distribution of $\varphi_{\mathbf{H}_s}$ is

$$P(\phi/R) = [2\pi I_o(XR^2)]^{-1} \exp[XR^2 \cos(2\phi + \xi)], \quad (A4)$$

where ξ is defined in (2)–(5) and X in (15). Clearly, ($A4$) has a unique maximum at $2\varphi_{\mathbf{H}_s} = -\xi$ when XR^2 is large.

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The Use of Continuous Atomic Distributions in Structural Investigations

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Abstract

A simple method of describing the scattering from an atom continuously distributed in the unit cell is proposed. Some experimental applications in structural investigations are presented.

1. Introduction

It is not unusual in structural analysis that an atom does not occupy a definite point position in the unit cell but is distributed among a number of positions, discretely or continuously. The problems connected with atomic disorder in crystals have been discussed extensively for a long time (Krivoglaz, 1969; Dunitz, Schomaker & Trueblood, 1988; Kuhs, 1992). If the number of occupied positions is finite, it is possible to refine these positions with partial populations. For more complicated distributions, caused by statistical displacements or thermal vibrations, a general approach has been introduced by Johnson (1969). It is based on a differential expansion of the atomic Gaussian probability density function (p.d.f.), which after Fourier transformation leads to a series expansion of tensorial coefficients. The limitations of this approach were discussed by Kuhs (1992). However, there are many cases when one wishes to express the p.d.f. for disordered atoms in real space. This p.d.f. will not only be similar to the Guassian or Johnson expansions but, also, its type may be established on the basis of physical considerations. Sometimes, it is possible to parametrize such a p.d.f. with a small number of parameters and use these as variables in the refinement. This direct approach to define the p.d.f. of disordered atoms was applied in the structural investigations of two compounds. Preliminary results were published in brief (Zhukov, 1991; Chernyshev, 1992). In this paper, a more detailed description is presented.

2. An atom uniformly distributed on a sphere

Let us define the average unit cell (a.u.c.) as that obtained by averaging the crystal unit cells. Such a.u.c.'s are used in ordinary structure-factor calculations. Let atom A in the a.u.c. be continuously distributed with equal probability on some set of positions on a sphere of radius R. Assuming scattering from a crystal with a.u.c.'s to be the same as that from a real crystal, one may calculate the scattering from atom A as follows.

It is possible to represent the sphere as a sum of n sets with equal areas. Let atom A be situated in set j with probability $1/n$, radius vector $\mathbf{r}_j$, form factor $f_A(H)$ and isotropic temperature factor $t_A(H,U_{\rm iso})$. The structure-factor contribution from such a disordered atom is

$$(1/n)\sum_{j=1}^{n} f_A(H)t_A(H,U_{\rm iso})\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)$$

$$= f_A(H)t_A(H,U_{\rm iso}) \times \left[(1/4\pi R^2)\sum_{j=1}^{n}\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)(4\pi R^2/n)\right]. \quad (1)$$

When $n\rightarrow\infty$, the area of a sphere surface element $4\pi R^2/n$ tends to $R^2\sin\theta\,{\rm d}\theta{\rm d}\varphi$ and the expression in square brackets is equal to

$$(1/4\pi)\int_0^{2\pi}{\rm d}\varphi\int_0^{\pi}\exp(2\pi iHR\cos\theta)\sin\theta\,{\rm d}\theta = \sin p/p, \quad (2)$$

where $p = 2\pi HR = 4\pi R\sin\theta/\lambda$.

