APPENDIX 2

Crystal-chemical model of Pb atom distributed on the sphere surface

The distance between the Pb position (0,0,0) and the O atoms in the structure of lead magneso-niobate, 2.857 Å, seems to be rather long in comparison with the average Pb—O distance (about 2.814 Å) in crystal structures containing 12-coordinated Pb atoms. However, the difference is not so dramatic as to cause strong disorder of the Pb atom, because in the structures of $Rb_2PbCu(NO_2)_6$ (Takagi, Joesten & Lenhert, 1976) and $Cs_2PbCu(NO_2)_6$ (Klein & Reinen, 1978) these distances are 2.843 and 2.847 Å, where the Pb atoms occupy fixed positions.

The fact of strong disorder of the Pb atom in PMN can be explained in terms of a bond-valence model. Let us assume that the Mg and Nb atoms are isomorphously distributed in the crystal lattice. Then, different kinds of O atoms exist: O atoms connected to two Nb atoms, to two Mg atoms and to one Nb and one Mg atom. If the second and third coordination spheres are taken into account, the number of different kinds may be increased. So the bond order of Pb—O will range from 1/12 to 1/3 of a valence unit depending on the local surroundings. The vector sum of the Pb—O interactions will differ from zero and will have a random direction, causing the shift of the Pb atom from the centre of the polyhedron.

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Effects of Noncrystallographic Symmetry on the Σ_1 Relationship. I. Bicentric Arrangements in $P\bar{1}$

BY URI SHMUELI* AND GEORGE H. WEISS

Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Heath, Bethesda, Maryland 20892, USA

Abstract

An exact Fourier representation of the probability for the Σ_1 relationship is derived, which takes into account the presence of noncrystallographic centrosymmetry in the asymmetic unit of the space group $P\bar{1}$. Illustrative examples show that the main effect of noncrystallographic symmetry is to decrease the probability that E_{2h} is positive, as compared to the corresponding probability in the absence of such symmetry. The effect appears to be more pronounced in the equal-atom case than it is for a structure having a heterogeneous atomic composition.

* Permanent address: School of Chemistry, Tel Aviv University, 69 978 Tel Aviv, Israel.

Introduction

One of the earliest and simplest relationships in direct methods of phase determination is the expression for the probability that the sign of the normalized structure factor E_{2h} is positive conditioned on the magnitudes $|E_{2h}|$ and $|E_h|$. This expression is a probabilistic version of the Σ_1 relationship (*e.g.* Giacovazzo, 1980) and is usually referred to as the Σ_1 formula. This relationship was first defined by Hauptman & Karle in their *Monograph* (Hauptman & Karle, 1953). Early studies of this relationship yielded approximations based on the central limit theorem (Vand & Pepinsky, 1953; Cochran & Woolfson, 1955), which are still implemented in most software packages for crystal structure determination. Several higher approximations for Σ_1 have been proposed during the following three decades [for references, see Giacovazzo (1980)], and an exact representation of the expression for this probability was derived by Shmueli & Weiss (1985a) for the space group $P\bar{1}$ in the form of a Fourier series. However, all these studies only took atomic composition and crystallographic symmetry into account; no additional structural or physical effects were considered.

It occurred to us that since noncrystallographic symmetry strongly affects the probability density function (p.d.f.) of the magnitude of the structure factor (Rogers & Wilson, 1953; Shmueli, Weiss & Kiefer, 1985), it is also likely to affect sign and phase relationships. Our recent work on Fourier representations of univariate and multivariate structure-factor statistics allowed us to test this hypothesis quantitatively and we decided to derive and compute an exact expression for the Σ_1 relationship. Such an expression should be of interest in connection with the study of effects of noncrystallographic symmetry on direct methods of phase determination. Our derivation is presented in the next section and the paper concludes with two illustrative examples along with their interpretation.

Derivation

We derive an expression for the probability that the sign of the normalized structure factor E_{2h} is positive, given the magnitudes $|E_h|$ and $|E_{2h}|$, together with a noncrystallographic center of symmetry in the asymmetric unit. The derivation is given for the space group $P\bar{1}$.

We proceed along the lines of the derivation of the exact Σ_1 formula by Shmueli & Weiss (1985a), with modifications related to the functional form of the structure factor. We assume that:

(1) The position vectors, $\mathbf{r}_j$, of all the atoms and that of the noncrystallographic center, $\mathbf{d}$, have

rationally independent components, from which it follows that the phase factors $2\pi\mathbf{h}^T\mathbf{r}_j$ and $2\pi\mathbf{h}^T\mathbf{d}$, each taken modulo 2π, are uniformly distributed in the interval $(-\pi,\pi)$.

