$$\frac{I(S=1/d)-I(S=3/2d)}{I(S=1/d)}=0{\cdot}1 \qquad (26)$$

to describe the critical ratio, we find for the limiting value of d

$$d_c=\frac{\sqrt{4{\cdot}8}}{\sqrt{\alpha}} . \qquad (27)$$

For the materials treated in this paper, the limiting repeat spacings are 9490 Å for PE, 3430 Å for PTFE, and 1370 Å for the Al–Zn alloy.

Discussion

In order for a material to show this effect, the plates need not be broad. For the case of a stack or colony of lamellae embedded in a matrix of the same average electron density, the results still hold, with the proviso that the amplitude function be corrected for the finite platelet width. (The effect of less broad lamellae is itself to broaden the diffraction peaks.)

If the real number of elements in the stack is limited, one needs to solve the exact equation (14). In this case, the numerator can no longer be set equal to unity. Calculations for finite stacks are beyond the scope of the present work. It is expected, however, that the results will be similar to those for the larger aggregates.

The limiting values of d calculated here indicate that advances in low angle resolution to d's in excess of 1μ will be of limited help in studying lamellar systems. It is, for example, evident that the band structure in slowly cooled PTFE (see Geil, 1963) and most eutectic or eutectoid colonies in alloys cannot be observable, due to the combination of high μ and d.

Conclusions

The effect of absorption on X-ray scattering from lamellar stacks has been shown to produce the following characteristics:

(1) Small angle diffraction peaks are broadened, proportionally to the linear absorption coefficient μ and the square of the repeat distance d.

(2) Proceeding to mth order peaks, these should be *sharpened* relative to the first order according to $1/m$.

(3) The effective number of scattering elements decreases sharply with denser material.

(4) Effective upper limits of d which can be resolved can be calculated. For most polymers, these values will be greater than 1000 Å, while for metals the value will be of the order of hundreds of Ångströms.

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On Refinement of the Crystal Orientation Matrix and Lattice Constants with Diffractometer Data

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An alternative to the procedure suggested by Busing & Levy [*Acta Cryst.* (1967) **22**, 457] for refining the crystal orientation matrix and (if desired) the crystal lattice parameters is proposed, in which linear observational equations are written with Miller indices as coefficients. Constraining equations appropriate to the crystal symmetry (exact to first order in the corrections) are presented for monoclinic, hexagonal, orthorhombic, tetragonal, and cubic systems.

In a recent paper and an associated report, Busing & Levy (1967*a*,*b*) have presented equations in matrix notation for single-crystal diffractometer angles in terms of the lattice constants and the crystal orientation matrix. In connection with these equations these authors have suggested procedures for refining the orien-

tation matrix, and if desired also the lattice constants, with precise diffractometer data. If the lattice constants as well as the orientation parameters are to be refined, measurement of the directions (two angles each) and the lengths (from the Bragg angles) of three non-coplanar reciprocal lattice vectors suffices for the determination or refinement of the three orientation parameters and the six lattice constants of a triclinic crystal.

If the lattice constants are not to be refined, measurement of the directions of any two non-collinear reciprocal lattice vectors will suffice to establish the orientation. However, since diffractometer measurements and lattice constants are subject to error, it is in general impossible to orient the crystal so that two or more non-collinear reciprocal lattice vectors are at the same time exactly parallel to the directions found for them by diffractometer measurements. The same difficulty can exist even if the lattice constants are to be refined, if the relative directions of the chosen reciprocal lattice vectors are fixed by crystal symmetry. Busing & Levy get around this difficulty by assuming that one vector is precisely in the direction found for it, and that the second is in the plane defined by this direction and the second direction and as close to the latter as possible. An objection to this procedure is that it arbitrarily ascribes all of the measurement error to one direction and none of it to the other. Recognizing this fact, and the fact that one will frequently wish to make measurements on several reflections in order to reduce the effect of random errors, Busing & Levy proposed that the lattice and orientation parameters be refined by least squares, and presented a procedure for such refinement (Busing & Levy, 1967*b*) that includes provision for constraints due to crystal symmetry.

