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Electron-Density Studies. II. Further Comments on the Electron Density in Diamond

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X-ray powder diffraction data for diamond have been re-analysed, in terms of an 'at rest' deformation-density model of monopole, octupole, hexadecapole and hexacontatettarapole terms of exponential form. The values of the parameters describing the third and fourth-order terms, and the refinement indices, are no different from those of an 'at rest' valence-density model. Unlike earlier analyses, however, the model is consistent with experimental measurements of the absolute scale, and with independently determined values of the Debye–Waller parameter. The predicted values of physical properties such as the gradient of the electric-field gradient at the carbon nucleus are shown to be strongly model-dependent. It is noted that the fit to the data, and in particular to the observed structure factor of the overlapping 333–511 reflection, is poor for all published charge-density analyses. Recent theoretical (crystal 'Hartree–Fock') calculations indicate, within the convolution and harmonic approximations, an experimental B value of $0\cdot172 \pm 0\cdot006$ Å^2 and a scale factor of $1\cdot004 \pm 0\cdot002$. These theoretical results are, however, in poor agreement with the experimental structure factors.

Introduction

In conventional structure analyses the mean of the 'goodness-of-fit' (GoF)* index for the high-order data is frequently of the order of unity, while that for the inner data is ten or more. This indicates that the harmonic approximation is adequate for most purposes, but that the atomic approximation is deficient. A variety of methods for improving the representation of the charge density have been proposed (Dawson, 1967*a*; Hirshfeld, 1971; Stewart, 1972*a*, 1973*a*; Sygusch, 1974). For structures of moderate complexity computational costs prohibit the detailed testing of all the various charge-density models. Such testing is feasible for the diamond structure as the high site symmetry reduces the number of unknown parameters.

An accurate, absolutely-scaled set of powdered-diamond diffraction data has been collected by Göttlicher & Wölfel (1959), and analysed successively by Dawson (1967*b*), McConnell & Sanger (1970), Kurki-Suonio & Ruuskanen (1971), Stewart (1973*b*,*c*) and by Harel, Hecht & Hirshfeld (1975). The scale factor for the data was treated as a variable parameter and differs significantly from unity in most cases, in conflict with experiment. The analyses also differ significantly in the determined B values which, in general, are substantially higher than the value of 0·149–0·150 Å^2 calculated (Stewart, 1973*b*) from phonon-dispersion curves measured by inelastic neutron scattering. The calculation is supported by a recent value of 0·14–0·17 Å^2, obtained by a neutron powder diffraction experiment (Price, Maslen & Moore, 1978). Most of the studies have not reported the GoF index, but reconstruction of the models described gives values of approximately 3, the lowest value (2·7) being that of Stewart (1973*c*).

Euwema & Greene (1975) have published theoretical X-ray structure factors for diamond calculated by a crystal Hartree–Fock formalism, which appear to differ significantly from the experimental values. Because of the increasing importance of charge-density analyses in the study of crystalline materials (Hirshfeld, 1971; Harel & Hirshfeld, 1975; Harel, Hecht & Hirshfeld, 1975; Berkovitch-Yellin & Leiserowitz, 1975; Price, Varghese & Maslen, 1978) it was considered necessary to resolve the conflict between the various experimental results, and to reassess the reliability of the theoretical structure factors.

Earlier charge-density models

The charge-density models can be classified as describing the thermally averaged density or as describing the 'at rest' density, where the pseudo-atom model and the convolution approximation allow the deconvolution of the thermal motion. They either parameterize the deformation density (where the molecular density is written as the sum of the Hartree–Fock atomic densities and atomic deformation terms) or the valence density (where the density is written as the sum of the Hartree–Fock 1*s* core densities and one-centre valence-density terms). The site symmetry of the diamond structure allows only single first-order

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* GoF = $[\Sigma\, \omega_i(\Delta F_i)^2/(n-m)]^{1/2}$ where ω_i is the weight of the ith structure factor, F_i, n is the number of observed structure factors and m is the number of parameters.

(monopole), third-order (octupole), fourth-order (hexadecapole), sixth-order (hexacontatettarapole), *etc.* terms, with the angular form of the Kubic Harmonics. The freedom of the various models is in the extent of the multipole expansion and the radial form of the density terms.

The analyses of Dawson (1967*a,b*) and of McConnell & Sanger (1970) described the thermally smeared deformation density in terms of an octupole and hexadecapole function with Gaussian radial functions:

$$f(r) = Pr^n \exp(-\gamma r^2). \qquad (1)$$

The radial order, n, was fixed at 2, and the Gaussian exponent, γ, was constrained to be the same for both functions. The population parameter, P, was independently varied. The model of Kurki-Suonio & Ruuskanen (1971) also described the thermally smeared deformation density. The values of the Fourier–Bessel transform of the radial-density functions were evaluated directly from the data. This necessitated the choice of the radius, R, of the deformed atom. These authors investigated the significance of deformation terms of orders 0, 3, 4, 6, 7 and 8. Unfortunately, the terms were strongly dependent on the choice of the size parameter, R. Harel, Hecht & Hirshfeld's (1975) model described the at-rest deformation density in terms of an octupole and hexadecapole function with Gaussian radial functions of orders 3 and 4 respectively. Stewart's (1973*c*) analysis was of the at-rest valence density. The pseudo-atom valence density was written as the sum of monopole, octupole and hexadecapole terms of exponential radial form:

$$f(r) = PN(\zeta,n)\, r^n \exp(-2\zeta r) \qquad (2)$$

where $N(\zeta,n)$ is a normalization coefficient. The population, P, of the monopole term was fixed at four electrons, and the radial orders, n, were fixed at 2, 3 and 4 respectively. There was no evidence that the exponents, ζ, were different for the different terms.

The results from the different models are similar in their description of broad charge-density features such as the electron count of the lobes of the octupole and hexadecapole functions, and in their fit to the data (GoF $\simeq$ 3). They differ in the values determined for the temperature-factor coefficient, B, and for the higher-order gradients of the electric field at the carbon nuclei. Deformation-density models had B values of 0·20–0·21 Å^2 while the valence-density-model values were in the range 0·17–0·18 Å^2.

Cusp constraint

Stewart (1973*b*) pointed out that the Hartree–Fock wavefunctions for the first-row atoms, tabulated by Clementi (1965), do not satisfy the nuclear cusp condition (Kato, 1957; Pack & Brown, 1966),

$$[(\partial\bar{\rho}/\partial r)/\bar{\rho}]_{r_j=0} = -2Z \qquad (3)$$

where $\bar{\rho}$ is the spherically averaged one-electron density function about the jth nucleus with an atomic number of Z. A cusp-constrained core-density function was defined as

$$\rho_{cc} = 2[0{\cdot}957605\,(\chi_{1s}^{\rm SCF})^2 + 0{\cdot}042395\,N\chi_{1s}^{\rm SCF}\chi_{2s}^{\rm STO}] \qquad (4)$$

where $\chi_{1s}^{\rm SCF}$ is the Clementi self-consistent-field atomic orbital for $C(^3P)$ and $\chi_{2s}^{\rm STO}$ is a Slater-type orbital of standard molecular exponent (Hehre, Stewart & Pople, 1969). The valence-density analysis with this core-density function (Stewart, 1973*c*) resulted in a B value of 0·140 ± 0·004 Å^2, quite close to the lattice-dynamic values.

