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A Re-evaluation of Bonding Features in Diamond and Silicon

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Published X-ray powder measurements on diamond and three different sets of published X-ray data on silicon have been re-analysed for bonding features using full-matrix least-squares refinement combined with a statistical analysis of the results obtained. In all cases a highly significant improvement in the fit between observed and calculated structure factors was obtained by introducing a tetrahedral distortion of the spherical 'prepared' charge distribution, but subsequent introduction of a fourth-order cubic distortion proved to be highly significant only for the diamond data and one set of the silicon data. Hartree–Fock calculations gave a better fit to the diamond measurements than calculations based on Hartree–Fock–Slater wave functions. The necessity for placing restrictions on the form of the radial functions associated with the non-spherical distortions, the large estimated standard deviations of the distortion parameters and the dependence of the parameter values on the set of basis wave functions chosen to describe the spherical 'prepared' charge distribution indicate the need for exercising caution in analysing the experimental measurements for bonding features.

Introduction

The diamond powder measurements of Göttlicher & Wölfel (1959) have recently been analysed for bonding features by Dawson (1967*b*) using a general structure factor formalism, Dawson (1967*a*). Similar bonding features in silicon have also been described by Dawson (1967*c*), who analysed the three different sets of X-ray data for silicon at present available† in the literature, *i.e.* the powder measurements of Göttlicher & Wölfel (1959) and the perfect single-crystal measurements of DeMarco & Weiss (1965) and Hattori, Kuriyama, Katagawa & Kato (1965).

Another approach, reported by Weiss (1964) and DeMarco & Weiss (1965), has also been used to analyse the X-ray data on diamond and silicon for bonding features. The similarities and differences between this and the approach of Dawson (1967*a*) are discussed in detail by Dawson & Sanger (1967) where it is shown that only the latter's approach permits adequate interpretation of the experimental data.

In the present paper the experimental measurements for diamond and silicon have been re-analysed for the features of bonding using the formalism of Dawson (1967*a*). However, this time the method of least squares has been used to determine the various parameters associated with the non-spherical distortions of the spherical 'prepared' charge distribution and the significance tests of Hamilton (1964, 1965*a*) are applied before discussing the bonding features in these compounds.

Theory

The space group of diamond is $Fd3m$ (O_h^7) and the complete lattice may be built up from two atomic positions with point group symmetry $\bar{4}3m$ (T_d) combined with the normal face-centred translations.

Application of the formalism of Dawson (1967*a*) shows that, in the calculation of structure factors for the diamond lattice, allowance must be made for non-

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[†] Hart & Milne (1969) have recently reported the measurement of the 220 reflexion in silicon. However, their results have not been used here since they do not represent a complete set of data for silicon.

centrosymmetry in the distribution of electronic charge about each reference nuclear position. These considerations finally lead to the structure factor expressions,

$$\begin{aligned} F(\mathrm{S}) &= 8f'_c(\mathrm{S}), && \text{for } h+k+l=4n \\ &= 4\sqrt{2}[f'_c(\mathrm{S})+f'_a(\mathrm{S})], && \text{for } h+k+l=4n+1 \\ &= 8f'_a(\mathrm{S}), && \text{for } h+k+l=4n+2 \\ &= 4\sqrt{2}[f'_c(\mathrm{S})-f'_a(\mathrm{S})], && \text{for } h+k+l=4n+3 \end{aligned} \quad (1)$$

where $F(\mathrm{S})$ is the structure factor and the subscripts c and a denote the terms which respectively possess centrosymmetry and antisymmetry about the reference atomic positions. The various terms in equation (1) are defined by the relations,

$$\begin{aligned} f'_c(\mathrm{S}) &= \bar{f}_c(S)T_c(S)+\delta f'_c(\mathrm{S}) \\ f'_a(\mathrm{S}) &= A_3(\theta,\varphi)f_a(S) \\ \delta f'_c(\mathrm{S}) &= B_4(\theta,\varphi)\delta f_c(S) \end{aligned} \quad (2)$$

where

$$\begin{aligned} \bar{f}_c(S) &= \int_0^\infty 4\pi r^2\bar{\rho}_c(r)j_0(kr)\mathrm{d}r \\ f_a(S) &= -\int_0^\infty 4\pi r^2F(r)j_3(kr)\mathrm{d}r \\ \delta f_c(S) &= \int_0^\infty 4\pi r^2G(r)j_4(kr)\mathrm{d}r \\ T_c(S) &= \exp\left(-B\frac{\sin^2\theta}{\lambda^2}\right) \\ A_3(\theta,\varphi) &= \frac{hkl}{(h^2+k^2+l^2)^{3/2}} \\ B_4(\theta,\varphi) &= \left[\frac{(h^4+k^4+l^4)}{(h^2+k^2+l^2)^2}-\frac{3}{5}\right]. \end{aligned} \quad (3)$$

The $j_n(kr)$ are spherical Bessel functions of order n, $k=2\pi S=4\pi\sin\theta/\lambda$ and $\bar{\rho}_c(r)$ is the spherical 'prepared' component of the atomic charge density.

