DMR-76-80847) facilitated this work. The research was supported by the US Army Research Office under grant No. DAAG29-78-G-0156.

References

BANUS, M. D. & REED, T. B. (1970). *The Chemistry of Extended Defects in Non-Metallic Solids*, edited by L. EYRING & M. O'KEEFE, pp. 488–522. Amsterdam: North-Holland.

BATTERMAN, B. W., DEMARCO, J. J. & WEISS, R. J. (1961). *Phys. Rev.* **122**, 68–74.

BORIE, B. & SPARKS, C. J. (1971). *Acta Cryst.* A**27**, 198–201.

CASTLES, J. R., COWLEY, J. M. & SPARGO, A. E. C. (1971). *Acta Cryst.* A**27**, 376–383.

GEHLEN, P. C. (1969). *Rev. Sci. Instrum.* **40**, 718–721.

GOODENOUGH, J. B. (1972). *Phys. Rev. B*, **5**, 2764–2774.

GRAGG, J. E. JR, BARDHAN, P. & COHEN, J. B. (1971). *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. MILLS, E. ASCHER & R. I. JAFFEE, pp. 309–337. New York: McGraw-Hill.

HAYAKAWA, M. & COHEN, J. B. (1975). *Acta Cryst.* A**31**, 635–644.

HAYAKAWA, M., MORINAGA, M. & COHEN, J. B. (1973). *Defects and Transport in Oxides*, edited by M. S. SELTZER & R. I. JAFFEE, pp. 177–199. New York: Plenum Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LIFSHITZ, I. M. (1964). *Adv. Phys.* **13**, 483–536.

MORINAGA, M. (1977). *Acta Metall.* **25**, 957–962.

MORINAGA, M. (1978). PhD Thesis, Northwestern Univ., Evanston, IL 60201.

REED, T. B. & POLLARD, E. R. (1968). *J. Cryst. Growth*, **2**, 243–247.

SAUVAGE, M. & PARTHÉ, E. (1974). *Acta Cryst.* A**30**, 239–246.

SCHWARTZ, L. H., MORRISON, L. H. & COHEN, J. B. (1964). *Adv. X-ray Anal.* **7**, 281–301.

SHAW, B. W. (1968). *Phys. Rev.* **174**, 769–781.

SUORTTI, P. (1972). *J. Appl. Cryst.* **5**, 325–331.

TAYLOR, A. & DOYLE, N. J. (1970). *The Chemistry of Extended Defects in Non-metallic Solids*, edited by L. EYRING & M. O'KEEFE, pp. 523–540. Amsterdam: North-Holland.

TERAUCHI, H. & COHEN, J. B. (1978). *J. Phys. Chem. Solids*, **39**, 681–686.

TERAUCHI, H., COHEN, J. B. & REED, T. B. (1978). *Acta Cryst.* A**34**, 556–561.

WATANABE, D., CASTLES, J. R., JOSTSONS, A. & MALIN, A. (1967). *Acta Cryst.* **23**, 307–313.

WATANABE, D., TERASAKI, O., JOSTSONS, A. & CASTLES, J. R. (1968). *J. Phys. Soc. Jpn*, **25**, 292.

WATANABE, D., TERASAKI, O. JOSTSONS, A. & CASTLES, J. R. (1970). *The Chemistry of Extended Defects in Non-Metallic Solids*, edited by L. EYRING & M. O'KEEFE, pp. 238–258. Amsterdam: North-Holland.

WILLIAMS, R. O. (1972). Report ORNL-5140. Oak Ridge National Laboratory, Tennessee.

WOLFF, P. M. DE (1956). *Acta Cryst.* **2**, 682–683.

ZIMAN, J. M. (1970). *Proc. R. Soc. London Ser. A*, **318**, 401–420.

Acta Cryst. (1979). A**35**, 652–658

The Use of Electric Field Gradient Calculations in Charge Density Refinements. I. Hirshfeld-Type Deformation Functions and the Calculation of Electric Field Gradients by Fourier Series

BY D. SCHWARZENBACH AND NGO THONG

Institut de Cristallographie, Université de Lausanne, Bâtiment des Sciences Physiques, 1015 *Lausanne, Switzerland*

(*Received* 20 *January* 1979; *accepted* 26 *February* 1979)

Abstract

Single-crystal X-ray diffraction data contain in principle complete information on the spatial distribution of the bonding electrons. However, this information is subject to a variety of errors. Nuclear quadrupole resonance spectroscopy (NQR) provides a very sensitive measurement of an electrostatic property of the deformation density; the electric field gradient tensor at the site of a nucleus. It is proposed that diffraction and NQR data are combined so that more reliable charge densities can be obtained. Well known multipole deformation functions are used to describe a quasi-static and parametrized deformation density. The electric field gradient is computed by a Fourier series and expressed as a function of the same deformation parameters. These can then be refined by least-squares calculations simultaneously with respect to diffraction intensities and NQR results. Overlap corrections of the neutral spherical atoms and the effect of temperature vibrations are discussed.