The 'at rest valence density with exponential functions' model of Stewart (1973*c*) gives the best fit to the data, but the improvement in the GoF index is barely significant when compared with those of the other models. This is primarily because of the small size of the diamond cell. There is rather limited sampling of the low-Bragg-angle region of reciprocal space, where the valence scattering is large. Consequently the uncertainty in the GoF index is much bigger than similar GoF uncertainties for data of comparable quality from larger cells.

Model dependence of physical properties

Stewart (1972*b*) has used charge-density methods to predict physical properties such as electric-field gradients at the nuclei. He recommends assessment of the validity of such predictions as a means of differen-

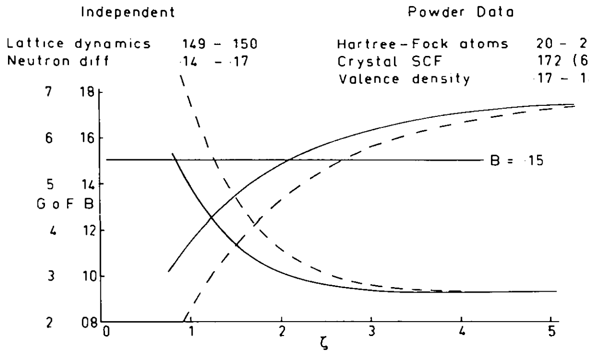

Fig. 1. The dependence of the determined B value (Å^2, curves of negative curvature) and of the fit to the data (GoF, curves of positive curvature) on the chosen value of the cusp constraint ζ [bohr^{-1}, see equation (4)]. Solid lines: with Clementi's (1965) SCF core wavefunction; dashed lines: with the Bagus–Gilbert (1967) SCF core wavefunction. Stewart (1973*c*), with ζ = 1·72 and using Clementi's χ_{1s}, obtained B = 0·140 (4).

tiating between charge-density models, but the nature of the dependence of the results on the model has not been fully explored.

Since (4) was an *ad hoc* choice of a cusp constraint and as the exponent of the $\chi_{2s}^{\rm STO}$ orbital had been arbitrarily fixed at the standard molecular value of 1·72 bohr^{-1} we have investigated the dependence of the result on the choice of exponent. Although the $C(^3P)$ SCF wavefunction of Bagus & Gilbert (1967) has a slightly lower energy than that of Clementi (1965), used by Stewart (1972*b*), the cusp discrepancy is somewhat larger. We repeated our analyses using the Bagus–Gilbert $\chi_{1s}^{\rm SCF}$. The results of these two investigations are illustrated in Fig. 1.

The B value is strongly dependent on the choice of the exponent and on the particular $\chi_{1s}^{\rm SCF}$ chosen. If the exponent is sufficiently large the cusp constraint has a negligible effect on the B value ($0{\cdot}178 \pm 0{\cdot}003$* Å^2) or on the GoF parameter (2·68). As the exponent decreases so does the B value, and the GoF parameter increases. As expected, the changes are larger for the analysis with the Bagus–Gilbert core-density function with its bigger cusp discrepancy. These results show that this form of a cusp constraint is not particularly useful, in that if it results in a lower B value it worsens the fit to the data.

The present models

Valence-density models of the same general type as those used by Stewart (1972*b*) have proved rather successful for the representation of valence density for atoms with atomic numbers less than ten. We have further explored these models. An analysis of accurate *Pendellösung* data for silicon (Price, Maslen & Mair, 1978) has shown that valence-density models do not extend readily to heavier atoms. We have therefore explored a deformation-density model with exponential functions, which does extend to heavier atoms, as an alternative. At the same time we have endeavoured to establish which physical properties will be reliably determined by such analyses.

Third and fourth-order deformation density functions were initially chosen with the same form as the valence-density functions of Stewart (1972*b*), *i.e.* exponential radial functions of orders 3 and 4 respectively [equation (2)]. The normalization of the angular functions, which are proportional to the third and fourth-order Kubic Harmonics, was chosen so that the electron content of the positive (or negative) parts was one electron. Thus the population parameters, O for the octupole and H for the hexadecapole, represent the number of electrons redistributed from the negative parts to the positive parts of the function. The octupole density function is then

$$\rho_3(\mathbf{r}) = O[ZO^{NO+3}/(NO+2)!]r^{NO}\exp(-ZOr)[2xyz/r^3] \tag{5}$$

and the hexadecapole density function is

$$\rho_4(\mathbf{r}) = H[ZH^{NH+3}/(NH+2)!]r^{NH}\exp(-ZHr) \times[160/27\sqrt{3\pi}][x^4+y^4+z^4-(3/5)r^4]/r^4 \tag{6}$$

with NO and NH initially set to 3 and 4 respectively, and with ZO and ZH initially constrained to be equal. These exponents should be comparable to twice Stewart's (1972*b*) exponent ζ.

Table 1 shows the results of the valence-density analysis, model I, and this deformation-density analysis, model II. The four parameters of the former are the B value, the valence-density function exponent, 2ζ, and the populations O and H of the octupole and hexadecapole functions. The latter model has the valence exponent, 2ζ, replaced by the octupole and hexadecapole exponent, ZO. The charge-density parameters, O, H and ZO or 2ζ, agree closely for the two models. The refinement indices,* R_w and GoF, are not significantly different. The B values, however, are quite different.

Inclusion of the overall scale factor, K, of the data as a variable parameter resulted in a value of $0{\cdot}998 \pm 0{\cdot}006$, in support of Göttlicher & Wölfel's (1959) claim that their measurements were absolutely scaled. The correlation coefficient between the scale factor and the B value was 0·89. (In the refinements for models I, II and III in Table 1 the scale factor was fixed at unity.)

Inclusion of ZH as a separate parameter resulted in a value close to ZO. In subsequent analyses with $NO = 3$ and $NH = 4$, ZH was constrained to equal ZO. As is discussed in more detail below, it is the positions of the maxima of the functions $r^2\rho_3(\mathbf{r})$ and $r^2\rho_4(\mathbf{r})$ which are well determined, and these occur at $r_3 = (NO+2)/ZO$ and $r_4 = (NH+2)/ZH$. Varying these radial orders NO and NH thus necessitates separate refinement of the exponents ZO and ZH.