We present here a refinement procedure that differs from that of Busing & Levy in several respects (see *Discussion*), and we present also constraining equations for monoclinic, hexagonal, orthorhombic, tetragonal, and cubic systems, in a form consistent with the Busing & Levy (1967*a*) equations and notation. For a given crystal system one set of two to five constraining equations will apply if the lattice constants are to be refined (*i.e.* the only constraints are from crystal symmetry); additional ones to a total of six will apply if lattice constants are not to be refined. These constraints may be used if desired to minimize the number of observations needed for determining the desired parameters, or they may be used in a least-squares-with-constraints treatment of an overdetermining set of observations.

We assume that from precise measurements of diffractometer angles we have obtained values of the coordinates of several reciprocal lattice points,†

$$\mathbf{h}_{\varphi j} \equiv \{h_{\varphi 1 j}, h_{\varphi 2 j}, h_{\varphi 3 j}\} ,$$

together with their uncertainties (from which weights for use in the least-squares refinement can be derived), in a *Cartesian* axial system affixed to the φ-circle of the diffractometer. The third axis of this system, which is the 'φ-axis system' of Busing & Levy, is parallel to the axis of φ rotation. These coordinates are in general not integers; they have dimensions of reciprocal length. The coordinates of each reciprocal lattice point in this system are related to the Miller indices of the reciprocal lattice point by the expressions [equations (2) and (4) of Busing & Levy (1967*a*)]:

$$\mathbf{h}_{\varphi j} = \mathbf{U}\mathbf{B}\mathbf{h}_j \equiv \mathbf{V}\mathbf{h}_j \tag{1}$$

where

$$\mathbf{h}_j \equiv \{h_{1j}, h_{2j}, h_{3j}\}$$

is the set of three Miller indices (integers), **B** is a matrix from which Cartesian coordinates in a standard frame of reference – the 'crystal Cartesian axis' system of Busing & Levy – are derived from the Miller indices, and **U** is a unitary 'orientation matrix' from which the reciprocal lattice coordinates in the φ system are derived from the crystal Cartesian coordinates. In the crystal Cartesian system the first coordinate axis is taken parallel to the reciprocal lattice vector $\mathbf{a}^*$ and the third is taken parallel to the direct lattice vector **c**. In this paper all axial systems are assumed to be right-handed.

We also assume that we already have at our disposal 'preliminary' values to moderate precision for the lattice constants and the orientation parameters. These quantities, and the matrices calculated from them, will be identified with zero subscripts (*e.g.* $a_0^*, \mathbf{B}_0$).

Given the diffractometer measurements on reflections with known Miller indices, equation (1) may be taken to represent three observational equations (equations of condition) for each reflection j:

$$\sum_{k=1}^{3} V_{ik} h_{kj} = h_{\varphi ij}, \; i = 1,2,3 . \tag{2}$$

To obtain observational equations in a form more amenable to application of constraints, let us multiply both sides of equation (1) on the left by the 'preliminary' matrix

$$\mathbf{V}_0^{-1} \equiv \mathbf{B}_0^{-1}\mathbf{U}_0^{-1} .$$

We obtain

$$\mathbf{V}_0^{-1}\mathbf{V}\mathbf{h}_j = \mathbf{V}_0^{-1}\mathbf{h}_{\varphi j} = \mathbf{h}'_j \tag{3}$$

where h'_j, k'_j and l'_j are numbers that would be integers equal to the Miller indices if our original knowledge of the lattice constants and orientation parameters were exact; in actuality they differ from integers by small amounts. We may rewrite equations (3), *our new observational equations*, as

$$\mathbf{D}\mathbf{h}_j = \mathbf{h}'_j \tag{4}$$

where the elements of

$$\mathbf{D} \equiv \mathbf{V}_0^{-1}\mathbf{V} = \mathbf{B}_0^{-1}\mathbf{U}_0^{-1}\mathbf{U}\mathbf{B} = \mathbf{B}_0^{-1}\mathbf{d}\mathbf{B} \tag{5}$$

