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Exact Random-Walk Models in Crystallographic Statistics. III. Distributions of $|E|$ for Space Groups of Low Symmetry

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Abstract

Exact univariate probability density functions (p.d.f.'s) of the magnitude of the normalized structure factor, taking into account space-group symmetry and the chemical composition of the asymmetric unit, have been investigated. The p.d.f.'s that represent distributions for centrosymmetric space groups are given by single Fourier series, while those for the non-centrosymmetric ones can be obtained from double Fourier series or, more conveniently, from single Fourier-Bessel expansions. Analytical expressions for the expansion coefficients are given for all triclinic, monoclinic and orthorhombic space groups, except *Fdd*2 and *Fddd*. These results are applied to a comparison of simulated distributions, based on a C_9U asymmetric unit and the space groups *P*1, *P*$\bar{1}$, *P*2 (or *Pm*), *P*2/*m*, *P*222, *Pmm*2 and *Pmmm*, with the theoretical p.d.f.'s derived here and with approximate generalized p.d.f.'s given by previously published five-term Hermite and Laguerre expansions. The performance of the Fourier and Fourier-Bessel p.d.f.'s is very good throughout the range of symmetries investigated, while that of the approximate ones is rather poor for the lowest symmetries and improves - albeit not uniformly - for the higher ones. Pertinent programming considerations, which suffice for the implementation of the new results in appropriate software, are presented.

Introduction

Exact univariate and multivariate distributions of the normalized structure factor have recently been introduced in crystallographic statistics, and their performance in situations arising in intensity statistics, as well as their application to simple sign relationships, have been discussed and illustrated (*e.g.* Shmueli, Weiss, Kiefer & Wilson, 1984; Shmueli, Weiss & Kiefer, 1985; Shmueli & Weiss, 1985). The principles of the derivation of probability density functions (p.d.f.'s) that account explicitly for crystal symmetry and composition have been given in some detail (Shmueli & Weiss, 1985), and their applications to specific cases are now possible. We started from the simplest instance, the p.d.f. of the magnitude of one normalized structure factor, and tried to represent it for a range of space-group symmetries. Preliminary results of our work on this subject have been presented elsewhere (Weiss, Shmueli, Kiefer & Wilson, 1985).

Probability distributions of one structure factor are of interest in the field of intensity statistics, and find their use in the resolution of space-group ambiguities. It is well known that the presence of outstandingly heavy atoms can cause serious discrepancies between observed distributions and those based on the central limit theorem (Wilson, 1949), and can give rise to difficulties in space-group determination. This problem has been extensively studied using truncated Gram-Charlier p.d.f.'s (*e.g.* Shmueli, 1979; Shmueli & Wilson, 1981, 1983; Shmueli & Kaldor, 1981, 1983), and such generalized p.d.f.'s, appropriate to all the space groups, are available for the case of all the atoms occupying general positions. These approximate p.d.f.'s perform well in cases of moderate atomic heterogeneity, and for many space groups of higher symmetries. However, their performance is least satisfactory for low symmetries, and especially when the composition is strongly heterogeneous and the number of atoms in the asymmetric unit is small. It is therefore desirable to develop and present expressions for the exact p.d.f.'s for the low-symmetry space groups.

The purpose of this paper is to present a classification of the exact p.d.f.'s that have been found to be most useful, to derive their functional forms for the triclinic, monoclinic and orthorhombic space groups and to compare their performance with that of the older approximate statistics using simulated distributions based on highly heterogeneous asymmetric units. The results presented in this paper can form the basis of application software, and such software, in which both the exact and the approximate

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approaches are implemented, is presently being developed.

Probability density functions

The normalized structure factor will be written as

$$E(\mathbf{h}) = \sum_{j=1}^{N/g} n_j T_j(\mathbf{h}) = A(\mathbf{h}) + iB(\mathbf{h}), \quad (1)$$

where

$$T_j(\mathbf{h}) = \xi_j(\mathbf{h}) + i\eta_j(\mathbf{h}) = \sum_{s=1}^{g} \exp[2\pi i \mathbf{h}^T(\mathbf{P}_s\mathbf{r}_j + \mathbf{t}_s)] \quad (2)$$

