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The Electron Distribution in Diamond: a Comparison Between Experiment and Theory

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Abstract

Deformation and valence electron densities in diamond are derived *via* Fourier summation and pseudoatom multipole refinement of the recently reported structure factors derived from X-ray *Pendellösung* beats [Takama, Tsuchiya, Kobayashi & Sato (1990). *Acta Cryst.* A**46**, 514-517]. The results are significantly different from those reported previously and are generally in excellent agreement with theoretical calculations.

Introduction

Because of its simple structure, high symmetry and low thermal motion, diamond occupies a unique position in the history of electron-density studies. The electron distribution in diamond was first examined by X-ray diffraction by Brill, Grimm, Hermann & Peters (1939) in an attempt to compare the covalent bonding in diamond with the ionic bonding in NaCl. The data set collected by those authors was subsequently analysed by Brill (1950, 1959, 1960) and Carpenter (1960). A more accurate, absolutely scaled, data set was later obtained from a powder sample by Göttlicher & Wölfel (1959; referred to as GW), and it is this data set which has since been analysed by many workers (Weiss, 1964, 1966; Dawson, 1967, 1975; Dawson & Sanger, 1967; Kurki-Suonio & Ruuskanen, 1971; McConnell & Sanger, 1970; Stewart, 1973*a*, *c*; Harel, Hecht & Hirshfeld, 1975; Price & Maslen, 1978) usually supplemented by the value of the 'forbidden' 222 reflection measured by Renninger (1937, 1955) or Weiss & Middleton (1965; see Dawson, 1967).

In this work we take advantage of the recent measurement of nine low-order structure factors using the *Pendellösung* beat method (Takama, Tsuchiya, Kobayashi & Sato, 1990; referred to as TTKS). These data are significantly different from those reported by GW, and a preliminary electron-density analysis performed by TTKS suggests that the resulting electron distribution is also somewhat different from those obtained previously. The new data, in conjunction with an independently measured value for the 222 reflection, deserve a careful critical analysis in the manner we have previously performed on silicon (Spackman, 1986) and germanium (Brown & Spackman, 1990). In this way we hope to ascertain the degree of current accord (or otherwise) between experiment and theory for this important archetype of covalent bonding and, with reference to the similar studies on silicon and germanium, explore the nature of any trends which may be revealed as we descend this column of the Periodic Table.

We analyse the recent *Pendellösung* data of TTKS combined with a measurement of the 222 reflection, pursuing both Fourier methods and a rigid pseudoatom model (Stewart, 1973*b*, 1976). Where possible, standard deviations (e.s.d.'s) in the results are determined from the estimated errors in the experimental observations and the curvature of the least-squares-error surface at the minimum. The structure of the present paper parallels the earlier study on silicon. In the following section we discuss details of the data set chosen for the study, then describe

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the various analyses of the data. This is followed by presentation of Fourier maps and maps resulting from the summation of pseudoatoms in the crystal and a comparison of these present results with other experimental results and with theory.

The data set

The nine *Pendellösung* beat measurements of TTKS have been described in some detail by those authors. We note here that the reported structure factors comprise an average of several measurements obtained at many different wavelengths (typically between 0·3 and 1·0 Å) and for different irradiated regions of a wafer-like crystal. TTKS note that wavelength dependence is not obvious; an important consequence of this is that no corrections for anomalous dispersion (which is less than 0·006 e per atom) need be made, nor indeed can they be made to the structure factors as published. TTKS have compared their measurements with the GW powder data and observe that, with the exception of the lowest-order reflection, 111, their data are systematically higher than those of GW. This of course has important implications for the derived isotropic thermal motion parameter, *B*, as discussed in detail by TTKS. In addition, the TTKS measurement of the 311 reflection compares extremely well with an earlier *Pendellösung* measurement by Lang & Mai (1979).

The important 222 reflection has been measured several times. Published values are 1·1 to 1·2 (Renninger, 1955), 1·15 (8) (Weiss & Middleton, 1965) and 0·95 (5) (Rosenberg, Kolosovsky, Kleshchinsky, Feldman, Kiselev & Shokhirev, 1984; Rosenberg, Kleshchinskii, Shokhirev, Kolosovskii, Sizykh & Rotner, 1987). These are all in good agreement with one another if the experimental errors are taken into account. For the present analysis we use the value from Weiss & Middleton as it is the median of the three, and also because it is the most commonly employed in analyses of the GW data. It turns out not to be a critical choice; as we report below, an analysis of just the nine TTKS data yields a result for $\rho(\mathbf{r})$ virtually indistinguishable from that obtained with inclusion of the 222 reflection. The combined data set of ten reflections comprises a complete sphere of data out to $(\sin\theta)/\lambda = 0{\cdot}8\ \text{Å}^{-1}$.

