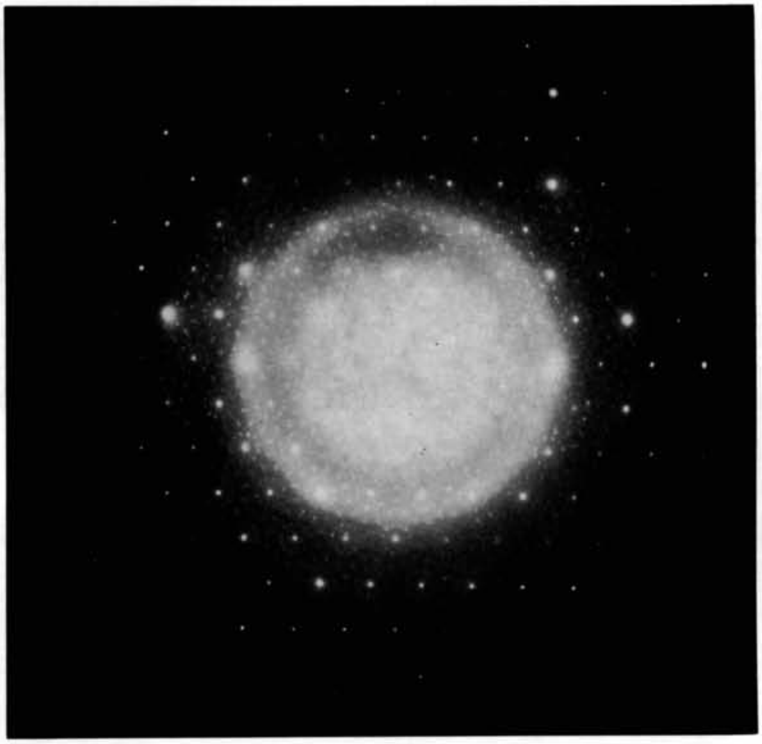

Fig. 1. Electron-diffraction pattern of CuSe. The specimen is twinned on $(11\bar{2}0)$ planes, and the orientation is near [0001].

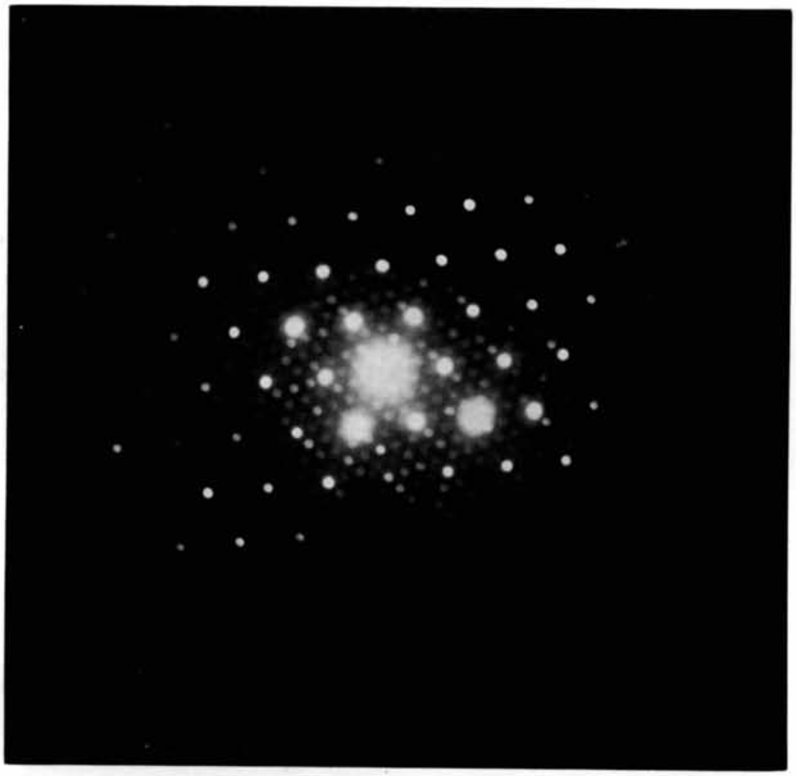

Fig. 2. CuSe: single twin component. Orientation $[12\bar{3}\bar{1}]$.

Fig. 3. CuSe: one twin component predominating. Orientation $[31\bar{4}\bar{1}]$.