In the analysis of the electron density in crystalline silicon (Price, Maslen & Mair, 1978) it was found necessary to include a monopole term in the deformation density. Simultaneous determination of a population for a similar monopole and the B value from the X-ray data alone was not possible for diamond, because the terms were correlated too strongly, the correlation coefficient calculated from the least-squares matrix being 0·99. The possible existence of a monopole term was therefore explored with the B value

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* All least-squares error estimates have been multiplied by the GoF.

* The refinement indices, R and R_w are defined

$$R = \Sigma\,|\Delta F_i|/\Sigma\,|F_{i,\rm obs}|$$
$$R_w = [(\Sigma\,\omega_i\Delta F_i^2/\Sigma\,\omega_i F_{i,\rm obs}^2)]^{1/2}$$

where ω_i is the weight of the ith observed structure factor, $F_{i,\rm obs}$.

fixed at 0·15 Å² (the lattice-dynamics value). Initially, an analysis was made with a term of the general form

$$\rho_0(\mathbf{r}) = (1/4\pi)\{PA'[N_0 + N_0(Z-12)r - N_1(Z-9)r^2] + PB'[-N_2r^2 + N_3r^3] + PC'[-N_2r^2 + N_4r^4]\}e^{-Zr} \quad (7)$$

where the $N_i = Z^{i+3}/(i+2)!$ are normalization constants. This function integrates to zero and leaves the cusp condition unaltered. The correlation coefficients between the three populations PA', PB' and PC' were greater than 0·9. The Fourier transforms of the corresponding density functions are not readily distinguishable from one another, within the range of the accessible data. It was clear that separate coefficients could not validly be extracted. PA' and PB' were arbitrarily set to zero. PC' and the corresponding exponent Z were included as variable parameters in the analysis.* The results of this analysis are also shown in Table 1 as model III. Some of the results of McConnell & Sanger's (1970) analysis are included in Table 1 under the heading 'M & S' for purposes of comparison.

Table 1. *Results of the charge-density refinements with models* I, II *and* III (*see text*)

The orders of the octupole and hexadecapole radial functions were fixed at 3 and 4 respectively. In model I all the valence exponents were constrained to be equal. In models II and III the octupole (ZO) and hexadecapole (ZH) exponents were constrained to be equal. In model III the B value was fixed at 0·15 Å². Comparable results of McConnell & Sanger's (1970) analysis are included under the heading 'M & S'. Units are Å² for B, e for PC, O and H, and bohr⁻¹ for ζ, Z, and ZO.

	Valence density	Deformation density		
	I	II	III	M & S
		$B\ O\ ZO\ H$	$PC\ Z\ O\ ZO\ H$	
	$B\ \zeta\ O\ H$	($PC = 0·0$)	($B = 0·15$)	$B_c\ O\ B^b\ H$
B	0·178 (5)^a	0·209 (4)	(0·15)	0·206 (3)
PC	–	–	0·092 (13)	–
Z	–	–	0·22 (3)	–
O	0·31 (5)	0·33 (4)	0·32 (4)	0·32 (12)
ZO	[3·12 (4)]^c	3·08 (17)	3·08 (18)	0·62 (4)^b
H	–0·24 (7)	–0·24 (7)	–0·24 (7)	–0·18 (7)
$r_{m,3}{}^d$	[0·55]	0·56 (3)	0·56 (3)	0·62 (3)
R_w	0·0084	0·0090	0·0090	0·0101
R	0·0089	0·0094	0·0094	0·0097
GoF	2·66	2·86	2·97	–

(*a*) Estimated standard deviations in the last figure quoted in parentheses. (*b*) McConnell & Sanger's (1970) Gaussian breadth parameter, B, is in units of bohr⁻². (*c*) This is 2ζ which should be comparable to ZO. (*d*) The position of the maximum of the function $r^2\rho_3(\mathbf{r})$ is expressed as a fraction of the bond length.

The parameters, O, ZO and H, of the third and fourth-order deformation functions, and the refinement indices, R_w and GoF, are very similar for the three models. McConnell & Sanger's (1970) R_w factor is a little larger, but the amplitudes of the octupole and hexadecapole functions are the same as those with the other models. The positions of the maxima of the various functions $r^2\rho_3(\mathbf{r})$ are the same within the errors. The B values, however, are quite different. Model III, with the monopole term, is the only published analysis consistent with the lattice-dynamic or neutron-diffraction B value. The monopole term is a sharp function (core deformation) redistributing charge from near (within 0·13 Å, or 0·09 of the bond length) the nucleus to regions further from the nucleus.

The electron contents of the lobes of the octupole and hexadecapole functions are simply related to the populations O and H. The tetrahedral octupole function has four positive lobes in the bonding directions and four negative lobes in the antibonding directions. Because of the normalization employed in (5) the electron content of each lobe is equal to $O/4$. The hexadecapole function has eight negative lobes in the bonding and antibonding directions of electron content equal to $-H/8$. The electron contents of the octupole lobes are then 0·078 ± 0·012, 0·082 ± 0·010 and 0·080 ± 0·010 (electrons) for models I, II and III, to be compared with Stewart's (1973*c*) value of 0·070 ± 0·011 with the cusp-constrained valence density model, and that of McConnell & Sanger (1970) of 0·081 ± 0·029 using Gaussian radial density functions. The electron contents of the negative hexadecapole lobes are 0·030 ± 0·008 (models I, II and III), 0·032 ± 0·009 (Stewart, 1973*c*) and 0·022 ± 0·009 (McConnell & Sanger, 1970).

Residuals

Although model III is consistent with the lattice-dynamic B value the fit to the data (GoF $\simeq$ 3) is far from satisfactory. This has been the case for all published analyses of this data. Table 2 shows the observed, F_o, and calculated, F_c, structure factors, the difference, $\Delta F = F_0 - F_c$, and the weighted squared difference, $(\Delta F/\sigma)^2$, the sum of which is minimized by the least-squares. The mean of these terms is $(\mathrm{GoF})^2(1 - m/n)$ and for a GoF of unity this would be 0·7 to 0·8 for the models II and III considered here.

The most poorly fitted data point is that of the overlapping 333–511 reflexions when F_c is some 7–8σ less than F_o. The 220, 400 and 440 reflexions are also badly fitted but the F_c values are greater than the F_o

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* Following the normalization ideas embodied in (5) and (6), that the population parameter of a deformation term should indicate the number of electrons transferred from the negative regions to the positive regions, we quote the monopole population, PC, where

$$PC = PC' \int_R^\infty (N_4r^4 - N_2r^2)e^{-Zr}r^2\,\mathrm{d}r = PC'[0·328533]$$

with $R = \sqrt{30}/Z$ satisfying $\rho_0(\mathbf{R}) = 0$.

values. If we assume that the F_o's and σ's are reliable experimental values then the charge-density model is clearly deficient. The simplest alternatives are to vary the radial form of the multipoles or to extend the level of the multipole expansion.

