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ABSTRACT

If $\sigma_\wedge(x)$ is the standard deviation of an atomic coordinate, the standard deviation of position of that atom in the direction of the corresponding reciprocal axis is $\underline{a}\,\sigma(x) \cos \underset{\sim\sim}{aa}^*$, where $\underset{\sim\sim}{aa}^*$ is the angle between the direct and reciprocal axes. When this standard deviation is independent of direction, the statistical correlation coefficient of two coordinates of the atom is given by the cosine of the angle between the corresponding reciprical axes. In the method of least squares, if the standard deviation of a coordinate is calculated with neglect of cross terms, it tends to be low by the factor $\cos \underset{\sim\sim}{aa}^*$. It is shown that crystallographic independence does not imply statistical independence.

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INTRODUCTION

The distance ℓ between two atoms in a crystal is a function of the co-ordinates x_1, y_1, z_1, x_2, y_2, z_2 of the two atoms and the dimensions $\underline{a}$, $\underline{b}$, $\underline{c}$, α, β, γ of the unit cell. The variance of ℓ is given by an expression (Arley and Buch, 1950):

$$\sigma^2(\ell) = \left[\frac{\partial \ell}{\partial x_1} \, \sigma(x_1) \right]^2 + \cdots$$

$$+ 2 \frac{\partial \ell}{\partial x_1} \frac{\partial \ell}{\partial y_1} \sigma(x_1) \, \sigma(y_1) \, r(x_1, y_1) + \cdots \qquad (1)$$

where there is a term of the first kind for each variable and a term of the second kind for each pair of variables. The factor $\sigma(x_1) \, \sigma(y_1) \, r(x_1, y_1)$ is the covariance of x_1 and y_1, and $r(x_1, y_1)$ is the correlation coefficient. The correlation coefficient is zero if the two variables are statistically in-dependent. It has one of the extreme values +1 or -1 if the two variables are related by symmetry (except in hexagonal coordinates, where sometimes a co-coordinate is a function of two other coordinates). Ordinarily the coordinates determined by x-ray diffraction, when expressed as fractions of the unit cell, are independent of the cell dimensions. It is commonly assumed (though not necessarily true, as shown below) that coordinates of two crystallographically independent atoms are statistically independent. It is well known that in oblique coordinate systems two different coordinates of an atom are not in general statistically independent of each other. Their correlation is related in a simple way to the angles of the reciprocal lattice, as shown below, when certain conditions are satisfied.

CORRELATION DUE TO INCLINATION OF AXES

In the following discussion it is assumed that no correlation occurs between coordinates of different atoms, and no consideration is given to errors in the unit cell dimensions. The variance of position of an atom, p^2, is defined as the sum of the terms in (1) which contain only the coordinates of that atom. When $\underset{\sim}{\ell}$ lies in the direction of $\underset{\sim}{a}^*$, the derivatives with respect to y and z vanish, and

$$p = \underset{\sim}{a} \cos \underset{\sim\sim}{aa}^* \quad \sigma(x) = \sigma(x)/\underset{\sim}{a}^* \tag{2}$$

where $\underset{\sim\sim}{aa}^*$ represents the angle between the direct and reciprocal $\underset{\sim}{a}$ axes. For monoclinic crystals, $\cos \underset{\sim\sim}{aa}^* = \sin \beta$. When p is independent of the direction of $\underset{\sim}{\ell}$, the error is isotropic. Errors are frequently found to be approximately isotropic when reasonably symmetrical three-dimensional data are used. If p is isotropic, one can evaluate the correlation coefficients from (1) by examination of special cases. For example, in the monoclinic case, consider $\underset{\sim}{\ell}$ in the direction of the bisector of β^* (Fig. 1). Since p is assumed to be isotropic, it is the same as in the direction of $\underset{\sim}{a}^*$:

$$p = \underset{\sim}{a} \sigma(x) \sin \beta \tag{3}$$

By (1), since $\underset{\sim}{a} \sigma(x)$ is assumed equal to $\underset{\sim}{c} \sigma(z)$:

$$p^2 = 2 \left[\underset{\sim}{a} \sigma(x) \cos(\beta/2) \right]^2 + 2 r(x,z) \left[\underset{\sim}{a} \sigma(x) \cos(\beta/2) \right]^2 \tag{4}$$

Eliminating p from (3) and (4) and solving for $r(x,z)$:

$$r(x,z) = \frac{\sin^2 \beta - 2 \cos^2(\beta/2)}{2 \cos^2(\beta/2)} = -\cos \beta = \cos \beta^* \tag{5}$$

That this value of r gives an isotropic p can be checked by consideration of more general cases, but the algebra becomes tedious.

