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Some Lattice Indeterminacies

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Small departures of crystal lattices from high symmetry may be incapable of direct detection from powder patterns. It is shown, however, that the nature of such small departures may be approximately gathered from a study of small discrepancies between the lattice constants deduced from different reflexion planes.

Introduction

A large proportion of the crystals examined by the powder method of X-ray diffraction have been assigned cubic symmetry, but lattices departing slightly from cubic symmetry may yield powder patterns indistinguishable to a first order from those given by exactly cubic lattices. The same may be said to a lesser degree of lattices departing slightly from hexagonal and other symmetries. It is the purpose of this paper to list the indeterminacies which limit the information derivable from powder crystallography, and to show how the nature of a slight departure from high symmetry can be approximately gathered from a study of small discrepancies between the lattice constants deduced from different reflexion planes.

Indeterminacies of the cubic system

In the cubic system, a maximum of 48 reflexion planes co-operate to produce one diffraction line. If a cubic lattice were so deformed as to become slightly rhombohedral, the 48 reflexions would no longer exactly coincide on the film, but would move apart, to a first order into six groups of eight lines each. It is of interest to consider how small a deformation can be detected.

In a triclinic lattice we have

$$d_{hkl} = \frac{(1-\cos^2\lambda-\cos^2\mu-\cos^2\nu+2\cos\lambda\cos\mu\cos\nu)^{\frac{1}{2}}}{\{\Sigma(h/a)^2\sin^2\lambda-2\Sigma(kl/bc)(\cos\lambda-\cos\mu\cos\nu)\}^{\frac{1}{2}}}, \quad (1)$$

where a, b, c, are the lattice spacings and λ, μ, ν are the interaxial angles. If this expression be differentiated with respect to the various parameters $a, b, c, \lambda, \mu, \nu$, and if in the result the cubic characteristics be substituted ($a = b = c$, $\lambda = \mu = \nu = 90°$), then the movements of the components of compound lines can be deduced from

$$d = d_o+(dd/d\lambda)\delta\lambda \quad \text{etc.},$$
$$2d\sin\theta = \text{wavelength}, \quad (2)$$

where d_o corresponds to the centroid of the group.

For computational purposes it is more convenient to deduce from each observed Bragg angle the value of the lattice constant a_o (the subscript indicating 'observed') which would be obtained on the assumption of an exactly cubic lattice, namely

$$a_o = \sqrt{(h^2+k^2+l^2)}.d_{hkl}. \quad (3)$$

The various components of the line hkl would (if resolved) yield values of a_o differing from the above by

$$da_o = \{h^2da+k^2db+l^2dc - a(kld\lambda+lhd\mu+hkd\nu)\}/\{h^2+k^2+l^2\}. \quad (4)$$

Consider the effect of a change in one side of the cube by 1%, i.e. $db = a/100$, $da = dc = 0$. The 100 and 010 lines will give displacements differing by $a/100$. If these reflexions occur at an angle $\theta = 45°$ in a 19 cm. camera, the equation

$$dS = -D(da_o/a)\tan\theta, \quad (5)$$

where S measures the arc on the film and D is the camera diameter, shows that the lines will be separated on the film by 2 mm. If, on the other hand, the general breadth of the lines is such that an increase of $\frac{1}{2}$ mm. or less cannot be detected, then it can only be asserted that the cube sides differ by less than $\frac{1}{4}$%.

According to (4), the components of the 100 group will not be moved *at all* by small changes in the interaxial *angles*, for hk, kl, lh, are all zero. It would be necessary to proceed to a second differentiation of equation (1) to estimate the least detectable change. On the other hand, the group 210 *would* be split to a first order by angular changes, for kl could be either 2 or 0. If, as before, the maximum line-broadening due to the moving asunder of the group is not to exceed $\frac{1}{2}$ mm., then the angles can only be stated to differ from 90° by less than 12′.

Thus, from a powder pattern containing these two lines, it would only be possible to affirm that the sides of the cube differed by less than $\frac{1}{4}$% and that the angles lay between 89° 48′ and 90° 12′.

The uncertainty would be less for higher values of hkl.

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Indeterminacies of other systems

Similar deductions may be made from the corresponding equations for tetragonal and orthorhombic lattices, in which, respectively,

$$da_o = \{h^2da+k^2db+l^2dC.a/C^3 - a(kld\lambda+lhd\mu)/C-ahkdv\}/\{h^2+k^2+l^2/C^2\} \quad (6)$$

$(C = c/a$; 16 components);

$$da_o = a(h^2da/a^3+k^2db/b^3+l^2dc/c^3-kld\lambda/bc - lhd\mu/ca-hkdv/ab)/(h^2/a^2+k^2/b^2+l^2/c^2) \quad (7)$$

(8 components).