The radial orders, NO and NH, of the octupole and hexadecapole functions were varied, with the exponents ZO and ZH separately refined. The fit to the data was insensitive to these parameters, with a shallow minimum at $NO \simeq 4$ and $NH \simeq 10$, when the fit to the 400, 333–511 and 440 data points was slightly improved.

The multipole expansion was extended by the addition of a sixth-order or hexacontatettarapole term of the form:

$$\rho_6(\mathbf{r}) = (P6)\, N(Z6,N6)\, r^{N6} \exp(-Z6r)(\mathrm{KH}_6) \qquad (8)$$

where KH_6 is the sixth-order Kubic Harmonic. Initially, the parameter $N6$ was fixed at 6, and $P6$ and $Z6$ were refined. This resulted in an insignificant improvement and the $P6$ parameter was determined as 0·4 of its e.s.d. Some improvement was obtained by varying the radial order, $N6$, but only by allowing it to go to physically unreasonable values. The term appears to have the right symmetry to reduce the residuals, provided its Fourier transform could be made sufficiently sharp by an appropriate choice of $N6$ and $Z6$. However, even with extreme values for these coefficients, the broadening produced by convolution with the thermal-smearing function is such that improvement is limited to the 333–511 and 400 reflexions.

Table 2. *Residuals after the analyses with models* II *and* III

		F_c		ΔF		$(\Delta F/\sigma)^2$	
$h\,k\,l$	F_o	II	III	II	III	II	III
1 1 1	18·57	18·57	18·57	−0·01	−0·01	0·0	0·0
2 2 0	15·29	15·46	15·47	−0·17	−0·18	5·6	6·5
3 1 1	9·01	9·02	9·01	−0·01	−0·01	0·0	0·1
2 2 2	1·15	1·08	1·08	0·07	0·08	0·7	0·9
4 0 0	11·11	11·35	11·34	−0·24	−0·23	11·1	10·1
3 3 1	8·29	8·30	8·30	−0·01	−0·01	0·2	0·1
4 2 2	10·50	10·49	10·49	0·01	0·02	0·4	1·5
333–511	7·21	7·00	6·99	0·22	0·23	59·6	64·5
4 4 0	9·08	9·35	9·34	−0·27	−0·26	13·9	13·1
5 3 1	6·26	6·29	6·28	−0·03	−0·03	3·4	2·1
6 2 0	8·35	8·32	8·31	0·03	0·04	0·6	0·9
5 3 3	5·70	5·75	5·75	−0·05	−0·05	3·8	3·7
551–711	5·07	5·11	5·11	−0·04	−0·04	5·5	5·7
6 4 2	6·76	6·78	6·78	−0·02	−0·02	0·4	0·8
553–731	4·58	4·60	4·61	−0·02	−0·02	0·2	0·3
660–822	5·58	5·51	5·53	0·08	0·06	5·7	3·3
555–751	3·76	3·75	3·77	0·00	−0·01	0·0	0·1
753–911	3·44	3·40	3·42	0·04	0·02	3·2	0·8
$\chi^2 = \Sigma(\Delta F/\sigma)^2$						114·51	114·50
GoF						2·86	2·97
R_w						0·0090	0·0090
R						0·0094	0·0094

It would seem that the data are incompletely described by charge-density models with radial functions of single-exponential or Gaussian form. Models with two-term radial functions may resolve the discrepancies. Of course, the poor fit could be caused by unreliable F_o's and the associated experimental error estimates. There may be a significant extinction correction, as found in a diamond-powder neutron diffraction experiment (Price, Maslen & Moore, 1978). Such an extinction correction cannot be applied to this data set at present, as powders of three diameters, 2·5, 5 and 10 μm, were used.

However, it is worth noting that Bentley (1974) has found that the Hartree–Fock theoretical densities for the first-row diatomic hydrides project into a valence-density model with density functions of single-exponential form only to an accuracy of $R_w \simeq 0{\cdot}015$, where R_w is a residual which should be comparable to experimental R_w factors.

Physical properties

Stewart (1972*b*) has recommended the estimation of such physical properties as local electric-field gradients from the parameters determined by a charge-density analysis. There are dangers in such a procedure which are best appreciated by reviewing certain aspects of least-squares fitting.

Let $\{x_i,y_i,\sigma\}$ be a set of experimental data points and the associated e.s.d.'s, where there is a linear function given exactly by $y = f(p_1,\ldots p_n;\ x)$ where $\{p_k\}$ is a set of parameters, and let $g[y_i$ (calc.)] be an unbiased estimate given by the function $g[y]$, with an associated error calculated from estimates of the parameter errors, $\{\sigma_k\}$. If the exact form of the function f is not known some model function $y = f'(\{p_k\};\ x)$ may be an adequate fit over the range of data, but the estimates of the properties $g'[y_i$ (calc.)] and the e.s.d.'s will now be biased by the assumptions of the model.

This is the situation in electron-density analyses. The exact functional relation is not known and the models only seek to describe adequately those charge-density features determined from the range of data. Estimates of properties which depend upon the structure factors in a highly nonlinear manner will be biased by the model and the error estimates will be unreliable. Electric-field gradients at each nucleus depend strongly on the shape of the electron density in regions near the nucleus, but such features contribute only weakly to the low-angle structure factors.

We illustrate this point by investigating the model dependence of estimates of the gradient of the electric-field gradient at the carbon nucleus in diamond. Fig. 2 shows the effect of varying the radial order, NO, of the octupole between 1 and 9. The GoF is relatively

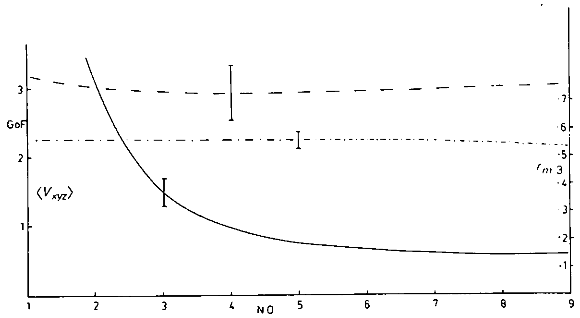


Fig. 2. The dependence of the GoF (dashed line), the estimate of the gradient of the electric-field gradient, $\langle V_{xyz} \rangle$ (units of 10^{32} J m^{-3} C^{-1}; solid line), and of $r_{m,3}$, the position of the maximum of the function $r^2\rho_3(\mathbf{r})$, (as a fraction of the C—C bond length; chain-dotted line), on the radial order, *NO*, of the octupole function. Stewart's (1973*c*) estimate of $\langle V_{xyz} \rangle$ shown with error bars. When $NO = 1$ the $\langle V_{xyz} \rangle$ integral diverges.