So, in the case of isotropic thermal vibrations, the continuous distribution of atomic statistical positions for the atom may be simply accounted for by multiplying the atomic form factor $f(H)$ by some function $S(\mathbf{H},\mathbf{x})$. The vector $\mathbf{x}$ defines the parameters of the set of atomic position distributions. For a sphere of radius R, we have

$$S(\mathbf{H},\mathbf{x}) = S(H,R) = \sin 2\pi HR/2\pi HR, \quad (3)$$

where the parameter x is simply R. Expression (3) [and expression (4) in §3] has been known in crystallography for a long time (Bijvoet & Ketelaar, 1932; Verweel & Bijvoet, 1938; King & Lipscomb, 1950; Bennett, Hutcheon & Foxman, 1975). The present method of calculation of $S(\mathbf{H},\mathbf{x})$ is general and simple as it reduces to an integration of the function $\exp(2\pi i\mathbf{H}\cdot\mathbf{r})$ over sets of continuous atomic position distributions of arbitrary form.

3. An atom uniformly distributed on a ring and a line segment

With the procedure described above, it is not difficult to obtain the expression for $S(\mathbf{H},\mathbf{x})$ if the atom is statistically distributed on a ring or on a line segment. For a ring of radius R,

$$S(\mathbf{H},\mathbf{x}) = \lim_{n\rightarrow\infty}(1/n)\sum_{j=1}^{n}\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)$$

$$= (1/2\pi R)\lim_{n\rightarrow\infty}\sum_{j=1}^{n}\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)(2\pi R/n)$$

$$= (1/2\pi)\int_0^{2\pi}\exp(2\pi iHR\cos\varphi\sin\psi){\rm d}\varphi$$

$$= {\rm J}_0(2\pi HR\sin\psi). \quad (4)$$

${\rm J}_0$ is the zero-order Bessel function and ψ is the angle between $\mathbf{H}$ and the ring-plane normal. For the calculation of (4), Hansen's integral (Watson, 1952) and a spherical coordinate system were used with $\mathbf{H} = H(\sin\psi,0,\cos\psi)$ and $\mathbf{r} = r(\cos\varphi,\sin\varphi,0)$. In this case, the vector $\mathbf{x}$ consists of four parameters, the radius R and the direction cosines of the unit vector normal to the plane of the ring.

For a line segment with length $2a$,

$$S(\mathbf{H},\mathbf{x}) = (1/2a)\int_{-a}^{a}\exp(2\pi iHr\cos\psi){\rm d}r = \sin p/p. \quad (5)$$

$p = 2\pi Ha\cos\psi$ and ψ is the angle between $\mathbf{H}$ and the line.

4. Insertion in the least-squares refinement programs

Since we have $S(\mathbf{h},\mathbf{x})$ in analytical form, we may insert it into refinement programs for powder or single-crystal diffraction data and get quantitative values of the parameters $\mathbf{x}$. For this, one needs only to multiply the atomic form factor by the function $S(\mathbf{H},\mathbf{x})$ and then calculate the moduli of the structural amplitudes and their derivatives. It should be noted that for a statistically distributed atom A the radius vector $\mathbf{r}_A$ represents the coordinates with respect to the centre of the set, for example, the centre of the sphere. However, the positional derivatives are not affected. Some additional derivatives of the parameters $\mathbf{x}$ must be added. These corrections were introduced into the single-crystal *AE*1 (Chernyshev *et al.*, 1992) and the powder *MRIA* (Zlokazov & Chernyshev, 1992) refinement programs. The refinement results for some experimental single-crystal X-ray data are presented in §5.

5. Examples of use in structural investigations

5.1. Pb *atom distributed on a sphere*

We start from the results of the refinements for lead magnesoniobate (PMN), $\rm Pb(Mg_{1/3}Nb_{2/3})O_3$ (Zhukov, 1991), space group $Pm\bar{3}m$. A spherical crystal of diameter 0.30 (1) mm was used for the data collection on a CAD-4 diffractometer at two temperatures, 293 and 573 K (Mo $K\alpha$ radiation). Since PMN has a very high linear absorption coefficient of 66.8 mm^{-1}, the spherical absorption correction for $\mu R = 10$, from Table 5.3.6*B* of *International Tables for X-ray Crystallography* (1959) was applied to aver-

Table 1. *Structure data of lead magnesoniobate,* $Pb(Mg_{1/3}Nb_{2/3})O_3$

In refinement $U_{iso}(Nb) = U_{iso}(Mg)$ is assumed.