In neither of these cases will a first-order change in interaxial angle split a group of the form $(h00)$.

The corresponding relation for hexagonal lattices is

$$da_o = \{h(h+k/2)da+k(h/2+k)db+\tfrac{3}{4}al^2dC/C^3 - a[(h/2+k)d\lambda+(h+k/2)d\mu]l/C - a(h^2+5hk/2+k^2)dv/\sqrt{3}\}/\{h^2+k^2+hk+\tfrac{3}{4}l^2/C^2\} \quad (8)$$

($C = c/a$; 24 components formed by transformations $hkl \rightarrow hk\bar{l} \rightarrow \bar{h}\bar{k}l \rightarrow khl \rightarrow \bar{k},h+k,l \rightarrow h+k,\bar{h},l$).

Particular points to be noted here are: (1) a change in interaxial angles λ, μ, has a first-order effect on da_o, but the lines move symmetrically so that their centroid remains fixed; (2) the term $\frac{3}{4}al^2dC/C^3$ has the same value for all the co-operating reflexions, i.e. a change in axial ratio is shown by a bodily displacement of the whole compound line. This will find a use later (Appendix).

Finally, for rhombohedral lattices the indeterminacy relation is

$$da_o = \{-\Sigma[h(l+k-h)\cos\lambda-h^2]da-a\Sigma[h(h-l-k) \times\cos\lambda+kl]\cot\tfrac{1}{2}\lambda d\lambda+a\{[\Sigma h^2(1+\cos\lambda) -2\Sigma hk\cos\lambda][\sin 2\lambda/2\,(\cos\lambda-\cos 2\lambda)]\Sigma d\lambda\}\} /\{\Sigma h^2(1+\cos\lambda)-2\Sigma hk\cos\lambda\} \quad (9)$$

(12 components);

but here the symmetry has been so reduced as to obscure any indeterminacies.

Lattice-spacing discrepancies

If the deviations of a lattice from high symmetry are so small that the components of a nominally hkl line are not resolved, their centroid may yet appear to shift, so that values of a_o calculated on the assumption of an exact symmetry will err.

If all the cooperating reflexions had the same intensity, the movement of the centroid would produce an apparent change in lattice spacing a_o by an amount $d\bar{a}_o$, where $d\bar{a}_o$ is the average of the da_o's of all the planes in the group. It will be instructive to apply this consideration to hexagonal lattices rather than to the simpler cubic system.

Averaging expression (8) over the 24 co-operating planes yields

$$d\bar{a}_o = -(da+db)/2+aAdC+a(1+AC)dv/2\sqrt{3},$$

where

$$A = A(hkl) = -l^2/C^3f^2, \quad (10)$$
$$f^2 = (4/3)(h^2+k^2+hk)+l^2/C^2.$$

Thus the lattice spacings a_o calculated on the assumption of an exactly hexagonal lattice will only be the same for all hkl *if*

$$\left.\begin{aligned} da+db &= adv/\sqrt{3}, \\ dC+Cdv/2\sqrt{3} &= 0. \end{aligned}\right\} \quad (11)$$

These conditions are unlikely to be fulfilled. If, in fact, the sides a, b, c, of the lattice and the angles $\lambda = \mu = 90°$ are unchanged but the angle ν is displaced slightly from its nominal 120°, measurement of the powder pattern will indicate a change in lattice spacing of

$$da_o = adv/2\sqrt{3}, \quad (12)$$

together with a change in axial ratio

$$dC = -Cdv/2\sqrt{3}. \quad (13)$$

For an axial ratio of the order of 1·6 quoted to five figures, this indicates that the value so quoted can be considered significant only if ν differs from 120° by considerably less than 40″.

Anomalous values of a and C were in fact found in a series of experiments with zinc oxide (Archard, 1953). These will be referred to later.

The expression (10) also shows that to a first order changes $d\lambda, d\mu$, in λ, μ, fail to affect da_o. If these are investigated to the second order, quantities of the form $A^2d\lambda^2$ enter, but insertion of numerical values makes it certain that second-order deformations will inevitably be accompanied by resolution of the co-operating lines.

Similar expressions can be deduced for the cubic and other lattices; in particular it is always found that small changes in angles nominally 90° cannot to a first order be detected.

The foregoing considerations have assumed that the intensities of co-operating lines are equal, which is not in general the case. Detailed consideration of every existing form of hexagonal lattice, however, has shown that sub-groups of different intensities superimpose their centroids, so that for complete co-operating groups the formulas remain true.