The lattice parameter we use for the structure-factor calculations, $a_0 = 3{\cdot}56703\ (10)$ Å is the mean of a large number of independent determinations, each corrected to 298 K (Parrish, 1960).

Analyses of the data

The analysis of the data is similar to that described previously for silicon (Spackman, 1986). We use a rigid pseudoatom model to obtain an estimate of the isotropic thermal parameter, *B*, and a deconvolution of the electron distribution from its thermal motion. Our nomenclature is that of Stewart (1973*b*, 1976). For the C atom in space group *Fd*3*m* the allowed multipoles up to fourth order are monopole, octopole and hexadecapole. In Stewart's notation the allowed multipoles are o_4, h_1 and h_9, each with a variable population, $O4$, $H1$ and $H9$, with the constraint $H1 = H9$. We consider only isotropic thermal motion; as discussed by Stewart (1973*a*, *c*), this is firmly justified as the Debye temperature of diamond is greater than 2200 K and 86% of the lattice-dynamic value for *B* is due to zero-point motion. We do not allow for the possibility that the thermal motion of the valence electrons may differ from that of the core, although this has been suggested elsewhere (Rosenberg *et al.*, 1987; Reid & Pirie, 1980). The present X-ray data set would need to be far more extensive before we could entertain that possibility.

The remaining flexibility in our pseudoatom model is the nature of the radial functions. As for silicon, we use the density-localized *K* and *L* shells obtained by Stewart (1980) from the Hartree–Fock atomic wavefunction of Clementi (1965) and allow for spherical deformation of the valence electron density by inclusion of a κ parameter which accounts for expansion or contraction of the valence electron density (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). The use of a density-localized *L* shell facilitates comparison of our model results with theory as the density-localized shell is essentially nodeless and similar to the radial functions obtained in pseudopotential calculations, with which we compare our results below. Jacobi fits to the density-localized shell scattering factors have been reported by van der Wal & Stewart (1984).

We assume the experimental data are on an absolute scale and hence no variable monopole populations or scale factors were included in the least-squares refinements. Octopole and hexadecapole radial functions are single exponential, $r^{n_l}\exp(-\alpha_l r)$ with $n_3 = 3$ (octopole) and $n_4 = 4$ (hexadecapole). Other choices of n_l yield virtually identical results to those we report, provided α_l is adjusted accordingly (*i.e.* refined in the least-squares process). Our choices for n_3 and n_4 are identical to those of Stewart (1973*c*) and as described in that work can be related to the products of appropriate Slater-type orbitals. As for silicon, α_3 and α_4 can be varied separately but do not differ significantly. It was decided to constrain $\alpha_3 = \alpha_4 = \alpha$. There is of course a practical reason for introducing constraints such as this (apart from the fact that it is the usual practice). Our data set comprises only ten experimental observations and it is most desirable to minimize the number of degrees of freedom in the fit.

In an attempt to reduce the number of variables in our model to an irreducible minimum, the model structure factors, F_c, were obtained using several

Table 1. *Refined variables and figures of merit for various electron-density models*

Model	B	$B, O, \alpha = \alpha_{\rm at}$	$B, O, \alpha = \alpha_{\rm sm}$	B, O, α	B, O, κ, α	B, O, H, α	B, O, H, κ, α
B (Å^2)	0·143 (19)	0·140 (8)	0·141 (9)	0·140 (8)	0·140 (9)	0·140 (9)	0·140 (10)
$O4$	-	−0·307 (42)	−0·273 (44)	−0·337 (119)	−0·338 (171)	−0·336 (144)	−0·337 (191)
$H9$	-	-	-	-	-	−0·002 (66)	−0·003 (75)
κ	1·0*	1·0*	1·0*	1·0*	0·999 (16)	1·0*	0·999 (18)
α (bohr^{-1})	-	3·18*	3·44*	2·93 (24)	2·92 (34)	2·93 (27)	2·92 (37)
ε	940·80	144·87	190·52	127·00	126·98	126·99	126·95
GOF	10·22	4·26	4·88	4·26	4·60	4·60	5·04
$R(F)$ (%)	3·62	1·00	1·24	0·85	0·85	0·85	0·85
$wR(F)$ (%)	2·81	1·01	1·16	0·95	0·95	0·95	0·95
$R(F^2)$ (%)	5·85	1·86	2·55	1·23	1·22	1·23	1·21
$wR(F^2)$ (%)	5·16	2·02	2·32	1·89	1·89	1·89	1·89
Correlation (α, $O4$)	-	-	-	0·918	0·953	0·912	0·940

* Indicates a value held fixed in the refinement.

models. We label these by the variables included in the refinement: (B, $O4$, $H1 = H9$, κ, α) is our most flexible multipole model and (B, $O4$, α) the least flexible, with $H1 = H9 = 0$ and $\kappa = 1{\cdot}0$. Optimum values of variables were obtained by minimization of

$$\varepsilon = \sum w(|F_o|^2 - |F_c|^2)^2,$$

with $w = \sigma^{-2}(|F_o|^2)$, $|F_o|$ being the observed structure-factor amplitude. Details of the least-squares procedure have been outlined previously (Spackman, 1986).