0567-7394/79/040652-07$01.00

Introduction

In recent years, the determination of bonding electron distributions with least-squares refinements using aspherical atom formalisms has shown great promise (Hansen & Coppens, 1978). The asphericity of an atom is generally described by the electron populations of a set of nucleus-centred functions $R(r)Y(\theta,\varphi)$ where the angular part Y is a spherical harmonic (Stewart, 1973) and the radial part is of the form $R(r) = r^n\exp(-\alpha r)$. Hirshfeld (1971) and Harel & Hirshfeld (1975) use a set of non-orthogonal functions which are linear combinations of spherical harmonics. Assuming that the electron cloud follows the vibrating nucleus, the aspherical atomic electron density at rest is convoluted with a standard Gaussian thermal displacement distribution. These multipolar models provide thus a *parametrized* estimate of the *static* charge density (Hirshfeld, 1977*a*).

The calculation of certain physical properties from the charge density distribution was proposed by Stewart (1972). Electrostatic quantities in crystals such as electric fields, field gradients, and dipole moments of molecular species are almost exclusively determined by the deformation density. Fields and field gradients at the atomic centers in a crystal composed of spherically symmetric neutral atoms (procrystal) are small and due only to atomic overlap. The electric field gradient at the position of a nucleus possessing a quadrupole moment can be measured by NQR, or by Mössbauer spectroscopy, and is therefore of special interest since it can serve as an independent check on the quality of an experimental deformation density. There are, however, two fundamental difficulties in such a procedure:

(*a*) The thermally averaged deformation density is obtained from X-ray diffraction, whereas NQR gives the vibrational average of the field gradient. The latter is determined in good approximation by the static deformation density (see below). The use of a multipole model is therefore essential to achieve an approximate deconvolution of temperature vibrations and charge density.

(*b*) The field gradient at a nuclear site is strongly dependent on a possible quadrupole deformation of the core electron distribution resulting from chemical bonding, since the contribution of a volume element at a distance r from the nucleus is proportional to r^{-3}. The deformation density near the atomic center can, however, not be determined reliably from diffraction data. Hirshfeld & Rzotkiewicz (1974) have shown that dipole core deformations due to chemical bonding are probable. Stewart (1977) concludes from theoretical calculations on N_2 that the relevant quadrupole deformations are well within the resolution of the diffraction experiment, indicating that meaningful field gradients can indeed be computed from deformation densities.

The precision of an experimental charge density determination is subject to a variety of errors (Coppens, 1975). The information contained in the structure factors on the distribution of the valence electrons is weak but complete, subject to the experimental resolution and assuming that the phases are known. The electric field gradient tensor depends only on the quadrupole component of the *total* charge density centered on the nucleus. Qualitatively similar electron distributions can produce rather different gradient tensors. The information obtained by NQR is thus reliable but incomplete. The effective tensor $\nabla\mathbf{E}$ is in fact described by at most five independent terms, its trace $\nabla E_{11} + \nabla E_{22} + \nabla E_{33}$ with respect to a Cartesian coordinate system being zero. How then should a charge density determined by X-ray diffraction be modified if it does not reproduce the measured field gradient? To answer this question, both types of experimental evidence must be expressed as functions of the same parameters, and we can then refine these parameters simultaneously with respect to diffraction intensities and NQR results. For this purpose, we propose to use the population factors and exponents of an aspherical atom formalism.

Hirshfeld's deformation functions

We use in the following the deformation functions given by Hirshfeld to describe the bonding density in a crystal. This choice was dictated to a large degree by the availability of a well established and documented computer program (Hirshfeld, 1977*b*). The spherical harmonics of the program *MOLLY* (Hansen & Coppens, 1978) would serve equally well.

The electron density of a stationary atom in the crystal is assumed to be

$$\rho = \rho_0 + \sum_n N^{(n)}\left[\sum_l c_l^{(n)} r^n \cos^n \Phi_l^{(n)}\right]\exp(-ar),$$

$$1 \le l \le \tfrac{1}{2}(n+1)(n+2),\ N^{(n)} = \frac{(n+1)\alpha^{n+3}}{4\pi(n+2)!}. \qquad (1)$$

ρ_0 is the spherical free-atom density, $\Phi_l^{(n)}$ is the angle between the radius vector $\mathbf{r}$ and the axis of the lth deformation function of order n, and $c_l^{(n)}$ is an occupation factor. $N^{(n)}$ normalizes the integral over even functions to unity. The corresponding scattering factor is then