is the trigonometric structure factor, which contains the explicit dependence on the space-group operators $(\mathbf{P}, \mathbf{t})$, n_j is the normalized scattering factor, $n_j = f_j/(\sum_{k=1}^{N} f_k^2)^{1/2}$, N is the number of atoms in the unit cell and g is the number of asymmetric units in the cell (order of the point group times the multiplicity of the Bravais lattice). We confine our calculations to the case of all the atoms being located in general positions, and assume that (i) effects of rational dependence are negligible (*cf.* Shmueli, Weiss, Kiefer & Wilson, 1984; Shmueli & Weiss, 1985) and (ii) the contributions of different atoms, within the asymmetric unit, to the structure factor are independent. These assumptions permit one to treat the atomic phase factors as random variables, uniformly distributed over the $[0, 2\pi]$ range.

The principle of the derivation of exact p.d.f.'s of the structure factor in the form of Fourier series consists of two elementary premises:

(i) A centrosymmetric normalized structure factor, or the real or imaginary part of a non-centrosymmetric one, must be confined to the $[-E_M, E_M]$ range, where E_M is the sum of the normalized scattering factors.

(ii) Since the probability of finding (a real) E, or either of A and B, outside the $[-E_M, E_M]$ interval is zero, probability density functions of these quantities can be regarded as bounded and the p.d.f.'s can therefore be expanded in Fourier series on this interval.

As shown by Shmueli & Weiss (1985), the above applies to any number of structure factors, and the general features of the underlying formalism have been given in the above study. For consistency of notation, we shall designate the reciprocal of the sum of the scattering factors by

$$\alpha = \left(\sum_{j=1}^{N} n_j\right)^{-1}. \quad (3)$$

Centrosymmetric space groups

The p.d.f. of $|E|$ is given for these space groups by

$$p(|E|) = \alpha\left[1 + 2\sum_{u=1}^{\infty} C_u \cos(\pi\alpha u|E|)\right], \quad (4)$$

where

$$C_u = \prod_{j=1}^{N/g} C_{uj}, \quad (5)$$

and

$$C_{uj} = \langle \exp(\pi i \alpha n_j u \xi_j)\rangle, \quad (6)$$

where ξ_j is the (real) trigonometric structure factor of the jth atom. (4) has been applied to the space group $P\bar{1}$, and the coefficients (5) were derived for crystallographic and non-crystallographic symmetry (Shmueli, Weiss, Kiefer & Wilson, 1984; Shmueli, Weiss & Kiefer, 1985; see also Appendix *A*).

Non-centrosymmetric space groups

Following the method of Shmueli & Weiss (1985), we can write the joint p.d.f. of the real and imaginary parts of E as the double Fourier series

$$p(A, B) = (\alpha/2)^2 \sum_u \sum_v C_{uv} \exp[-\pi i\alpha(uA + vB)], \quad (7)$$

where

$$C_{uv} = \prod_{j=1}^{N/g} C_{uvj} \quad (8)$$

and

$$C_{uvj} = \langle \exp[\pi i \alpha n_j (u\xi_j + v\eta_j)]\rangle, \quad (9)$$

where $T_j = \xi_j + i\eta_j$ is the trigonometric structure factor of the jth atom. Some examples of the averaging to be done in (9) are given in Appendix *A*.

Since we are interested, in the present context, in the p.d.f. of the magnitude $|E|$ of the normalized structure factor, we transform (7) by introducing the variables $|E|$ and φ, where φ is the phase of the structure factor, as $A = |E|\cos\varphi$ and $B = |E|\sin\varphi$, and integrate out the phase. The result is

$$p(|E|) = \frac{\pi}{2}\alpha^2|E| \sum_u \sum_v C_{uv} J_0[\pi\alpha(u^2 + v^2)^{1/2}|E|]. \quad (10)$$

Equation (10), with coefficients given by (8) and (9), is applicable to any non-centrosymmetric space group. This equation was first given by Weiss, Shmueli, Kiefer & Wilson (1985).