	$T = 293$ K	$T = 573$ K
a (Å)	4.0401 (8)	4.044 (1)
Number if unique reflections	79	63
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.99	0.90

Atom	Position	Occupancy
Pb	0, 0, 0	1
Nb	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{2}{3}$
Mg	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{3}$
O	$\frac{1}{2}, \frac{1}{2}, 0$	1

Table 2. *Results of the refinements of lead magnesoniobate at two temperatures*

First line $T = 293$ K, second line $T = 573$ K.

Model A – harmonic (isotropic) thermal vibrations for the Pb atom. Model B – anharmonic thermal vibrations for the Pb atom. Model C – Pb atom uniformly distributed on a sphere. r = radius of an ideal mosaic block. Minimization $\sum w_2|F^2_{obs} - F^2_{kin}|^2 \rightarrow$ minimum, $F_{kin} = \text{Scale} \times y^{1/2}F_{calc}$, y = extinction coefficient, $w_2 = \sigma^{-2}(F^2_{obs})$,

$$R = \sum|F_{obs} - F_{kin}|/\sum|F_{obs}|,$$

$$R_w = [w|F_{obs} - F_{kin}|^2/\sum wF^2_{obs}]^{1/2},$$

$$\text{GOF} = [\sum w|F_{obs} - F_{kin}|^2/\sum(n-p)]^{1/2},$$

$w = \sigma^{-2}F_{obs}$, n = number of reflections, p = number of variables.

	A	B	C
Scale	4.8 (4)	3.27 (11)	2.95 (7)
	3.2 (2)	2.56 (5)	2.73 (9)
Lead			
U_{iso} (Å^2)	0.079 (4)	0.045 (1)	0.020 (1)
	0.063 (3)	0.044 (1)	0.033 (2)
$d_{1111} \times 10^7$		−93 (5)	
		−65 (4)	
$d_{1122} \times 10^7$		−36 (3)	
		−27 (2)	
R_{Pb} (Å)			0.286 (2)
			0.244 (5)
(Niobium, magnesium)			
U_{iso} (Å^2)	0.019 (3)	0.0101 (8)	0.0110 (5)
	0.018 (1)	0.0114 (5)	0.0143 (8)
Oxygen			
U_{iso} (Å^2)	0.037 (6)	0.023 (3)	0.022 (1)
	0.032 (4)	0.028 (1)	0.033 (6)
r (μm)	9 (1)	5.6 (5)	3.0 (3)
	3.7 (5)	2.0 (2)	2.3 (4)
Variables	5	7	6
R	0.127	0.060	0.037
	0.070	0.030	0.045
R_w	0.213	0.091	0.052
	0.094	0.037	0.055
GOF	3.53	1.58	1.10
	1.36	0.59	0.95

aged intensities.* Atomic scattering factors for the neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Some structural information concerning PMN is given in Table 1.

Initially, two models for the thermal vibrations of lead were refined: model A – harmonic (isotropic) thermal vibration for lead; and model B – anharmonic thermal vibration. Gram–Charlier series expansion up to the fourth order was used in model B [*International Tables for X-ray Crystallography* (1974), p. 316; see also Appendix 1 of the present paper]. The isotropic primary-extinction parameter (Becker & Coppens, 1974) was also refined. The minimization was on F^2. Although the F refinement has the same global minimum as F^2 refinement, the minimization process on F for model A converges to different local minima depending on the initial values of the variables. The refinement results are displayed in Table 2. One can see from Table 2 that model A is unsuitable for the two experimental data sets. Model B gives satisfactory results at 573 K and is not so good at 293 K. The fact that the absolute values of the anharmonic parameters of the Pb atom at 293 K are much higher than those at 573 K indicates strong disorder of lead at room temperature. All attempts to find suitable split positions for it failed. On the basis of the discussion in Appendix 2, model C – in which lead is uniformly distributed on a sphere of radius R_{Pb} – was proposed for the refinement. Model C gives the most satisfactory result for the experimental set at 293 K.