The refined variables and figures of merit for the various electron-density models are listed in Table 1. Refinement of a separate scale factor in each instance yielded a value insignificantly different from 1·0; the data indeed appear to be on an absolute scale. The models reported in Table 1 range from the simple spherical-atom model (B) to the most complicated model where five variables are optimized with respect to the ten observations (B, O, H, κ, α), a less than desirable situation. Several important conclusions emerge from the results in Table 1:

(i) The isotropic thermal parameter, B, is extremely robust, with no significant change between models. The result we obtain, 0·140 (9) Å^2, agrees well with that of 0·142 (9) Å^2 deduced by TTKS. As observed by those authors this value is in good agreement with that calculated by numerical integration of phonon dispersion curves by Stewart (1973*a*), 0·149–0·150 Å^2, and the neutron-diffraction value of 0·14–0·17 Å^2 from Price, Maslen & Moore (1978). It also agrees well with the model lattice-dynamical values of 0·144 to 0·145 Å^2 obtained by Reid & Pirie (1980). The present value is quite different from the estimates of 0·17–0·22 Å^2 obtained from analyses of the GW data.

(ii) The optimum radial exponent of the higher multipole functions, $\alpha = 2{\cdot}93\,(24)$ bohr^{-1}, is marginally less than the 'atomic' value, $\alpha_{\rm at} = 3{\cdot}18$ bohr^{-1} (Clementi & Raimondi, 1963) and significantly less than the 'standard molecular' value, $\alpha_{\rm sm} = 3{\cdot}44$ bohr^{-1} (Hehre, Stewart & Pople, 1969). It is also marginally less than the values obtained by Stewart (1973*c*) [3·12 to 3·18 bohr^{-1} for various models] and Price & Maslen (1978) [3·08 to 3·12 bohr^{-1}] in similar analyses of the GW data.

(iii) The contraction/expansion factor for the valence monopole function, κ, is not significantly different from 1·0. This is in contrast to the result we obtained for silicon (Spackman, 1986) where a significant expansion of the valence shell is detectable. It is, however, in accord with the correlation observed by Coppens *et al.* (1979) between refined κ values and corresponding point charges for a range of substances. In that work a linear relationship between κ and q (net charge) is demonstrated for both C and N atoms and in both cases a net charge of zero corresponds to a κ value very close to 1·0. Further support for a value of κ close to 1·0 in diamond comes from recent model studies of the κ-refinement procedure by Brown & Spackman (1991), using Hartree–Fock-level diatomic wavefunctions. In that work $\kappa(q)$ values of 1·006 (+0·112) and 0·994 (−0·036) were obtained for C in CO and CH respectively.

(iv) The octopole population, $O4$, is significant and well defined, with a range of −0·27 (4) to −0·34 (12) depending on the model. These results are compatible with results reported by Price & Maslen (1978) of 0·31 (5) to 0·33 (4) and Stewart (1973*c*) of 0·28 (4) to 0·36 (6).*

(v) The population of the hexadecapole function is insignificant. This is in disagreement with the analyses of the GW data, where the hexadecapole term leads to significant improvement over a model containing monopole and octopole terms (Stewart, 1973*c*; Price & Maslen, 1978). As described by Stewart (1973*c*) and Dawson (1967), the hexadecapole func-

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* The normalization in all cases is such that the absolute value of the octopole function integrates to 2·0 electrons, leading to a ready physical interpretation of the population parameter $O4$ (Hansen & Coppens, 1978). The sign difference between the present results and the others cited reflects a different choice of coordinate system. Our choice has Cartesian axes parallel to the unit-cell axes and for an atom at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ a negative octopole population reflects the build-up of electron density between nearest neighbours.