insensitive to the parameter, there being a shallow minimum at $NO \simeq 4$. The GoF is not significantly greater at $NO = 1$ or $NO = 9$, and hence the data are not sufficient to determine this parameter. The estimate of the gradient of the electric-field gradient $\langle V_{xyz} \rangle$, however, is strongly dependent upon the assumed value of *NO*, the integral diverging when $NO = 1$. Stewart's (1973*c*) estimate of $1{\cdot}5 \pm 0{\cdot}2 \times 10^{32}$ J m^{-3} C^{-1} is seen to be a consequence of his choice of 3 for this parameter. Also shown on Fig. 2 is the model estimate of the position of the maximum of the function $r^2\rho_3(\mathbf{r})$, which is the radial amplitude, per unit solid angle, of the octupole deformation function. The estimate is $0{\cdot}56 \pm 0{\cdot}03$ of the C—C bond length for $1 \leq NO \leq 6$ and is reasonably independent of the *NO* parameter.

Which properties are well determined?

The above results suggest that the position of the peak of the function $r^2\rho_3(\mathbf{r})$ is well determined, independently of details of the analysis such as the radial order, *NO*, or even whether $\rho_3(\mathbf{r})$ is a Gaussian or exponential function. One might hope to be able to determine the position, electron content, peak height and 'width' of these deformation functions. However, with only two adjustable parameters, *O* and *ZO*, this is impossible. Some idea of which properties will be well-determined can be obtained by approximating the fitting procedure. The fitting is in reciprocal space with an experimental weighting function. If the radial dependence of the experimental octupole was exactly described by an exponential function of some fixed order, $N - 2 \neq NO$, then we can visualize the least-squares adjustment of the shape of the function, *via* the model parameters *O* and *ZO*, to minimize χ^2. If the fitting was in real space rather than reciprocal space, then we can solve the problem exactly for the best parameters *O* and *ZO* for each *NO*, and investigate the expected *NO* dependence of such results as the position of the maximum, the electron content and the peak height. The difficulty is in converting the expression for χ^2 from a reciprocal-space sum to a real-space integral.

In reality, we minimize a residual, χ^2, given by

$$\chi^2 = \Sigma[\Delta F/\sigma(F)]^2 \tag{9}$$

where $\Delta F = F_o - F_c$ is the difference between the observed and calculated structure factors, $\sigma(F)$ is the experimental uncertainty in F_o, and the sum is over all the observed reflexions. The latter usually means a sum over all reflexions up to the $\sin\theta/\lambda$ cut-off. If there is no correlation between the octupole deformation function and the other parameters then the octupole contribution to F_o, F_c, $\sigma(F)$ and hence χ^2 is, in principle, separable. Writing

$$F_{\rm oct}(\mathbf{S}) = f_3(S)[\mathrm{KH}_3(\theta_0,\varphi_0)] \tag{10}$$

as the product of a radial term and the third-order Kubic Harmonic, results in

$$\chi^2_{\rm oct} = \sum_i \omega_i(\Delta f_{3,i})^2 \tag{11}$$

with

$$\omega_i = (\mathrm{KH}_{3,i}/\sigma_{{\rm oct},i})^2. \tag{12}$$

The radial scattering factor, $f_3(S)$, is the Fourier–Bessel transform of the radial part of the octupole density function, $R_3(\mathbf{r})$

$$f_3(S) = \int_0^\infty r^2R_3(r)j_3(Sr)\,\mathrm{d}r. \tag{13}$$

When the radial function, $R_3(r)$, is an exponential function as in (5) then $f_3(S)$ is proportional to the integral

$$f^S_{n,k}(S,Z) = \int_0^\infty r^n\exp(-Zr)j_k(Sr)\,\mathrm{d}r \tag{14}$$

with $k = 3$. This is given by Stewart, Davidson & Simpson (1965) as

$$f^S_{n,k}(S,Z) = \frac{2^{k+\frac{1}{2}}(n+k)!}{S^{n+1}(2k+1)!!\,\beta^{k+\frac{1}{2}}(1+\alpha^2)^{(n+\frac{1}{2})/2}} \times {}_2F_1\{n+\tfrac{1}{2}; -n+\tfrac{1}{2}; k+\tfrac{3}{2}; (1+\beta^2)^{-1}\} \tag{15}$$

where $\beta = \alpha + (1+\alpha^2)^{1/2}$ and $\alpha = Z/S$.

If the radial function $R_3(r)$ is of Gaussian form then $f_3(S)$ is proportional to

$$f^G_{n,k}(S,Z) = \int_0^\infty r^n\exp(-Zr^2)j_k(Sr)\,\mathrm{d}r \tag{16}$$

with $k = 3$. This integral is found in Watson (1952) as

$$f^G_{n,k}(S,Z) = \frac{\Gamma^1[(n+k+1)/2]S^k}{2Z^{(n+k+1)/2}(2k+1)!!}\exp(-S^2/4Z) \times {}_1F_1\{1+(k-n)/2; k+3/2; S^2/4Z\}. \tag{17}$$

The octupole contribution to χ^2 of (11) can then be rewritten as an integral

$$\chi^2_{\text{oct}} = \int_0^\infty \omega(S) \left\{ \int_0^\infty \Delta[r^2 R_3(r)] j_3(Sr) \mathrm{d}r \right\}^2 \mathrm{d}S \qquad (18)$$

where the weighting function $\omega(S)$ takes into account the crystal field [so that $\omega(S)$ is a sum of delta functions], the sin θ/λ cut-off [so that $\omega(S) = 0$ for $S > S_{\max}$] and the S^2 dependence of the volume element, in addition to the experimental ω_i's of (12). In principle this integral can be rewritten in real space as

$$\chi^2_{\text{oct}} = \int_0^\infty \omega(r) \{\Delta[r^2 R_3(r)]\}^2 \mathrm{d}r \qquad (19)$$

where the weighting function $\omega(r)$ will be a function of the experimental σ_i's, the sin θ/λ cut-off, the crystal field and unknown properties of the Fourier–Bessel transform of (13).

