2_1-operation, whereas the reflexion (200), for which the structure amplitude vanishes in relation with the 4_1-operation, is not forbidden.

The present result, further, can be applied also to the symmetrical spot pattern given by the incident beam parallel to a zone axis which is not the principal axis. Fig. 2 shows the spot pattern obtained from a crystal of diamond-type structure with the incident beam parallel to $[01\bar{1}]$-axis. In this pattern, the reflexion (200), for which the structure amplitude vanishes by the presence of the screw axis 4_1 perpendicular to $[01\bar{1}]$, is not forbidden by the same reason as considered above. The reflexion (222) is also not forbidden because the extinction of the structure amplitude of it is due to the special positions of atoms and is not directly related to the symmetry operations.

An easy understanding of the above results may be obtained in the following way. The appearance of forbidden reflexions is caused by the dynamical double reflexions, and the amplitude of doubly reflected wave on the net planes (hkl) and ($h'k'l'$) may be regarded as proportional to $V_{hkl} \cdot V_{h'k'l'}$ at least approximately. In the example of Fig. 1 we have the relations $V_{hk0} = -V_{h\bar{k}0}$ (h: odd) and $V_{hk0} = V_{h\bar{k}0}$ (h: even), assuming the coordinate origin on the 4_1-axis parallel to the x-axis. Then, the double reflexions can not contribute to (100) because the products $V_{hk0} \cdot V_{1-h,\bar{k},0}$ and $V_{h\bar{k}0} \cdot V_{1-h,k,0}$ have always the opposite sign of one another, while (200) may appear because $V_{hk0} \cdot V_{2-h,\bar{k},0}$ and $V_{h\bar{k}0} \cdot V_{2-h,k,0}$ have the same sign. The similar argument can be applied to explain the appearance of (200) in Fig. 2.

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A twinning interpretation of 'superlattice' reflexions in X-ray photographs of synthetic klockmannite, CuSe.

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Introduction

X-ray diffraction studies of klockmannite were begun by Earley (1949) who observed strong X-ray reflexions consistent with a hexagonal unit cell of dimensions $a = 3{\cdot}94$ Å, $c = 17{\cdot}25$ Å, and containing six CuSe units. Its similarity with covellite (CuS) suggested that the compounds were isostructural and Berry (1954) gave a possible solution which resembled that for covellite, but the agreement between the observed and calculated reflexions was rather unsatisfactory. Earley and Berry both noted the occurrence of 'superlattice' reflexions corresponding to a much larger cell but did not investigate them further. Dr Gabrielle Donnay suggested that the extra reflexions might be investigated by optical-transform methods. She supplied us with photographs taken with Cu $K\alpha$ radiation using synthetic crystals in the form of thin hexagonal plates prepared by Dr G. Kullerud of the Geophysical Laboratory, Washington D.C. The complete structure has not been determined, but in view of the current interest in the twinning phenomena which occur in various minerals (e.g. Donnay, Donnay & Kullerud, 1958) it was thought that a short note on the progress made so far would be worth publishing.

The problem

Fig. 1 is a representation of the $hk0$ section of the weighted reciprocal lattice; there are no indications of any multiplication of the c axis and for all the three lattices discussed later the c dimension remains 17·25 Å. The very strong reflexions (indicated conventionally by encircled discs) correspond to the cell of side $a = 3{\cdot}94$ Å which will be referred to as the sub-cell. The additional reflexions lie on a hexagonal reciprocal net which corresponds in real space to a cell of side $13 \times a^{\text{sub}} = 51{\cdot}2$ Å. This would contain 1,014 CuSe units, and, at the beginning of the present investigation, was taken to be the true cell of the structure. Dr Donnay observed that the extra reflexions also lay on circles surrounding the strong reflexions (see Fig. 1). It was from this point that the optical-transform investigation began. Details of the steps in the solution will be published when the complete structure has been worked out, and only a brief outline will be given here.

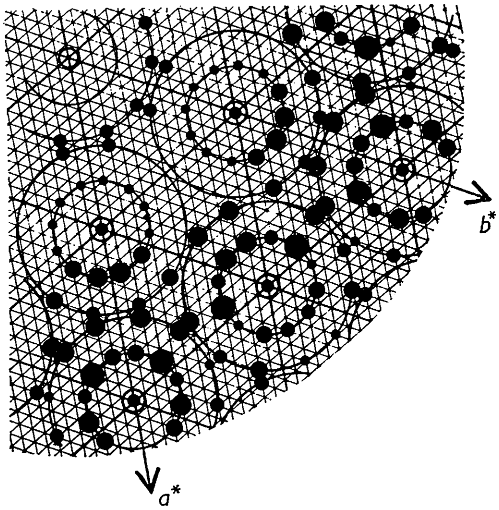

Fig. 1. Part of the $hk0$ section of the weighted reciprocal lattice; a^* and $a^*/13$ nets indicated. The encircled reflexions are very intense compared with the others.

