

The Phase Problem in the Analysis of X-ray Diffraction Data in Terms of Electron-Density Distributions

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Abstract

The refinement of electron-density distributions for non-centrosymmetric crystals from X-ray diffraction data may lead to a very good fit between model and data but to totally meaningless electron densities. This is to a large extent because varying certain parameters, or combination of parameters, in the model mainly leads to a change in the phases of the structure factors. A formal analysis of why this happens, when using multipole models, is given as well as specific examples using real data: the contributions of odd-order multipoles, which are invariant under crystal-class symmetry operations, are poorly determined. The importance of applying constraints on the models is stressed. The conclusions of this analysis can be carried over to refinements of anharmonic atomic vibrations.

1. Introduction

What are the consequences of the fact that in any diffraction experiment we only determine the structure-factor moduli and not the phases of the complex structure factors? The conclusions drawn from the discussion below applies not only to the analysis of X-ray diffraction data in terms of electron-density distributions but to any interpretation of single-crystal diffraction data going beyond the atomic structure and harmonic thermal motions of the atoms.

Until about ten years ago, it was speculated whether reliable electron-density distributions from X-ray diffraction data for crystals belonging to non-centrosymmetric classes could be obtained. Since then, a series of successful studies of organic and organometallic compounds indicated that this was indeed possible, but recent studies of highly symmetric non-centrosymmetric structures gave results depending sensitively on the data set or the details of the model, *e.g.* boron nitride, zinc-blende-type structure (Eichhorn, Kirfel, Grochowski & Serda, 1991), hexamethylenetetramine (Kampermann, Ruble & Craven, 1994, and work cited therein). We have analyzed existing data for GaAs, work which will be presented below, and have also been involved in a study of the

electron-density distribution of LiB_3O_5 [space group $Pna2_1$ (Le Hénaff, Hansen, Protas & Marnier, 1996)] for which the analysis also does not give an unambiguous result.

In the past, the problem of undetermined, or poorly determined, parameters and density distributions has been discussed for some specific cases: third-order cumulants in the zinc-blende-type structure (Hazell & Willis, 1978); and a more general discussion of the electron density and anharmonicity of thermal vibrations in hexamethylenetetramine (space group $I43m$) for which Terpstra, Craven & Stewart (1993) recently published a study based on X-ray and neutron diffraction measurements. Short discussions concerning the phase problem when using the Gram–Charlier expansion were published some years ago (Nelmes & Tun, 1987, 1988; Hansen, 1988): the former authors showed that skewness can be detected by using a limited Gram–Charlier expansion, but that this is not the case for the Edgeworth expansion, whereas Hansen drew attention to the fact that the result is not unique. In a recent study of GaAs (Stevenson, 1994), there is also some discussion about poorly determined parameters (here third-order anharmonicity), which is explained by high correlations between these parameters.

The first section will be concerned with the effect of phase factors in structure-factor expressions. We will recall what form phase factors may take and we will apply these general principles to the multipole expansion of electron-density distributions. In the following sections, we examine the two examples, GaAs and LiB_3O_5 , more closely. Finally, we consider how one may build into the charge-density analysis an automatic detection of when the problem becomes serious, and we will conclude by discussing the means that we may use to solve the problem.

2. The information contained in the phase of the structure factor

In this and the following section, it will be demonstrated from basic principles that, if only the structure-factor moduli are known, a refinement of the population

coefficients of the odd-order multipoles that are invariant under symmetry transformations of the crystal class leads to inaccurate and highly correlated parameters. The arguments can also be carried over to the models for anharmonic atomic motions.

Modeling of the structure and the electron-density distribution using moduli of the structure factors implies prejudicing their phases. We will show that knowing only the moduli does not in general allow us to make a unique choice of phases. The arbitrariness of this choice leads to the problem described in the previous paragraph, and by examination of the expression of the structure factor for specific models it becomes clear that a change of the phases of a structure-factor set in some well defined manner is equivalent to modifying certain parameters.

In order to analyze the problem, consider two electron-density distributions corresponding to the same set of moduli. The corresponding structure factors, $F(\mathbf{H})$ and $F'(\mathbf{H})$, respectively, are then related by

$$F'(\mathbf{H}) = F(\mathbf{H}) \exp[i\Phi(\mathbf{H})], \quad (1)$$

where $\Phi(\mathbf{H})$ is a real scalar function, which we may represent by a tensor expansion:

$$\Phi(\mathbf{H}) = d_0 + d_1^r h_r + d_2^{rs} h_r h_s + d_3^{rst} h_r h_s h_t + \dots \quad (2)$$

(Einstein summation convention), h_1, h_2, h_3 are the components of the scattering vector \mathbf{H} .

We will suppose that the two density distributions are real (a physical constraint) and that they have the same space-group symmetry (the space group is in general known before one starts a fine analysis of experimental data) and we will then investigate what constraints this imposes on $\Phi(\mathbf{H})$.

The consequences of the condition that the density is real is that, for any set of structure factors, Friedel's law must be satisfied, $F(-\mathbf{H}) = F^*(\mathbf{H})$, *i.e.* we neglect at present the anomalous dispersion (its effect will be discussed later). One therefore obtains

$$\Phi(-\mathbf{H}) = -\Phi(\mathbf{H}) + 2\pi n \quad (3)$$

(n is any integer; it may depend on \mathbf{H}) and therefore that all even-order terms in the expansion (2) are equal to zero or $\pi \pmod{2\pi}$, thus the coefficients $d_2^{rs}, d_4^{rstu}, \dots \in \{0, \pi \pmod{2\pi}\}$ (throughout, phases will be given by their value modulo 2π).

The effect of imposing the crystal symmetry is that the odd-order coefficients d_1^r, d_3^{rst}, \dots must form tensors that are invariant under the crystal-class symmetry operations. This follows from

$$F(\mathbf{HR}) = F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{t}), \quad (4)$$

where a symmetry operation is represented by

$$\hat{\mathbf{S}}\mathbf{r} = \mathbf{R}\mathbf{r} + \mathbf{t} = \mathbf{r}'. \quad (5)$$

Points \mathbf{r} and \mathbf{r}' are related by symmetry, \mathbf{R} is the rotational and \mathbf{t} the translational part. Since this equality

must also be satisfied by the modified structure-factor set $\{F'(\mathbf{h})\}$, we get the following condition:

$$\Phi(\mathbf{HR}) = \Phi(\mathbf{H}) + 2\pi n. \quad (6)$$

A sufficient condition is that the tensors d_m^{rst}, \dots are invariant under the crystal-class operations or that some of the coefficients take the special values 0 and π . These are also the only two values allowed for centrosymmetric crystal structures.

These two conditions show that we can limit ourselves to tensors d_m^{rst}, \dots of odd rank, m , which are invariant under crystal-class symmetry.