When the coefficients C_{uv} in (10) depend on $(u^2 + v^2)^{1/2}$ only, *i.e.* they have radial symmetry in the (u, v) index space, we can, following Barakat (1974), represent the p.d.f. of the magnitude $|E|$ by a single Fourier–Bessel series (Berg & McGregor, 1966), which takes the form

$$p(|E|) = 2\alpha^2|E| \sum_{u=1}^{\infty} D_u J_0(\alpha\gamma_u|E|), \quad (11)$$

where

$$D_u = [J_1^2(\gamma_u)]^{-1} C(\alpha\gamma_u) \quad (12)$$

and

$$C(\alpha\gamma_u)=\prod_{j=1}^{N/g} C_{uj}, \qquad (13)$$

where $J_1(x)$ is the Bessel function of the first kind, of the first order, and γ_u is the uth root of the equation $J_0(x)=0$ (*cf.* Shmueli, Weiss, Kiefer & Wilson, 1984; Weiss, Shmueli, Kiefer & Wilson, 1985).

Numerical computations of the p.d.f.'s from single Fourier-Bessel series are of course faster than those using the double Fourier series (10), but both representations converge fairly rapidly.

Examples and discussion

The formalism of the previous section was applied to the derivation of analytical forms of the Fourier and Fourier-Bessel expansion coefficients for the monoclinic and orthorhombic symmorphic space groups. These coefficients, together with those given by Shmueli, Weiss, Kiefer & Wilson (1984) for $P1$ and $P\bar{1}$, extend the exact p.d.f.'s to all the space groups of the first three crystal systems, with the exception of *Fdd*2 and *Fddd*. This is so since, for these systems, the moments of the trigonometric structure factor are associated with the point groups rather than with the space groups (Shmueli, 1979; Shmueli & Kaldor, 1981, 1983) and so are the moments of the structure factor and its p.d.f.'s. The atomic contributions to the expansion coefficients are listed in Table 1 and some of their derivations are briefly illustrated in Appendix *A*.

These exact p.d.f.'s, the previously given approximate Gram-Charlier expansions (Shmueli & Wilson, 1981; Shmueli, 1982*a*) and simulated distributions of $|E|$ - all for a C_9U asymmetric unit - were computed and compared. The calculations were carried out for all the point groups listed in Table 1, represented by symmorphic space groups with *P*-type lattices, and the simulation was carried out as described elsewhere (Shmueli, 1982*b*; Shmueli, Weiss, Kiefer & Wilson, 1984). Some simulated and theoretical p.d.f.'s are shown in Fig. 1, and a list of the χ^2 and R discrepancy criteria, evaluated as detailed by Shmueli, Weiss, Kiefer & Wilson (1984), is given in Table 2.

It is seen that the exact p.d.f.'s, shown by solid lines in Fig. 1 agree very well with the simulated distributions throughout the range of symmetries considered, while the performance of the Gram-Charlier p.d.f.'s (dashed lines) is rather poor for the triclinic space groups and improves as the symmetry increases. In one case, for the space group $P222$, the exact p.d.f. seems to offer only a marginal improvement over that achieved by the five-term Gram-Charlier expansion appropriate to this space group. It is also interesting to note that the distribution for *Pmm*2 is clearly on the 'centric' side, while that for *Pmmm* is similar to the bicentric one (*e.g.* Shmueli, 1982*b*). One must, of course, keep in mind the rather high atomic heterogeneity (one U and nine C atoms in the asymmetric unit) that was assumed and the consequent strong effect of the heavy atom on the distribution.

Table 1. *Atomic contributions to the expansion coefficients of Fourier and Fourier-Bessel p.d.f.'s*

The table lists the point-group symbols and the corresponding analytical expressions of the atomic contributions to the expansion coefficients. These expressions are applicable to all the space groups that are based on the point group in a given entry, except those given in the footnotes. The superscripts (1), (2), or (3) indicate that the contribution pertains to the single Fourier p.d.f., equation (4), the single Fourier-Bessel p.d.f., equation (11), or the double Fourier p.d.f., equation (10), respectively. The abbreviations in the Table are:

$$a_{uj}=g\pi\alpha n_j u,\ b_{uj}=g\alpha n_j\gamma_u \text{ and } c_{uvj}=g\alpha n_j\pi(u^2+v^2)^{1/2},$$

where g is the order of the point group times the multiplicity of the Bravais lattice, u and v are summation indices, n_j is the normalized scattering factor of atom j and α is given by equation (3).