(2) Contributions of different atoms within the asymmetric subunit to the structure factor are statistically independent.

(3) Effects of anomalous dispersion are not taken into account.

Assumption (1) implies that all the atoms, as well as the noncrystallographic center, are located in general positions of the space group.

Following Shmueli & Weiss (1985a), the joint p.d.f. of the two structure factors involved is given by the two-dimensional Fourier series

$$p(E_h, E_{2h}) = (\alpha^2/4)\sum_s\sum_t C_{st} \exp[-i\pi\alpha(sE_h + tE_{2h})],$$
(1)

where the indices s and t range from $-\infty$ to ∞ and α is the reciprocal of the maximum allowable value of $|E|$. In order to obtain the coefficients, C_{st}, we use the result obtained by Shmueli, Weiss & Kiefer (1985) for the normalized structure factor in the present bicentric arrangement. This structure factor is given by

$$E_h = 4\cos\psi \sum_{j=1}^{N/4} n_j\cos(\theta_j - \psi),$$
(2)

where $\theta_j = 2\pi\mathbf{h}^T\mathbf{r}_j$, $\psi = 2\pi\mathbf{h}^T\mathbf{d}$, n_j is the normalized scattering factor of the jth atom and N is the number of atoms in the unit cell. The characteristic function corresponding to the p.d.f. given by (1) is therefore defined by

$$C(\omega_1,\omega_2) = \langle \exp[i(\omega_1 E_h + \omega_2 E_{2h})]\rangle,$$
(3)

$$C(\omega_1,\omega_2) = \left\langle \prod_{j=1}^{N/4} \exp\{4in_j[\omega_1\cos\psi\cos(\theta_j - \psi) + \omega_2\cos 2\psi\cos(2\theta_j - 2\psi)]\}\right\rangle.$$
(4)

The averaging in (4) is first carried out with respect to the θ_j's and finally with respect to ψ. If we introduce the abbreviations $x_{j1} = 4\omega_1 n_j\cos(\psi)$ and $x_{j2} = 4\omega_2 n_j\cos(2\psi)$ and recall that θ_j is uniformly distributed in $(-\pi,\pi)$, the average in (4) can be written as

$$C(\omega_1,\omega_2) = (1/2\pi)\int_{-\pi}^{\pi}\left\{\prod_{j=1}^{N/4}\left[(1/2\pi)\right.\right.$$
$$\times \int_{-\pi}^{\pi} \exp\{i[x_{j1}\cos(\theta - \psi)$$
$$\left.\left.+ x_{j2}\cos(2\theta - 2\psi)]\}d\theta\right]\right\}d\psi.$$
(5)

The multiple integral indicated in (5) can, at least in principle, be evaluated numerically. However, it is

also possible to reduce the expression for $C(\omega_1,\omega_2)$ to a single integral by making use of the identity

$$\exp\,(iu\cos\beta) = \sum_{m=-\infty}^{\infty} i^m J_m(u)\exp\,(im\beta) \qquad (6)$$

(e.g. Gradshteyn & Ryzhik, 1980; entry 8.511-4). By substituting this expansion for the exponentials in (5), we obtain

$$C(\omega_1,\omega_2)$$

$$= (1/2\pi)\int_{-\pi}^{\pi}\prod_{j=1}^{N/4}\sum_p\sum_q i^{p+q}J_p(x_{j1})J_q(x_{j2})$$

$$\times\left[(1/2\pi)\int_{-\pi}^{\pi}\exp\,[i(p+2q)(\theta-\psi)]\mathrm{d}\theta\right]\mathrm{d}\psi, \quad (7)$$

where

$$(1/2\pi)\int_{-\pi}^{\pi}\exp\,[i(p+2q)(\theta-\psi)]\mathrm{d}\theta$$

$$=\begin{cases}1, & \text{if } p=-2q \\ 0, & \text{if } p\neq-2q\end{cases}. \qquad (8)$$