We do not know how to exploit analytically the condition that the electron density should be overall positive.

Let us consider as an example the polar crystal class 2 with its twofold axis parallel to the crystallographic b axis. The invariance imposes that a phase factor, satisfying the above conditions, may be written

$$\Phi(\mathbf{H}) = d_1^2 k + d_3^{222} kkk + d_3^{123} hkl + d_3^{112} h^2 k + d_3^{223} kl^2 + 5\text{th and higher orders.} \quad (7)$$

(Note that all superscripts on the coefficients are the contravariant indices of tensor elements.)

To be specific, consider the first-order term in (7). A non-zero value of the coefficient d_1^2 means that the two density functions have different origins of the unit cell since

$$\begin{aligned} & \exp(id_1^2 k) \sum_j f_j \exp 2\pi i(hx_j + ky_j + lz_j) \\ &= \sum_j f_j \exp 2\pi i[hx_j + k(y_j + d_1^2/2\pi) + lz_j]. \end{aligned} \quad (8)$$

In order to illustrate the effect of third-order terms, consider the cumulant expansion of the structure factor

$$\begin{aligned} F(\mathbf{H}) &= \sum_j f_j \exp 2\pi i(h_s x_j^s) \exp(-h_s h_t \beta_{jt}^{st}) \\ &\times \exp(-ih_s h_t h_u \beta_{jst}^{stu}) \dots \end{aligned} \quad (9)$$

The multiplication with a phase factor composed of the third-order terms is equivalent to changing the values of the corresponding cumulants, *i.e.* those that are invariant under crystal-class operations. The argument may of course be carried over to any odd-order cumulants.

We can approach the problem differently. The third-order cumulants for two atoms, j and j' , related by a twofold axis parallel to \mathbf{b} must satisfy

$$\begin{aligned} \beta_j^{111} &= -\beta_{j'}^{111}; & \beta_j^{222} &= \beta_{j'}^{222}; & \beta_j^{333} &= -\beta_{j'}^{333}; \\ \beta_j^{112} &= \beta_{j'}^{112}; & \text{etc.} & & & \end{aligned} \quad (10)$$

Consider a third-order cumulant expansion of the structure factors,

$$F(\mathbf{H}) = \sum_j f_j \exp 2\pi i(h_s x_j^s) \exp(-h_s h_t \beta_j^{st}) \\ \times \exp(-ih_s h_u \beta_j^{su}).$$

Separate out a common factor:

$$F(\mathbf{H}) = \exp(-iB^{stu} h_s h_t h_u) \sum_j f_j \exp 2\pi i(h_s x_j^s) \\ \times \exp(-h_s h_t \beta_j^{st}) \exp[-ih_s h_t h_u (\beta_j^{su} - B^{stu})] \\ = \exp(-iB^{stu} h_s h_t h_u) F'(\mathbf{H}). \quad (11)$$

If the set $\{F'(\mathbf{H})\}$ also obeys crystal symmetry, we must require that $\beta_j^{stu} = \beta_j^{st} - B^{stu}$ still satisfies (10), which means that B^{stu} can take any value for the components stu for which $\beta_j^{su} = \beta_j^{st}$ but must be zero for the others. Changing the value of a component, which is invariant, for all atoms in the unit cell only leads to a change in the phase of the structure factors. Refining these cumulants for all atoms will therefore lead to a singular least-squares normal-equations matrix. As a consequence, we cannot refine all individual values for β_j^{222} , β_j^{123} , β_j^{112} and β_j^{233} from diffraction data.

The cumulant expansion is from a mathematical point of view an extremely simple case, since the phase problem is not 'disguised'; by this we mean that it leads to truly singular normal equations. Of other expansions of the electron-density distribution based on the notion 'atoms in crystals', one may consider the Gram-Charlier expansion, which is mainly used for describing anharmonicity of atomic thermal motions, and the multipole expansion for modeling valence-electron-density distributions or a combination of the two. The close resemblance between the cumulant and the Gram-Charlier expansions has already been pointed out by other authors (*e.g.* Kuhs, 1983) and the merits of the latter expansion was discussed by Nelmes & Tun (1987). The multipole expansion has a more complex form than the other two expansions but this is justified by physicochemical arguments and by the fact that it converges rapidly in practice. A convenient feature of the Gram-Charlier and multipole expansions is that the terms can be Fourier transformed individually contrary to the cumulant expansion leading to an infinite series. The next chapter is dedicated to the discussion of the multipole expansion but most of the arguments can be carried over to the Gram-Charlier expansion with only minor modifications and the general conclusions are identical.

3. Multipole expansion of valence-electron charge densities

Several expansions have been proposed in the past for the refinement of electron-density distributions from X-ray diffraction data (*e.g.* Stewart, 1976; Hirshfeld, 1971; Hansen & Coppens, 1978; Craven, Weber & He, 1987). For our discussion, they can be considered as

equivalent. The form that we will use for the general discussion is that the electron density of an atom may be expressed as

$$\rho_j(\mathbf{r}) = \rho_{j\text{core}}(\mathbf{r}) + \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l P_{jlm} R_{jl}(r) y_{lm}(\mathbf{r}/r); \quad (12)$$

the corresponding atomic scattering factor is then given by the expression

$$f_j(\mathbf{H}) = f_{j\text{core}}(H) + \sum_l i^l \sum_m P_{jlm} \varphi_{jl}(H) y_{lm}(\mathbf{H}/H). \quad (13)$$

$f_{j\text{core}}$ is the Fourier transform of the spherically symmetric function $\rho_{j\text{core}}$ representing the density of the atomic core electrons. y_{lm} are real spherical harmonic functions; each subset of y_{lm} having one value of l forms a rotationally invariant set, which means that the capability of a limited multipole expansion to describe a density function is independent of the choice of coordinate system; we therefore consider the situation where, for each atom, we choose the origin of the coordinate system at its nucleus and the axes for all of the atoms are oriented the same way. φ_{jl} is the Fourier-Bessel transform of the radial functions R_{jl} :

$$\varphi_{jl}(H) = 4\pi \int_0^\infty R_{jl}(r) j_l[4\pi(\sin \theta)\lambda r] r^2 dr. \quad (14)$$

It is important to note that all terms in the expression for the atomic scattering factor are real with the exception of i^l . We may therefore reorganize (13) as follows:

$$f_j(\mathbf{H}) = f_{j\text{core}}(H) + \sum_l^{\text{even}} \sum_m P_{jlm} \varphi'_{jl}(H) y_{lm}(\mathbf{H}/H) \\ + i \sum_l^{\text{odd}} \sum_m P_{jlm} \varphi'_{jl}(H) y_{lm}(\mathbf{H}/H) \\ = a_j(\mathbf{H}) + ib_j(\mathbf{H}), \quad (15)$$

where $\varphi_{jl} = \varphi'_{jl}$ for $l = 0, 4, 8, \dots, 1, 5, 9, \dots$ and $\varphi_{jl} = -\varphi'_{jl}$ for $l = 2, 6, 10, \dots, 3, 7, 11, \dots$