In the above equations the non-spherical components of the atomic charge density have been expanded to fourth order terms only in the Kubic Harmonics of Von der Lage & Bethe (1947) and the corresponding radial functions $F(r)$ and $G(r)$ refer directly to the vibrating atom. Also, an isotropic temperature factor, $T_c(S)$, has been used in equation (2) since diamond and silicon have high values of the Debye temperature ($\Theta_M>1800$°K, $\Theta_M=543$°K respectively) and consequently any effects caused by anharmonic vibrations in these substances are very small at room temperature.

The conventional reflexions for the diamond lattice correspond to $h+k+l=4n, 4n+1, 4n+3$. The set $h+k+l=4n+2$ includes the 'forbidden' 222 reflexion and arises from the antisymmetric component of the atomic charge density. Reference to equation (1) shows that measurements of the structure factors of reflexions of class $h+k+l=4n+1, 4n+3$ can supplement the evidence provided by the 222 reflexion for the antisymmetric component, $f_a(\mathrm{S}')$. On the other hand, reflexions in the class $h+k+l=4n$ can reveal only centrosymmetric non-spherical features which are absent in the 'prepared' atom.

The form chosen for the radial functions $F(r)$ and $G(r)$ is influenced by the necessity to satisfy the condition of zero value at the nuclear position (Dawson & Sanger, 1967) and the requirement imposed by data limitations to describe these radial functions by a particular type of elementary function. Following Dawson (1967*a*,*b*) elementary functions of the form $Pr^2\exp(-Qr^2)$ have been used here, and further restrictions imposed due to data limitations are described in the sections to follow [see equation (7)].

X-ray data for diamond

Accurate structure factors for diamond have been obtained by Göttlicher & Wölfel (1959), who carried out X-ray measurements on fine diamond powder at room temperature and placed their measurements on an 'absolute' scale by comparison with powder measurements on LiF and NaCl. These values, [F_{obs}(GW)], are given in Table 1 together with the authors' estimates of their reliability. Table 1 also includes a value of 1·15 ± 0·08 for the magnitude of the structure factor of the 222 reflexion. This is the value given by Weiss & Middleton (1965) which is in agreement with the value $|F(222)|=1{\cdot}1$ to 1·2 reported by Renninger (1955). In each case the value given was claimed to be on an 'absolute' scale.

Conventional full-matrix least-squares refinement of the complete set of diamond data (*i.e.* using the spherical 'prepared' model) gave the isotropic temperature factor $B=0{\cdot}204$ (0·011) Å^2, when the scale factor was fixed at unity. The term in brackets represents the estimated standard deviation (e.s.d.) of the parameter B_c as calculated by the least-squares procedure. In this case the spherical 'prepared' model was based on the charge density $\bar{\rho}_c(r)$, set up from the Hartree–Fock (HF) wave functions of Clementi (1965) for C(^3P). The calculated structure factors were obtained by numerical integration* at the exact values of $(\sin\theta)/\lambda$ using Simpson's rule over the 441-point mesh of Herman & Skillman (1963). The lattice parameter of diamond, $a=3{\cdot}5667$ Å (Swanson & Fuyat, 1967) was also used in these calculations. Structure factors, $\bar{F}_{\mathrm{calc}}$(HF), based on these parameters are included in Table 1 and the agreement factors, unweighted $R(R_u)$ and weighted $R(R_w)$ as defined below, are shown at the bottom of this Table.

$$R_u=\Sigma|F_{\mathrm{obs}}-F_{\mathrm{calc}}|/\Sigma F_{\mathrm{obs}} \quad (4)$$

$$R_w=\left[\frac{\Sigma w(F_{\mathrm{obs}}-F_{\mathrm{calc}})^2}{\Sigma wF_{\mathrm{obs}}{}^2}\right]^{1/2}. \quad (5)$$

This conventional refinement of the complete set of diamond data using HF wave functions was repeated,

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* Hanson, Herman, Lea & Skillman (1964) showed that this method is numerically accurate to seven significant figures.

this time allowing the scale factor as well as the isotropic temperature factor B_c to vary. However, there was no significant change in the scale factor from the value of unity, nor any significant improvement in the fit to the observed data as judged by using the significance tests of Hamilton (1964, 1965*a*).

