ions, for example: serine, 1·26 and 1·27 Å (Shoemaker, Barieau, Donohue & Lu, 1953); hydroxyproline, 1·25 and 1·27 Å (Donohue & Trueblood, 1952); threonine, 1·24 and 1·25 Å (Shoemaker *et al.*, 1950); histidine, 1·25 and 1·27 Å (Donohue, Lavine & Rollett, 1956).

The simple valence-bond theory thus accounts satisfactorily for the observed carbon–oxygen distances, but not for the nitrogen–oxygen distances. The latter discrepancies may possibly be connected with the fact that for both the nitrate ion and the nitro group the contributing resonance forms have opposite formal changes on the nitrogen and oxygen atoms. This situation might be expected to shorten the distances from those predicted, as is observed. Precise determination of the N–O bond length in an amine oxide, such as $(CH_3)_3N^+–O^-$ would be of interest on this point.

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A Direct Vector Method for Obtaining Symmetry-Independent Solutions to Crystallographic Problems Applied to Reflections and Single Rotations in Crystals

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By using vector methods within the sixfold system of coordinates that comprise both the direct- and the reciprocal-lattice vectors, the symmetry-independent crystallographic solutions to vector equations are obtained directly. The technique is applied to the study of arbitrary reflections and single rotations in crystals. The symmetry-independent solution to the reflection problem is identical to a recently published solution obtained less directly by the matrix method. The symmetry-independent solution to the rotation problem has not heretofore been given.

Introduction

The treatment of problems in geometrical crystallography by traditional vector methods frequently involves complicated algebraic manipulations which result from the non-orthogonality of the coordinate axes. The solution of some of the problems is simplified by the matrix method. In this method the crystallographic problem is referred to a Cartesian coordinate system by means of a matrix transformation. The problem is then solved in the Cartesian system and the solution is finally referred back to the crystallographic coordinates by a second matrix transformation. The mechanics of solution by either of these

methods is complicated and is liable to manipulative and conceptual errors.

This paper describes a direct vector method that reduces to a minimum the possibility of error, since the symmetry-independent crystallographic solutions to vector equations are obtained directly. By considering both the direct- and the reciprocal-lattice vector systems from a common origin, solutions to vector equations are obtained in terms of the components of the vectors upon all six coordinate axes in a form that does not depend upon the symmetry of the crystal. We are concerned in this report only with the method of deriving such symmetry-independent solutions. In order to obtain an explicit solution to the vector equation for a particular crystal from the symmetry-independent solution it is necessary to know the six components of each vector, while in general only three components of each vector are given. Transformation equations for evaluating the undetermined components of the vectors are presented and the method for obtaining explicit solutions is outlined.

In order to demonstrate the elegance of the direct vector method the transformation equations that relate to arbitrary reflections and single rotations in crystals are developed in a form that does not depend upon the symmetry of the crystal. The problems to be considered involve the determination of the crystallographic components of a vector $\mathbf{R}_2$ which is related to an initial vector $\mathbf{R}_1$ either through reflection across an arbitrary plane $(h_0k_0l_0)$ in any crystal, as in Fig. 1(*a*); or by means of a rotation about an arbitrary axis $\mathbf{R}_0$ by some angle φ in any crystal, as in Fig. 1(*b*).

A vector treatment of these problems has been given by Decker (1944), and more recently Andrews & Johnson (1955) have obtained the symmetry-independent solution to the reflection problem by the matrix method. The direct vector method is markedly different from the vector method used by Decker. Since in Decker's treatment the reciprocal lattice lies in reciprocal space, which is a transformation of real space, corresponding vectors in the two lattices are reciprocally related. The direct vector method, in contrast, operates within a single space and the direct and reciprocal lattices are considered as two coordinate systems, or as a combined coordinate system, in the same space. Since vectors and vector equations are independent of coordinate systems, corresponding vectors in the direct and reciprocal lattices are identical. The consideration of the relationship between the direct and the reciprocal lattice as one that involves a transformation of space or as one that involves simply a transformation of coordinates thus distinguishes the two vector methods.