After refinements B and C, the p.d.f.'s of lead were calculated (see Appendix 1) at two different temperatures. The plots of these p.d.f.'s along the [100] direction are displayed in Fig. 1. It is necessary to mention that these p.d.f.'s at 573 K are qualitatively different but the R factors for different models are close. Probably, a model that takes into account the disordering and the anharmonic thermal motion of the Pb atom should be used. Certainly, by increasing the number of terms of the Gram–Charlier representation of the temperature factor of the Pb atom, one may obtain more acceptable results for the refinement of model B at room temperature. However, in that case the number of variables also increases. The direct approach of the representation of the p.d.f. for the Pb atom in PMN at room temperature achieves the required goal.

At 573 K, the atomic thermal vibrations in PMN give a more important contribution to the scattered intensities and it is not surprising that taking into account the anharmonic thermal vibrations of the Pb atom gives the best results in this case.

5.2. H *atoms in fully disordered methyl groups*

Expression (4) was successfully used in the structure refinement of (α-hydroxy-α-phenyl-

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* Lists of F_{obs} (after averaging and absorption correction) and refinement results at $T = 293$ and 573 K have been deposited with the IUCr (Reference: AL573). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

acetato)trimethyltin (Sizova *et al.*, 1993). Crystal data: $C_{11}H_{16}O_3Sn$, monoclinic, space group $P2_1/c$, $a = 7.887\ (2)$, $b = 22.002\ (4)$, $c = 15.592\ (3)$ Å, $\beta = 100.11\ (2)^\circ$, $Z = 8$ (two independent molecules in the asymmetric unit). Of the total of 7731 reflections recorded on a CAD-4 diffractometer (Mo $K\alpha$ radiation, $\Theta_{\max} = 30^\circ$) at room temperature, only 4861 with $I > 2.5\sigma(I)$ were used in the refinement after empirical absorption correction. As was seen from a difference electron-density map, all methyl groups attached to the Sn atom were rotationally disordered and for the H atoms of these groups the following procedure was used. The methyl H atoms were assumed to be uniformly distributed on a ring and the parameters refined were the radius, the coordinates of the centre of the ring and the isotropic displacement parameter. The total occupation of the H atoms was equal to 3. The values obtained for the radii of the rings varied from 0.85 (2) to 0.90 (2) Å, which gave the values 0.98–1.05 Å for C–H distances in the methyl groups. The total number of refined parameters was 356 and the final error indices obtained were $R = 0.034$, $R_w = 0.035$, goodness of fit (GOF) = 1.5. It should be noted that the model used for the methyl H atoms decreases the number of refined parameters per methyl group from 12 to 5.

6. Concluding remarks

The approach presented for accounting for atomic disorder may be very useful in structural investigations as shown above. It is easy to obtain a set of analytical functions $S(\mathbf{H},\mathbf{x})$ for various types of disordering with regular geometric shape. Further, these functions may be inserted in refinement programs for powder and single-crystal diffraction data, which can lead to considerable improvement in the fitting. A physical picture of the crystal interior can be obtained, coupled with quantitative values of the parameters $\mathbf{x}$.