It is instructive to consider fitting a calculated octupole radial function, $R_{3,\text{calc}}(r)$, to an observed function, $R_{3,\text{obs}}(r)$, by the minimization of (19) when $\omega(r)$ is approximated by the simple form,

$$\omega(r) = r^p. \qquad (20)$$

Let us consider the observed and calculated density functions to be of exponential form, as in (5),

$$r^2 R_{3,\text{calc}}(r) = O[Z^{n+1}/n!] r^n e^{-Zr} \qquad (21)$$

and with $r^2 R_{3,\text{obs}}(r)$ given by the same expression with O replaced by O_0, Z replaced by ζ and n replaced by N. Here n is fixed at integer values not necessarily equal to N, and O and Z are parameters adjusted to minimize (19). The results are

$$\frac{Z}{\zeta} = \frac{n + (p+1)/2}{N + (p+1)/2} \qquad (22)$$

and

$$\frac{O}{O_0} = \frac{[n + (p+1)/2]^{n+p} [N + (p+1)/2]^{N+1}}{[(N+n)/2 + (p+1)/2]^{N+n+p+1}} \times \frac{2^n n! \, (N+n+p)!}{2^N N! \, (2n+p)!}. \qquad (23)$$

The peak height of the calculated function is

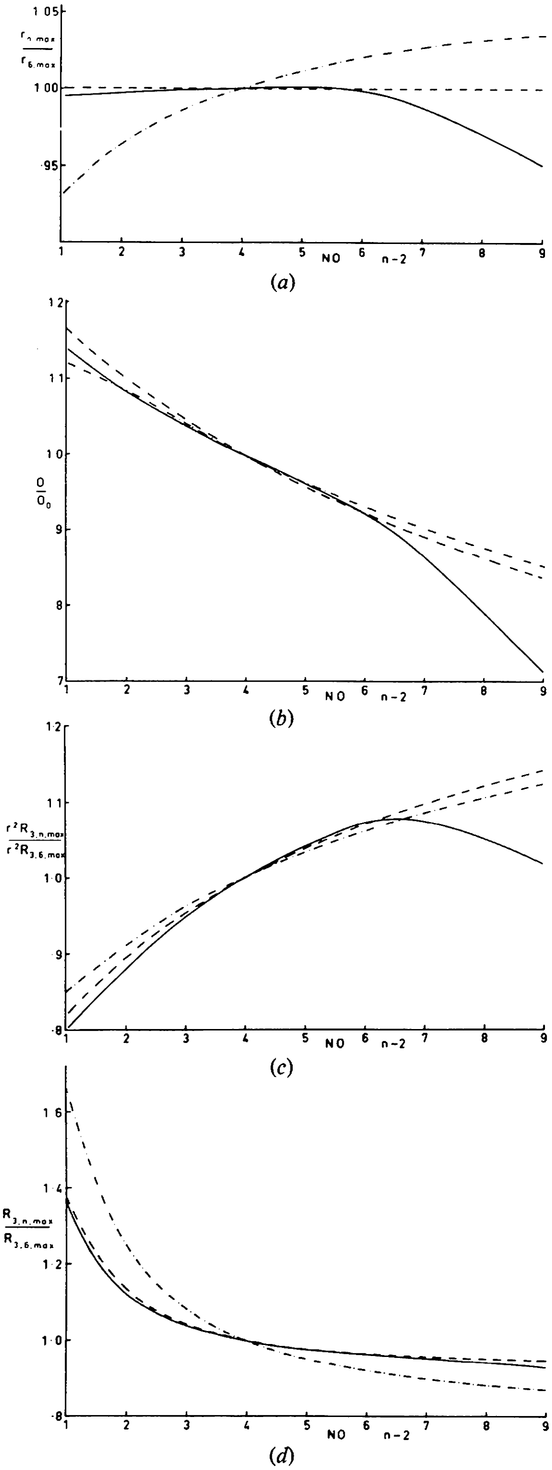
$$r^2 R_{3,\text{calc}}(r)]_{\max} = OZ \, n^n e^{-n}/n!. \qquad (24)$$

The position of the maximum of $r^2 R_3(r)$ is at

$$r_{n,\max} = n/Z. \qquad (25)$$

Thus, from (22), this is a well-determined quantity if $p = -1$.

Also of interest are the position and height of the maximum of the density function $R_3(r)$ itself. The position of this maximum is at $r = (n-2)/Z$. From



(a)

(b)

(c)

(d)

Fig. 3. The ratios of (a) the determined position, $r_{n,\max}$, of the maximum of $r^2 R_{3,n}$ to the 'true' value, $r_{6,\max}$; (b) the determined electron content, O, of the octupole function to the 'true' value O_0; (c) the calculated peak height, $r^2 R_{3,n}$ ($r = r_{n,\max}$) to the 'true' value $r^2 R_{3,6}$ ($r = r_{6,\max}$); (d) the calculated peak height $R_{3,n}$(max) to the 'true' value $R_{3,6}$(max.). Solid line: experimental results, dashed line: expected results with $p = -1$, chain-dotted line: with $p = 0$.

(22) this would be well-determined if $p = -5$. The calculated peak height is

$$R_{3,\mathrm{calc}}(r)]_{\max} = OZ^3(n-2)^{n-2}e^{-(n-2)}/n!. \qquad (26)$$

Fig. 3(*a*), (*b*), (*c*) and (*d*) depict these [equations (25), (23), (24), (26) respectively] results graphically for $p = 0$ and $p = -1$, with $N = 6$ ($NO = 4$) and $\zeta = 3{\cdot}66$ bohr^{-1} (the experimental result for ZO when $NO = 4$ which gave the lowest experimental GoF). Also shown are the experimental results for (*a*) the ratio of the positions of the maxima, $r_{n,\max}/r_{4,\max}$, (*b*) the ratio of the electron contents or areas O_n/O_4, (*c*) the ratio of the peak heights of r^2R; $r^2R_{3,n}$ $(r = n/Z)/r^2R_{3,6}$ $(r = 6/\zeta)$ and (*d*) the ratio of the peak heights of R;

$$R_{3,n}[r = (n-2)/Z]/R_{3,6}\,(r = 4/\zeta).$$

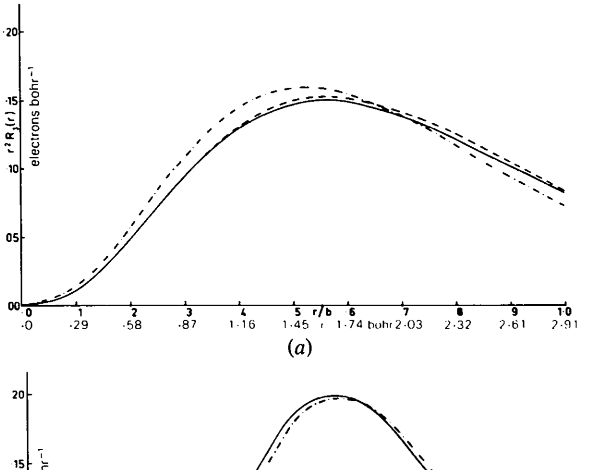


Fig. 4. The functions $r^2R_{3,n}(r)$ for (*a*) $n = 3$, $NO = 1$; (*b*) $n = 8$, $NO = 6$ and (*c*) $n = 11$, $NO = 9$. r is expressed both as a fraction of the bond length (r/b) and in bohr units (r). The area under each curve is the electron content, O. Solid line: experimental results, dashed line: expected results with $p = -1$, chain-dotted line: with $p = 0$. By constraint, the three curves are coincident for $NO = 4$. [In Fig. 4(*b*) ($NO = 6$) the experimental and $p = -1$ curves are coincident.]