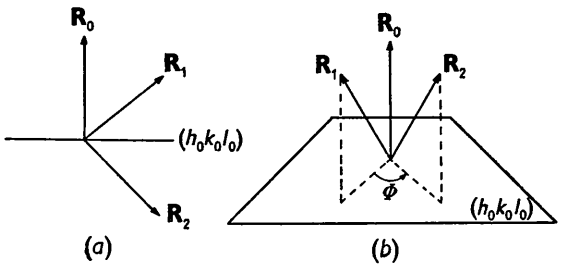

Fig. 1. (*a*) Reflection: The problem is to determine the components of the vector $\mathbf{R}_2$ which is related to an initial vector $\mathbf{R}_1$ by reflection across some plane $(h_0k_0l_0)$ in any crystal. (*b*) Rotation: The problem is to determine the components of the vector $\mathbf{R}_2$ which is related to an initial vector $\mathbf{R}_1$ by the rotation of $\mathbf{R}_1$ about some axis $\mathbf{R}_0$ through an arbitrary angle φ in any crystal.

Development of the direct vector method

Vector equations that pertain to certain geometrical problems involve the products of vectors in addition to their sums and differences. Our problem is to find the crystallographic solutions to such equations. We begin by considering a general system of crystallographic coordinates that comprises the direct- and the reciprocal-lattice vectors, and derive general expressions for vectors and for vector products in terms of the components of the vectors. These expressions are inserted into the vector equations, which then become linear functions of the basic lattice vectors. Advantage is taken of the fact that the sum of the components of all the vectors in a vector equation resolved in any direction equals zero. By resolving the vector equation along each of the coordinate axes, expressions are obtained that involve only the crystallographic components of the vectors and certain numerical factors. The component equations, so obtained, constitute the symmetry independent crystallographic solution to the vector equation.

We let all the basic lattice vectors **a**, **b**, **c**, and **a***, **b***, **c*** have a common origin and serve as coordinate axes in space. Since vectors and vector equations are independent of coordinate systems, it follows that any vector $\mathbf{R}_q$ in any crystal can be expressed variously as

$$\begin{aligned}\mathbf{R}_q &= u_q\mathbf{a}+v_q\mathbf{b}+w_q\mathbf{c} = \alpha_{qi}\mathbf{a}_i \\ &= h_q\mathbf{a}^*+k_q\mathbf{b}^*+l_q\mathbf{c}^* = \alpha^*_{qi}\mathbf{a}^*_i\,.\end{aligned} \qquad (1)\dagger$$

Since $\mathbf{a}_i \cdot \mathbf{a}^*_j = \delta_{ij}$, the dot product of two vectors is

$$\mathbf{R}_p \cdot \mathbf{R}_q = \alpha_{pi}\alpha^*_{qi} = \alpha^*_{pi}\alpha_{qi}\,, \qquad (2)$$

$$\mathbf{R}_q \cdot \mathbf{R}_q = |\mathbf{R}_q|^2 = \alpha_{qi}\alpha^*_{qi}\,. \qquad (3)$$

† **a**, **b**, **c** and **a***, **b***, **c*** are the basic lattice vectors in the direct and the reciprocal lattice respectively; the parameters $[u_qv_qw_q]$ are the components of the vector $\mathbf{R}_q$ in the direct lattice which specify its crystallographic direction; the parameters $(h_qk_ql_q)$ are the components of $\mathbf{R}_q$ in the reciprocal lattice and are proportional to the Miller indices of the planes in the direct lattice that are perpendicular to $\mathbf{R}_q$. For convenience these components and vectors are expressed in the notation $\alpha_{qi}\mathbf{a}_i$, where the convention is used that a repeated dummy index occurring in a product implies the summation over the index, i.e.:

$$\alpha_{qi}\mathbf{a}_i = \alpha_{q1}\mathbf{a}_1+\alpha_{q2}\mathbf{a}_2+\alpha_{q3}\mathbf{a}_3 = u_q\mathbf{a}+v_q\mathbf{b}+w_q\mathbf{c}\,.$$

If we take the dot product of $\alpha_{qi}\mathbf{a}_i = \alpha^*_{qi}\mathbf{a}^*_i$, first with $\mathbf{a}_j$ then with $\mathbf{a}^*_j$, we see that the components of the vectors are related by

$$\alpha^*_{qj} = \mathbf{a}_j \cdot \alpha_{qi}\mathbf{a}_i; \quad \alpha_{qj} = \mathbf{a}^*_j \cdot \alpha^*_{qi}\mathbf{a}^*_i . \tag{4}$$