Table 2. *Experimental data* [$|F_o|$ *with* $\sigma(|F_o|)$ *in parentheses*] *and residuals* [$\Delta|F| = |F_o| - |F_c|$] *after pseudoatom refinement using the* (B, O, α) *model*

h	k	l	$(\sin\theta)/\lambda$ (Å^{-1})	$\lvert F_o\rvert$	$\Delta\lvert F\rvert$	Δ/σ
1	1	1	0·243	18·37 (6)	−0·006	−0·105
2	2	0	0·396	15·36 (4)	−0·004	−0·092
3	1	1	0·465	9·32 (2)	0·013	0·667
2	2	2	0·486	1·15 (8)	0·137	1·708
4	0	0	0·561	11·93 (5)	−0·218	−4·355
3	3	1	0·611	8·39 (4)	0·019	0·471
4	2	2	0·687	10·90 (8)	0·127	1·588
5	1	1	0·728	7·41 (1)	0·052	5·196
3	3	3	0·728	7·28 (3)	0·124	4·130
4	4	0	0·793	9·58 (2)	−0·152	−7·579

tion, if populated, represents interactions between next-nearest-neighbour carbon atoms. The apparent non-existence of this term in diamond and increasing importance in Si [0·10 (2) electrons (Spackman, 1986)] and Ge [0·16 (6) electrons (Brown & Spackman, 1990)] would suggest increasing importance of next-nearest-neighbour interactions on descending the Group IV* column. This may be interpreted as an increasing tendency towards less directional bonding (*i.e.* less covalent) and hence metallic character. In this context we note that the band gaps for the Group IV elements descend in the following manner: 580 kJ mol^{-1} (C), 107 kJ mol^{-1} (Si), 64 kJ mol^{-1} (Ge), 8 and 0 kJ mol^{-1} (α-Sn and β-Sn respectively) (Greenwood & Earnshaw, 1984). The correspondence between small band gap and increased metallic character suggests a rationale for the increased significance of the hexadecapole term for Si and Ge. A more conclusive result will have to await more extensive and accurate data sets for Ge and an electron-density refinement using accurate diffraction data for α-Sn.

From the points (i) to (v) above and a consideration of refinement indices in Table 1, especially $wR(F)$ and goodness of fit (GOF), it is quite clear that the best electron-density model for diamond, with the minimum number of variables, is that labelled (B, O, α) in Table 1. This model yields the lowest GOF (4·26) and a value of $wR(F^2)$ insignificantly higher than that for the most complex model in the table and we choose it for more detailed discussion and for mapping of Fourier and direct-space electron-density functions in the subsequent sections. Table 2 gives the residuals $\Delta|F|$ and the ratio $\Delta|F|/\sigma(|F|)$ for the (B, O, α) multipole refinement; the latter ratio is a good estimate of the contribution of that reflection to the residual ε.

From the values of Δ/σ in Table 2 it is evident that four reflections (400, 511, 333 and 440) comprise 95% of ε, which largely explains the apparently high figures of merit for a multipole refinement of this type. By comparison with $wR(F^2) = 1{\cdot}89\%$ for the present refinement, values of 0·27 and 0·23% were obtained for Si (Spackman, 1986), 0·52% for Ge (Brown & Spackman, 1990) and typically 0·84 to 1·19% for analyses of the GW diamond data (Stewart, 1973*c*). These comparisons, coupled with the rather large goodness of fit in the present work, suggest that the e.s.d.'s reported by TTKS underestimate the true errors in the data. Indeed, the mean error quoted by TTKS for the present data set is 0·35%, which seems extraordinarily low and approaching the errors obtained in earlier measurements on Si [~0·1% (Aldred & Hart, 1973; Teworte & Bonse, 1984)] and the very recent work on Ge [<0·25% (Deutsch, Hart & Cummings, 1990)]. In this regard we note that in the report by Deutsch *et al.* (1990) a comparison is made between structure factors of type *hhh*, corrected for dispersion and thermal motion, obtained by Deutsch *et al.* and those from other sources. Of particular relevance to the present study is the 111 reflection, reported to a precision of 0·19% by Deutsch *et al.* and 0·33% by Takama & Sato (1981) (using the same technique employed for the present data set on diamond), yet the two values disagree by 2·4%. This comparison may be complicated by uncertainties in the dispersion corrections applied, but it does support the assertion above that the TTKS data may not be as precise as suggested by the e.s.d.'s reported.

Despite these reservations about the precision of the TTKS data, there are no systematic trends evident in the residuals reported in Table 2 for the (B, O, α) model. The residual electron density obtained by Fourier summation of $F_o - F_c$ is shown in Fig. 1. The maxima in the map are 0·05 (2) e Å^{-3} and the minima −0·09 (2) e Å^{-3}. The contour interval used for the map in Fig. 1 (0·015 e Å^{-3}) reflects the size of the e.s.d.'s derived from $\sigma(|F_o|)$ and as such from the

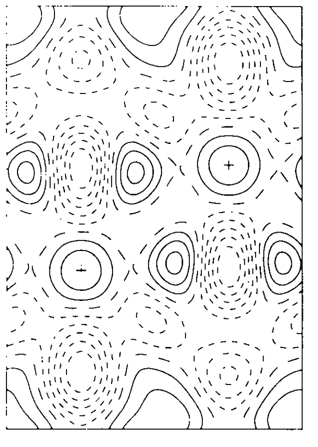

Fig. 1. Residual electron-density map after (B, O, α) multipole refinement. Nuclear positions in the plane are marked with +. The contour interval is 0·015 e Å^{-3} with zero and negative contours shown as dashed lines. The map is $a_0/2^{1/2}$ horizontally (along [110]) and a_0 vertically (along [001]).