† A sequence of quantities enclosed in curly brackets here represents the set of components of a *column* vector.

are now the unknowns to be found (by least-squares or otherwise) and where

$$\mathbf{d}\equiv\mathbf{U}_0^{-1}\mathbf{U}\simeq \begin{pmatrix} 1 & d_{12} & d_{13} \\ -d_{12} & 1 & d_{23} \\ -d_{13} & -d_{23} & 1 \end{pmatrix}\simeq\begin{pmatrix} 1 & -L_3\xi & L_2\xi \\ L_3\xi & 1 & -L_1\xi \\ -L_2\xi & L_1\xi & 1 \end{pmatrix} \quad (6)$$

is a unitary matrix corresponding to a rotation around an axis with direction cosines L_1, L_2, L_3, through a very small angle ξ. Since (with small ξ) the matrices $\mathbf{U}_0^{-1}$ and $\mathbf{U}$ approximately commute, the matrix $\mathbf{d}$ effectively represents the *orientation correction* for the crystal Cartesian axis system with respect to the φ-axis system, *i.e.* the resultant of the reverse of the preliminary rotation $\mathbf{U}_0$ followed by the newly estimated rotation $\mathbf{U}$. The matrix elements on the right in equation (6) are correct to first order in the angle ξ.†

The constraints due to symmetry, as well as any that relate to the values of the lattice constants themselves, are transformed by equation (5) into necessary relations among the elements D_{ij}. This is most easily seen by considering first the simplest case, that of the cubic system, in which

$$\mathbf{B}=a^*\mathbf{l}=(1/a)\mathbf{l};\ \mathbf{B}_0^{-1}=(1/a_0^*)\mathbf{l}=a_0\mathbf{l} \quad (7)$$

where $\mathbf{l}$ is the identity matrix. We obtain immediately from equation (5)

$$\mathbf{D}=\frac{a^*}{a_0^*}\mathbf{d}=\frac{a_0}{a}\mathbf{d} \quad (8)$$

whence the five constraining equations required by symmetry are immediately evident from equation (6):

$$\begin{aligned} D_{11}-D_{22}&=0\\ D_{11}-D_{33}&=0\\ D_{12}+D_{21}&=0\\ D_{13}+D_{31}&=0\\ D_{23}+D_{32}&=0 \end{aligned} \quad (9)$$

If the lattice constant is not to be refined, we may in principle add a sixth constraint,

$$D_{11}-1=0\,, \quad (10)$$

although it is doubtful whether this would be significantly advantageous in practice.

The cases of lower symmetry are more complicated. We omit consideration of the triclinic case, where there are no constraints if the lattice constants are being refined, and where the expression for $\mathbf{D}$ is of formidable complexity. We shall develop the expression for $\mathbf{D}$ in the monoclinic case, and specialize later to higher symmetries. For economy of presentation we shall confine ourselves to expressions containing reciprocal lattice lengths and angles; the corresponding expressions in direct lattice parameters can easily be obtained. In the monoclinic system (where we adopt the *'first setting'* – c axis unique – in order to derive later the equations for the hexagonal system) equation (3) of Busing & Levy becomes

$$\mathbf{B}=\begin{pmatrix} a^* & b^*\cos\gamma^* & 0 \\ 0 & b^*\sin\gamma^* & 0 \\ 0 & 0 & c^* \end{pmatrix} \quad (11)$$