Since the basic lattice vectors $\mathbf{a}_i$ and $\mathbf{a}^*_i$ do not have integral values, equation (4) shows that only one of the two sets of components α_{qi} and α^*_{qi} of any vector $\mathbf{R}_q$ can have integral values. The components α_{qi} are proportional to the zonal parameters when $\mathbf{R}_q$ is parallel to a crystal zone and the components α^*_{qi} are proportional to the Miller indices when $\mathbf{R}_q$ is normal to a crystal face. We consider also the cross product

$$\mathbf{R}_s = \mathbf{R}_p \times \mathbf{R}_q = (\alpha^*_{pi}\mathbf{a}^*_i) \times (\alpha^*_{qi}\mathbf{a}^*_i) . \tag{5}$$

Since

$$\mathbf{a}_i = \Delta(\mathbf{a}^*_j \times \mathbf{a}^*_k) ,$$

where $\Delta = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ and i, j, and k maintain the cyclical order of 1, 2, and 3, it follows that

$$\mathbf{R}_s = \frac{1}{\Delta}\begin{vmatrix} \mathbf{a}_1 & \alpha^*_{p1} & \alpha^*_{q1} \\ \mathbf{a}_2 & \alpha^*_{p2} & \alpha^*_{q2} \\ \mathbf{a}_3 & \alpha^*_{p3} & \alpha^*_{q3} \end{vmatrix} = \frac{1}{\Delta}\det(\mathbf{a}_i \alpha^*_{pi} \alpha^*_{qi}) \tag{6}$$
$$= \Delta \det(\mathbf{a}^*_i \alpha_{pi} \alpha_{qi}) .$$

The problem of reflection

Let $\mathbf{R}_0$ (Fig. 1(*a*)) be a vector normal to the reflection plane $(h_0k_0l_0)$, $\mathbf{R}_1$ be any initial vector, and $\mathbf{R}_2$ its reflection across $(h_0k_0l_0)$. Decker (1944) has shown that for such reflections

$$\mathbf{R}_2 = \mathbf{R}_1 - 2(\mathbf{R}_1 \cdot \mathbf{R}_0)\mathbf{R}_0/(\mathbf{R}_0 \cdot \mathbf{R}_0) . \tag{7}$$

Using relations (1), (2) and (3), we can immediately write

$$\alpha_{2j}\mathbf{a}_j = \alpha_{1j}\mathbf{a}_j - 2(\alpha_{1i}\alpha^*_{0i})\alpha_{0j}\mathbf{a}_j/(\alpha_{0i}\alpha^*_{0i}) , \tag{8a}$$

$$\alpha^*_{2j}\mathbf{a}^*_j = \alpha^*_{1j}\mathbf{a}^*_j - 2(\alpha_{1i}\alpha^*_{0i})\alpha^*_{0j}\mathbf{a}^*_j/(\alpha_{0i}\alpha^*_{0i}) . \tag{8b}$$

Since the sum of the components of all the vectors in a vector equation resolved in any direction must equal zero, equations (8) yield directly the components of $\mathbf{R}_2$ upon each coordinate axis in terms of the components of the vectors $\mathbf{R}_1$ and $\mathbf{R}_0$. Thus the components of the vector $\mathbf{R}_2$ along the coordinate axes are given directly by

$$\alpha_{2j} = \alpha_{1j} - 2A\alpha_{0j} , \tag{9a}$$

$$\alpha^*_{2j} = \alpha^*_{1j} - 2A\alpha^*_{0j} , \tag{9b}$$

where

$$A = (\alpha_{1i}\alpha^*_{0i})/(\alpha_{0i}\alpha^*_{0i}) = (\alpha^*_{1i}\alpha_{0i})/(\alpha_{0i}\alpha^*_{0i}) .$$