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* Group 4 in IUPAC (1988) nomenclature.

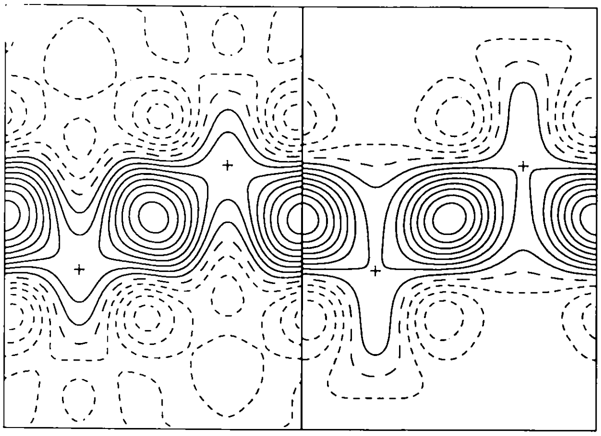
foregoing discussion is probably an underestimate of the true e.s.d.'s. It is difficult therefore to attach much significance to any of the residual features in the map, especially those far removed from the nuclear sites.

Fourier and pseudoatom electron-density maps

In this section we discuss the deformation electron density, $\Delta\rho(\mathbf{r})$, and the valence electron density, $\rho_{\text{val}}(\mathbf{r})$, obtained from both summation of Fourier coefficients and mapping of subsets of the model electron-density function [in all cases (B, O, α)] corrected for the effects of thermal motion. Deformation electron densities were constructed by Fourier summation using the coefficients $F_o - F_{\text{IAM}}$ (Fig. 2*a*) and $F_c - F_{\text{IAM}}$ (Fig. 2*b*) where the F_{IAM} are obtained from the wavefunction of Clementi (1965). Both deformation-density maps show elongated peaks in the bond characteristic of the C–C bond. There is little difference between the maps, as noted above with respect to the residual density function. The observed structure factors give a peak at the bond midpoint of 0·43 (2) e Å^{-3} and deficits behind the nuclei, along the C–C vector, of −0·22 (2) e Å^{-3}; the calculated structure factors yield peak and trough values of similar magnitude. The only really discernible difference between the two maps in Fig. 2 is that the elongated bond peak in Fig. 2(*a*) is more extended perpendicular to the bond than is the case in Fig. 2(*b*) using the model structure factors. Whether this is a deficiency of the present model or a result of errors in one or two structure factors cannot be determined as yet.

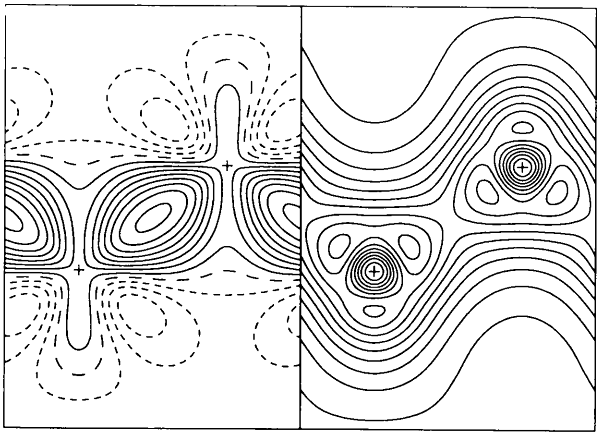
In Fig. 3(*a*) we give the static deformation density map obtained by summing the model electron-density functions in direct space. In the absence of any monopole deformation in the (B, O, α) model (*i.e.* $\kappa = 1{\cdot}0$), the map in Fig. 3(*a*) is a result of just the octopole function. The direct-space map reproduces all of the features of the Fourier map, Fig. 2(*b*), although the bond peak appears even more elongated along the bond than in the Fourier map. Maxima and minima in Fig. 3(*a*) are 0·41 (6) and −0·19 (5) e Å^{-3} respectively, in agreement with the values obtained by Fourier summation. The rather large e.s.d.'s reported for these maxima and minima are a direct result of the relatively large uncertainty in the value of $O4$ (35%) from the (B, O, α) refinement, although this is somewhat reduced as the e.s.d.'s reported for Fig. 3 take into account the large covariance of $O4$ and α (the correlation coefficient is 0·918). It is clear that the present data set implies a peak in the deformation density for diamond of slightly more than 0·4 e Å^{-3} [TTKS also report a maximum $\Delta\rho$ value of 0·44 (17) e Å^{-3}], considerably less than the value of 0·64 e Å^{-3} obtained by Dawson (1967) from an analysis of the GW data. This result is not an artefact of the particular 222 reflection employed; the present analysis used the same 222 structure factor used by Dawson in his analysis and the TTKS result was obtained in the absence of a 222 reflection (*i.e.* just the nine TTKS structure factors were used in the fitting procedure). The present result is more in accord with recent theoretical calculations, as we demonstrate below.