$$f = f_0 + \sum_n\sum_l c_l^{(n)}\,\delta f_l^{(n)}(\alpha). \qquad (2)$$

With n ranging from 0 to 4, 35 deformation functions and 36 deformation parameters may be refined for an atom in a general position. The anisotropic temperature factor is applied to the total scattering factor. The axes of the deformation functions are chosen in a local atom-centered Cartesian coordinate system in directions related by cubic symmetry: $100\circlearrowleft$ for $n = 1$; $1\pm10\circlearrowleft$ for $n = 2$; $1\pm10\circlearrowleft$, 111 and $\bar{1}\bar{1}1\circlearrowleft$ for $n = 3$; $100\circlearrowleft$ and $A\pm1\pm1\circlearrowleft$ for $n = 4$ ($\circlearrowleft$ means cyclic permutation, $A = \sqrt{2} - 1$). These 35 non-orthogonal functions can be expressed as sums of spherical harmonics, comprising three monopole terms ($n = 0, 2, 4$), two dipole terms ($n = 1, 3$), two quadrupole terms ($n = 2, 4$), one octopole ($n = 3$) and one hexadecapole term ($n = 4$). They represent thus a very flexible expansion of the atomic asphericity. Their transformation properties are in general not simple. They can be derived by writing the sum of the $\frac{1}{2}(n+1)(n+2)$ functions of order n in the algebraic form

$$\sum_l c_l^{(n)} r^n \cos^n \Phi_l^{(n)} = \sum_0^n \sum_0^n \sum_0^n a_{uvw}^{(n)} x^u y^v z^w, \quad (u + v + w = n), \tag{3}$$

where the $\frac{1}{2}(n + 1)(n + 2)$ coefficients $a_{uvw}^{(n)}$ transform as the totally symmetric tensor of order n. The number $Z^{(n)}$ of independent functions or coefficients of order n for an atom with a given point symmetry can thus be obtained by group theoretical methods (Bhagavantam, 1966). If $\chi^{(n)}(x)$ is the character of the transformation of the deformation functions for the symmetry operation x, and h the order of the group:

$$Z^{(n)} = \frac{1}{h} \sum_x \chi^{(n)}(x), \tag{4}$$

the sum extending over all symmetry operations. The $c_l^{(n)}$ and $a_{uvw}^{(n)}$ are related by a system of linear equations.

The characters are listed in Table 1 for $n = 1$ through 6. While (4) is useful as a check against errors, the relevant symmetry constraints are easily derived by inspection for all subgroups of $m3m$. One of the advantages of Hirshfeld's deformation functions is in fact their intuitive simplicity. Hexagonal and higher symmetries require, however, special considerations. A tensor of order x possesses cylindrical symmetry in the presence of proper rotations of order $x + 1$ or higher. This implies the same relations between the occupation factors $c_l^{(4)}$ ($n = 4$) for all hexagonal groups. Denoting these occupation factors by the indices of their main axes and orienting the cylinder axis along 001, we obtain:

$$\begin{aligned}
&(11A) = (\bar{1}1A) = (1\bar{1}A) = (\bar{1}\bar{1}A);\\
&(100) = (010) = 8/(2 + A^2)^2\,\{(11A)\};\\
&(A11) = (A\bar{1}1) = (A1\bar{1}) = (A\bar{1}\bar{1}) = (1A1)\\
&\qquad = (\bar{1}A1) = (1A\bar{1}) = (\bar{1}A\bar{1});\ (001).
\end{aligned}$$

These relations become more complicated for $A \neq \sqrt{2} - 1$.

Spherical symmetry for $n = 4$, *i.e.* a pure monopole, implies the same occupation factors for all functions $100\circlearrowleft$ and for all $A\pm1\pm1\circlearrowleft$ with the additional condition $(A11) = (10{\cdot}5 - 6\sqrt{2})\{(100)\}$. The cylindrical symmetries for all other n can be derived by inspection. The effect of a sixfold inversion axis $\bar{6}$ on the functions $n = 3$ introduces, however, special constraints. The $c_l^{(3)}$ are for $\bar{6}2m$ (twofold axis along 100):

$$\begin{aligned}
&(111) = (1\bar{1}\bar{1}) = -(\bar{1}\bar{1}1) = -(\bar{1}1\bar{1});\\
&(101) = (10\bar{1}) = -2B\{(111)\};\\
&(110) = (1\bar{1}0) = -B\{(111)\};\quad (011) = (01\bar{1}) = 0;\\
&B = 2\sqrt{2}/3\sqrt{3}.
\end{aligned}$$

For symmetry $\bar{6}$, we obtain:

$$\begin{aligned}
&(111) = -(\bar{1}\bar{1}1);\ (1\bar{1}\bar{1}) = -(\bar{1}1\bar{1});\\
&(110) = -B\{(111)\};\quad (1\bar{1}0) = -B\{(1\bar{1}\bar{1})\};\\
&(101) = (10\bar{1}) = -B\{(111) + (1\bar{1}\bar{1})\};\\
&(011) = (01\bar{1}) = -B\{(111) - (1\bar{1}\bar{1})\}.
\end{aligned}$$

With these relations, all point symmetries of atomic sites can be treated. Only the group $\bar{6}$ presents a complicated situation.