The component equations (9), with j taking on the values of 1, 2, and 3, constitute the symmetry-independent solution to the reflection problem. Expressed in terms of components from equation (1), equations (9) can be written as

$$\left.\begin{aligned} u_2 &= u_1 - 2Au_0 , \\ v_2 &= v_1 - 2Av_0 , \\ w_2 &= w_1 - 2Aw_0 , \end{aligned}\right\} \tag{10a}$$

$$\left.\begin{aligned} h_2 &= h_1 - 2Ah_0 , \\ k_2 &= k_1 - 2Ak_0 , \\ l_2 &= l_1 - 2Al_0 , \end{aligned}\right\} \tag{10b}$$†

where

$$A = \frac{h_0u_1 + k_0v_1 + l_0w_1}{h_0u_0 + k_0v_0 + l_0w_0} = \frac{h_1u_0 + k_1v_0 + l_1w_0}{h_0u_0 + k_0v_0 + l_0w_0} .$$

Equations (10) are the identical equations that were obtained much less directly by Andrews & Johnson (1955), using matrix methods. Equations (10) are the symmetry-independent form of the transformation equation for the reflection across the plane $(h_0k_0l_0)$ of (*a*) the directions $[u_1v_1w_1]$ and (*b*) the planes $(h_1k_1l_1)$ into (*a*) the directions $[u_2v_2w_2]$ and (*b*) the planes $(h_2k_2l_2)$. The parameters $u_0v_0w_0$ and $h_0k_0l_0$ are the components of the reference vector $\mathbf{R}_0$ in the direct and the reciprocal lattice respectively. Equation (4) expresses the relationship between these components.

The problem of single rotation

The problem, in a crystal with fixed coordinates, is to determine the crystallographic direction of a vector $\mathbf{R}_2$ (Fig. 1(*b*)) which is related to an initial vector $\mathbf{R}_1$ by a counterclockwise rotation of $\mathbf{R}_1$ about an arbitrary axis $\mathbf{R}_0$ through some angle φ. An equivalent statement of the problem is the following: Let a fixed direction in space be established such that it lies parallel to a known direction $\mathbf{R}_1$ in a crystal. Let the crystal be rotated clockwise about an arbitrary axis $\mathbf{R}_0$ through some angle φ. The fixed direction now lies parallel to the crystallographic direction $\mathbf{R}_2$ which is to be determined. Decker (1944) has shown that for such rotations

$$\mathbf{R}_2 = \mathbf{R}_1 \cos\varphi + \mathbf{R}_1 \cdot \mathbf{R}_0(1-\cos\varphi)\mathbf{R}_0/\mathbf{R}_0 \cdot \mathbf{R}_0 + \sin\varphi(\mathbf{R}_0 \times \mathbf{R}_1)/|\mathbf{R}_0| . \tag{11}$$

From relations (1), (2), (3), and (6) we can express (11) directly as

$$\alpha_{2i}\mathbf{a}_i = \alpha_{1i}\mathbf{a}_i \cos\varphi + (\alpha_{1n}\alpha^*_{0n})(1-\cos\varphi)\alpha_{0i}\mathbf{a}_i/(\alpha_{0n}\alpha^*_{0n}) + \sin\varphi \det(\mathbf{a}_i\alpha^*_{0i}\alpha^*_{1i})/\Delta/(\alpha_{0n}\alpha^*_{0n}) \tag{12}$$

and

$$\alpha^*_{2i}\mathbf{a}^*_i = \alpha^*_{1i}\mathbf{a}^*_i \cos\varphi + (\alpha_{1n}\alpha^*_{0n})(1-\cos\varphi)\alpha^*_{0i}\mathbf{a}^*_i/(\alpha_{0n}\alpha^*_{0n}) + \Delta\sin\varphi \det(\mathbf{a}^*_i\alpha_{0i}\alpha_{1i})/\Delta/(\alpha_{0n}\alpha^*_{0n}) . \tag{13}$$

Thus the symmetry-independent solution to the single-rotation problem is

$$\alpha_{2i} = \alpha_{1i}\cos\varphi + A(1-\cos\varphi)\alpha_{0i} + \sin\varphi(\alpha^*_{0j}\alpha^*_{1k} - \alpha^*_{1j}\alpha^*_{0k})/\Delta B \tag{14}$$

and

$$\alpha^*_{2i} = \alpha^*_{1i}\cos\varphi + A(1-\cos\varphi)\alpha^*_{0i} + \Delta\sin\varphi(\alpha_{0j}\alpha_{1k} - \alpha_{1j}\alpha_{0k})/B , \tag{15}$$

† Equations (10*b*) and (15) are based upon the assumption that planes transform in the same way as their vector normals. While this assumption is not always valid, it holds for the special cases here considered.