Point group(s)	Atomic contribution
1	$C^{(2)}_{uj}=J_0(b_{uj})$ or $C^{(3)}_{uvj}=J_0(c_{uvj})$
$\bar{1}$	$C^{(1)}_{uj}=J_0(a_{uj})$
2, m	$C^{(2)}_{uj}=J_0^2(b_{uj}/2)$ or $C^{(3)}_{uvj}=J_0^2(c_{uvj}/2)$
$2/m$	$C^{(1)}_{uj}=J_0^2(a_{uj}/2)$
222	$C^{(3)}_{uvj}=(2/\pi)\int_0^{\pi/2} J_0(\lvert X+Y\rvert)J_0(\lvert X-Y\rvert)\,d\theta$ where $X=(a_{uj}/2)\cos\theta$ and $Y=(a_{uj}/2)\sin\theta$
*mm*2*	$C^{(2)}_{uj}=(2/\pi)\int_0^{\pi/2} J_0^2[(b_{uj}/2)\cos\theta]\,d\theta$ or $C^{(3)}_{uvj}=(2/\pi)\int_0^{\pi/2} J_0^2[(c_{uvj}/2)\cos\theta]\,d\theta$
mmm†	$C^{(1)}_{uj}=(2/\pi)\int_0^{\pi/2} J_0^2[(a_{uj}/2)\cos\theta]\,d\theta$

* Not applicable to *Fdd*2.
† Not applicable to *Fddd*.

It was found in this and previous studies that the dependence of the fourth moment of $|E|$ on a range of symmetries and a somewhat more moderate atomic heterogeneity, given by Shmueli & Wilson (1981), provides a good qualitative indicator of space-group symmetries which are likely to be problematic. This is seen from the comparison of *Pmm*2 with *Pmmm*, and is also expected to be found in the pairs (*P*4*mm*, *P*4/*mmm*) and (*P*6*mm*, *P*6/*mmm*) and perhaps in some other space groups. It is therefore likely that some space groups of higher symmetries will be studied by the methods of this paper; some analytical work still needs to be done in order to reduce the readily available formal expressions to a form lending itself to routine computation. However, in most space groups of higher symmetries the departures from the asymptotic centric and acentric distributions (Wilson, 1949) are usually smaller than those in the space groups here treated, and the available (for all the space groups) four-term Gram-Charlier expansions (Shmueli & Wilson, 1981; Shmueli & Kaldor, 1981,

Table 2. *Discrepancies between the theoretical and simulated distributions given in Fig.* 1

The table lists the χ^2 and R discrepancy factors between the Fourier (and Fourier-Bessel) and Gram-Charlier p.d.f.'s and the histograms which were simulated for the composition C_9U of the asymmetric unit in each of the space groups shown.

Explanation of Table headings:

(h-ex) - comparison of histogram with the p.d.f. computed from Fourier or Fourier-Bessel expansion.

(h-GC) - comparison of histogram with the p.d.f. computed as a five-term Gram-Charlier expansion.

$\bar{\chi}^2(2\delta)$ - approx. '95% confidence' expected value of χ^2 (Shmueli, Weiss, Kiefer & Wilson, 1984).

$\bar{R}$ - expected value of R (*cf.* above reference).

Note: the expected values of χ^2 and R pertain to the comparison of the histogram and the Fourier or Fourier-Bessel p.d.f.

Space group(s)	χ^2(h-ex)	χ^2(h-GC)	$\bar{\chi}^2(2\delta)$	R(h-ex)	R(h-GC)	$\bar{R}$
*P*1	4·72	1160·71	14·48	0·032	0·507	0·036
P$\bar{1}$	10·99	236·89	30·00	0·052	0·245	0·070
*P*2 (*Pm*)	16·88	528·68	27·31	0·060	0·339	0·067
*P*2/*m*	18·96	115·47	35·27	0·065	0·150	0·076
*P*222	23·58	54·93	32·65	0·071	0·094	0·070
*Pmm*2	19·91	295·44	33·96	0·066	0·311	0·074
Pmmm	28·67	94·45	42·97	0·072	0·181	0·069

1983) are likely to perform reasonably well for many higher symmetries, even in cases of conspicuous atomic heterogeneity.