In a centrosymmetric structure, the deformation model simply parametrizes the residual electron density found in a difference synthesis, as far as it is flexible enough to account for all significant features, and it filters random errors. We do not try to attach any physical significance to the individual parameters which are often highly correlated and we do not attempt to reduce the number of parameters by introducing local or chemical symmetries if the available memory space in the computer permits this. In non-centrosymmetric structures where the phases cannot be deduced from the spherical atom model, there may well be several combinations of deformation functions capable of adequately reproducing the observed structure factors. If the structure possesses centrosymmetric projections, the danger of such ambiguities will certainly be reduced. The introduction of supplementary information such as electric field gradients is also expected to favor a unique solution.

Table 1. *Characters $\chi^{(n)}(x)$ of the transformation matrices of deformation functions of order n for rotations $\pm 2\pi/x$*

The characters for rotation–inversions $\bar{x}$ are $\chi^{(n)}(\bar{x}) = (-1)^n \chi^{(n)}(x)$.

$x =$	1	2	3	4	6
$\chi^{(1)}$	3	−1	0	1	2
$\chi^{(2)}$	6	2	0	0	2
$\chi^{(3)}$	10	−2	1	0	1
$\chi^{(4)}$	15	3	0	1	0
$\chi^{(5)}$	21	−3	0	1	0
$\chi^{(6)}$	28	4	1	0	1

Electrostatic quantities and Fourier series

With respect to a Cartesian coordinate system, any electrostatic quantity $\boldsymbol{\varepsilon}$ at the position $\mathbf{R} = (R_1 R_2 R_3)$ is given by

$$\boldsymbol{\varepsilon} = \int g(\mathbf{R} - \mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{5}$$

where $\rho(\mathbf{r})$ describes the distribution of all charges in the crystal, i.e. electrons and nuclei, and the integration extends over the complete crystal volume. For the potential Φ, the field $\mathbf{E}$ and the field gradient tensor element ∇E_{mn}, we obtain respectively

$$g(\mathbf{r}) = \frac{1}{|\mathbf{r}|};\quad \frac{\mathbf{r}}{|\mathbf{r}|^3};\quad -\frac{3r_mr_n - \delta_{mn}|\mathbf{r}|^2}{|\mathbf{r}|^5}, \tag{6}$$

with $|\mathbf{r}|^2 = r_1^2 + r_2^2 + r_3^2$.

The trace of $\nabla\mathbf{E}$ is zero. It is conceivable to carry out the integration in direct space and to express $\boldsymbol{\varepsilon}$ in terms of monopole, dipole and higher moments which are all functions of the deformation parameters. Overlap corrections for neighboring atoms and the effect of the electron cloud around the position $\mathbf{R}$ would have to be included. A summation in reciprocal space is, however, preferable (Bertaut, 1952, 1978) since $\boldsymbol{\varepsilon}$ is the convolution of $g(\mathbf{r})$ with $\rho(\mathbf{r})$. The Fourier transforms $G_g(\mathbf{s})$ of $g(\mathbf{r})$ are

$$G_g(\mathbf{s}) = \frac{1}{\pi|\mathbf{s}|^2}, [\Phi];\quad \frac{2i}{|\mathbf{s}|^2}\mathbf{s}, [\mathbf{E}];$$
$$\frac{4\pi}{3|\mathbf{s}|^2}(3s_ms_n - \delta_{mn}|\mathbf{s}|^2), [\nabla E_{mn}], \tag{7}$$

$\mathbf{s} = (s_1s_2s_3)$ is a reciprocal vector. The Fourier transform $G_\rho(\mathbf{s})$ of a *periodic* charge distribution is given by the structure factors including the nuclei

$$G_\rho(\mathbf{s}) = V^{-1}F_{\mathbf{s}} = \int \rho(\mathbf{r}) \exp(2\pi i\mathbf{s}\mathbf{r})\,\mathrm{d}\mathbf{r}$$
$$\text{for } \mathbf{s} = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^* \tag{8}$$

and is zero otherwise. The mean charge density as seen by a nucleus executing thermal vibrations is, however, not strictly periodic. $\boldsymbol{\varepsilon}$ is equal to the Fourier transform of G_gG_ρ;

$$\boldsymbol{\varepsilon} = \int G_gG_\rho \exp(-2\pi i\mathbf{s}\mathbf{R})\,\mathrm{d}\mathbf{s}, \tag{9}$$

which, for a periodic charge distribution, gives

$$\Phi = \frac{1}{\pi V}\sum_{\mathbf{s}} \frac{1}{|\mathbf{s}|^2} F_{\mathbf{s}} \exp(-2\pi i\mathbf{s}\mathbf{R}),$$

$$\mathbf{E} = \frac{2i}{V}\sum_{\mathbf{s}} \frac{1}{|\mathbf{s}|^2} \mathbf{s}F_{\mathbf{s}} \exp(-2\pi i\mathbf{s}\mathbf{R}),$$