It follows that

$$C(\omega_1,\omega_2) = (1/2\pi)\int_{-\pi}^{\pi}\left\{\prod_{j=1}^{N/4}\sum_q i^{3q}J_{2q}(x_{j1})J_q(x_{j2})\right\}\mathrm{d}\psi \quad (9)$$

$$\equiv (1/2\pi)\int_{-\pi}^{\pi}\left\{\prod_{j=1}^{N/4}[R_j(\omega_1,\omega_2,\psi)\right.$$

$$\left.+iI_j(\omega_1,\omega_2,\psi)]\right\}\mathrm{d}\psi, \qquad (10)$$

where

$$R_j(\omega_1,\omega_2,\psi) = J_0(x_{j1})J_0(x_{j2})$$

$$+2\sum_{m=1}^{\infty}(-1)^m J_{4m}(x_{j1})J_{2m}(x_{j2}) \qquad (11)$$

and

$$I_j(\omega_1,\omega_2,\psi) = 2\sum_{m=0}^{\infty}(-1)^{m+1}J_{4m+2}(x_{j1})J_{2m+1}(x_{j2}).$$

$$(12)$$

The Fourier coefficients are obtained in a manner similar to that presented by Shmueli & Weiss (1985a). If we make the replacements $\omega_1\rightarrow\pi\alpha s$ and $\omega_2\rightarrow\pi\alpha t$ and introduce the abbreviations

$$R_{jst}(\psi) = R_j(\pi\alpha s,\pi\alpha t,\psi), \qquad (13)$$

$$I_{jst}(\psi) = I_j(\pi\alpha s,\pi\alpha t,\psi), \qquad (14)$$

the expression for the Fourier coefficient can be written

$$C_{st} = (1/\pi)\int_0^{\pi}\left\{\prod_{j=1}^{N/4}[R_{jst}(\psi)+iI_{jst}(\psi)]\right\}\mathrm{d}\psi \quad (15)$$

$$\equiv \mathscr{R}_{st}+i\mathscr{I}_{st}, \qquad (16)$$

where $\mathscr{R}_{st}$ and $\mathscr{I}_{st}$ are the real and imaginary parts, respectively, of the integral on the right-hand side of (15).

In our test calculations, we assume that there are only two kinds of atoms in the asymmetric subunit. There are M_L equal light atoms and M_H equal heavy ones. The product in (15) then reduces to

$$(R_{Lst}+iI_{Lst})^{M_L}(R_{Hst}+iI_{Hst})^{M_H}, \qquad (17)$$

where $M_L+M_H=N/4$, a similar simplification being valid for the representation of $C(\omega_1,\omega_2)$ given in (5).

Equation (1) can now be computed directly. However, this calculation is significantly simpler when symmetry properties of the real and imaginary parts of the Fourier coefficient are taken into account, with respect to changes in sign of s and t. A direct inspection of (11) and (12), with the appropriate replacements as made above, shows that $R_{jst}(\psi)$ is invariant under the change of the signs of s or t or both, for any j and ψ. Further, I_{jst} is invariant with respect to a change in sign of s but changes its sign when t changes sign. The real and imaginary parts of the integrand in (15) have the same symmetry as that of $R_{jst}(\psi)$ and $I_{jst}(\psi)$ (cf. Shmueli & Weiss, 1985a) and the same is true for the integral in (15). We therefore have

$$\mathscr{R}_{st} = \mathscr{R}_{\bar{s}t} = \mathscr{R}_{s\bar{t}} = \mathscr{R}_{\bar{s}\bar{t}}, \qquad (18)$$

$$\mathscr{I}_{\bar{s}t} = \mathscr{I}_{st} \quad\text{and}\quad \mathscr{I}_{s\bar{t}} = -\mathscr{I}_{st}. \qquad (19)$$

Since the symmetry of the Fourier coefficients in the presence of noncrystallographic symmetry is the same as that in its absence, we can use the results of Shmueli & Weiss (1985a) by simply replacing R_{st} and I_{st} of that reference with the present $\mathscr{R}_{st}$ and $\mathscr{I}_{st}$, respectively. The final result for the probability that the sign of E_h is positive, given the magnitudes $|E_{2h}|$ and $|E_h|$, is therefore given by

$$p_+(2\mathbf{h}|\mathbf{h}) = \tfrac{1}{2}(1+\Omega_b/\Gamma_b), \qquad (20)$$

where

$$\Omega_b = \sum_{s=1}^{\infty}\sum_{t=1}^{\infty}\mathscr{I}_{st}\cos\,(\pi\alpha s E_h)\sin\,(\pi\alpha t|E_{2h}|) \quad (21)$$

and

$$\Gamma_b = \tfrac{1}{4}\left\{1+2\sum_{s=1}^{\infty}\mathscr{R}_{s0}[\cos\,(\pi\alpha s E_h)+\cos\,(\pi\alpha s E_{2h})]\right.$$

$$\left.+4\sum_{s=1}^{\infty}\sum_{t=1}^{\infty}\mathscr{R}_{st}\cos\,(\pi\alpha s E_h)\cos\,(\pi\alpha t E_{2h})\right\}. \quad (22)$$

Equations (20), (21) and (22), with $\mathscr{R}_{st}$ and $\mathscr{I}_{st}$ given by (16) and (15) and based on (11) and (12), are the basis of numerical computations of the exact probability for Σ_1 in the presence of noncrystallographic centrosymmetry in a $P\bar{1}$ structure.