For $1 \le NO \le 6$ the observed positions of the maxima closely follow the predicted values with $p = -1$. The $p = 0$ predictions are a poor description of the observed results. Similarly, for $1 \le NO \le 6$, the observed peak heights [Fig. 3(*c*) and (*d*)] closely follow the predicted values with $p = -1$. The qualitative result is the same with $p = 0$ but the quantitative agreement with the experimental results is not as good. The results for the electron contents (Fig. 3*b*) are the reverse of these, with the $p = 0$ line lying a little closer to the experimental results than that with $p = -1$.

Graphs of the functions $r^2R_3(r)$ for $NO = 1$, 6 and 9 [Fig. 4(*a*), (*b*) and (*c*) respectively] show that for $1 \le NO \le 6$ the $p = -1$ functions closely follow the experimentally fitted functions (the agreement at $NO = 4$ is constrained to be exact) except that the $p = -1$ peak heights are slightly larger. The $p = 0$ functions, however, are quite different from the experimentally fitted functions, even though the total areas (electron contents) may be very similar. Thus, for $1 \le NO \le 6$ the least-squares fitting of structure factors with experimental weights [the minimization of (18)] appears to be well-described by the approximate procedure of minimizing (19) with weighting function $\omega(r) = 1/r$.

The minimization of (19) is equivalent to the minimization of

$$\chi^2_{\mathrm{oct}} = \int_0^\infty \omega'(r)\,[\Delta(R_3(r)]^2\,r^2\,\mathrm{d}r \qquad (19')$$

with $\omega'(r) = r^2\omega(r)$. If $\omega'(r) = r^{p'}$ then $p' = p + 2$. Thus the minimization of (18) appears similar to the minimization of (19′) with $p' = 1$ but not with $p' = 2$. The results with $p' = 0$ were considerably worse. Fig. 5 shows the predicted fitted curves with $p = -1$ for $NO = 1$ to 9.

For $7 \le NO \le 9$ the actual parameters deviated significantly from the expected results with $p = -1$ or $p = 0$. The amplitudes of the actual curves were considerably below the expected results and the positions of the peak maxima shifted towards the centre of the atom [Figs. 3(*a*), (*b*), (*c*) and 4(*c*)]. These radial functions become increasingly sharp as the NO parameter increases and their Fourier transforms [equation (13)] extend further into reciprocal space. The different behaviour for $7 \le NO \le 9$ may thus be the effect of the sin θ/λ cut-off.

In summary, it appears that, at least for $1 \le NO \le 6$, (18) can be approximated by (19) with $\omega(r)$ given by (20) with $p = -1$. Fig. 5 shows the results for the fitted functions if the 'true' function had $NO = 4$ and

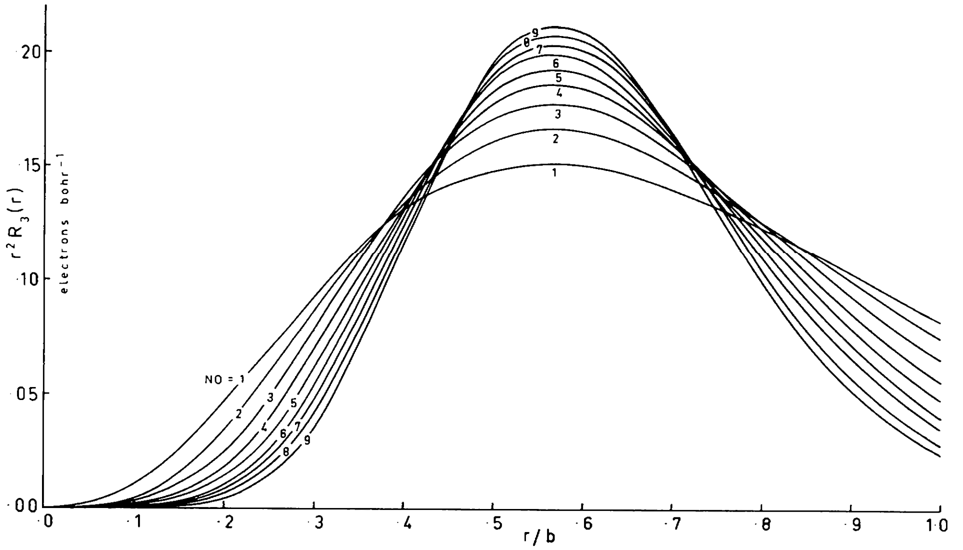


Fig. 5. The least-squares octupole functions $r^2R_{3,n}(r)$ with $p = -1$ assumed. The 'true' function is $r^2R_{3,6}(r)$ ($NO = 4$). Results for $NO = 1$ ($n = 3$) to 9 ($n = 11$) shown. r/b is r as a fraction of the C—C bond length.

$ZO = 3{\cdot}66$ bohr^{-1}. If we cannot determine this width parameter, NO, from the least-squares, then we can expect the position of the maximum of the constrained function to be well-determined, but the peak height (per unit solid angle) and electron content will vary, in this analysis by up to 20%. Fig. 3(*d*) indicates that the predicted peak height of $R_3(r)$ can be expected to be overestimated by some 40% if an NO value of 1 is chosen when the 'true' value is 4. If NO is chosen too large, on the other hand, the peak heights are underestimated by only a few per cent. The position of the maxima of $R_3(r)$ is overestimated by 50% when $NO = 1$ and underestimated by 20% when $NO = 8$.

The determination of gross atomic charges has been a prime goal of charge-density analyses. The case of diamond illustrates the effect of cell size on the precision of estimates of gross atomic charge. The carbon atom in diamond has exactly six electrons but in a trial refinement we treated the valence population as a variable parameter. The large e.s.d. in the result, $3{\cdot}66 \pm 0{\cdot}22$ e, illustrates the problem of determining gross charges for structures with small cell dimensions. This was encountered in charge-density analyses on a number of oxalate structures by Allen-Williams, Delaney, Furina, Maslen, O'Connor, Varghese & Yung (1975). It contrasts with the well defined populations obtained for structures with larger dimensions (Price, Varghese & Maslen, 1978).

