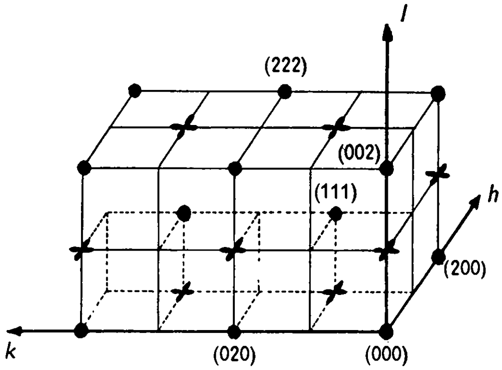

Fig. 2. The reciprocal lattice of the CuAu superlattice containing anti-phase domains. Circles: normal reflexion points; crosses: superlattice reflexion points.

the superlattice reflexions for which $h+k$ is odd must vanish (the c axis corresponds to l and is perpendicular to the alternate planes of gold and copper) and the crosses should remain only in those cases in which their planes are perpendicular to the c axis, as shown in Fig. 2. Consequently, the observed crosses belong only to such a set in which the c axis is perpendicular to the film surface. The reflexion spots $(001)_{//1}$, $(00\bar{1})_{//1}$, $(001)_{//2}$ and $(00\bar{1})_{//2}$ in Fig. 1(*b*), corresponding to the other two sets, show the elongation in a perpendicular or in a horizontal direction, which arises from the intersection of platelets with the reflexion sphere.

When the film showing the crosses was heated above the transition point and, after quenching, was again annealed at about 400° C., the crosses disappeared; this might be due to the vanishing of the orientation in which the c axis was perpendicular to the film surface.

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A graphical method for the determination of the unit-cell dimensions of non-cubic materials from X-ray powder photographs.

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It is often necessary to determine the unit-cell dimensions of a non-cubic substance from powder photographs when there is an insufficiency or even an absence of suitable reflexions; and it is the purpose of the present note to describe a simple graphical method of doing this that is always applicable to tetragonal and hexagonal crystals, and may be applied to orthorhombic crystals in many instances. It requires that the measured spacings be first corrected for the usual errors, e. g. by reference to an internal standard. The method due to Cohen (1935) achieves, of course, both the correction of the spacings and the determination of the unit-cell dimensions, but it involves a considerable amount of computation. This is avoided in the present method by carrying out the correction of the spacings and the determination of the unit-cell dimensions in two stages. The method also avoids the danger of a systematic drift which is often inherent in methods of successive approximation.

For a tetragonal crystal we have

$$1/d^2_{hkl} = (h^2+k^2)a^{*2}+l^2c^{*2}\ ,$$

where the symbols have their usual significance. This may be written

$$c^{*2} = \frac{1}{l^2d^2_{hkl}} - \left(\frac{h^2+k^2}{l^2}\right)a^{*2}\ . \qquad (1)$$

A series of values for c^{*2} may be found from this expression by taking the observed spacings for a series of hkl reflexions and assuming a value for a^*. A good value for a^* may sometimes be obtained by one of the well known extrapolation techniques, or by a method such as that described by Bacon (1948), using the $hk0$ reflexions; but if there is no $kh0$ reflexion, or if there are only one or two, perhaps at small angles, difficulties at once arise. However, let us accept the need for putting a poor value for a^* in equation (1). For a^* we must now put $(a^*+\delta a^*)$, where δa^* is the error in a^*, and (1) becomes

$$c^{*2}_{\text{obs.}} = \frac{1}{l^2d^2_{hkl}} - \left(\frac{h^2+k^2}{l^2}\right)(a^*+\delta a^*)^2\ ,$$

or, neglecting δa^{*2},

$$c^{*2}_{\text{obs.}} = c^{*2} - \left(\frac{h^2+k^2}{l^2}\right).\ 2a^*\delta a^*\ . \qquad (2)$$

But $2a^*\delta a^*$ is a constant, so that by plotting $c^{*2}_{\text{obs.}}$ against $\{(h^2+k^2)/l^2\}$ a straight line is obtained which, at the value $\{(h^2+k^2)/l^2\} = 0$, cuts the $c^{*2}_{\text{obs.}}$ ordinate at the correct value of c^{*2}. Moreover, the correct value of a^* may be obtained from the slope of the line. Alternatively, a value may be obtained by plotting the observed values of a^{*2} against $\{l^2/(h^2+k^2)\}$.

The method is clearly applicable, *mutatis mutandis*, to the hexagonal system, and may be applied to the orthorhombic system as shown below.