Examples and discussion

The probability that the seminvariant E_{2h} will be positive, given the magnitudes $|E_{2h}|$ and $|E_h|$ in addition to a bicentric arrangement of the unit-cell contents, was evaluated for $|E_{2h}|$ fixed at 1.75, $|E_h|$ varying from 1.0 to 3.0 and two compositions of the asymmetric unit of space group $P\bar{1}$: (i) C_{32} and (ii) $C_{30}Cd_2$. In the bicentric arrangement, this consists of two identical subunits. The probability computed for this arrangement is represented by dashed lines in Figs. 1(a) and (b) and is referred to as the *probability for the bicentric* Σ_1. The solid lines in these figures represent the corresponding exact probabilities for the Σ_1 relationship for the same values of $|E|$ and the same compositions but in the *absence* of noncrystallographic symmetry – computed from the results of Shmueli & Weiss (1985a). The latter is referred to as *probability for the centric* Σ_1.

The computation of the probability for the centric Σ_1 is rapid and straightforward since the coefficients of the relevant Fourier expansion are given by an expression equivalent to the *integrand* in (15) with $\psi = 0$. The Fourier coefficients needed for the probability for the bicentric Σ_1, on the other hand, require the evaluation of the angular integral in (15). This numerical integration converges slowly, especially in the equal-atom case. The dashed lines in Fig. 1 are a result of some smoothing of the computed bicentric Σ_1 relation.

While the present treatment is valid for an arbitrary atomic heterogeneity, it appears interesting to find the expression for the probability of a bicentric Σ_1 relationship for the equal-atom case. This is of probable importance in practical applications and

would bring out more clearly the dependence of the probability on the number of atoms in the unit cell.

This investigation of the effect of noncrystallographic symmetry on exact multivariate crystallographic statistics indicates that, in the important equal-atom case, the presence of a bicentric arrangement significantly decreases the probability that the sign of the structure seminvariant E_{2h} is positive. Such a decrease also occurs as a result of a heterogeneous composition [Fig. 1(b)] but the effect is practically absent when the magnitude of E_h is sufficiently large.

It was recalled by one of the referees that structures with more than one molecule in the asymmetric unit are more difficult to solve by direct methods than they should be. This may indeed have to do with the decreased probability of sign/phase relationships, associated with noncrystallographic symmetry. Of course, the bicentric arrangement is only one such unfavorable situation.

The present calculations were planned so that an exact probability for the Σ_1 relationship should be evaluated for a partially bicentric arrangement (Shmueli & Weiss, 1985b). This is a situation – not unfrequently encountered in real crystals – where the asymmetric unit of $P\bar{1}$ contains a large centrosymmetric fragment and some atoms not related by the non-crystallographic center. The Fourier coefficient can then be obtained as a product of centric and bicentric contributions. It will be of interest to examine this situation when more extensive calculations of effects of noncrystallographic symmetry are undertaken.

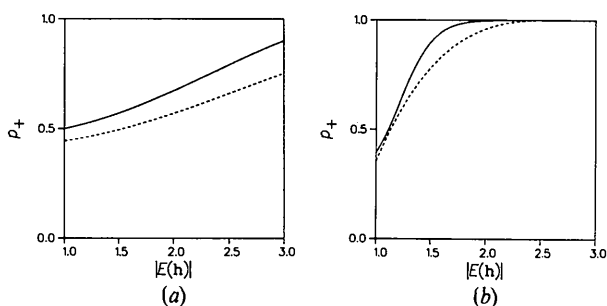Fig. 1. The Σ_1 relationship in the presence and absence of noncrystallographic symmetry. The solid curves denote the probability for the positive sign of E_{2h} in the absence of noncrystallographic symmetry (Shmueli & Weiss, 1985a) and the dashed curves refer to in its presence, as derived in the text. The magnitude $|E_{2h}|$ is fixed at 1.75. Composition of the asymmetric unit: (a) C_{32}, (b) $C_{30}Cd_2$.

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