$$\nabla E_{mn} = \frac{4\pi}{3V}\sum_{\mathbf{s}} \frac{1}{|\mathbf{s}|^2}(3s_ms_n - \delta_{mn}|\mathbf{s}|^2)F_{\mathbf{s}}$$
$$\times \exp(-2\pi i\mathbf{s}\mathbf{R}), \tag{10}$$

the sums extending over all reciprocal lattice vectors. These formulae obviously represent real quantities since $F_{-\mathbf{s}} = F_{\mathbf{s}}^*$. The Fourier summations are more efficiently calculated if the coordinate system is defined by the unit translations of the crystal lattice where $\mathbf{R} = \sum x_i\mathbf{a}_i$ and $\mathbf{s} = \sum h_i\mathbf{a}_i^*$. The tensors $\boldsymbol{\varepsilon}$ are defined in the reciprocal coordinate system. They transform covariantly with the coordinates h_i and contravariantly with the coordinates x_i. Introducing the superscript (c) to denote the crystal coordinate system and replacing $\mathbf{s}$ by $\mathbf{h}$, we obtain finally the tensor components

$$\Phi^{(c)} = \frac{2}{\pi V}\sum_{+\mathbf{h}} \frac{1}{|\mathbf{h}|^2}[A_{\mathbf{h}}\cos(2\pi\mathbf{h}\mathbf{R})$$
$$+ B_{\mathbf{h}}\sin(2\pi\mathbf{h}\mathbf{R})],$$

$$E_m^{(c)} = \frac{4}{V}\sum_{+\mathbf{h}} \frac{h_m}{|\mathbf{h}|^2}[A_{\mathbf{h}}\sin(2\pi\mathbf{h}\mathbf{R}) - B_{\mathbf{h}}\cos(2\pi\mathbf{h}\mathbf{R})],$$

$$\nabla E_{mn}^{(c)} = \frac{8\pi}{V}\sum_{+\mathbf{h}} [h_mh_n/|\mathbf{h}|^2 - (\mathbf{a}_m\mathbf{a}_n)/3]$$
$$\times [A_{\mathbf{h}}\cos(2\pi\mathbf{h}\mathbf{R}) + B_{\mathbf{h}}\sin(2\pi\mathbf{h}\mathbf{R})],$$

$$\mathbf{h}\mathbf{R} = h_1x_1 + h_2x_2 + h_3x_3;\quad F_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}}. \tag{11}$$

The sums ($+\mathbf{h}$) extend over half the reciprocal space. The condition that trace ($\nabla\mathbf{E}$) = 0 is now expressed by

$$\sum_{m,n} \nabla E_{mn}^{(c)}(\mathbf{a}_m^*\mathbf{a}_n^*) = 0, \tag{12}$$

which can be verified by recognizing that $\sum_{m,n}(\mathbf{a}_m\mathbf{a}_n)(\mathbf{a}_m^*\mathbf{a}_n^*)$ = trace $(\mathbf{M}.\mathbf{M}^*) = 3$, $\mathbf{M}$ and $\mathbf{M}^*$ being the direct and reciprocal metric tensors respectively. In fact, by calculating the derivatives of $\Phi^{(c)}$ with respect to x_i, div grad $\Phi = \Delta\Phi = 4\pi\rho(\mathbf{R})$ is obtained.

The crystal symmetry is introduced in the same way as in an electron density calculation. Considering the symmetry transformation $(B, \mathbf{t}_B)$ acting on the coordinates in real space where (B) and $\mathbf{t}_B$ are the rotational and translational parts respectively, the structure factor of the reflection $\mathbf{h}' = (\tilde{B})\mathbf{h}$ is

$$F_{\mathbf{h}'} = F_{\mathbf{h}} \exp(-2\pi i\mathbf{h}\mathbf{t}_B). \tag{13}$$

The sum over a set of equivalent reflections then becomes

$$\Phi^{(c)}(\mathrm{sym}) = \frac{1}{\pi V|\mathbf{h}|^2}F_{\mathbf{h}}\sum_B \exp[-2\pi i\mathbf{h}(B\mathbf{R} + \mathbf{t}_B)] \tag{14}$$

and similarly for $\mathbf{E}$ and $\nabla\mathbf{E}$. The calculations are thus reduced to sums over symmetrically independent terms. The results may finally be transformed back into a Cartesian base by $\mathbf{E} = (R)\mathbf{E}^{(c)}$ and $\nabla\mathbf{E} = (R)\nabla\mathbf{E}^{(c)}(\tilde{R})$, where (R) transforms the reciprocal coordinates and the real coordinate axes into the Cartesian system.

Equivalent charge densities and overlap corrections

As is well known (Bertaut, 1952), the series (11) do not converge due to the nuclear point charges. However, equivalent charge distributions can be derived which yield the same electrostatic quantities. Thus, any spherical neutral charge distribution, corresponding to the condition $\int 4\pi r^2\rho(r)\,\mathrm{d}r = 0$, will not contribute to the quantities $\boldsymbol{\varepsilon}$, provided that it does not extend to the position **R**. Equivalent charge distributions can therefore be obtained by subtracting spherical neutral non-overlapping atoms centered on the nuclear positions, the number of their electrons being equal to the nuclear charges. For the potential Φ, the contribution of the electrons of the atom centered at **R** has to be added, their contribution to the field and the field gradient being zero. By subtracting free spherical atoms as used in a normal structure refinement, *i.e.* the electron density of the procrystal, the deformation density discussed above is obtained. However, these atoms overlap at **R** and an appropriate overlap correction for nearest neighbors must be devised.