The static valence electron density is mapped in Fig. 3(*b*) and results from the addition of the localized valence monopole to the static deformation density map in Fig. 3(*a*). The main features of the map are the twin peaks in the bond, 0·38 Å from the nuclear



(*a*) (*b*)

Fig. 2. Deformation electron densities, $\Delta\rho(\mathbf{r})$, obtained by Fourier summation of (*a*) $F_o - F_{\text{IAM}}$ and (*b*) $F_c - F_{\text{IAM}}$, with F_c from the (B, O, α) model. Contours at intervals of 0·05 e Å^{-3}. Map dimensions as in Fig. 1.



(*a*) (*b*)

Fig. 3. (*a*) Static deformation electron density calculated from the (B, O, α) model. The contour interval is 0·05 e Å^{-3}. (*b*) Static valence electron density calculated from the (B, O, α) model; note that the valence electron density is a minimum (but not zero) at the nuclei. The contour interval is 0·20 e Å^{-3} and the lowest contour is 0·20 e Å^{-3}. Map dimensions as in Fig. 1.

sites, reaching a maximum of 2·07 (5) e Å^{-3}, the saddle point at the bond midpoint having a value of 1·57 (6) e Å^{-3}, and a smaller peak behind the nuclei of 1·83 (2) e Å^{-3}. The valence electron density is actually a minimum (but not zero) at the nuclei; the specific nature of $\rho_{\rm val}(\mathbf{r})$ in the vicinity of the nuclei is strongly dependent upon the valence monopoles added to $\Delta\rho(\mathbf{r})$. Although none of the earlier analyses of the GW data report electron-density contour maps [with the exception of Dawson (1967)] the valence density from the refinement reported by Stewart (1973*c*) has been given by Stewart & Spackman (1981). The map reported in that work is qualitatively similar to the present one, with peaks in the bond, nearer the nuclei, in excess of 2·0 e Å^{-3}, but the saddle point has a value closer to 1·8 e Å^{-3}, again reflecting the larger peak in the deformation density resulting from analysis of the GW data.

Comparison with theory

As in the earlier analysis of the Si data, we compare the present results obtained from multipole refinement with theoretical calculations. We do this by a comparison of (i) theoretical $\Delta\rho(\mathbf{r})$ and (ii) theoretical $\rho_{\rm val}(\mathbf{r})$ with the (B, O, α) model results and (iii) theoretical structure factors with a set of structure factors derived from the experimental values by correcting for harmonic thermal motion.

(i) *Deformation density*

There is only one theoretical calculation of $\Delta\rho(\mathbf{r})$ in diamond known to us, that reported recently by Orlando, Dovesi, Roetti & Saunders (1990) from an *ab initio* Hartree–Fock calculation with a 6-21G* basis set. The bond peak obtained in that calculation is ~0·60 e Å^{-3} with a deficit behind the nucleus of ~0·15 e Å^{-3}. The bond peak is in substantial disagreement with the present result of 0·41 (6) e Å^{-3}. This overestimate of the deformation density at the bond centre is further exaggerated in the total electron density at bond midpoint, where Orlando *et al.* report an *ab initio* value of 1·96 e Å^{-3}, far greater than the value of 1·58 (6) e Å^{-3} obtained from the (B, O, α) model. Orlando *et al.* (1990) unfortunately do not report $\rho_{\rm val}(\mathbf{r})$ or structure factors, which would enable further comparison with experiment.

(ii) *Valence density*

There are numerous theoretical maps of $\rho_{\rm val}(\mathbf{r})$ for diamond in the literature. As for silicon, it is impossible to be exhaustive in our comparison, but we discuss a number of results and compare them with Fig. 3(*b*).