The multipoles with l odd give an imaginary contribution to the complex atomic scattering factor because the corresponding density function is odd with respect to the inversion of the position vector \mathbf{r} . We recall that the real spherical harmonic functions can be expressed in polynomial form (see *e.g.* Hansen & Coppens, 1978):

$$y_{lm}(\mathbf{H}/H) = H^{-l} \text{Pol}_m^l(h, k, l), \quad (16)$$

where Pol_m^l is a homogeneous polynomial of degree l . We may therefore rewrite the imaginary part of f_j as

$$b_j = \sum_l^{\text{odd}} H^{-l} \varphi'_{jl}(H) \sum_{rst\dots m} C^{rst\dots m} P_{jlm} h_r h_s h_t \dots \quad (17)$$

$$= (\varphi'_{j1}/H) B_1^r h_r + (\varphi'_{j3}/H^3) B_3^{rst} h_r h_s h_t + \dots; \quad (18)$$

the Einstein summation convention is to be applied. The real part may be expressed in a similar manner but this is

without consequences for our discussion. This expansion differs from the cumulant expansion in two respects:

(a) ϕ_{ji}/H' is a radial function of H but the important point is that each term has the same transformation properties under symmetry operations as the cumulants $[\beta_{ji}^{rst\dots}, \text{equation (9)}]$ have.

(b) The terms $\phi_{ji}/H'B_1^{rst}h_r h_s h_t \dots$ do not appear as the arguments of a complex exponential function but in the limit $b_j \ll a_j$ we may make the following approximation for f_j :

$$\begin{aligned} f_j(\mathbf{H}) &= a_j(\mathbf{H})[1 + ib_j(\mathbf{H})/a_j(\mathbf{H})] \\ &\cong a_j(\mathbf{H}) \exp[ib_j(\mathbf{H})/a_j(\mathbf{H})]. \end{aligned} \quad (19)$$

The condition $b_j \ll a_j$ is reasonably well satisfied for most atoms since a_j contains the scattering factor of the core electrons, which is dominating; the heavier the atom, the more true this is. Hydrogen is considered to be without core electrons but the spherical part of the valence electrons also contributes to a_j .

It should be stressed that b_j is a linear function of the multipole population coefficients. Multiplying a structure factor set by a phase factor therefore corresponds to modifying the populations P_{jlm} of certain odd-order multipoles on all atoms if, among the functions y_{lm} invariant under the crystal-class symmetry operations, functions c_{lm} exist such that for all atoms (index j)

$$\partial[b_j(\mathbf{H})/a_j(\mathbf{H})]/\partial P_{jlm} \cong s_{jlm}c_{lm}(\mathbf{H}), \quad (20)$$

where s_{jlm} are non-zero constants. For all reasonable models, c_{lm} will tend rather rapidly to zero for $\sin \theta/\lambda > 1 \text{ \AA}^{-1}$, since c_{lm} reflects the distribution of the valence-electron density.

We must also comment on the more general case when anomalous scatterers are present in the crystal. Then the strict equality of (19) becomes (the real part of the anomalous dispersion has been included in a_j)

$$\begin{aligned} f_j(\mathbf{H}) &= a_j(\mathbf{H})[1 + i\Delta f_j''/a_j(\mathbf{H})][1 + ib_j(\mathbf{H})/a_j(\mathbf{H})] \\ &\quad + \Delta f_j'' b_j(\mathbf{H})/a_j(\mathbf{H}). \end{aligned} \quad (19a)$$

When the last term can be neglected, the situation is similar to that without anomalous dispersion, *i.e.* modifying the contribution $b_j(\mathbf{H})$ corresponds to rotating the atomic scattering factor in the complex plane.

If $\Delta f_j''$ is reasonably large, the expression cannot be simplified as above [(19)] and it might be possible to obtain populations either by comparing Friedel pairs of reflections or using data collected with radiation at different wavelengths. Concerning the use of polynomial expansions of the Debye-Waller factors, the 'phase problem' cannot be solved this way since the Debye-Waller factor is a multiplicative correction to the atomic scattering factor and not additive as for the multipole expansion.

Because of all the possible ways in which we may choose radial functions for the multipoles, it is difficult to

push the general discussion any further. We will therefore illustrate what happens with a couple of examples to which the discussion by Terpstra *et al* (1993) of the refinement of hexamethylenetetramine may be added.

Before going into this discussion, we shall make a comment concerning least-squares refinements of structure-factor models. If a change of a certain combination of parameters only leads to a change in the phases of all observed structure factors, then the least-squares normal-equations matrix becomes singular. In the multipole model (contrary to the cumulant expansion), this will not be strictly true since (19) is only approximate. In most cases, it will therefore be possible to find a unique solution to the optimization problem but it is not necessarily physically meaningful.

It should also be emphasized that the problem of indetermination, or in reality imprecise determination of certain parameters, does not depend in any direct way on the quality of the experimental data set: the normal-equations matrix is constructed from derivatives of calculated structure factors and weight factors, one element of the matrix being given by

$$\sum_{\mathbf{H}} [\partial|F(\mathbf{H})|/\partial p_i][\partial|F(\mathbf{H})|/\partial p_j] w_{\mathbf{H}}.$$

4. Multipole refinements of GaAs

The experimental structure-factor moduli used in the present study are taken from the work of Matsushita & Hayashi (1977) for the strong reflections and from Pietsch, Tsirelson & Ozerov (1986) for the weak reflections. An X-ray diffraction study of the valence-charge-density distribution has also been published by Levallois & Allais (1986).

The space group of GaAs having the zinc-blende-type structure is $F43m$. Ga was placed at $0,0,0$ and As at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. Since both atoms occupy sites of $43m$ symmetry, for each of them the multipole expansion through fourth order reduces to

$$\begin{aligned} f_j(\mathbf{H}) &= f_{j\text{core}}(H) + P_v f_{j\text{valence}}(H/\kappa') \\ &\quad + P_{j4} \varphi_{j4}(H) c_4(\mathbf{H}/H) \\ &\quad + i[P_{j32} - \varphi_{j3}(H)] y_{32-}(\mathbf{H}/H). \end{aligned} \quad (21)$$

$f_{j\text{core}}$ and $f_{j\text{valence}}$ are calculated for the ground state of the atoms. These functions are modified by a radial scaling parameter κ' ,

$$\begin{aligned} c_4(\mathbf{H}/H) &\propto (h^4 + k^4 + l^4)/H^4 - \frac{3}{5} \\ y_{32-}(\mathbf{H}/H) &= 2hkl/H^3. \end{aligned}$$

The radial density functions corresponding to φ_{j3} and φ_{j4} have been chosen:

$$R_3(r) \propto r^8 \exp(-\zeta r)$$

$$R_4(r) \propto r^{10} \exp(-\zeta r).$$

The value of ζ is given in Table 1.