Each of the various refinements of the complete sets of diamond and silicon data, to be described in the sections to follow, was carried out twice; first of all with the scale factor fixed at unity and then with the scale factor allowed to vary. In all of the refinements where the scale factor was allowed to vary, there was no significant difference between the resulting value of the scale factor and the value of unity, and the inclusion of this extra parameter in the refinement did not produce a significantly better fit to the observed data as judged by the significance tests of Hamilton (1964, 1965*a*). Consequently, any reference to the significance tests of Hamilton in the rest of this paper will be confined to examining the effects of introducing non-spherical distortions of the spherical 'prepared' charge distribution in order to give a better fit to the observed data.

Non-spherical analysis of diamond data using HF wave functions

Examination of the values given in Table 1 for the observed structure factors for diamond and those calculated on the basis of a spherical 'prepared' model shows that significant differences occur mainly at small values of (sin θ)/λ. Using equation (1) these differences can be seen to correspond to the relations

$$\begin{aligned} F_{\rm obs}(S)-\bar{F}_{\rm calc}(S) &= 8B_4(\theta,\varphi)\delta f_c(S), \text{ for } h+k+l=4n \\ &= 4\sqrt{2}[B_4(\theta,\varphi)\delta f_c(S)+A_3(\theta,\varphi)f_a(S)], \\ &\qquad\qquad \text{for } h+k+l=4n+1 \qquad (6) \\ &= 8A_3(\theta,\varphi)f_a(S), \text{ for } h+k+l=4n+2 \\ &= 4\sqrt{2}[B_4(\theta,\varphi)\delta f_c(S)-A_3(\theta,\varphi)f_a(S)], \\ &\qquad\qquad \text{for } h+k+l=4n+3 \end{aligned}$$

and the experimental measurements thus give information about the Fourier transforms $f_a(S)$ and $\delta f_c(S)$ and hence about the radial functions $F(r)$ and $G(r)$.

In order to fit non-spherical components to these differences, simple radial functions $F(r)$ and $G(r)$ of the form

$$\begin{aligned} F(r) &= Ar^2 \exp(-Br^2) \\ G(r) &= Cr^2 \exp(-Br^2) \qquad (7) \end{aligned}$$

were chosen, following Dawson (1967*a,b*). These have the general form given previously and furthermore have been given the same exponents. There is no *a priori* reason why these functions should have the same radial behaviour, or even the same form, but in view of the limited data available here, it was considered that no more than three adjustable distortion parameters should be used in the least-squares analysis.

The first stage of the non-spherical analysis was to determine the values of the two parameters A and B associated with the tetrahedral distortion f_a(S), while

Table 1. *Structure factors for diamond on an absolute scale*

hkl	sin θ/λ (Å^{-1})	$F_{\rm obs}$(GW)	$\bar{F}_{\rm calc}$(HF)	$F_{{\rm calc},\,T}$(HF)	$F_{{\rm calc},\,TC}$(HF)	$\bar{F}_{\rm calc}$(HFS)	$F_{{\rm calc},\,TC}$(HFS)
111	0·2428	18·566 ± 0·040	17·012	18·570	18·568	17·538	18·611
220	0·3965	15·288 ± 0·072	15·211	15·210	15·459	15·710	15·886
311	0·4649	9·006 ± 0·040	9·515	9·080	8·991	9·727	9·232
222	0·4856	− 1·150 ± 0·080*	0·000	− 1·242	− 1·102	0·000	− 1·144
400	0·5607	11·112 ± 0·072	11·905	11·902	11·302	12·019	11·470
331	0·6111	8·287 ± 0·028	7·981	8·151	8·249	8·023	8·327
422	0·6868	10·504 ± 0·016	10·453	10·449	10·512	10·467	10·530
333	0·7284	7·212 ± 0·028	7·082	6·969	7·073	7·083	7·048
511	0·7284	7·212 ± 0·028	7·082	7·100	6·996	7·083	6·997
440	0·7930	9·080 ± 0·072	9·348	9·344	9·371	9·339	9·367
531	0·8294	6·256 ± 0·017	6·346	6·324	6·324	6·338	6·311
620	0·8866	8·352 ± 0·040	8·391	8·387	8·333	8·377	8·315
533	0·9193	5·696 ± 0·028	5·700	5·721	5·733	5·690	5·734
551	1·0011	5·069 ± 0·017	5·127	5·130	5·132	5·117	5·126
711	1·0011	5·069 ± 0·017	5·127	5·122	5·089	5·117	5·077
642	1·0491	6·760 ± 0·024	6·791	6·785	6·784	6·777	6·773
553	1·0768	4·582 ± 0·045	4·618	4·603	4·609	4·609	4·599
731	1·0768	4·582 ± 0·045	4·618	4·617	4·603	4·609	4·595
660	1·1895	5·584 ± 0·032	5·530	5·525	5·519	5·516	5·507
822	1·1895	5·584 ± 0·032	5·530	5·525	5·505	5·516	5·492
555	1·2140	3·756 ± 0·034	3·766	3·769	3·768	3·756	3·762
751	1·2140	3·756 ± 0·034	3·766	3·760	3·754	3·756	3·746
753	1·2772	3·439 ± 0·023	3·410	3·410	3·405	3·399	3·397
911	1·2772	3·439 ± 0·023	3·410	3·407	3·391	3·399	3·380
Agreement factors			R_u = 0·0325 R_w = 0·0372	R_u = 0·0140 R_w = 0·0140	R_u = 0·0097 R_w = 0·0101	R_u = 0·0327 R_w = 0·0312	R_u = 0·0147 R_w = 0·0133