We may write this as

$$\mathbf{B}=\mathbf{B}_0+\delta\mathbf{B} \quad (12)$$

where

$$\delta\mathbf{B}=\begin{pmatrix} \delta a^* & [\cos\gamma_0^*\,.\,\delta b^*-b_0^*\sin\gamma_0^*\,.\,\delta\gamma^*] & 0 \\ 0 & [\sin\gamma_0^*\,.\,\delta b^*+b_0^*\cos\gamma_0^*\,.\,\delta\gamma^*] & 0 \\ 0 & 0 & \delta c^* \end{pmatrix}. \quad (13)$$

From this point on the derivation of the matrix $\mathbf{D}$ is automatic; we give the result to first order in the matrix elements d_{ik} and other correction quantities:

$$\mathbf{D}=\begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix}$$

$$\simeq\begin{pmatrix} \left[1+\cot\gamma_0^*\,.\,d_{12}+\dfrac{\delta a^*}{a_0^*}\right] & \left[\dfrac{b_0^*}{a_0^*\sin\gamma_0^*}(d_{12}-\delta\gamma^*)\right] & \left[\dfrac{c_0^*}{a_0^*}(d_{13}-\cot\gamma_0^*\,.\,d_{23})\right] \\ \left[-\dfrac{a_0^*}{b_0^*\sin\gamma_0^*}\,.\,d_{12}\right] & \left[1-\cot\gamma_0^*\,.\,d_{12}+\dfrac{\delta b^*}{b_0^*}+\cot\gamma_0^*\,.\,\delta\gamma^*\right] & \left[\dfrac{c_0^*}{b_0^*\sin\gamma_0^*}\,d_{23}\right] \\ \left[-\dfrac{a_0^*}{c_0^*}\,d_{13}\right] & \left[-\dfrac{b_0^*}{c_0^*}(\cos\gamma_0^*\,.\,d_{13}+\sin\gamma_0^*\,.\,d_{23})\right] & \left[1+\dfrac{\delta c^*}{c_0^*}\right] \end{pmatrix}. \quad (14)$$

In the case of the monoclinic system, if we are refining lattice constants as well as orientation parameters, there are only two independent constraints due to symmetry, corresponding to the specification that α^* and β^* are both equal to 90°. Examination of equation (14) easily results in the derivation of a pair of equations of contraint:

† The elements of $\mathbf{d}$ have been derived from those of the matrix given in *International Tables for X-ray Crystallography*, (1959), page 63. With the conventions here employed, the matrix given there is the *transpose* of a matrix representing a rotation of a point around an axis having the direction cosines l_1, l_2, l_3 in a right-handed Cartesian axial system, through an angle α the positive rotational direction of which is that of a right-hand screw driven along the axis in its positive direction. The same directional convention applies here to ξ.

$$\frac{c_0^*}{a_0^*} D_{31} + \frac{a_0^*}{c_0^*} D_{13} + \frac{b_0^* \cos\gamma_0^*}{c_0^*} D_{23} = 0 ,$$

$$-\frac{c_0^* \cos\gamma_0^*}{a_0^*} D_{31} + \frac{c_0^*}{b_0^*} D_{32} + \frac{b_0^* \sin^2\gamma_0^*}{c_0^*} D_{23} = 0 . \quad (15)$$

Additional equations can be derived in the same way from equation (14), but they are not independent of equations (15). If the lattice constants are not to be refined, four additional constraining equations are needed, which may be taken as the following, obtained from equation (14) by setting δa^*, δb^*, δc^* and $\delta\gamma^*$ equal to zero:

$$\begin{aligned} &D_{11} + D_{22} - 2 = 0 , \\ &D_{11} + \frac{b_0^* \cos\gamma_0^*}{a_0^*} D_{21} - 1 = 0 , \\ &D_{33} - 1 = 0 , \\ &\frac{b_0^*}{a_0^*} D_{21} + \frac{a_0^*}{b_0^*} D_{12} = 0 . \end{aligned} \quad (16)$$