Method of approach

The complete weighted reciprocal-lattice section was treated as the product of three functions. The first is a lattice function defining the points of the fine reciprocal lattice corresponding to the super-cell. The second is a function, zero everywhere except around the circles drawn in Fig. 1, accounting for the large number of reflexions, possible in terms of the first function, which are in fact absent. The third is a modulation function which would account for the variations in intensity of the extra reflexions. Since the complete weighted reciprocal-lattice section is the product of these three functions, the structure in real space may be regarded as the convolution of the separate transforms of these three functions (Lipson & Taylor, 1958). The three functions may therefore be treated separately. The third function which corresponds to the detailed structure has not yet been elucidated. The second function seemed most likely to yield useful information and when a solution for it was found it led to the twinning hypothesis discussed below. This approach through the convolution principle is particularly useful because in investigating the second function it is not necessary to know what kind of differences are likely to occur between the small pseudo cells.

Preliminary results

Fig. 2 shows that all the reciprocal lattice points at which weak reflexions occur lie at the nodes of one or the other of two hexagonal nets which have sides $1/\sqrt{13}$ times that of the reciprocal cell defined by the strong reflexions, and that these two nets are related by a mirror plane parallel to $(11\bar{2}0)$. When transformed to real space this new cell has side $\sqrt{13}a_{\text{sub}}$ and the two new lattices appear to correspond to the two individuals of a twin.

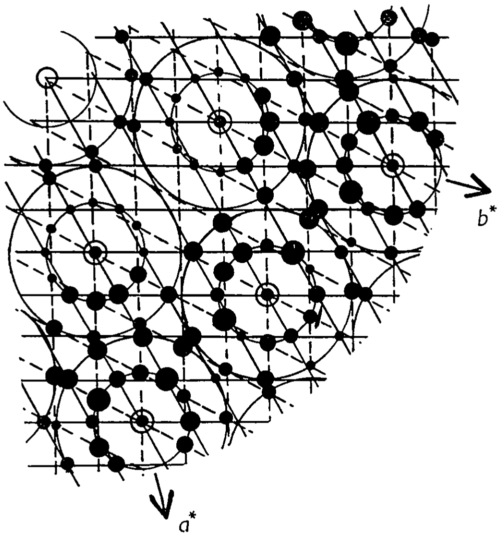

Fig. 2. As Fig. 1 with two $a^*/\sqrt{13}$ nets indicated instead of a^* and $a^*/13$ nets.

Table 1. *Dimensions of hexagonal cells in klockmannite*

Sub-cell	a	3·954 Å	a^*	0·2920 Å^{-1}
True cell	$\sqrt{13}a$	14·26	$a^*/\sqrt{13}$	0·0810
Super-cell	$13a$	51·40	$a^*/13$	0·0225

For all the cells $c = 17{\cdot}25$ Å.
a-Dimension from Donnay (1954–55).

Fig. 3 shows the relationship between this new cell—now called the true cell—and the sub and super cells already described; Table 1 gives the real and reciprocal dimensions for all three. The sub and super lattices are continuous for both individuals of the twin. The interesting points to note are that all three lattices are hexagonal, and that the geometrical relationship of the sub-cell to the true cell is exactly the same as that of the true cell to the super-cell.

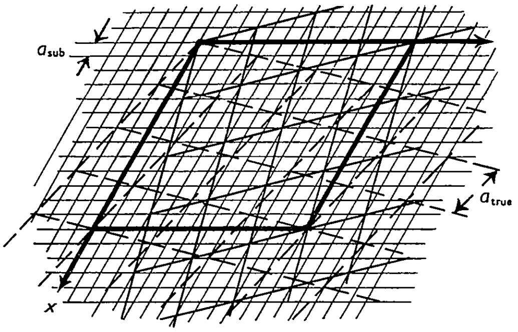

Fig. 3. 001 projection showing the relationship between the twinned true cells ($\sqrt{13}a$), the sub-cell (a) and the super-cell ($13a$, indicated by the boldest lines).

The twinning is of the type described as 'twinning by reticular merohedry' (Friedel, 1926; Cahn, 1954; Donnay & Donnay, 1959). The twin obliquity is 0, the twin law is $(11\bar{2}0)$ with respect to the super-cell, and the twin index 13.

Problems remaining

The true cell contains 78 CuSe units and a high proportion of these atoms probably lie close to the sites proposed by Berry. Work is now proceeding on the details of this structure.

The original problem, that of placing 2,028 atoms, seemed at first sight to be almost impossible; the twinning hypothesis makes the problem much more straightforward, but there may still be considerable difficulties in arriving at a complete solution.

We are grateful to Prof. and Mrs Donnay for suggesting this problem and for their continued interest and assistance.

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