As is obvious from the underlying assumptions (see above), the present results are applicable to structures having all the atoms in general positions and in which effects of rational dependence are negligible, especially among the heavy scatterers. While the problem of special positions calls for a calculation of characteristic functions (*e.g.* Kendall & Stuart, 1969) for the appropriate forms of the trigonometric structure factor, and is soluble at least in principle, the problem of accounting for rational dependence is clearly a much more serious one. In any case, it seems more advisable to compare the histogram of experimental $|E|$ values with the best available p.d.f.'s than to carry out statistical tests using only moments and cumulative distributions; the latter may be easier to compute, but they do not reveal the shape of the distribution and may well conceal 'surprises'.

Another important consideration is the percentage of weak or 'unobserved' reflections removed from the data set. Such removal may distort the experimental distribution as a whole, and will affect mainly its low end. Thus, for example if the low end of a $P\bar{1}$ distribution is artificially underpopulated the resulting histogram acquires apparent 'acentric' features, and it may be difficult to recognize the true symmetry without consulting the detailed distribution that is expected for the above space group, for the given atomic composition. The discrimination between other space groups, *e.g.* *Pmm*2 and *Pmmm*, is also likely to be difficult in such circumstances.

Programming considerations

The coefficients for the space groups *P*1, *P*$\bar{1}$, *P*2 (or *Pm*) and *P*2/*m* are most conveniently computed from polynomial approximations for $J_0(x)$ and $J_1(x)$ that are given in the literature (*e.g.* Abramowitz & Stegun, 1972). The roots ('zeros') of $J_0(x)=0$, required for Fourier-Bessel expansions, are rapidly and accurately obtainable by taking the first five tabulated roots (Abramowitz & Stegun, 1972, Table 9.5) and generating the remaining ones from McMahon's formula (*e.g.* Shmueli, Weiss, Kiefer & Wilson, 1984, Appendix *A*).

More care is needed in numerical evaluation of the integrals for *P*222, *Pmm*2 and *Pmmm*, since the integrands are oscillatory functions and the frequency

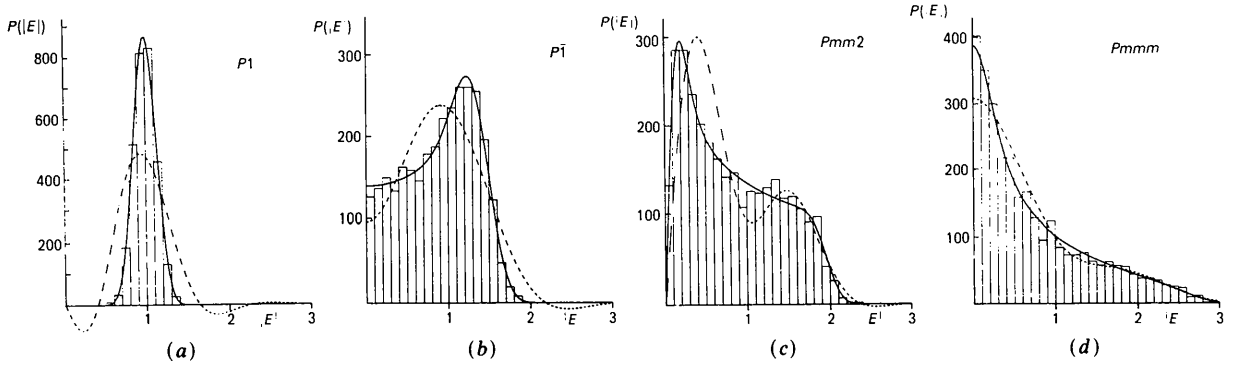

Fig. 1. Simulated and theoretical distributions for space groups of low symmetries. The histograms and theoretical p.d.f.'s were calculated assuming that the asymmetric unit of each space group contains nine carbon atoms and one uranium. The histograms are constructed from 3000 simulated $|E|$ values each, in 30 equal channels and in the range $0<|E|<3$. The p.d.f.'s computed from Fourier and Fourier-Bessel expansions (see text) are drawn using solid lines, and the p.d.f.'s drawn using dashed lines are computed from five-term Hermite and Laguerre expansions of the Gram-Charlier type (Shmueli, 1982*a*). All the p.d.f.'s are scaled to the corresponding histograms. An interval between successive divisions on the vertical axis of a drawing corresponds to 100 (channel) counts of the histogram shown. The triclinic and achiral orthorhombic symmetries are selected for this figure. For all the low symmetries, in the context of comparison between exact and approximate expressions, see Table 2. (*a*) *P*1, (*b*) *P*$\bar{1}$, (*c*) *Pmm*2, (*d*) *Pmmm*.

of these oscillations increases with increasing value of the constant coefficient of the sine or cosine. For rough calculations, Simpson's rule or Gaussian quadrature appear to be sufficient; however, the theoretical p.d.f. (and mainly its tail $|E|$ values) is then likely to be affected by ripples. We avoided this by using Romberg's adaptive integration algorithm (*e.g.* Davis & Rabinovitz, 1967), as implemented in the *DCADRE* routine in the locally available *IMSL* program library.