International Tables for X-ray Crystallography (1974) quote the free spherical atom form factors in the analytical approximation

$$f = \sum_{i=1}^{4} a_i \exp(-b_i\lambda^{-2}\sin^2\theta) + c, \tag{15}$$

all neutral atoms having positive b_i values. The coefficients are optimized in the $\sin\theta/\lambda$ region from 0 to 2 Å^{-1}. The more uncertain scattering factor at larger reciprocal distances is, however, mainly due to the atomic cusp density which behaves as an electric monopole at distances not too near to the atomic center. The Fourier inversion of (15) is therefore sufficiently accurate for the required overlap correction. The charge density for atomic number Z is thus given by

$$\rho(r) = \delta(r)(Z-c) - 8\pi^{3/2}\sum_{i=1}^{4} a_i b_i^{-3/2}\exp(-\tfrac{1}{2}r^2\sigma^{-2})\,\mathrm{d}\mathbf{r}, \tag{16}$$

i.e. by a sum of Gaussian distributions with variances $\sigma_i^2 = b_i/(8\pi^2)$. In a Cartesian coordinate system, the electrostatic quantities $\boldsymbol{\varepsilon}$ at position **d** due to a Gaussian charge distribution centered at the origin are, in analogy to (5),

$$\boldsymbol{\varepsilon} = (2\pi)^{-3/2}\sigma^{-3}\int g(\mathbf{d}-\mathbf{r})\exp(-\tfrac{1}{2}r^2\sigma^{-2})\,\mathrm{d}\mathbf{r}. \tag{5$'$}$$

This integral can be directly evaluated for Φ, **E** and ∇**E**:

$$\Phi = \frac{1}{|\mathbf{d}|}\Gamma(t),$$

$$\mathbf{E} = \frac{\mathbf{d}}{|\mathbf{d}|^3}\left[\Gamma(t) - \sqrt{\frac{2}{\pi}}\,t\exp(-\tfrac{1}{2}t^2)\right],$$

$$\nabla E_{mn} = -\frac{3d_md_n - \delta_{mn}|\mathbf{d}|^2}{|\mathbf{d}|^5} \times\left[\Gamma(t) - \frac{2}{3\sqrt{2\pi}}(t^3+3t)\exp(-\tfrac{1}{2}t^2)\right],$$

$$\Gamma(t) = \frac{2}{\sqrt{2\pi}}\int_0^t \exp(-\tfrac{1}{2}x^2)\,\mathrm{d}x,$$

$$t = \frac{|\mathbf{d}|}{\sigma}. \tag{17}$$

The vector **d** points *away* from the origin. Insertion into (16) gives for the field gradient due to the complete atom;

$$\nabla E_{mn} = -\frac{3d_md_n - \delta_{mn}|\mathbf{d}|^2}{|\mathbf{d}|^5}\left\{Z - c - \sum_{i=1}^{4} a_i\left[\Gamma(t_i) - \frac{2}{3\sqrt{2\pi}}(t_i^3 + 3t_i)\exp(-\tfrac{1}{2}t_i^2)\right]\right\},$$

$$t_i = 2\pi|\mathbf{d}|\sqrt{(2/b_i)}. \tag{18}$$

This converges to zero for $|\mathbf{d}| = 0$ or ∞, since the trace of the tensor is zero and $\sum a_i + c = Z$. The overlap correction is therefore easily evaluated. For the site of Al in the low-quartz structure of $\mathrm{AlPO_4}$, it amounts to a few percent of the observed field gradient and is opposite in sign to the contribution of the deformation functions (Ngo Thong & Schwarzenbach, 1979). This shows that ∇E is due almost exclusively to the deformation density.