For the triclinic case consider the axial directions on a stereographic projection (Fig. 2) and $\underset{\sim}{\ell}$ in a direction in the $\underset{\sim}{a}^* \underset{\sim}{b}^*$ plane (i.e., $\underline{\perp} \underset{\sim}{c}$). The projections of $\underset{\sim}{a}$ and $\underset{\sim}{b}$ on the plane of $\underset{\sim}{a}^*$ and $\underset{\sim}{b}^*$ are $\underset{\sim}{a}'$ and $\underset{\sim}{b}'$. Since $\underset{\sim\sim}{aa}'\underset{\sim}{\ell}$ are right spherical triangles,

$$\cos \underset{\sim}{a}\underset{\sim}{a}' \ \cos \underset{\sim}{a}'\underset{\sim}{\ell} = \cos \underset{\sim}{a}\underset{\sim}{\ell}, \ \text{etc.,} \tag{6}$$

and the variance can be written:

$$p^2 = \left[(\underline{a} \cos \underset{\sim}{a}\underset{\sim}{a}') \ \sigma \ (\underline{x}) \cos \underset{\sim}{a}'\underset{\sim}{\ell} \right]^2 + \cdots \tag{7}$$

This expression is equivalent to that for a monoclinic case with an axis of $(\underline{a} \cos \underset{\sim}{a}\underset{\sim}{a}')$ in the direction of $\underset{\sim}{a}'$ and an axis $(\underline{b} \cos \underset{\sim}{b}\underset{\sim}{b}')$ in the direction of $\underset{\sim}{b}'$, but with the same directions of $\underset{\sim}{a}^*$ and $\underset{\sim}{b}^*$. Therefore, by (5) with change of naming of axes:

$$r \ (x,y) = \cos \gamma^* \tag{8a}$$

Similarly, by permutation of axes:

$$r \ (x,z) = \cos \beta^* \tag{8b}$$

$$r \ (y,z) = \cos \alpha^* \tag{8c}$$

The expressions in terms of angles of the direct cell are much less simple. The application of these relations to other crystal systems is obvious.

To illustrate the magnitude of the effects of correlation, there is plotted in Fig. 3 the angular dependence of p for a monoclinic $\beta = 120^\circ$. The solid circle represents the isotropic p corresponding to r = 1/2. The curve shows the dependence of p for independent coordinates, or no correlation. The latter curve would be appropriate, for example, when x and z were obtained from independent projections. Note that the curves coincide in the directions of the reciprocal axes. The broken circle is drawn with radius $\underline{a} \ \sigma \ (x)$ to show the effect of omitting the factor $\cos \underset{\sim}{a}\underset{\sim}{a}^*$.

The variances and covariances of coordinates are themselves subject to experimental uncertainty. Therefore when the error is reasonably isotropic it may be better (and certainly is simpler) to assume an isotropic error given by some average of the various determinations, than to calculate the error by (1).

