in the normal way by the settings of the ζ potentiometers and the multipliers are used to give a point to point scan across the convergent beam discs. Apart from the multipliers very little additional hardware is required since for small angles the change in angle $\Delta\theta$ across a disc is linearly related to the change in each ζ_n by the relation $\Delta\zeta_n=(2\theta_n/\lambda)\Delta\theta$, where θ_n is the Bragg angle.

The intensities from distorted crystals are given by solving equation (45) of Howie & Whelan (1961) rewritten in the present notation as

$$\frac{dU_n}{dz}=2\pi i(\zeta_n+\beta'_n)U_n+i\sigma\sum_h E_{n-h}\,.\,U_h\,, \qquad (8)$$

where $\beta'_n=d[\mathbf{g}\,.\,\mathbf{R}(z)]/dz$ and $\mathbf{g}$ is the reciprocal lattice vector and $\mathbf{R}(z)$ the vector describing the displacement of the lattice at a depth z. Two function generators giving the x and y components of $d\mathbf{R}/dz$ are sufficient to permit the calculation of β'_n for all n, since

$$\beta'_n=|\mathbf{g}_n|\,.\left(c_n\frac{dR_x}{dz}+d_n\frac{dR_y}{dz}\right),$$

where c_n and d_n are constants defining the angle between $\mathbf{g}$ and $\mathbf{R}$. Changing the slope of a ramp function generator which feeds the function generators allows the depth of the distortion within the crystal to be varied with the twist of a knob.

The n-beam electron microscope image of dislocations within a crystal can be rapidly obtained by using the foregoing technique on analog computers equipped with independently switched integrators and control logic.

In conclusion, the analog computer is seen as an invaluable adjunct to the digital machine in the field of dynamic electron diffraction computation when it is sufficient to include the interactions between a few strong beams. Additionally the analog circuit offers a fresh way of visualizing diffraction problems.

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Indexing of X-Ray Powder Patterns. Part I. The Theory of the Triclinic Case

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In a triclinic system, the squares of reciprocal spacings of any seven linearly independent X-ray powder lines which belong to the same lattice fulfill a Diophantine equation containing their Miller indices, which involves a 7×7 determinant. This can be expanded in minors which are integers. Theory is developed which breaks the problem of solving this equation into smaller steps, more easily amenable to numerical evaluation. The triclinic case has not yet been tried on a practical example, but the method has been already used in practice for systems of higher symmetry, for which the computational labor is much reduced.

Introduction

It would appear from literature that the indexing problem for a triclinic system is very unlikely to succeed in practice. Most authors restrict themselves to special cases: no arbitrary angles in the unit cell (Hesse, 1948; Lipson, 1949; Stosick, 1949), or with unusual classes of compounds, such as long-spacing compounds (Vand, 1948). The method of Ito (Runge, 1917; Ito, 1950) attacks the problem from the low symmetry

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rather than from the higher symmetry aspect and has to be followed by a cell-reduction procedure. Such procedures are discussed by Buerger (1957) and Azaroff & Buerger (1958). Lastly the work of de Wolff (de Wolff 1957, 1958, 1967) which uses concepts of zone relations, most closely approaches the theory described in this paper.

When working for the Joint Committee on Powder Diffraction Standards on automatic computer handling of X-ray powder data file, we have developed a useful theory for indexing X-ray powder patterns. We tested the theory by hand on actual powder patterns from the file up to orthorhombic symmetry and found it to work well. Since the higher symmetry procedures are only special cases of a more general triclinic case, we are presenting this case first, although we did not test the practical feasibility of the computation in practice. The triclinic case is too complex to be solved by hand, but it is within practical feasibility limits of electronic computers. We hope to write the necessary computer programs in the near future.

We hope that this paper will be followed by others where the theory will be developed for all crystal systems and Bravais lattices, and in which practical examples will be presented where available.

Initial equations

All the indexing methods for X-ray powder patterns are based on the consideration of the equation (quadratic form) for the square of the reciprocal lattice vector, which for triclinic the system is

$$Q_j = Ah_j^2 + Bk_j^2 + Cl_j^2 + Dk_jl_j + El_jh_j + Fh_jk_j\,, \quad (1)$$

where

$$Q_j = 1/d_j^2$$

and where d_j is the direct spacing of the jth powder line of the pattern, and h_j, k_j, l_j are the Miller indices.

The six constants $A, B, \ldots F$ are related to the edges and angles of the reciprocal unit cell by

$$A = a^{*2},\ B = b^{*2},\ C = c^{*2},\ D = 2b^*c^* \cos\alpha^*,$$
$$E = 2c^*a^* \cos\beta^*,\ F = 2a^*b^* \cos\gamma^*\,. \quad (2)$$

Once $A, B, \ldots F$ are known, the reciprocal cell constants can be calculated from relations

$$a^* = \sqrt{A},\ b^* = \sqrt{B},\ c^* = \sqrt{C}$$

$$\cos\alpha^* = D/2\sqrt{BC},\ \cos\beta^* = E/2\sqrt{CA},\ \cos\gamma^* = F/2\sqrt{AB}$$

Direct cell constants can then be obtained from the reciprocal constants by the usual methods.