Two things are remarkable about the results reported in Table 1. The octupolar populations of both atoms are numerically very large; we may compare with a result for silicon, $P_{32-} = 0.45(5)$ (Spackman, 1986); but what clearly shows that there is a problem is their large standard deviations and that they are highly correlated. A calculation of their sum and difference gives

$$P_{32-}(\text{Ga}) + P_{32-}(\text{As}) = -4.0(21)$$

$$P_{32-}(\text{Ga}) - P_{32-}(\text{As}) = 0.4(2)$$

(standard deviations in parentheses). Thus, the sum is very poorly determined. This agrees with the discussion in the previous section. In GaAs, the site symmetry of the

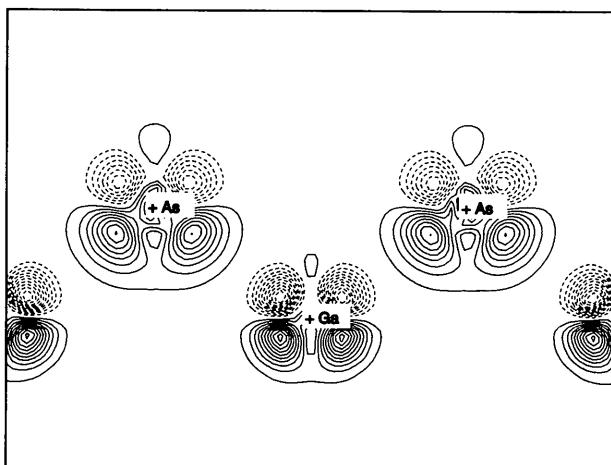


Fig. 1. GaAs static valence-electron density distribution from an unconstrained refinement (see text). Contours at intervals of $0.5 \text{ e } \text{Å}^{-3}$, solid lines positive, dashed lines negative.

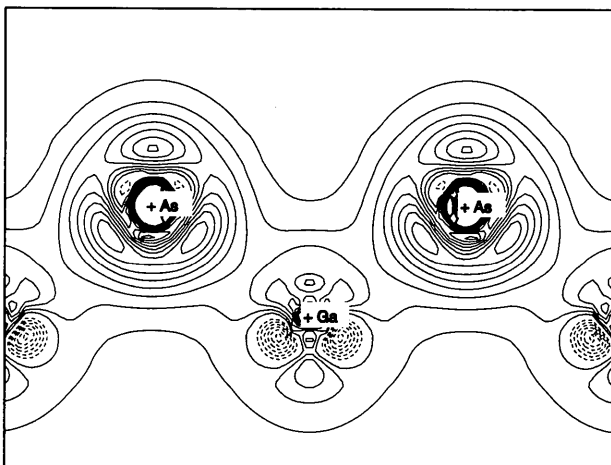


Fig. 2. GaAs static valence-electron density distribution from a constrained refinement (see text). Contours at intervals of $0.1 \text{ e } \text{Å}^{-3}$, solid lines positive, dashed lines negative.

Table 1. Results from a refinement of GaAs

Parameters for	Ga	As
P_v	2.4 (6)	5.6 (6)
κ'	1.09 (14)	1.02 (4)
P_{32-}	-1.8 (11)	-2.2 (11)
P_{40}	0.19 (11)	0.15 (12)
P_{44+}	0.14	0.11
$\zeta (\text{Bohr}^{-1})^*$	9.0 (13)	7.5 (3)

$P_v(\text{Ga}) + P_v(\text{As}) = 8$ by constraint (electroneutrality). Correlation coefficient $\gamma[P_{32-}(\text{Ga}), P_{32-}(\text{As})] = 0.984$. $P_{44+} = 0.740 P_{40}$ by constraint (see Hansen & Coppens, 1978). $R(F) = 0.44\%$, $R_w(F) = 0.45\%$. $R(F) = \sum |F_{\text{obs}}(\mathbf{H})| - |F_{\text{calc}}(\mathbf{H})| / \sum |F_{\text{obs}}(\mathbf{H})|$. $R_w(F) = \{ \sum w_{\mathbf{H}} [|F_{\text{obs}}(\mathbf{H})| - |F_{\text{calc}}(\mathbf{H})|]^2 \}^{1/2} / \{ \sum w_{\mathbf{H}} |F_{\text{obs}}(\mathbf{H})|^2 \}^{1/2}$. * 1 Bohr = 1 Bohr radius = 0.529 Å .

atoms is equal to the crystal-class symmetry, which implies that by adding a constant amount to P_{32-} for each of the atoms mainly affects the phases of the structure factors and not their moduli. On the other hand, the difference of the populations is determined with a much higher accuracy.

In Fig. 1, we show the static model valence density in the (110) plane corresponding to the above-described model. This density must be considered as physically meaningless because of the very pronounced negative regions in the neighborhood of each atom. The main features come from the octupoles. We subsequently changed their populations such that their difference remained the same but their values have opposite signs: $P_{32-}(\text{Ga}) = -P_{32-}(\text{As}) = 0.18$. With these values and ζ fixed, we refined the model again. The fit was slightly poorer, $R(F) = 0.50\%$, $R_w(F) = 0.50\%$ compared to 0.45% found previously. The corresponding model valence density (Fig. 2) is now much more reasonable (note that the contour interval is $0.1 \text{ e } \text{Å}^{-3}$ compared with $0.5 \text{ e } \text{Å}^{-3}$ in Fig. 1) although it still shows regions of negative density.

5. Multipole refinements of LiB_3O_5

A charge-density study of LiB_3O_5 (LBO) has been published by Radaev, Genkina, Lomonov, Maksimov, Pisarevskii, Chelokov & Simonov (1991) and Radaev,

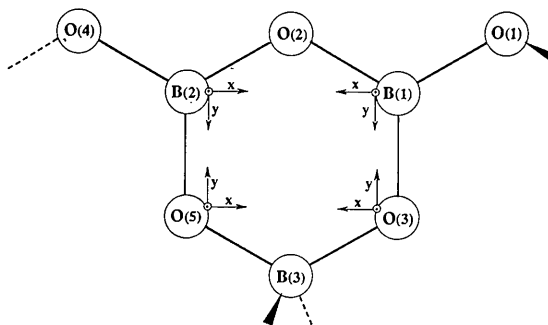


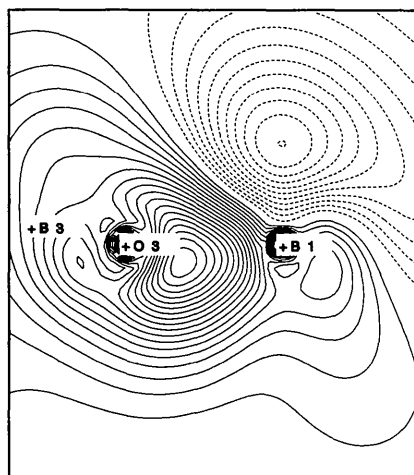
Fig. 3. Schematic representation of a fragment of the structure of LiB_3O_5 . The local coordinate systems used for the constrained multipole refinement of the electron density are indicated.