Comparison with crystal 'Hartree–Fock' results

Euwema & Greene (1975) have recently published X-ray structure factors for diamond calculated by their crystal Hartree–Fock formalism. Within the harmonic and convolution approximations, the effect of thermal motion should be to reduce the structure factors by the temperature factor, $\exp[-B(\sin\theta/\lambda)^2]$. Fig. 6 is a plot of the natural logarithm of the ratio of the experimental to the theoretical structure factors against the value of $(\sin\theta/\lambda)^2$ for the structure factors calculated by Euwema & Greene (1975). Within the above approximations these points should lie on a line with a gradient equal to (minus) the B value and an intercept equal to the logarithm of the experimental scale factor, K. The least-squares line is shown. The parameter

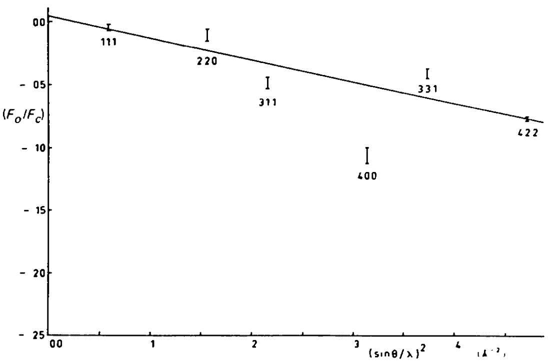


Fig. 6. A determination of the diamond B value and scale factor from Göttlicher & Wölfel's (1959) X-ray powder data with it assumed that the 'at-rest' electron density is that of Euwema & Greene's (1975) crystal SCF calculation. The ordinate is the natural logarithm of the ratio of the experimental to the theoretical structure factors. The abscissa is $(\sin\theta/\lambda)^2$. Within the harmonic and convolution approximations the B value is (minus) the slope of the line and the intercept is the logarithm of the experimental scale factor. The least-squares line [$B = 0{\cdot}172$ (6) scale $= 1{\cdot}004$ (2_2) GoF $= 5{\cdot}1$] is shown. [The 222 result, $\ln(F_o/F_c) = 0{\cdot}51$ (7), is well above the graph, but has a relatively large error bar.]

estimates are $B = 0{\cdot}172 \pm 0{\cdot}006$,* $K = 1{\cdot}004 \pm 0{\cdot}002$.* The line is a poor fit to the data, and the GoF parameter is 5·1.

Thus although the crystal Hartree–Fock results support the neutron-diffraction B value, and Göttlicher & Wölfel's (1959) claim that their data was absolutely scaled, they are not in good agreement with the lattice-dynamic B value and they are a poor fit to the experimental structure factors. Both of these may be due to the limited nature of the theoretical basis set. In calculations on isolated molecules it has been shown (Coppens, 1975; de With & Feil, 1975) that d-type polarization functions are necessary to adequately allow for the build up of charge in the bonding region.

Conclusion

The evidence that the diamond B value is less than the standard X-ray refinement value of 0·20–0·21 Å^2 is increasing, with the lattice-dynamic value of 0·149–0·150 Å^2, the neutron diffraction value of 0·14–0·17 Å^2 and the value of $0{\cdot}172 \pm 0{\cdot}006$ inferred from the recent theoretical calculations of Euwema & Greene (1975). If the B value is less than about 0·18 Å^2 then the valence density is negative near the nucleus. This can be seen in valence-density maps (Yang, 1975). It is unlikely to be due to the failure of the SCF core-density functions to satisfy the nuclear cusp condition. The spherical part of such core and valence deformation has been parameterized by the monopole term defined above.

The various charge-density models which have been used to describe the diamond powder data of Göttlicher & Wölfel (1959) are seen to be similar in their fit to the data and in their description of such broad charge-density features as the electron content of the lobes of the octupole and hexadecapole functions and of the position of the maximum of these functions. They differ in their estimates of the B value and in their estimates of the higher-order gradients of the electric field at the carbon nucleus. This is a result of strong correlation between the sharp monopole terms of the charge-density models and the B value, and between the radial order and exponent of the octupole or hexadecapole functions. A realistic charge-density analysis requires an independent, precise B value and the acceptance that the low-angle structure factors are relatively insensitive to the higher-order gradients of the electric field.

It was shown that if, as in this analysis, charge-density parameters such as NO cannot be determined reliably from the data, then even gross features such as electron contents and peak heights will be biased by the model. On the other hand, the positions of the maxima of the radial functions such as $r^2R_3(r)$ appear to be well-determined.

All of the published charge-density models have been poor fits to the experimental structure factors. An analysis resulting in a GoF of unity will have R factors near 0·3%, rather than near 1%, as at present. Our studies indicate that this will necessitate two-term radial functions for the octupole and hexadecapole functions.

Euwema & Greene's (1975) theoretical structure factors are in poor agreement with the experimental values. This is probably because of the absence of d-type polarization functions in their basis set, but may be partly because of the inadequacy of the convolution approximation (Price, Varghese & Maslen, 1978).

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* Unlike earlier least-squares parameter error estimates, these uncertainties have not been multiplied by the GoF.

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Electron-Density Studies.
III. A Re-evaluation of the Electron Distribution in Crystalline Silicon

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Highly accurate absolute measurements of the X-ray structure factors of silicon [Aldred & Hart, *Proc. R. Soc. London, Ser. A*, (1973), **332**, 223–238] have been used to analyse a number of models for the electron distribution. Initially, the valence-electron distribution (with the neon core assumed to be unmodified from that of the isolated silicon atoms) was built up with a radial basis of the form $r^n \exp(-\zeta r)$ and non-sphericity was allowed for by inclusion of octupole and hexadecapole terms. Improved representation was achieved with related models in which deformations from the total isolated-atom electron density were refined instead. The exact shape of the deformation electron density in the region of the bond was sensitively dependent on the monopole deformation term. The anomalous-dispersion contributions ($\Delta f'$) to the scattering factors were refined and found to be in agreement with recent interferometric measurements, but not with recent calculations. The octupole density term is slightly sharper at 293·2 than at 92·2 K, and the structure factor for the 222 reflection is predicted to be larger at the higher temperature. These effects may be due to a failure of the convolution approximation or to uncertainties in the anharmonic corrections to the structure-factor data.

Introduction

The one-electron density of a molecular system is a fundamental observable (Hohenberg & Kohn, 1964) which, in principle, can be measured by coherent X-ray scattering. The qualitative description of a molecule as a sum of deformed atoms (or 'pseudo-atoms') has long been popular in chemistry, and recent work by Bader and co-workers (see, for example, Srebrenik & Bader, 1975) indicates that this viewpoint may have a more rigorous basis in that the properties of a system may be expressible in terms of those of its component density fragments.

A variety of pseudo-atom definitions have been proposed for the analysis of X-ray diffraction data (Dawson, 1967*a*; Kurki-Suonio & Ruuskanen, 1971; Hirshfeld, 1971; Stewart, 1972, 1973*a*; Sygusch, 1974). The essential differences were discussed in a previous paper [Price & Maslen (1978), hereinafter referred to as paper II]. It was shown there that in the analysis of powdered-diamond diffraction data most of the models resulted in similar fits to the data (R and R_w factors of