The indexing problem consists in obtaining $A, B, \ldots F$, which are unknown, from the known set of Q_j, measured experimentally. Unfortunately, not only are the six irrational numbers A, B, ... F unknown, but also the Miller indices h_j, k_j, l_j. We therefore cannot solve the indexing problem by the methods of ordinary algebra, as no matter how many equations (1) we take, we have always more unknowns than knowns. However, as the Miller indices are integers, it is possible to obtain a solution to the problem by application of number theory (Diophantine equations).

The indexing method

Because (1) contains six irrational numbers A, B, ... F, we must take at least seven different equations (1) to introduce a constraint and so make them soluble. Let us choose any seven lines of the powder pattern, label them $j = 1, \ldots 7$, and construct a determinant

$$\Delta = \begin{vmatrix} Q_1 Q_2 \ldots\ldots\ldots Q_7 \\ h_1^2 h_2^2 \ldots\ldots\ldots h_7^2 \\ k_1^2 k_2^2 \ldots\ldots\ldots k_7^2 \\ \cdot\ \ldots\ldots\ldots\ldots \\ \cdot\ \ldots\ldots\ldots\ldots \\ h_1k_1h_2k_2\ \ldots\ h_7k_7 \end{vmatrix}\,. \quad (3)$$

If the seven Q_j are self-consistent through (1), this determinant is necessarily zero, because its first row is a linear combination of the remaining rows. Thus

$$\Delta = 0\,. \quad (4)$$

After expanding (3) into minors of Q_j,

$$\Sigma\, p_jQ_j = 0 \quad j = 1, \ldots 7\,, \quad (5)$$

where p_j is a minor obtained from (3) by omitting the first row of Q_j and the jth column containing Q_j.

The equation (5) is a Diophantine equation, as the minors p_j are integers.

The following six Diophantine equations are valid:

$$\begin{aligned} &\Sigma\, p_jh_j^2 = 0 \\ &\Sigma\, p_jk_j^2 = 0 \\ &\ldots\ldots\ldots \\ &\Sigma\, p_jh_jk_j = 0 \quad j = 1, \ldots 7\,. \end{aligned} \quad (6)$$

They can be obtained by replacing the row of Q_j in (3) by successive rows of (3) and by expanding into minors p_j. The result (6) follows, as any determinant with two identical rows is equal to zero.

The basic principle of our method is to take a septet of Q_j and then solve (5) in integers p_j. Each p_j represents a Diophantine equation in terms of the appropriate Miller indices hkl, which is solved next.

For example

$$p_7 = \begin{vmatrix} h_1^2 h_2^2 \ldots\ldots\ldots h_2^6 \\ k_1^2 k_2^2 \ldots\ldots\ldots k_6^2 \\ \cdot\ \ldots\ldots\ldots\ldots \\ \cdot\ \ldots\ldots\ldots\ldots \\ h_1k_1h_2k_2\ \ldots\ h_6k_6 \end{vmatrix}$$

represents a Diophantine equation with 18 unknown integers.

An easier procedure is to solve, after obtaining p_j, the equations (6) for Miller indices. The first three equations give the magnitudes of h_j,k_j,l_j, the last three their signs.

A question might be raised why the seven equations (1) should not be solved for *hkl* directly. The answer is that by breaking the problem into smaller steps (5) and (6) we reduce the formidable problem (1) into more amenable smaller units of computation which are just about of a size manageable on a present-day electronic computer.

The practical solution of equations (6) can be facilitated as follows:

The first three equations formally represent a single equation of a type

$$\Sigma p_j x_j^2 = 0\,, \quad j=1, \ldots 7\,. \tag{7}$$

This is a general form of the famous Legendre equation

$$ax^2+by^2=cz^2,$$

where a,b,c are natural numbers and x,y,z are integers. This equation is not always soluble.

In our case, because of (1), equation (7) is necessarily soluble, and it must have at least three independent solutions, one corresponding to the septet h_j, one to k_j, one to l_j. If a solution cannot be found (or if (5) cannot be fulfilled), Q_j do not form a self-consistent set, *i.e.* the seven powder lines cannot all correspond to the reciprocal points belonging to the same crystal lattice. At least one of the Q_j must belong to an impurity, β line or other experimental error.

It is therefore only necessary to solve one equation (7) and then assign to its three independent solutions the three sets of Miller indices. It is irrelevant which solution is used for which set, as this interchangeability merely corresponds to relabeling of the three crystal axes.

Geometrical interpretation

The above equations have the following geometrical interpretation. The values Q_j can be regarded as seven components of a known irrational vector **Q** in a seven-dimensional space. The integers p_j can be regarded as seven components of an auxiliary integer vector **p** orthogonal to **Q**. It is not obvious that such a vector exists, but equation (4) guarantees its existence. In the same space, there are six other unknown integer vectors, the components of which are $h_j^2,k_j^2,\ldots h_jk_j$. The vector **Q** is a linear combination of the six vectors. The vector **p** is orthogonal to all these six vectors, so that these and also **Q** must all lie in a single six-dimensional hyperplane, the normal of which is **p**. Our indexing method is based on the fact that it is easier to find the hyperplane and then the six unknown integer vectors within it *via* the auxiliary vector **p** than to look for them in the seven-dimensional space directly.