Maksimov, Simonov, Andreev & D'Yakov (1992). The present analysis is based on a data set collected at room temperature (Le Hénaff, Hansen, Protas & Marnier, 1996).

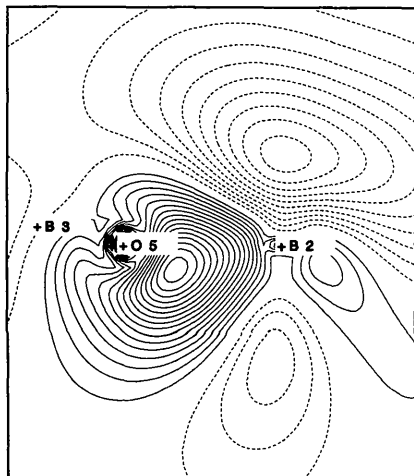
The space group is $Pna2_1$, $Z = 4$. We may consider the structure as a three-dimensional polymer formed from the fragments shown in Fig. 3, where the central B_3O_3 moiety is close to planar. The Li ions are located in channels running through the structure.

In order to illustrate what happens with this type of structure, we have carried out two refinements. In both of them, lithium was treated as a free +1 ion. For the other atoms, the multipole expansion was carried through to the third-order level (*i.e.* including octupoles). In the first refinement, no other constraints than the electroneutrality was imposed, whereas in the second we supposed that

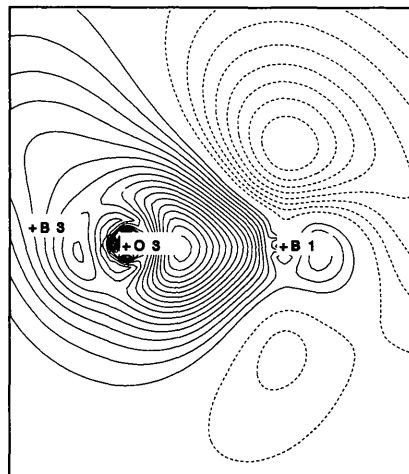
the pairs of atoms B(1), B(2) and O(3), O(5), respectively, had identical deformations. The fits obtained are almost equally good for both [unconstrained model: $R(F) = 1.41\%$; constrained model: $R(F) = 1.51\%$] and the residual density maps are low and quite similar ($\Delta\rho_{\text{res}} \leq 0.15 \text{ e \AA}^{-3}$). In Fig. 4, we show the static deformation density ($\Delta\rho = \rho_{\text{multipole}} - \rho_{\text{independent atoms}}$ calculated directly from the multipole model) in a plane through the B(1)—O(3) and B(2)—O(5) bonds and perpendicular to the pseudo molecular plane (B_3O_3 moiety). For the unconstrained model, it should be noted that the deformation density is very asymmetric with respect to the B_3O_3 plane and what we may term 'the bond peak' is displaced off the line connecting B(1) with O(3) and B(2) with O(5) and to the same side of the plane. When we constrain the model as described above, the deformation density becomes more symmetric with respect to the plane (Fig. 5), though not yet satisfactory to our mind, and the bond peaks are now



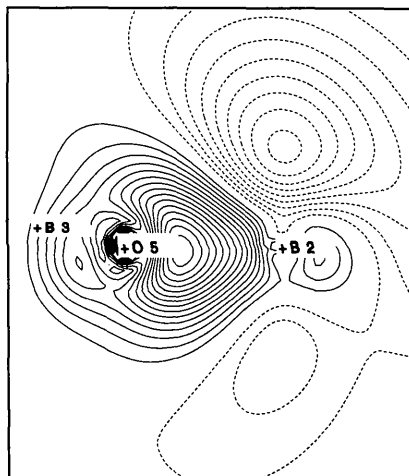
(a)



(b)



(a)



(b)

Fig. 4. LiB_3O_3 static electron deformation density in planes perpendicular to the hexagonal plane (B_3O_3) seen in Fig. 3 following an unconstrained refinement (a) containing the bond B(1)—O(3), (b) containing the bond B(2)—O(5). Contours at intervals of 0.05 e \AA^{-3} , solid lines positive, dashed lines negative.

Fig. 5. As Fig. 4 but for a constrained refinement (see text).

on the connecting lines. For a more detailed discussion of the electron-density distribution in LBO, we refer to the work by Le Hénaff *et al.* (1996) and in the next section we will explain why the constraints have made the model density more realistic.

6. Detection of ‘close to singular situations’ – remedies

We have described how we can determine from crystal symmetry what coefficients in the multipole expansion are poorly determined by an X-ray diffraction experiment. We will recall how an automatic diagnosis of this type of problem can be made during a least-squares refinement. The discussion will be based on the ideas of the ‘singular value decomposition’ (*e.g.* Press, Flannery, Teukolsky & Vetterling, 1990).

The least-squares normal equations can be expressed as (*e.g.* Hamilton, 1964)

$$\mathbf{B}\Delta\mathbf{p} = \mathbf{b}, \quad (22)$$

$$B_{ij} = \sum_{\mathbf{H}} w_{\mathbf{H}} (\partial C_{\mathbf{H}} / \partial p_i) (\partial C_{\mathbf{H}} / \partial p_j), \quad (23)$$

$$b_i = \sum_{\mathbf{H}} w_{\mathbf{H}} (\partial C_{\mathbf{H}} / \partial p_i) (O_{\mathbf{H}} - C_{\mathbf{H}}), \quad (24)$$

$\mathbf{B} = \{B_{ij}\}$ is a symmetric $n \times n$ matrix, $C_{\mathbf{H}}$ denotes the modulus of the calculated structure factor, $O_{\mathbf{H}}$ its observed value, $w_{\mathbf{H}} > 0$ is a weight factor, Δp_i change of parameter i , $\Delta\mathbf{p} = \{\Delta p_i\}$ is a vector in n -dimensional space and $\mathbf{b} = \{b_i\}$ likewise. It is assumed that the errors of the observations are not correlated.