METHOD OF LEAST SQUARES

In the method of least squares, one derives a matrix A of elements:

$$a_{ij} = \sum w \frac{\partial F}{\partial x_i} \frac{\partial F}{\partial x_j} \tag{9}$$

The inverse of A is A^{-1} with elements b_{ij}. If the discrepancies $\Delta = F_o - F_c$ represent random errors, then the variance of a coordinate is:

$$\sigma^2(x_i) = b_{ii} \sum w \Delta^2/(u-v) \tag{10}$$

where u - v is the excess of data over the number of variables. A covariance is given by the same expression, with b_{ij} in place of b_{ii}. Therefore, a correlation coefficient is:

$$r(x_i, x_j) = b_{ij}(b_{ii}b_{jj})^{-1/2} \tag{11}$$

Sometimes the complete matrix A is not available, and the variance is approximated by using $1/a_{ii}$ in place of b_{ii} in (10). The standard deviation calculated in this way will be called $s(x_i)$. According to Sparks (1958), experimental data suggest that $s(x)$ is less than $\sigma(x)$ by a factor similar to cos aa^*. It is shown below that this is true when the errors are isotropic and the only correlation is that among coordinates of a single atom because of the inclination of the axes. The latter restriction permits A to be factored into matrices of order 3 x 3, which can be considered one at a time.

From geometry,

$$\cos^2 aa^* = \frac{1 - \cos^2 a^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}{1 - \cos^2 \alpha^*} \tag{12}$$

From (8) and (11),

$$\cos \alpha^* = b_{23} (b_{33}b_{22})^{-1/2}, \text{ etc.} \tag{13}$$

Substituting (13) and similar relations in (12), the terms can be arranged in the form:

$$\cos^2\underset{\sim\sim}{aa}^* = \frac{b_{11}b_{22}b_{33} - b_{11}b_{23}^2 - b_{22}b_{13}^2 - b_{33}b_{12}^2 + 2b_{12}b_{13}b_{23}}{b_{11}(b_{22}b_{33} - b_{23}^2)} \tag{13}$$

The numerator is the expanded form of the determinant of A^{-1}, while the denominator is the product of b_{11} and its cofactor. Since a cofactor divided by a determinant is an element of the inverse matrix, (13) reduces to:

$$\cos \underset{\sim\sim}{aa}^* = (a_{11}b_{11})^{-1/2} \tag{14}$$

But, from the definition of $s(x)$:

$$s(x) = \sigma(x) (a_{11}b_{11})^{-1/2} \tag{15}$$

Thus $s(x)$ differs from $\sigma(x)$ by just the factor $\cos \underset{\sim\sim}{aa}^*$. This result indicates the importance in distinguishing $\sigma(x)$ and $s(x)$ in reporting experimental results.

CRYSTALLOGRAPHIC AND STATISTICAL INDEPENDENCE

Crystallographic independence does not necessarily imply statistical independence of coordinates. Consider a structure consisting of three similar atoms in a unit cell of no symmetry. Unless an origin is selected, a particular atom is as likely to be one place as another, and the variance of its position is infinite. Suppose the origin is placed at the first atom. Then

the variance of position of that atom is zero. Assume that the x coordinates

of the other two atoms, and the variances of these coordinates, are determined

as well as possible from the data. Then, if these coordinates are statistical-

ly independent,

$$\sigma(x_1 - x_2) < \sigma(x_3 - x_2).$$

This inequality can be reversed by placing the origin at the third atom. There-

fore it must be concluded that the coordinates are not statistically independent

in this case when the origin is chosen in this way.

I thank Dr. R. A. Sparks for his suggestion concerning $s(x)$, and Prof.

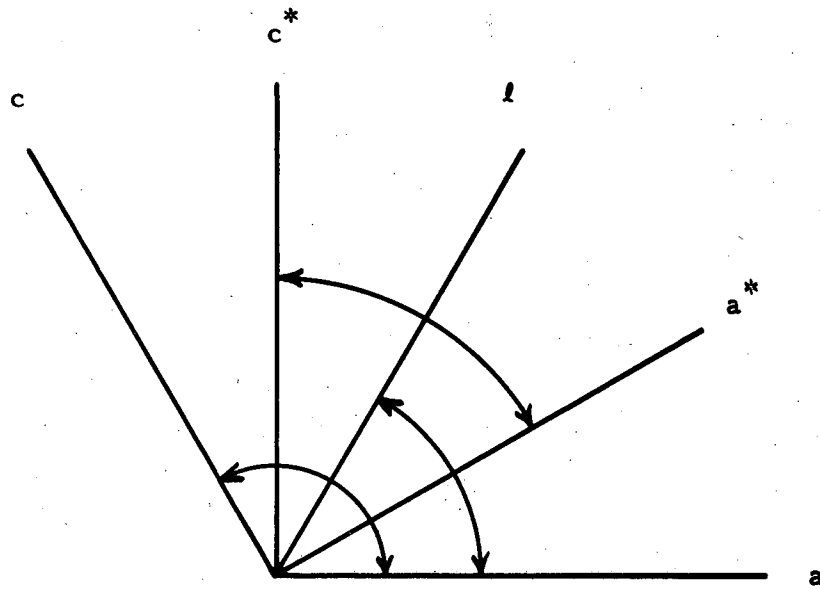J. Waser and Prof. K. N. Trueblood for helpful discussions.