Yin & Cohen (1981) reported *ab initio* density-functional pseudopotential results for the valence density in both diamond and silicon. As we have reported earlier (Spackman, 1986), these calculations on silicon are in excellent agreement with the model results obtained from highly accurate data. For diamond, Yin & Cohen report a valence density with twin peaks of magnitude 1·99 e Å^{-3} just 0·39 Å from the nuclei, a result in excellent agreement with Fig. 3(*b*). Jones & Lewis (1984) have presented a valence-charge-density map for diamond obtained using a tight-binding method. Their results give a twin peak in $\rho_{\rm val}(\mathbf{r})$ of height ~1·97 e Å^{-3} at 0·38 Å from the nuclei and a saddle point at the bond midpoint of ~1·54 e Å^{-3}. Both results agree very well with the present model, in particular the low saddle-point value.

Pseudopotential density-functional results of Denteneer & van Haeringen (1985) give a twin peak in $\rho_{\rm val}(\mathbf{r})$ of ~2·01 e Å^{-3} at 0·36 Å from the nucleus, a saddle point at the bond midpoint of ~1·54 e Å^{-3} and a smaller peak behind the nucleus of ~1·70 e Å^{-3}. Similar calculations by van Camp, van Doren & Devreese (1986) yield a twin peak of 1·90 e Å^{-3} at 0·43 Å from the nucleus, a saddle-point value of ~1·53 e Å^{-3} and a peak behind the nucleus of ~1·60 e Å^{-3}. Recent *ab initio* pseudopotential calculations by Rodriguez, Casali, Peltzer y Blanca & Cappannini (1987) show twin peaks of ~1·97 e Å^{-3} at 0·45 Å from the nucleus, a value of ~1·61 e Å^{-3} at the bond midpoint and ~1·65 e Å^{-3} behind the nuclei. Similar results have also been reported by Chelikowsky & Louie (1984) and Bachelet, Greenside, Baraff & Schlüter (1981).

Taken together, the theoretical results, particularly the density-functional pseudopotential calculations, are in excellent agreement with the model $\rho_{\rm val}(\mathbf{r})$ in Fig. 3(*b*). In particular, they strongly support the lower value at the bond midpoint and in turn a value of $\Delta\rho(\mathbf{r})$ of ~0·4 e Å^{-3} at this position, rather than the earlier result obtained from the GW data. The present TTKS data set would therefore appear to provide a more reliable estimate of the electron distribution in diamond than did the powder data of GW.

(iii) *Comparison with theoretical structure factors*

We have noted previously that not all calculations of the electronic structure of crystalline solids also report maps of either $\Delta\rho(\mathbf{r})$ or $\rho_{\rm val}(\mathbf{r})$, but that most report several low-angle structure factors (Spackman, 1986). For diamond such calculations report either $\rho_{\rm val}(\mathbf{r})$ or structure-factor amplitudes, but no calculation reports both quantities. Therefore a comparison between experimental and theoretical structure factors enables us to extend the comparison of experiment with theory. For this purpose, in Table 3 we report the TTKS structure factors corrected for thermal motion using $B = 0{\cdot}140$ Å^2. We also include the value of the 222 reflection of Weiss & Middleton (1965) treated in the same manner. The values in

Table 3. *Experimental structure factors for diamond corrected for thermal motion using* $B = 0{\cdot}140$ Å^2

Values are normalized to a single C atom. Figures in parentheses are e.s.d.s in the last figures of $|F_{\rm exp}|$.

h	k	l	$\lvert F_{\rm exp}\rvert$	h	k	l	$\lvert F_{\rm exp}\rvert$
1	1	1	3·274 (11)	3	3	1	1·563 (8)
2	2	0	1·963 (5)	4	2	2	1·455 (10)
3	1	1	1·699 (4)	5	1	1	1·411 (2)
2	2	2	0·149 (10)	3	3	3	1·386 (6)
4	0	0	1·559 (7)	4	4	0	1·308 (3)

Table 4. *Unweighted R factors for agreement between various theoretical structure-factor determinations and the values in Table* 3

N is the number of reflections compared in each case.

Calculation reference	$100 \times R$	N
von der Linden *et al.* (1986)	1·62	9
Dovesi *et al.* (1980)	1·62	9
Heaton & Lafon (1978)	2·15	9
Zunger & Freeman (1977), exchange	1·58	9
Zunger & Freeman (1977), exchange + correlation	1·63	9
Ivey (1974), $\alpha = 2/3$	0·82	10
Ivey (1974), $\alpha = 0{\cdot}75847$	0·78	10
Euwema, Wilhite & Surratt (1973)	1·14	10
Raccah *et al.* (1970), S	1·76	10
Raccah *et al.* (1970), KS	2·90	10
Raccah *et al.* (1970), S-RHF	2·11	10
Raccah *et al.* (1970), KS-RHF	2·52	10

Table 3 are normalized to one atom and are therefore effective atomic scattering factors for C atoms in the solid; this is the most common manner of presentation of theoretical structure factors, and is the same as the procedure we followed in our analysis on silicon.