The hexagonal case (applicable also to the rhombohedral lattice) is obtained from the monoclinic case by setting $\gamma_0^* = 60°$, $\delta\gamma^* = 0$, $b_0^* = a_0^*$, $\delta b^* = \delta a^*$. The constraining equations required by symmetry are four in number, and may be written

$$\begin{aligned} &D_{11} + D_{21} - D_{22} = 0 , \\ &D_{12} + D_{21} = 0 , \\ &\frac{c_0^*}{a_0^*} D_{31} + \frac{a_0^*}{c_0^*} D_{13} + \frac{a_0^*}{2c_0^*} D_{23} = 0 , \\ &-\frac{c_0^*}{2a_0^*} D_{31} + \frac{c_0^*}{a_0^*} D_{32} + \frac{3a_0^*}{4c_0^*} D_{23} = 0 . \end{aligned} \quad (17)$$

If lattice constants are not to be refined, two additional constraining equations are needed:

$$\begin{aligned} &D_{11} + D_{22} - 2 = 0 , \\ &D_{33} - 1 = 0 . \end{aligned} \quad (18)$$

In the orthorhombic case, the three constraining equations required by symmetry are

$$\begin{aligned} &\frac{a_0^*}{b_0^*} D_{12} + \frac{b_0^*}{a_0^*} D_{21} = 0 \\ &\frac{a_0^*}{c_0^*} D_{13} + \frac{c_0^*}{a_0^*} D_{31} = 0 \\ &\frac{b_0^*}{c_0^*} D_{23} + \frac{c_0^*}{b_0^*} D_{32} = 0 , \end{aligned} \quad (19)$$

and if the lattice constants are not to be refined there are three more,

$$\begin{aligned} &D_{11} - 1 = 0 \\ &D_{22} - 1 = 0 \\ &D_{33} - 1 = 0 \end{aligned} \quad (20)$$

In the tetragonal case, the four constraining equations required by symmetry are

$$\begin{aligned} &D_{11} - D_{22} = 0 \\ &D_{12} + D_{21} = 0 \\ &\frac{a_0^*}{c_0^*} D_{13} + \frac{c_0^*}{a_0^*} D_{31} = 0 \\ &\frac{a_0^*}{c_0^*} D_{23} + \frac{c_0^*}{a_0^*} D_{32} = 0 , \end{aligned} \quad (21)$$

and if the lattice constants are not to be refined there are two more,

$$\begin{aligned} &D_{11} - 1 = 0 \\ &D_{33} - 1 = 0 . \end{aligned} \quad (22)$$

The equations for the cubic case have already been given.

Once having refined the D_{ik} with the appropriate constraints, we may obtain the matrix $\mathbf{V} \equiv \mathbf{UB}$ with the equation

$$\mathbf{V} = \mathbf{V}_0 \mathbf{D} \quad (23)$$

obtained by multiplying equation (5) through by $\mathbf{V}_0$. This matrix is now available for calculating $\mathbf{h}_{\varphi j}$ for further diffractometer measurements with equation (1). In addition, we may determine the lattice constants (if they were refined) either by extracting the correction quantities (δa^*, *etc.*) from the elements of $\mathbf{D}$ using equation (14) or else by using equations (32)–(34) of Busing & Levy,

$$\tilde{\mathbf{V}}\mathbf{V} = \tilde{\mathbf{B}}\mathbf{B} = \mathbf{G}^{-1}; \; (\mathbf{G}^{-1})_{ik} = \mathbf{a}_i^* \cdot \mathbf{a}_k^* \quad (24)$$

where $\mathbf{G}^{-1}$ is the metric tensor for the reciprocal lattice.

The elements of the orientation correction matrix $\mathbf{d}$ can easily be extracted from the elements of $\mathbf{D}$ if they are desired, and from these the angle

$$\xi = (d_{12}^2 + d_{13}^2 + d_{23}^2)^{1/2} \quad (25)$$

and the direction cosines

$$L_1 = -d_{23}/\xi, \; L_2 = d_{13}/\xi, \; L_3 = -d_{12}/\xi \quad (26)$$

can easily be obtained.