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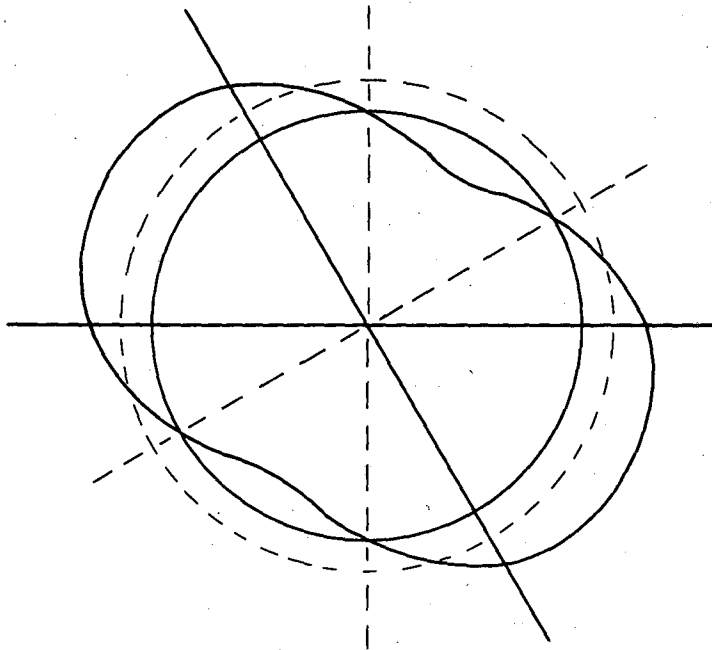
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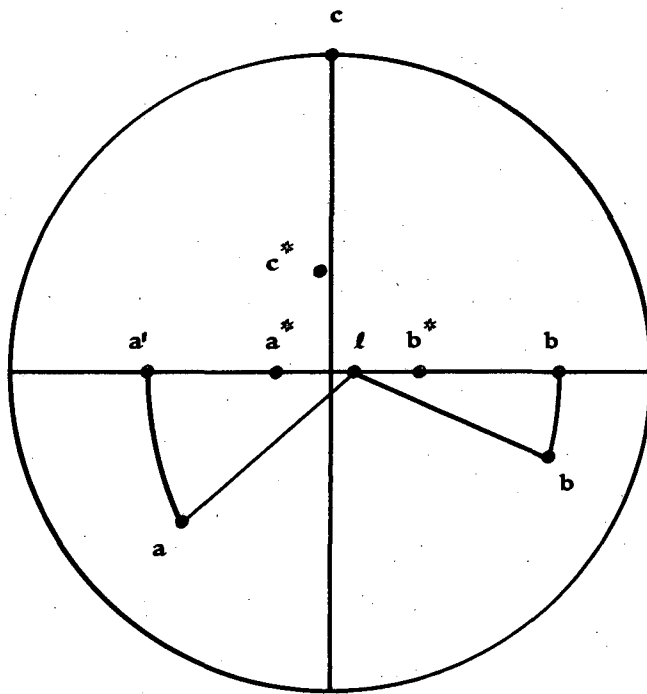
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Fig. 1. Monoclinic case: plane of a^* and c^*.

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Fig. 2. Triclinic case: stereographic projection of axial directions.

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Fig. 3. Variance of position with and without correlation, as explained
in the text.