We may solve (22) by diagonalization (eigenvalue analysis):

$$(\mathbf{T}\mathbf{B}\mathbf{T}^t)(\mathbf{T}\Delta\mathbf{p}) = (\mathbf{T}\mathbf{b}), \quad (25)$$

which may be reformulated as

$$\mathbf{B}'\Delta\mathbf{p}' = \mathbf{b}'. \quad (26)$$

\mathbf{T} is a unitary transformation matrix ($\mathbf{T}' = \mathbf{T}^{-1}$; \mathbf{T}' is \mathbf{T} transposed). We may consider (26), when compared to (22), as a change of parameters, *i.e.* a rotation in the n -dimensional parameter space. Thus, we may also write

$$B'_{ii} = \sum_{\mathbf{H}} w_{\mathbf{H}} (\partial C_{\mathbf{H}} / \partial p'_i)^2 \quad (27)$$

and

$$b'_i = \sum_{\mathbf{H}} w_{\mathbf{H}} (\partial C_{\mathbf{H}} / \partial p'_i) (O_{\mathbf{H}} - C_{\mathbf{H}}).$$

Each parameter combination $\{p_i\}$ or $\{p'_i\}$ is looked upon as a vector in an orthogonal space; this means that we have implicitly assumed a metric corresponding to the scalar product:

$$(p_1, p_2, \dots, p_n | q_1, q_2, \dots, q_n) = \sum_{i=1}^n p_i q_i. \quad (28)$$

Since \mathbf{B}' is diagonal, the solution to the normal equations in the primed parameter space is very simple:

$$\Delta p'_i = b'_i / B'_{ii}. \quad (29)$$

The solution in terms of the original parameters is

$$\Delta\mathbf{p} = \mathbf{T}'\Delta\mathbf{p}'.$$

Problems arise when some B'_{ii} values equal zero. This will only happen [see (27)] if the derivative $\partial C_{\mathbf{H}} / \partial p'_i$ is zero for all \mathbf{H} , which implies that b'_i is also equal to zero. In this case, any value of $\Delta p'_i$ satisfies the normal equations, *i.e.* its value is totally undetermined by the experiment. In several standard mathematical subroutine libraries, the action taken, when a close to singular problem is encountered, is to put $\Delta p'_i = 0$. Singularities may in some cases be avoided by measuring other reflections, but this is not often the case; the example of third-order cumulants in a structure belonging to the crystal class $\bar{4}3m$ cannot be solved this way. In such cases, we do need additional information to that contained in the diffraction data; it may come from imposing constraints on the parameters. The discussion below will be limited to linear constraints on the parameters which may be expressed by

$$\sum_{i=1}^n c_i p_i = C. \quad (30)$$

If a parameter p'_i is undetermined, the vector $\mathbf{c} = (c_1, c_2, \dots, c_n)$ must have a non-zero component parallel to p'_i in order to remove the singularity, *i.e.*

$$\mathbf{c} \cdot \mathbf{T}'\mathbf{p}'_i \neq 0, \quad \mathbf{p}'_i = (0, 0, \dots, p'_i, \dots, 0). \quad (31)$$

This can be illustrated graphically. Imagine a model only depending on two parameters, p_1 and p_2 (this can be generalized to any number of parameters). Fig. 6 shows a well behaved case. It is a contour plot of the weighted deviance (wD).

$$wD = \sum_{\mathbf{H}} w_{\mathbf{H}} [O_{\mathbf{H}} - C_{\mathbf{H}}(p_1, p_2)]^2, \quad (32)$$

which is the function that is minimized by the least-squares procedure. It is shown as a function of the two model parameters – the actual figure corresponds to a linear model. The contours are drawn at values of $+1, +2, \dots$ of the weighted deviance above its minimum at p_{01} and p_{02} . For a linear model, the contours are ellipses, the major axes of which correspond to the ‘eigenparameters’ (p'_1, p'_2). The ‘radii’ of the ellipse at $+1$ are equal to the standard deviations of the corresponding primed parameter (see Hamilton, 1964, ch. 4) and given by

$$\sigma(p'_i) = (1/B'_{ii})^{1/2}. \quad (33)$$

A linear constraint on the model parameters is represented by a line satisfying the equation

$$c_1 p_1 + c_2 p_2 = C. \quad (34)$$

Solving the least-squares problem under constraint means locating the minimum of wD on this line [on Fig. 6 this minimum is denoted (p_{c1}, p_{c2})].

In Fig. 7, a representation corresponding to a singular situation is shown. There is no unique solution to the problem since all points on the broken line have the same minimal value of wD . Imposing the constraint means that we only have to examine the points on the line [equation (34)]. Using 'eigenparameters', p'_2 (notation of Fig. 7) has a well defined value that is independent of the constraint (we still assume that both the refined model and the applied constraint are linear). For a non-singular situation, p'_2 depends on the constraint.

Complications arise when we have non-singular ill behaved normal equations, by which we mean that the normal-equations matrix is almost singular or in terms of the diagonalized equations that certain elements B'_{ii} are small, corresponding to ellipses in Fig. 6 with one very long major axis.

According to (33), if B'_{ii} is small, then the corresponding parameter has a large standard deviation but what we mean by 'large' depends very much on the type of parameter in question: e.g. for a coordinate of a non-H atom, a precision of 0.001 Å is good, but crystallographic programs are using fractional coordinates in the calculation, which implies that good precision means

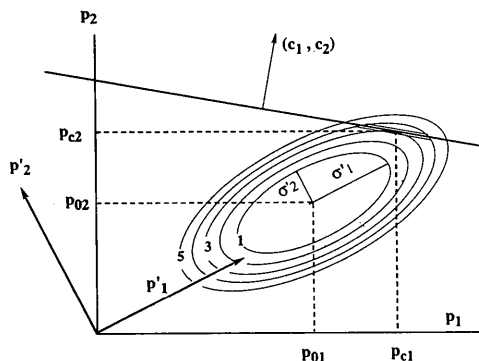


Fig. 6. Contour plot of the 'weighted deviance', wD , for a well behaved situation. The symbols are explained in the text.

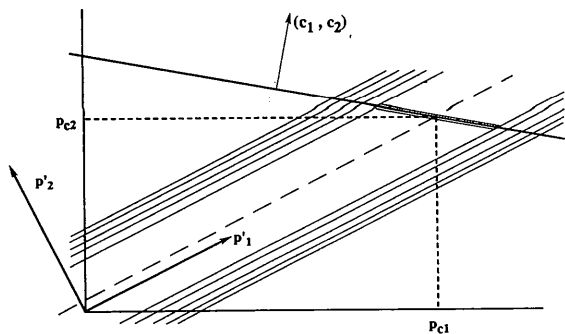


Fig. 7. As Fig. 6, but for singular least-squares normal equations. wD takes its minimum value at all points on the broken line.