Discussion

In principle the nine normal equations that would result from an unconstrained least-squares determination of the D_{ik} can be combined through the use of Lagrange undetermined multipliers with the n equations of constraint to give $9+n$ simultaneous linear equations in $9+n$ unknowns (the nine D_{ik} and the n multipliers) according to the general method described in standard textbooks (see for example Whittaker & Robinson, 1944). This procedure for including constraints, though 'brute force', can be programmed in general for all cases and may be the most straightforward, particularly in the monoclinic and hexagonal cases. In the other cases, however, the constraining equations contain at most two variables and permit the

number of least-squares variables to be reduced by direct substitution, without recourse to undetermined multipliers. Neither of these two methods is in fact quite as simple as the application of constraints in the Busing–Levy procedure, where the constraints are applied to the lattice parameters directly through (for example) the simple omission of rows and columns from the normal equations matrix.

Our procedure for refining lattice and orientation parameters has some advantages and some disadvantages (Busing & Levy, 1967*c*) relative to the Busing–Levy procedure. In our procedure the observational equations are linear in the parameters, and the refinement should converge in one cycle, while the Busing–Levy procedure may require two or three cycles. (However, if in our treatment constraints are to be applied, either one must have fairly good preliminary values of the parameters or else one must solve the normal equations with constraints in successive approximations.) The coefficients in our observations are simply the integer Miller indices, while in the procedure suggested by Busing & Levy the needed coefficients are to be obtained by numerical differentiation.

On the other side, in our procedure the observations h'_j, k'_j, l'_j are subject in some degree to correlated errors because in general all of them for a given reflection depend on the same three or four measured angles. (Even the angles themselves may be subject to correlated errors, depending on diffractometer geometry and measurement procedure.) However, in the absence of constraints the observational equations in the D_{ik}, and the normal equations resulting from them, divide into three independent sets, the first determining D_{11}, D_{12}, D_{13} from the h'_j, the second D_{21}, D_{22}, D_{23} from the k'_j, the third D_{31}, D_{32}, D_{33} from the l'_j. Within a given set the observations are completely uncorrelated and the least-squares treatment is completely valid. Such correlation of errors as may affect the least-squares refinement in cases other than triclinic arises only through the equations of constraint, which prevent the equations from dividing into independent sets. While the possible effects of correlated errors must be borne in mind in the use of our procedure, we believe that in nearly all cases the loss of accuracy in the refined parameters will be small.

A possible disadvantage of our procedure, relative to that of Busing & Levy, is that all three (or four) angles must be measured for each reflection. Partial information (*e.g.* Busing & Levy's Type 1 and Type 6 observations) cannot be used as the basis of refinement in our method. Whether this is a severe disadvantage will depend on the particular experimental procedures employed in the laboratory.

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Etude de la Symétrie de Quelques Configurations Magnétiques par la Méthode de Bertaut

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The representation method of Bertaut is applied to the analysis of spin structures in the following ionic compounds: α-Fe_2O_3 and Cr_2O_3, UX_2 (X = O, S, Se, Te), $FeSb_2O_4$, $MnWO_4$ and hexagonal $HoMnO_3$.

Nous décrivons dans cette note quelques configurations magnétiques par la méthode de Bertaut (Bertaut, 1968). Soit G_e le groupe d'espace d'un cristal dans la phase ordonnée magnétiquement; si l'énergie est d'ordre 2, la structure peut se décrire à l'aide des fonctions de base d'une représentation irréductible Γ_{kj} de G_e extraites de l'espace des coordonnées des moments magnétiques de la maille. Nous étudions successivement les structures magnétiques des composés: α-Fe_2O_3 (Dzialoshinsky, 1958) et Cr_2O_3 (Corliss & Hastings, 1964); UX_2 (Przystawa, 1967, 1968) (X = O, S, Se, Te); $CrCl_2$ (Wollan, Koehler & Wilkinson, 1959); $FeSb_2O_4$