Temperature vibrations

Relaxation times in a NQR experiment are of the order of seconds so a thermally averaged field gradient is observed. This is, however, not the same as the tensor computed from a thermally averaged charge density. The Debye–Waller temperature factor describes the average electron density in terms of smeared atomic densities which are convolutions of stationary densities ρ_0 with a probability distribution p, $\rho_T = \rho_0 {*} p$ (Cochran, 1954), *i.e.* ρ_T is a superposition of spherical densities. Assuming that the nuclei and their electron clouds execute the same vibrations, a neutral spherical atom not overlapping with position **R** does not contribute to the electrostatic quantities $\boldsymbol{\varepsilon}$, regardless of the form of p. Subtraction of anisotropically vibrating free atom densities from the thermally smeared total density thus leads to an equivalent thermally smeared density if the proper overlap corrections are considered for neighboring atoms. Equation (5) shows this correction to be the double convolution $\boldsymbol{\varepsilon}_T = g{*}p{*}\rho_0 = p{*}\boldsymbol{\varepsilon}_0$. This cannot be evaluated analytically if p is a general three-dimensional Gaussian distribution. An approximate solution is, however, obtained by a series expansion in terms of the atomic displacements. This leads to rather lengthy formulae which need not be reproduced here. From the observed anisotropic temperature parameters in $AlPO_4$ (Ngo Thong & Schwarzenbach, 1979), the overlap correction is changed by about 10% which is only a few e.s.d.'s of the observed tensor elements and hence negligible. $\nabla\mathbf{E}$ due to the thermally smeared charges can thus be obtained from the thermally smeared deformation functions in the same way as for the stationary crystal. As mentioned above, however, this is not the correct solution. The average $\nabla\mathbf{E}$ at a nuclear position, *i.e.* $\nabla\mathbf{E}$ as seen by the nucleus, depends on the *joint* probability distribution of this nucleus and the surrounding charge density $p(\mathbf{R},\mathbf{r})$. Bragg X-ray intensities do not contain any information about this joint distribution since the correlations between the atomic displacements give rise only to thermal diffuse scattering. In other words, the correct $\nabla\mathbf{E}$ has to be computed from a non-periodic charge distribution. Two limiting cases corresponding to independent and riding motion (Busing & Levy, 1964) can, however, be treated.

For entirely *uncorrelated vibrations*, $p(\mathbf{R},\mathbf{r})$ is the convolution of the individual probability functions $p'(\mathbf{R})$ and $p''(\mathbf{r})$. The temperature parameters of the atom at position $\mathbf{R}$ are therefore added to those of the neighboring atoms and the Fourier coefficients are then computed with these larger temperature factors. The atom at $\mathbf{R}$ itself is then, of course, considered to be at rest. The corresponding correction to $\nabla\mathbf{E}$ can be evaluated by integration in real space. Especially for the all-important nearest neighbors, this model is certainly very unrealistic.

Complete correlation implies a riding motion of neighboring atoms and their relative movement is then described by the difference of their temperature factors and that of the atom at $\mathbf{R}$. If this difference motion is assumed for *all* atoms, the charge density retains translational symmetry. The atom at $\mathbf{R}$ and all those equivalent by translation will then have zero temperature factors. The rotational symmetry of the crystal will in general be reduced to the point symmetry of position $\mathbf{R}$. The full space-group symmetry may be retained by assigning difference temperature factors only to the atoms in a properly chosen asymmetric unit which should contain the nearest neighbors of the central atom at $\mathbf{R}$. This model, although clearly unrealistic for distant neighbors, is expected to be a better approximation to the exact solution and is also easily computed.

Analogously, we use the sum of the temperature factors for all atoms in the asymmetric unit and a stationary atom at $\mathbf{R}$, and then apply the full space-group symmetry to obtain an estimate of the thermal correction to $\nabla\mathbf{E}$ in the worst case of uncorrelated vibrations. Our calculations on $AlPO_4$ (Ngo Thong & Schwarzenbach, 1979) indicate that this is negligible and that the stationary electron density gives satisfactory results. It is clear that any influence of the atomic vibrations on $\nabla\mathbf{E}$ is due to optical phonons.

Conclusion

Electrostatic quantities, and especially the field gradients at the sites of the atomic nuclei can be evaluated by a simple Fourier summation (11) with the structure factors derived from the deformation functions alone. Acceptable results are obtained for a stationary structure. The series converges as fast as an electron density summation. $\nabla\mathbf{E}$ is thus given in terms of the deformation parameters. Its derivatives with respect to these parameters are likewise obtained by Fourier summations, the coefficients being the derivatives of the structure factors. The calculation of the derivatives with respect to the positional parameters requires also the differentiation of (11) with respect to the components of $\mathbf{R}$. A structure factor least-squares program for the refinement of deformation parameters (Hirshfeld, 1977*b*) computes all the necessary quantities, and the calculation of $\nabla\mathbf{E}$ or any other electrostatic quantity can easily be introduced. Moreover, $\nabla\mathbf{E}(\text{deformation}) = \nabla\mathbf{E}(\text{observed}) - \nabla\mathbf{E}(\text{overlap})$ can be added as a supplementary observation and the deformation and positional parameters refined with respect to the structure factors and $\nabla\mathbf{E}$ simultaneously. This should result in more reliable electron density maps. We compute $\nabla\mathbf{E}$ and its derivatives first in the crystal coordinate system according to (11), then transform to an orthogonal coordinate system and sum the respective terms in the matrix of the normal equations with user-supplied weights. A temperature correction for uncorrelated motion may be introduced. The procedure will be effective if the deformation functions are flexible enough to simulate the total quadrupole distortion of an atom and at the same time the electron distribution between the atoms. The actual electron density near the atom centers will not be obtained more accurately.