The number of terms in a single Fourier or Fourier–Bessel summation was usually taken as 40, because of the highly heterogeneous composition for which the illustrative examples were computed. This seems to be an upper limit of what may usually be needed for a ten-atom unit, but more terms may be required for smaller units.

We thank Mrs Zafra Stein for skillful and helpful programming and computing assistance, and we are grateful to Professor A. Ben-Reuven for helping us to simplify one of the integrals that appeared in the coefficient for *P*222. All the computations were carried out on the Cyber 170–855 at the Tel Aviv University Computation Center. This research was supported in part by grant No. 84-00076 from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel.

APPENDIX *A*

The evaluation of the coefficients given in Table 1 involves calculation of definite integrals that lead to, or contain, Bessel functions of the first kind. The technique employed is illustrated below by several examples.

*Space group P*1

The trigonometric structure factor is $\xi_j + i\eta_j$, where $\xi_j = \cos\theta_j$ and $\eta_j = \sin\theta_j$, with $\theta_j = 2\pi(hx_j + kv_j + lz_j)$. Hence, using (9), the atomic contribution to the Fourier coefficient is given by

$$C_{uvJ} = \langle \exp[\pi i \alpha n_j (u\cos\theta_j + v\sin\theta_j)] \rangle \qquad (A1)$$

$$= \langle \exp[\pi i \alpha n_j (u^2+v^2)^{1/2} \cos(\theta_j - \Delta)] \rangle \qquad (A2)$$

$$= (2\pi)^{-1} \int_0^{2\pi} \exp[\pi i \alpha n_j (u^2+v^2)^{1/2} \times \cos(\theta - \Delta)]\, d\theta \qquad (A3)$$

$$= J_0[\pi \alpha n_j (u^2+v^2)^{1/2}], \qquad (A4)$$

where $\tan\Delta = v/u$. The introduction of polar coordinates, leading from (*A*1) to (*A*2), and the integral representation of the Bessel function $J_0(x)$ (*e.g.* Abramowitz & Stegun, 1972, entry 9.1.21), leading from (*A*3) to (*A*4), are frequently employed in these calculations.

Equation (*A*4) can be used in computing the Fourier coefficient for *P*1, for the double Fourier p.d.f. (10). In view of the rotational symmetry with respect to the index pair (u, v), the double Fourier series can be replaced by a single Fourier–Bessel expansion (see *e.g.* Spiegel, 1974) as shown in the text.

Space group Pmmm

The trigonometric structure factor is of the form $\xi_j = 8\cos\theta_j \cos\varphi_j \cos\psi_j$, where $\theta_j = 2\pi h x_j$, $\varphi_j = 2\pi k v_j$ and $\psi_j = 2\pi l z_j$. We thus have

$$C_{uj} = \langle \exp[8\pi i \alpha n_j u \cos\theta_j \cos\varphi_j \cos\psi_j] \rangle,$$

and integrating first over ψ we obtain

$$C_{uj} = (2/\pi)^2 \int_0^{\pi/2}\int J_0(8\pi\alpha n_j u \cos\theta \cos\varphi)\, d\theta\, d\varphi. \qquad (A5)$$

One of the angular variables in (*A*5) can be integrated out, if we make use of the known definite integral

$$\int_0^{\pi/2} J_0(2z\cos x)\, dx = (\pi/2) J_0^2(z) \qquad (A6)$$

(Gradshteyn & Ryzhik, 1980, entry 6.519.1), thus leading to the coefficient for *Pmmm* appearing in Table 1.