Table 2. Typical standard deviations for different parameters from a precise X-ray diffraction study

Scale factor	0.1%
x, y, z	10^{-3} Å
U_{ij}	10^{-4} – 10^{-5} Å ²
Multipole population coefficients	
P_{00}	5×10^{-2}
P_{lm}	2×10^{-2}

Table 3. Results of singular value decomposition analysis for refinement of the multipole population coefficients for GaAs

$$p'_i = g_{i32-}P_{32-}(\text{Ga}) + g_{i40}P_{40}(\text{Ga}) + a_{i32-}P_{32-}(\text{As}) + a_{i40}P_{40}(\text{As}).$$

For the definition of P_{40} , see the explanations in Table 1.

i	g_{i32-}	g_{i40}	a_{i32-}	a_{i40}	$\sigma(p'_i)$
1	0.76	0.08	0.64	0.09	0.38
2	-0.33	0.62	0.23	0.68	0.04
3	-0.56	-0.33	0.73	-0.22	0.03
4	0.05	-0.71	-0.07	0.70	0.008

$\sigma(x/a) \approx 10^{-4}$ assuming a lattice constant of the order of 10 Å. If the least-squares normal-equations matrix is diagonal ($B \cong B'$), this implies that $B_{ii} \ll 10^8$ should be considered small. For a multipole population parameter with the normalization used in the computer program MOLLY (Hansen & Coppens, 1978), a precise study of a centrosymmetric structure gives typically $\sigma(P_{lm}) \cong 0.05$, and now small means $B_{ii} \ll 400$. In Table 2, values that may be considered 'good standard deviations' are compiled. When working with a real case, we are confronted with the problem that a parameter p'_i is some combination of all types of parameters, thus we do not *a priori* have any idea of what 'small' and 'large' mean. In order to get more uniform values of B_{ii} , it seems reasonable to make a change of parameters by scaling such that typically good standard deviations are of the order of unity. This corresponds to changing the metric of the initial parameter space but we may introduce this as an intermediate transformation before the diagonalization [equation 22]:

$$(SBS)(S^{-1} \Delta p) = Sb,$$

where S is a diagonal matrix composed from the idealized standard deviations like those proposed in Table 2.

7. Singular value decomposition applied to GaAs

For simplicity, we apply the procedure described above on the converged model for GaAs but consider only the populations of the two cubic harmonic functions on each of the two atoms. In Table 3, we give the expression for the primed parameters in terms of the original population coefficients as well as their standard deviations. As already pointed out, the sum of the two octupolar populations is poorly determined. It would therefore be convenient if one could impose a constraint on this value

as we did when we put this sum equal to zero. It is nevertheless difficult to justify this constraint from chemical reasoning.

For GaAs, an alternative way of analyzing the electron density is to model it as was done by Levallois & Allais (1986) and by Pietsch (1985). Their models describe the density as formed from spherical electron-density distributions at the ion sites and an additional cylindrically symmetric density centered on the bond axis, a 'bond charge'. The parameters are the ion charges, the bond charge, its extent and position. This model converges to a very satisfactory density as shown by Levallois & Allais (1986). It also has the advantage over the multipole model that the positivity of the electron density may be ensured by the sufficient condition that the populations are positive. Nevertheless, the ambiguity remains since we cannot consider this as a unique density only depending on the experimental data, independent of preconceived ideas. We might imagine that we add some octupoles corresponding to the parameter p'_1 (Table 3) to the bond-charge model; this would not significantly deteriorate the fit to the experimental data but it does modify the electron density. Only if we believe that the bond-charge model possesses the right flexibility, may we consider the ambiguity owing to the lack of knowledge of the phases of the structure factors to be removed, but we cannot use the diffraction data to justify this belief!

8. Singular value decomposition applied to LBO

We consider the multipole analysis presented in a previous paragraph. The case is more complicated than GaAs for several reasons, but the problems may be repaired more easily:

(a) the number of parameters is large; there are 128 population coefficients in the unconstrained model that we employed;

(b) the multipole radial functions for boron and oxygen are quite different, so we are rather far from the more ideal situation described in the general section; in particular, the condition given in (20) is not satisfied;

(c) because the boron multipole functions are more diffuse, *i.e.* they contribute little to the diffraction, their population coefficients are much less precisely determined (their standard deviations are about ten times higher than those of the O atoms). The singular-value-decomposition analysis therefore becomes much less straightforward to interpret owing to interferences between parameters that are poorly determined because of the phase problem and parameters that are poorly determined for the above reason.

Nevertheless, looking at the lowest eigenvalues (B'_i), we observe that the corresponding parameters are mainly combinations of the populations for the dipoles oriented along the polar crystal axis, Dz :

$$\begin{aligned} p'_1 &\cong 0.30Dz(\mathbf{B}(1)) + 0.30Dz(\mathbf{B}(2)) + 0.80Dz(\mathbf{B}(3)) + \dots \\ p'_2 &\cong 0.56Dz(\mathbf{B}(1)) + 0.58Dz(\mathbf{B}(2)) + 0.39Dz(\mathbf{B}(3)) + \dots \end{aligned} \quad (35)$$

(we have left out contributions for which the coefficients are smaller than 0.2 – it is stressed that the eigenvectors, *i.e.* the rows of T , are normalized to 1). There are contributions from the O atoms to these parameters, although very weak, but if we only compare the oxygen contributions among themselves, we find again that the strongest admixture by far is from the dipoles parallel to the polar axis.

We will next analyze how the constraints help for the most poorly determined parameters. The constraints that we applied in the present study were that deformations of the two trigonally coordinated B atoms were the same when referred to their close-neighbor coordination. When expressing the multipole functions with respect to the local coordinate systems indicated in Fig. 3, the constraints are simply

$$P_{lm}^{\text{local}}(\mathbf{B}(2)) = P_{lm}^{\text{local}}(\mathbf{B}(1))$$

or, in a different form,

$$P_{lm}^{\text{local}}(\mathbf{B}(2)) - P_{lm}^{\text{local}}(\mathbf{B}(1)) = 0;$$

there is one constraint per coefficient P_{lm} . For the dipoles, it is easy to show how these constraints work since the parameter set (P_{11+}, P_{11-}, P_{10}) transforms like a position vector:

$$\begin{pmatrix} P_{lm}^{\text{local}} \\ P_{lm}^{\text{local}} \\ P_{lm}^{\text{local}} \end{pmatrix} = \{E_{ij}\} \begin{pmatrix} P_{11+}^{\text{cryst}} \\ P_{11-}^{\text{cryst}} \\ P_{10}^{\text{cryst}} \end{pmatrix}.$$