The use of dipole moments as supplementary observations in charge density refinements is also possible and does not require the calculation of Fourier series in the least-squares program. The difficulty of such a procedure lies in the fact that dipole moments of molecules in the crystalline environment cannot be measured. We would like to stress here that generally any introduction of supplementary observations has its inherent dangers and causes uncertainties of a different kind due to the additional approximations involved. The results should be considered as *model* rather than *experimental* charge densities. The electron distribution is not directly observed. It is constructed in such a way that it reproduces a set of physical measurements. This is of course true for any standard structure determination.

This project is supported by the Swiss National Science Foundation, grant no. 2.724-0.77.

References

Bertaut, E. F. (1952). *J. Phys. Radium*, **13**, 499–505.
Bertaut, E. F. (1978). *J. Phys. Chem. Solids*, **39**, 97–102.
Bhagavantam, S. (1966). *Crystal Symmetry and Physical Properties*, pp. 82–99. London & New York: Academic Press.
Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.
Cochran, W. (1954). *Acta Cryst.* **7**, 503–504.
Coppens, P. (1975). *International Review of Science, Physical Chemistry Series Two*, **11**, 21–56. London: Butterworths.
Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* A**34**, 909–921.
Harel, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* B**31**, 162–172.
Hirshfeld, F. L. (1971). *Acta Cryst.* B**27**, 769–781.
Hirshfeld, F. L. (1977*a*). *Isr. J. Chem.* **16**, 168–174.
Hirshfeld, F. L. (1977*b*). *Isr. J. Chem.* **16**, 226–229.
Hirshfeld, F. L. & Rzotkiewicz, S. (1974). *Mol. Phys.* **27**, 1319–1343.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Ngo Thong & Schwarzenbach, D. (1979). *Acta Cryst* A**35**, 658–664.
Stewart, R. F. (1972). *J. Chem. Phys.* **57**, 1664–1668.
Stewart, R. F. (1973). *J. Chem. Phys.* **58**, 1668–1676.
Stewart, R. F. (1977). *Chem. Phys. Lett.* **49**, 281–284.

Acta Cryst. (1979). A**35**, 658–664

The Use of Electric Field Gradient Calculations in Charge Density Refinements. II. Charge Density Refinement of the Low-Quartz Structure of Aluminum Phosphate.

By Ngo Thong and D. Schwarzenbach

Institut de Cristallographie, Université de Lausanne, Bâtiment des Sciences Physiques, 1015 *Lausanne, Switzerland*

(*Received* 19 *January* 1979; *accepted* 26 *February* 1979)

Abstract

The experimental determination of the electron distribution in quartz (SiO_2) is problematic since the structure is pronouncedly non-centrosymmetric. The structure of $AlPO_4$ is derived from the quartz structure by replacing half the Si atoms by Al and the other half by P. The physical properties of the two substances are similar. The electric field gradient tensor ∇E at the site of Al (site symmetry 2) has already been measured. This electrostatic information, which is not available for quartz itself, is used in the determination of the charge density. Deformation parameters describing multipolar deformation functions are refined by least-squares methods with respect to X-ray data and the elements of the field gradient tensor simultaneously. A κ refinement yielded the atomic charges $+1\cdot4$ for Al, $+1\cdot0$ for P and $-0\cdot6$ for O. The electron distribution obtained with a standard charge density refinement does not reproduce the correct ∇E. Inclusion of ∇E in the refinement leads to a different least-squares minimum. The minimum is ill-defined by the X-ray data alone, whereas ∇E stabilizes the phases of the superstructure reflections (l odd). ∇E is extremely sensitive to the deformation density distribution. The resulting deformation maps show the maxima and minima always in the same places, but the inclusion of ∇E changes the heights drastically and indicates the P—O bond to be more covalent than the Al—O bond. The trigonal arrangement of the lone-pair and bonding densities around the O atoms indicates sp^2 hybridization. This leads to bent covalent bonds, the angle Al—O—P being $142\cdot3°$. Double bonding appears to extend over nearly planar structural fragments defined by five atoms; metal—oxygen—metal—oxygen—metal.

Introduction

Several oxides with the composition $A^{III}B^{V}O_4$ form structures which can be derived from the isoelectronic SiO_2 modifications quartz, tridymite and cristoballite by replacing half the Si atoms by A and the other half by B. Buerger (1948) cites as examples BPO_4, $AlPO_4$, $FePO_4$, $GaPO_4$, $BAsO_4$ and $AlAsO_4$. The relationship between $AlPO_4$ and SiO_2 is particularly close. $AlPO_4$ forms all three structure types and shows the same polymorphic transformations at approximately the same temperatures as SiO_2. Large crystals of the low-quartz form of $AlPO_4$ (mineral name berlinite) were grown by hydrothermal synthesis (Stanley, 1954). Their physical properties are very similar to those of quartz (Schwarzenbach, 1966*a*); the density, hardness, refractive indices and optical rotatory power being all

0567-7394/79/040658-07$01.00