Structure-factor asymmetries

Another form of asymmetry will now be considered with particular relation to the ZnO-type structure. This crystal is hexagonal with an axial ratio of 1·60220 (Rymer & Archard, 1952) and has Zn atoms at points (0, 0, 0), $(-\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ and O atoms at points (0, 0, $-\frac{3}{8}$), $(-\frac{1}{3}, \frac{1}{3}, \frac{1}{8})$.

The structure factor is

$$|F|^2 = 2(f_O^2+f_{Zn}^2+2f_O f_{Zn}\cos 2\pi wl) \times(1+\cos 2\pi(hx+ky+lz)), \quad (14)$$

where

$$x = \tfrac{1}{3},\ y = -\tfrac{1}{3},\ z = \tfrac{1}{2},\ w = -\tfrac{3}{8}.$$

Now suppose that the relative positions of atoms in a unit cell are changed so that x becomes $(\frac{1}{3}+dx)$, y becomes $(-\frac{1}{3}+dy)$ and z becomes $(\frac{1}{2}+dz)$. The structure factors of co-operating lines will no longer form a symmetrical group. Consequently, first-order changes in the nominally 90° angles may now be expected to affect the apparent values of a_o. Suppose therefore that the the angles of the unit cell change thus:*

$$\left.\begin{aligned} d\lambda = -d\mu;\ d\nu = 0. \\ dx = -dy. \end{aligned}\right\} \quad (15)$$

Also, let:

Now average the da_o's of expression (8) with duly modified weighting factor (14). Simple if tedious analysis yields

$$d\bar{a}_o = aM dx dz d\lambda, \quad (16)$$

$$M = 4\pi^2C^2A(1+AC)f^2.\cos(\tfrac{2}{3}\pi|h-k|) \times\cos\pi l/[1+\cos(\tfrac{2}{3}\pi|h-k|)\cos\pi l].$$

This means that values of lattice spacing calculated on the assumption of an exactly hexagonal lattice will show discrepancies of the form

$$M = M(hkl).$$

The application of this theory to certain experimental results has already been described (Archard, 1953). Discrepancies of the form M were found, and numerical values obtained from their measurement indicated that

$$dx\,dz\,d\lambda \fallingdotseq 10^{-6}, \quad (17)$$

which could be satisfied, for example, by $dx = dz = 0{\cdot}03$, $d\lambda = 0{\cdot}001$. Such displacements would on a 19 cm. camera broaden the most sensitive lines observed (e.g. the 213 line) by $\frac{1}{2}$ mm., which on the films in question could hardly have been detected—certainly no resolution of the component lines would have been found.

There is a little evidence that the corresponding theory for cubic lattices might explain certain discrepancies found by Kochanovska (1946; also private communication) in α-brass, but the observations reported were insufficient to admit a rigid application of the theory.

Conclusion

It has been shown that small departures from high symmetry may to a first order be undetected on powder patterns, or may merely yield small discrepancies in the lattice constants deduced from different lines on the film. In general it may be said that the quotation of lattice constants to 1 in 10^5 implies that departure from assumed symmetry is less than a few parts in 1000 of the sides of the unit cell, and that the deformation of interaxial angles is less than a few minutes of arc. Actual values depend on the particular case and the particular lines measured—those with large values of hkl being the most sensitive.

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APPENDIX

Absorption in the specimen has not been considered specifically in the foregoing, since its effects can be eliminated by extrapolation. Thus, Nelson & Riley (1945) have shown that good straight-line extrapolations can be obtained by plotting the a_o's deduced from various lines against

$$\tfrac{1}{2}(\cos^2\theta/\theta+\cos^2\theta/\sin\theta). \quad (18)$$

The procedure to be adopted in order to examine lattice-spacing discrepancies is therefore to plot the best straight line through the values of a_o observed, to obtain the residuals of the various experimental points and to average for many films. The mean residuals would be statistically zero if no real discrepancies occurred; otherwise they would give the $d\bar{a}_o$'s of expressions such as (10).

In the experimental case quoted (hexagonal, ZnO) an additional difficulty was the presence in the expression $a_o = d_{hkl}.\sqrt{[\frac{4}{3}(h^2+hk+k^2)+l^2/C^2]}$ of the unknown axial ratio C. The procedure adopted was, first, to estimate C roughly, then to obtain the extrapolation, and then to change C until minimum variance was obtained. For truly hexagonal materials the final value of C should be the true one, but for 'nearly-hexagonal' materials where the angles of the cell had changed from normal, the C obtained by this method would differ from the true C by $Cd\nu/2\sqrt{3}$.

* These assumptions are merely to simplify computations and give the order of the effects.

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