*Space group P*222

The trigonometric structure factor is of the form $\xi_j + i\eta_j$, where $\xi_j = 4\cos\theta_j \cos\varphi_j \cos\psi_j$ and $\eta_j = -4\sin\theta_j \sin\varphi_j \sin\psi_j$, and θ_j, φ_j, ψ_j have the same meaning as in *Pmmm* above. Abbreviating to $\xi_j = K(\theta_j, \varphi_j)\cos\psi_j$ and $\eta_j = M(\theta_j, \varphi_j)\sin\psi_j$, and following the same steps as outlined for *P*1 above, we obtain

$$C_{uvj} = (2/\pi)^2 \int_0^{\pi/2}\int J_0[4\pi\alpha n_j (u^2\cos^2\theta\cos^2\varphi + v^2\sin^2\theta\sin^2\varphi)^{1/2}]\, d\theta\, d\varphi. \qquad (A7)$$

Equation (*A*7) can be rearranged to

$$C_{uvj} = (2/\pi)^2 \int_0^{\pi/2}\int J_0\{[P(\theta) + Q(\theta)\cos^2\varphi]^{1/2}\}\, d\theta\, d\varphi, \qquad (A8)$$

where

$$P(\theta) = 8(\pi\alpha n_j)^2 (u^2\cos^2\theta + v^2\sin^2\theta)$$

and

$$Q(\theta) = 8(\pi\alpha n_j)^2 (u^2\cos^2\theta - v^2\sin^2\theta).$$

Using the identity $\cos^2\varphi = \frac{1}{2} + \frac{1}{2}\cos 2\varphi$, introducing the variable $\tau = 2\varphi$ and comparing the correspondingly rearranged form of (*A*8) with the known definite integral

$$\int_0^{\pi} J_0[(x^2+y^2-2xy\cos\tau)^{1/2}]\, d\tau = \pi J_0(x) J_0(y) \qquad (A9)$$

(*cf.* Gradshteyn & Ryzhik, 1980, entry 6.684.1), we arrive at the expression given for this coefficient in Table 1.

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The Effect of Ionic Deformation on One-Phonon X-ray Scattering

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Abstract

Explicitly representing the deformation of ions by the lattice dynamical shell model, the one-phonon scattering is written in a form that is amenable to direct evaluation. An analytic expression for the shell scattering factor is introduced, and the percentage alteration in the scattering brought about by the ionic deformation during vibration is calculated. Contour plots of the effect are presented for GaAs, ZnS and Si as representative of the zinc-blende-structure compounds and group IV elements. The alteration produced by shell models is found to be negative, because for these materials the shell moves less than the core. Its maximum value varies from about −2·5 to −15% depending on the material and lattice dynamical model used. Its structure in reciprocal space should be measurable and could lead to a better understanding of deformation processes.

Introduction

Continuing interest on how the deformation of an ion during vibration affects the scattering factors led to an earlier study by Reid (1983*b*) on the modification of the Debye-Waller factor likely to arise from this process. Using different shell models to represent the deforming ions, a quantitative analysis was made for 14 zinc-blende-structure materials. Since then, Matthew & Yousif (1984) have highlighted the quantum-mechanical justification inherent in the shell model approach. It is therefore natural to complete the enquiry by asking what quantitative effects are expected from such deformation processes on one-phonon (X-ray) scattering. This scattering is of course not confined to Bragg reflections and therefore gives a better picture of the decay of the effect with increasing scattering vector than is provided by the Debye-Waller factors.

The additional scattering processes

Earlier studies of the effect of deforming atoms [*e.g.* Melvin, Pirie & Smith (1968); Reid (1974); March & Wilkins (1978)] followed the lead of Born (1942) by introducing deformation parameters $\beta(ll', kk', \mathbf{K})$ that described the dependence of the scattering factor for the atom (lk) on the motion of the atom $(l'k')$ for scattering vector $\mathbf{K}$. With a particular model of the deforming atom, such as the archetypal shell model, this approach is distracting and unnecessary. The usual one-phonon scattering cross section may be written in electron units per cell as

$$I(\mathbf{K})/N\sigma_0 I_0 = \sum_j (E/\omega^2)_{\mathbf{q}j} \left| \sum_k f_k(K) \exp(-W_k) \times \mathbf{K} \cdot \mathscr{E}(k/\mathbf{q}j)/m_k^{1/2} \exp[i\mathbf{G} \cdot \mathbf{r}(k)] \right|^2 \times \Delta(\mathbf{K}+\mathbf{q}, \mathbf{G}) \quad (1)$$

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