where i, j, and k maintain the cyclical order of 1, 2, and 3;

$$A=\alpha_{1n}\alpha^*_{0n}/\alpha_{0n}\alpha^*_{0n} \quad \text{and} \quad B^2=\alpha_{0n}\alpha^*_{0n}=h_0u_0+k_0v_0+l_0w_0.$$

Transposing directly to parameter form by means of equation (1), equations (14) and (15) become

$$\begin{aligned} u_2 &= u_1\cos\varphi+A(1-\cos\varphi)u_0+\sin\varphi(k_0l_1-k_1l_0)/\Delta B \\ &\cdot \\ &\cdot \\ h_2 &= h_1\cos\varphi+A(1-\cos\varphi)h_0+\Delta\sin\varphi(v_0w_1-v_1w_0)/B\,. \\ &\cdot \\ &\cdot \end{aligned} \tag{16}$$

Equation (14) yields the directions $[\alpha_{21}\alpha_{22}\alpha_{23}]$ and (15) the planes $(\alpha^*_{21}\alpha^*_{22}\alpha^*_{23})$ that initial directions $[\alpha_{11}\alpha_{12}\alpha_{13}]$ and initial planes $(\alpha^*_{11}\alpha^*_{12}\alpha^*_{13})$ will occupy after being rotated counterclockwise about the axis $\mathbf{R}_0=\alpha_{0i}\mathbf{a}_i=\alpha^*_{0i}\mathbf{a}^*_i$ through an angle φ in a crystal with fixed coordinates.

Consider a rotation of 180° about the axis $\mathbf{R}_0$. For $\varphi=2\pi$ equations (14) and (15) yield

$$\bar{\alpha}_{2j}=\alpha_{1j}-2A\alpha_{0j}\,, \tag{17a}$$

$$\bar{\alpha}^*_{2j}=\alpha^*_{1j}-2A\alpha_{0j}\,. \tag{17b}$$

Comparing (17) and (9) we deduce the well known result that the combined operation of a two-fold rotation about $\mathbf{R}_0$ followed (or preceded) by reflection across the plane normal to $\mathbf{R}_0$ transforms all initial directions and planes into the inverse directions and planes.

Discussion

The technique of applying the above equations to a particular crystal has been described previously (Davisson, 1957) and will only be outlined here. Since the equations contain the components of the vectors $\mathbf{R}_q$ upon the six coordinate axes $\mathbf{a}_i$ and $\mathbf{a}^*_i$ while we only know three of the components of each vector, either $[\alpha_{q1}\alpha_{q2}\alpha_{q3}]$ or $(\alpha^*_{q1}\alpha^*_{q2}\alpha^*_{q3})$ as the case may be, it is necessary to solve equation (4) to obtain the remaining components. The transformation equations are then solved by substitution of the components and the evaluation of Δ in the appropriate symmetry system. It is important to note from equations (1) and (2) that the components obtained from (4) usually cannot be reduced or factored before being applied to the solutions obtained by the direct vector method, but it can be shown that such factoring does not alter the reflection equations.

Since rotations and reflections are the elements of macroscopic symmetry, the above relationships may be of general interest to crystallographers. Their application to the study of X-ray diffraction patterns formed from twinned crystals is well known. Equations (9) and (17) apply to the study of reflectional and two-fold twinning respectively. The rotation equations are generally useful in problems of crystal orientation. Thus, without using their full potentialities, they can be used to determine the directions of surface features such as slip lines, edges of dislocation pits, and surface breakdown paths observed on crystal faces. The more general transformation equations developed previously (Davisson, 1957) are useful for determining the directions of volume paths in crystals.

The direct vector method can be used generally to obtain symmetry-independent solutions to crystallographic problems. With a little practice such solutions can be written down directly from an inspection of the vector equation. It is suggested that this method is more direct and simple than the methods of geometrical analysis presently used, which yield the symmetry independent solution only after a considerable amount of calculation. Certain advantages are gained when the geometry of crystals is described by the direct vector method: (1) Each problem is reduced to a single symmetry-independent solution in which all quantities are known except for certain components of the vectors. (2) Symmetry considerations are involved only in the evaluation of the components by means of equation (4), to which a single form of work sheet can be applied. It follows that the work of solving problems in the various symmetry systems becomes systematized and thereby simplified.

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