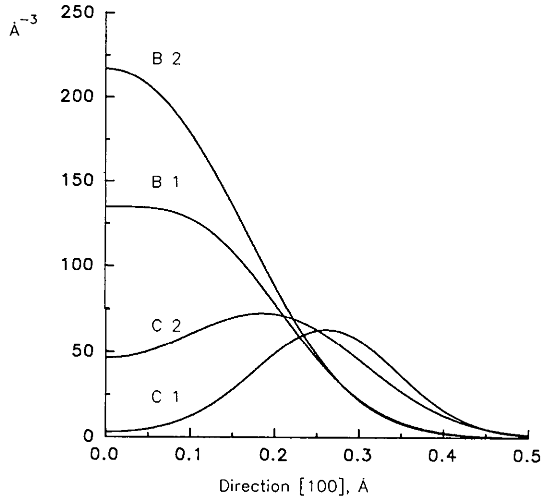

Fig. 1. P.d.f.'s of the Pb atom in direction [100]. *B*1, *B*2 – model *B* at 293 and 573 K. *C*1, *C*2 – model *C* at 293 and 573 K. Model *B* – anharmonic thermal vibrations of the Pb atom; model *C* – Pb atom uniformly distributed on the sphere.

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APPENDIX 1
Probability density functions for different models of the Pb atom

The harmonic temperature factor for lead (site symmetry $m\bar{3}m$) has the form $T_{\rm harm} = \exp[-\beta_{11}(h^2 + k^2 + l^2)]$. Then, p.d.f.$_{\rm harm}$ will be [see *International Tables for X-ray Crystallography* (1974), p. 314]:

$$\begin{aligned}\text{p.d.f.}_{\rm harm}(\mathbf{u}) &= \text{p.d.f.}_{\rm harm}(u)\\ &= (\pi/\beta_{11})^{3/2}\exp[-(3\pi^2/\beta_{11})u^2], \quad (A1)\end{aligned}$$

where $\mathbf{u}$ is the displacement vector of the Pb atom from the position (0,0,0).

If the temperature factor of lead is refined in a Gram–Charlier representation up to fourth order [*International Tables for X-ray Crystallography* (1974), p. 317], then

$$\begin{aligned}T_{\rm anharm} = T_{\rm harm}\{1 &+ [(2\pi i)^4/4!][d_{1111}(h^4 + k^4 + l^4)\\ &+ 4d_{1122}(h^2k^2 + h^2l^2 + k^2l^2)]\} \quad (A2)\end{aligned}$$

and p.d.f.$_{\rm anharm}$ will be

$$\begin{aligned}\text{p.d.f.}_{\rm anharm}(\mathbf{u}) = \text{p.d.f.}_{\rm harm}(u)\{1 &+ (1/4!)\\ &\times [d_{1111}(H_{1111}(\mathbf{u}) + H_{2222}(\mathbf{u})\\ &+ H_{3333}(\mathbf{u})) + 4d_{1122}(H_{1122}(\mathbf{u})\\ &+ H_{1133}(\mathbf{u}) + H_{2233}(\mathbf{u}))]\}. \quad (A3)\end{aligned}$$

H_{ijkl} are Hermite polynomials as defined in *International Tables for X-ray Crystallography* (1974, p. 316).

If lead is distributed on a sphere with radius R, for the p.d.f.$_{\rm sphere}$ calculation one can use the concept of the joint p.d.f. (Bachman & Schulz, 1984). Then, writing ($A1$) as p.d.f.$_{\rm harm}(u) = a\exp(-bu^2)$, one obtains

$$\begin{aligned}\text{p.d.f.}_{\rm sphere}(\mathbf{u}) &= \text{p.d.f.}_{\rm sphere}(u)\\ &= (1/4\pi)\int_0^{2\pi} {\rm d}\varphi \int_0^{\pi} {\rm d}\theta \sin\theta\, a\\ &\quad\times \exp[-b(R^2 + u^2 - 2Ru\cos\theta)]\\ &= \text{p.d.f.}_{\rm harm}(u)(1/4bRu)\exp(-bR^2)\\ &\quad\times [\exp(2bRu) - \exp(-2bRu)]. \quad (A4)\end{aligned}$$

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 magnesoniobate, 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 $\sum_1$ Relationship. I. Bicentric Arrangements in $P\bar{1}$

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Abstract

An exact Fourier representation of the probability for the $\sum_1$ 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 $E_{2\mathbf{h}}$ 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.

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