The use of invariants

One disadvantage of solving (1) or the smaller steps (5) and (6) directly in terms of Miller indices is that if one solution exists, there necessarily exists a family of an infinity of solutions obtained from it by unimodular transformations. It is therefore profitable to look for a solution in some intermediate quantities which are invariant to unimodular transformations, and convert these into Miller indices at a later stage. Let us consider an integer

$$D_{ijr}=\begin{vmatrix} h_i & h_j & h_r \\ k_i & k_j & k_r \\ l_i & l_j & l_r \end{vmatrix} \quad i,j,r=1, \ldots 7 \tag{8}$$

which has a geometrical interpretation as being equal to a volume in space of integer vectors h_j of a parallelepiped, the sides of which are the three vectors involved. Thus if these vectors are coplanar, $D_{ijr}=0$. Also D_{ijr} preserves its magnitude on unimodular transformation, only changing sign when the transformation is improper. There are 343 integers D_{ijr}, but since interchange of indices merely changes sign, and any two or three equal indices cause D_{ijr} to vanish, there are in general only 35 non-zero D_{ijr} which are different in magnitude, whereas there are 21 values of h_j,k_j,l_j for $j=1, \ldots 7$. Thus D_{ijr} are not all independent, and relations exist amongst D_{ijr} which are called fundamental Laplace identities. We are not going to enumerate all of them, because they are treated for example by Turnbull (1960). One typical example is

$$D_{123}D_{456}-D_{234}D_{156}+D_{134}D_{256}-D_{124}D_{356}=0\,. \tag{9}$$

When two subscripts become equal (for example if we change 4 into 6), we obtain a so-called extensional

$$D_{236}D_{156}-D_{136}D_{256}+D_{126}D_{356}=0\,. \tag{10}$$

These identities are useful for calculation of one D_{ijr} if the others within the identity are already known, or for checking purposes when all D_{ijr} were derived by other means.

All the following equations can be proved by the substitution of the expanded determinant (8) into them.

There are 21 equations

$$\Sigma p_i D_{ijk}^2=0 \quad i,j,k=1, \ldots 7 \tag{11}$$

and 105 equations

$$\Sigma p_i D_{ijk}D_{krs}=0 \quad i,j,k,r,s=1, \ldots 7 \tag{12}$$

which are analogous to the six equations (6). However, as D_{ijk} vanish when two or three subscripts become equal, from the computational point of view equations (11) have the advantage that each contains only five non-zero terms and equations (12) have only three non-zero terms and are therefore easier to handle than equations (6) with seven non-zero terms, each. In addition, not all the 126 equations (11) and (12) need be

used, as some of D_{ijr} can be obtained from the others by (9) and (10).

Once all the D_{ijk} are calculated, the next task is to calculate h_j, k_j, l_j from them. This can be best accomplished by using some of 35 equations of four terms each, exemplified by

$$x_1D_{234}-x_2D_{134}+x_3D_{124}-x_4D_{123}=0 \qquad (13)$$

where three independent solutions in x stand in turn for h, then k, then l.

Because there is an ambiguity in the choice of axes in a triclinic case, three hkl points can be freely chosen subject to one condition (13) and four others can be calculated from these. In this way, any one set of 21 Miller indices can be readily calculated. The one set of Miller indices will be one member of the infinite set obtainable by unimodular transformations. Again, not all the 35 equations (13) need be used, but only enough to determine all the Miller indices of the required set.

Conclusions

The above mathematics may appear too complex to an ordinary powder-diffractionist to be of any practical use, but the greatest practical computational problem is the solution of equation (5) in integers within observational tolerances. Once this equation is solved, all the rest of the equations deal in integers, are therefore exact, and are easier to solve than equation (5).

The treatment greatly simplifies when crystal systems of higher symmetry are considered. The hexagonal and tetragonal systems can be solved at once by the aid of a simple nomograph, and the solution of the orthorhombic system requires only a moderate computational effort. However, the monoclinic and the triclinic case will require the use of a computer.

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A Study of Optimal Phase Boundaries: The Case of Exsolved Alkali Feldspars

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A general theory of grain and phase boundaries (the *O*-lattice theory) is further developed and tested on alkali feldspars with exsolution lamellae, since measurements exist for the structures of the two-phase system (perthitic feldspars) as well as for the orientation of the phase boundary. It is shown that in this case the adaptation of two monoclinic structures is energetically preferable to the adaptation of a monoclinic and a triclinic one. The phase boundary energy is markedly lower in the former case. Thus, a pseudo-monoclinic structure is produced out of the triclinic by periodic submicroscopic twinning. The calculated orientation of the phase boundary is in close agreement with the measurements.

Introduction

Since most materials are polycrystalline, the importance of the study of crystal interfaces does not need to be emphasized. One usually distinguishes between subgrain boundaries consisting of distinct dislocation networks and high-angle boundaries where a dislocation density would be so high that the dislocation cores would merge so that at first sight a boundary might appear as a highly disturbed interface. A distinction