For this system we have

$$1/d^2_{hkl} = h^2a^{*2}+k^2b^{*2}+l^2c^{*2}\ .$$

Proceeding as before we may write, for example,

$$c^{*2}_{\text{obs.}} = c^{*2}-(2/l^2)(h^2a^*\delta a^*+k^2b^*\delta b^*)\ .$$

For the *hhl* reflexions this becomes

$$c^{*2}_{\text{obs.}} = c^{*2} - (2h^2/l^2)(a^*\delta a^* + b^*\delta b^*)\ ,$$

and the correct value for c^{*2} may be obtained by plotting $c^{*2}_{\text{obs.}}$ against h^2/l^2 for such reflexions. Similar considerations may be applied to a^* and b^*.

Fig. 1 gives an example of the application of the method to the determination of the *c* dimension of β-uranium. The values of the unit-cell dimensions of this material at 720° C. are (Thewlis, 1951, 1952)

$$a = 10{\cdot}759 \pm 0{\cdot}001,\quad c = 5{\cdot}656 \pm 0{\cdot}001\ \text{Å}\ .$$

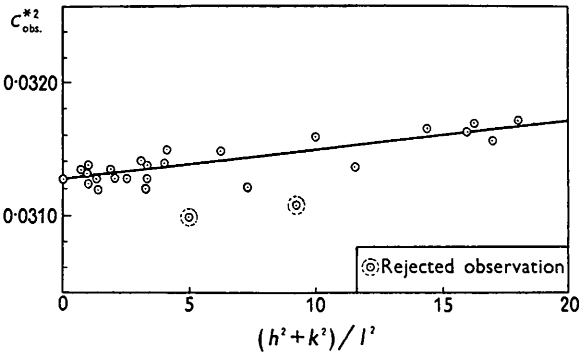

Fig. 1. Plot of $c^{*2}_{\text{obs.}}$ against $\{(h^2+k^2/l^2\}$ for β-uranium.

In drawing Fig. 1 a deliberately incorrect choice of *a* was made, the value being taken as 10·772 Å. The value of c^{*2} obtained is 0·03127. This corresponds to $c = 5{\cdot}655$ Å, which is in satisfactory agreement with the author's previous value.

As already mentioned, the value of a^*, and hence *a*, can be found from the slope of the line in Fig. 1.

From equation (2), the slope is $-2a^*\delta a^*$. From this a value for δa^* may be obtained by putting in the value of a^*. This is not known, however, but a moment's consideration will show that it is legitimate to insert the assumed value of a^*. The slope is positive (its value is actually 0·000022), hence δa^* is negative and the assumed value of a^* is too small, i.e. that of *a* is too high.

$$\text{We now have } \delta a^* = -\frac{0{\cdot}000022}{2a^*_{\text{assumed}}} = -0{\cdot}000118.$$

This reduces the value of *a* from that assumed, i. e. 10·772 Å, to 10·758 Å, which again is in satisfactory agreement with the author's previous value.

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The orientation of silver formed during electron bombardment of silver halides.

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Trillat (1951, 1952) has recently published results of an electron-diffraction study of the growth of silver which occurs during electron bombardment of thin films of oriented silver bromide (in transmission experiments). These results lead him to conclude that the silver produced during the bombardment is randomly oriented with respect to the orientation of the bromide. This is in apparent contradiction with reflexion experiments (electron diffraction) carried out by the author (Pashley, 1950, 1951, p. 39), who finds a prominent parallel orientation of silver in both silver bromide and silver chloride.

It could be argued that this parallel orientation was caused by the single-crystal substrates (mica, rocksalt etc.) on which the silver halide was supported during the bombardment. This point has been carefully considered, and checked by experiments such as the following. Silver bromide was deposited on to potassium bromide cleavage faces in two different ways: (1) with a parallel orientation between the substrate and the deposit; (2) with (111) silver bromide planes parallel to the (100) potassium bromide cleavage surface (for details see Pashley, 1952). In each case electron bombardment of the specimens caused growth of silver oriented parallel to the silver bromide. The orientation of the silver with respect to the potassium bromide was thus different in the two cases, and it therefore follows that the substrate was not responsible for initiating the orientation of the silver. A more detailed account of these results will be given later.

Trillat's experiments with detached thin films have been repeated by the author, with both silver bromide and silver chloride. It is found that although much randomly oriented silver is formed, some parallel oriented silver also forms, particularly in the case of silver chloride. In addition, the silver halide becomes appreciably disoriented during electron bombardment, giving halide diffraction rings. At least one such ring is also visible on Fig. 6 of Trillat's paper (1952). Subsequent decomposition of this disoriented halide will give rise to randomly oriented silver, which might be sufficient to mask the appearance of oriented silver. No such disorientation of the halide occurs with layers supported on substrates.

It is therefore to be concluded that the formation of parallel oriented silver is a genuine effect of the decomposition of silver bromide and silver chloride.

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