P_{lm}^{cryst} refers to functions defined with respect to identical coordinate axes parallel to the crystallographic axes for all atoms. The transformation matrices $\{E_{ij}\}$ for atoms B(1) and B(2) are related by $E_{1j}(\mathbf{B}(1)) = -E_{1j}(\mathbf{B}(2))$, the other components being identical, since the two atoms have their local x axes in opposite directions and the y and z axes parallel. The constraints on the three dipoles may therefore be written:

$$\begin{aligned} &E_{11} [P_{11+}^{\text{cryst}}(\mathbf{B}(1)) + P_{11+}^{\text{cryst}}(\mathbf{B}(2))] \\ &+ E_{12} [P_{11-}^{\text{cryst}}(\mathbf{B}(1)) + P_{11-}^{\text{cryst}}(\mathbf{B}(2))] \\ &+ E_{13} [P_{10}^{\text{cryst}}(\mathbf{B}(1)) + P_{10}^{\text{cryst}}(\mathbf{B}(2))] = 0, \\ &E_{21} [P_{11+}^{\text{cryst}}(\mathbf{B}(1)) - P_{11+}^{\text{cryst}}(\mathbf{B}(2))] \\ &+ E_{22} [P_{11-}^{\text{cryst}}(\mathbf{B}(1)) - P_{11-}^{\text{cryst}}(\mathbf{B}(2))] \\ &+ E_{23} [P_{10}^{\text{cryst}}(\mathbf{B}(1)) - P_{10}^{\text{cryst}}(\mathbf{B}(2))] = 0, \\ &E_{31} [P_{11+}^{\text{cryst}}(\mathbf{B}(1)) - P_{11+}^{\text{cryst}}(\mathbf{B}(2))] \\ &+ E_{32} [P_{11-}^{\text{cryst}}(\mathbf{B}(1)) - P_{11-}^{\text{cryst}}(\mathbf{B}(2))] \\ &+ E_{33} [P_{10}^{\text{cryst}}(\mathbf{B}(1)) - P_{10}^{\text{cryst}}(\mathbf{B}(2))] = 0. \end{aligned}$$

For the parameter p'_1 [equation (35)], the scalar product defined in (31) becomes, for each of the three constraints,

$$P_{11+}^{\text{loc}} : -E_{13}(0.30 + 0.30) \cong -0.6E_{13}$$

$$P_{11-}^{\text{loc}} : -E_{23}(0.30 - 0.30) \cong 0$$

$$P_{10}^{\text{loc}} : -E_{33}(0.30 - 0.30) \cong 0.$$

Therefore, the constraint on the dipole in the x direction of the local coordinate systems is the only one that can be efficient and only if E_{13} [the direction cosine of the local x axis of B(1) with respect to the c axis of the crystal] is large (close to ± 1), *i.e.* the local x axis must form an angle with the polar axis quite different from 90° . For LBO, this angle is 54° , $E_{13} = 0.58$.

For LBO, we could imagine other constraints. We might impose the electron density of the atoms B(1) and B(2) to be symmetric with respect to the plane formed by the three next-neighbor O atoms, and possibly also impose a local mirror symmetry on the tetrahedrally coordinated B(3) atom.

From inspection of the form of the parameters p'_1 and p'_2 [equation (35)], one sees that it is important to find a constraint that affects the dipole population coefficient of B(3).

We will not go any further into the analysis of the electron density of LBO but refer to the detailed analysis by Le Hénaff *et al.* (1996).

9. Conclusions

We will briefly examine a number of situations that at first sight seem to invalidate the conclusions that we have drawn from our analysis.

The existence of pseudo-forbidden reflections for some crystals implies that the atoms must have odd-parity components in their density distribution. The best known example of this is the 222 reflection of silicon, but since the space group is centrosymmetric it does not apply to the present discussion. Comparing with our analysis of GaAs, we may consider the constraint that was applied [$P_{32-}(\text{Ga}) = -P_{32-}(\text{As})$] as introducing a pseudo center of inversion into the structure. For a structure type such as zinc blende, 'forbidden' Bragg reflections of this type do not exist but a significant difference between observed structure amplitudes of the relatively weak $h + k + l = 4n + 2$ reflections and the calculated structure amplitudes for a model only taking into account centrosymmetric density functions on the atoms will be a clue to the importance of pile-up of bond density; *i.e.* in the multipole expansion there must be a significant contribution from the octupoles. Our analysis agrees with this but shows that we cannot decide from the data on which atom this deformation is preponderant.

Pseudo-extinctions analogous to those of the ' $4n + 2$ reflections' in silicon can occur in some non-centrosymmetric space groups. 'Violations' of these imply that

non-spherical deformations of the atomic densities must exist; but inspection of the space groups shows that these weak intensities never impose any values on the populations of the troublesome odd-order multipoles. As an example of this, consider the space group $P222_1$. If the atoms are on one type of special position, special conditions apply to the reflections $h0l$ or $0kl$, but the only invariant odd-order multipole ($l \leq 3$) in this class is y_{32-} , which does not contribute to these reflection groups. Their intensities are only affected by other multipoles.

Our approach to the problem could also have been based on the Patterson function. The general problem that has been discussed thoroughly in the past was whether a unique atomic structure can be found in all cases (it was tacitly assumed that the atomic density distributions are centrosymmetric). We are concerned with a more delicate problem: even if a unique structure can be found, the total density is not unique. This can easily be seen if we add a density function of odd parity (*e.g.* odd-order multipoles) to predominant spherically symmetric densities; all the mixed convolution integrals between even and odd functions cancel and the Patterson function is only modified to second order in the odd-parity functions. This is the analog to the approximation in (19).

The aim of the present analysis is to draw attention to the fact that for non-centrosymmetric crystal structures a 'truly experimental' electron density cannot be obtained from an X-ray diffraction experiment. This is contrary to the situation for centrosymmetric structures for which even crude models (*e.g.* structure factors calculated from non-interacting free-atom electron-density distributions) predict correct signs of the structure factors for the vast majority of Bragg reflections.

For the non-centrosymmetric cases, we should therefore always consider very carefully how we model the electron density, since the way we model or constrain the model limits the questions that we can ask about the electron density. The conclusion may be drawn that we should not attempt to analyze electron densities by modeling but content ourselves with comparing experimental structure-factor amplitudes with theory. At present, this would limit the compounds that we could study because of the quality of theoretical computations of electronic wave functions for big molecules or crystals.

When things seem to work out for organic crystals (with the exception of highly symmetric cases like hexamethylenetetramine), one reason is that constraints are almost always applied to the density models from the very beginning of the analysis, and mostly without any other justifications than: (i) to reduce the ratio of the number of variables to the number of measured reflections; (ii) that certain parameters (*e.g.* individual H-atom charges and multipole deformations) would be determined with low precision.

The possibly best way of improving the analysis of charge densities for non-centrosymmetric structures may be to introduce into the modeling true experimental phase information. Nevertheless, it may only be possible to obtain this with sufficient accuracy for simple structures – the only example we know of is BeO (Zuo, Spence, Downs & Mayer, 1993).

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