We use the experimental values in Table 3 to compare the various theoretical calculations with experiment. We compare twelve calculations of structure factors taken from von der Linden, Fulde & Bohnen (1986), Dovesi, Pisani, Ricca & Roetti (1980), Heaton & Lafon (1978), Zunger & Freeman (1977), Ivey (1974), Euwema, Wilhite & Surratt (1973) [actually the 'refined' results reported by Ivey (1974)] and Raccah, Euwema, Stukel & Collins (1970). In Table 4 we give unweighted R factors ($R = \sum ||F_{\rm exp}| - |F_{\rm theor}|| / \sum |F_{\rm exp}|$) for these theoretical calculations. Agreement factors are surprisingly poor in many instances and this is almost always due to a large underestimate of the 222 structure factor. The best agreement is found for the local-density calculations of Ivey (1974). Good agreement is also evident for the Hartree–Fock calculations by Dovesi *et al.* (1980), Euwema *et al.* (1973) and von der Linden *et al.* (1986) as well as the local-density functional results of Zunger & Freeman (1977). We note that although similar R factors are found for these particular calculations (between 1·14 and 1·63%), the local-density method yields values for F_{222} in good agreement with experiment (0·14 e) but all of the Hartree–Fock methods significantly underestimate F_{222} (typically by 40 to 50%); this underestimate is almost certainly a result of the near-minimal basis sets used to date in the Hartree–Fock calculations. Larger basis sets with polarization functions included would be likely to yield better agreement with experiment, but we note that the 6-21G* basis set used by Orlando *et al.* (1990) overestimates the bond peak in the deformation density, and hence is likely to do the same for F_{222}. The self-consistent orthogonalized plane wave (SCOPW) calculations of Raccah *et al.* (1970) are clearly somewhat inferior to the other methods, as in all four cases presented in Table 4 F_{222} is well described (values between 0·12 and 0·14 e) yet R factors are higher than for the other methods. Ivey (1974) has commented that the SCOPW calculations cannot adequately handle systems without core p states (*e.g.* first-row atoms); indeed, the SCOPW results for silicon, discussed by Spackman (1986), are in excellent agreement with the high-quality experimental data for that element. It is unfortunate that structure factors have not been reported for any of the calculations discussed in the previous section on the valence electron density. We suspect that the calculations of Yin & Cohen (1981), and probably several of the others discussed above, would yield R factors in better agreement with experiment than those tabulated in Table 4.

Concluding remarks

We have attempted in this work to analyse the recent X-ray data set on diamond reported by Takama *et al.* (1990) with the aim of assessing any significant differences between electron-density functions obtained from it and the earlier data reported by Göttlicher & Wölfel (1959), which has been analysed numerous times in the past several decades. In an obvious way we have made this work a companion piece to our previous work on silicon, and to a lesser extent that on germanium. In this manner it is possible to see chemical trends that would not be evident in any of the separate works.

Major conclusions of the analysis of the experimental data are:

(i) $\Delta\rho(\mathbf{r})$ for diamond is characterized by an elongated bond peak with a height approximately 0·42 e Å^{-3} and a corresponding deficit of electron density behind the nuclei with depth approximately −0·20 e Å^{-3}. The bond peak is substantially lower than that deriving from the GW data.

(ii) The valence density obtained from the pseudoatom model displays a distinct twin peak in the bond, with peaks of 2·07 (5) e Å^{-3} at 0·38 Å from the nucleus; the saddle point at bond midpoint is 1·57 (6) e Å^{-3} and the peak behind the nuclei reaches 1·83 (2) e Å^{-3}. These results are in excellent agreement with a large number of theoretical calculations.

(iii) As discussed by Takama *et al.* (1990) the present data set is compatible with the lattice-dynamical B value obtained by Stewart (1973*a*); the earlier data of GW yielded much higher values of B.

(iv) The pseudoatom model strongly suggests that there is no apparent radial modification of the valence electron density of the C atom evident in diamond. The octopole deformation term is large and in agreement with analyses of the GW data; in contrast, the hexadecapole deformation term is insignificantly small and this result suggests an increasing importance of next-nearest-neighbour interactions in the series C, Si, Ge, an observation which correlates nicely with the increasingly metallic character of these Group IV elements on descending that row of the Periodic Table.

We believe the results obtained from the present experimental data are significantly different from the earlier results derived from the GW data, and their agreement with other experimental data and with numerous theoretical calculations suggests a faithful representation of the electron distribution in diamond.

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