* Value due to Weiss & Middleton (1965).

the effects of the 4th order cubic distortion $\delta f_c(\mathrm{S})$ are neglected. Full-matrix least-squares refinement of the complete set of diamond data allowing A, B and an isotropic temperature factor B_C to vary, with the scale factor fixed at unity, gave the results

$$\begin{aligned} A &= 7{\cdot}78\ (1{\cdot}87) \\ B &= 2{\cdot}15\ (0{\cdot}19) \\ B_C &= 0{\cdot}205\ (0{\cdot}004)\ \text{Å}^2\,. \end{aligned} \tag{8}$$

Structure factors, $F_{\text{calc},\,T}(\text{HF})$, based on these parameters are listed in Table 1.

When the effects of the 4th order cubic distortion are included in the refinement the following results are obtained,

$$\begin{aligned} A &= 7{\cdot}05\ (1{\cdot}43) \\ B &= 2{\cdot}21\ (0{\cdot}14) \\ C &= -2{\cdot}11\ (0{\cdot}52) \\ B_C &= 0{\cdot}206\ (0{\cdot}003)\ \text{Å}^2\,. \end{aligned} \tag{9}$$

Structure factors, $F_{\text{calc},\,TC}(\text{HF})$, based on the parameters given in equation (9) are listed in Table 1.

Application of the significance tests of Hamilton (1964, 1965*a*) to the above results shows that the introduction of a tetrahedral distortion gives a highly significant improvement in the fit to the observed data, and further that a model including the effects of both a tetrahedral and a 4th order cubic distortion gives an even better fit to the experimental measurements. The various weighted R factor ratios to be compared in these two cases are shown in Table 2.

The validity of the significance tests depends on the linearity of the model being used in the least-squares refinement procedure (Hamilton, 1965*b*). A study of the dependence of the weighted R factor on each of the distortion parameters showed that the conditions of linearity were satisfied in the present analyses.

The parameters A, B and C of the radial functions $F(r)$ and $G(r)$ associated with the tetrahedral and 4th order cubic distortion can now be used to evaluate the electron redistribution of the spherical 'prepared' charge distribution due to these distortions. The details of these calculations and the resultant effects of bonding redistribution in the diamond lattice have been described by Dawson (1967*b*). However, some of the numerical features of these calculations will again be presented here, based on the parameters given in equation (9) together with an indication of their accuracies.

The electron content of each of the eight negative lobes, n_-, associated with the 4th order cubic distortion is defined by the relation

$$n_- = -\frac{27\sqrt{3}}{1280}\int_0^\infty \pi r^2 G(r)\mathrm{d}r\,. \tag{10}$$

If allowance is made for the errors in the parameters B and C defining $G(r)$ then an e.s.d. for n_- can be calculated using the equation

$$\Delta n_- = \left[\frac{\partial n_-}{\partial C}\right]_{B,C}\Delta C + \left[\frac{\partial n_-}{\partial B}\right]_{B,C}\Delta B \tag{11}$$

where Δn_-, ΔC and ΔB are the e.s.d.'s for n_-, C, and B respectively.

If the values given in equation (9) are used in equations (10) and (11) the following result is obtained,

$$n_- = 0{\cdot}0222\ (0{\cdot}0090)\ \text{electrons}\,. \tag{12}$$

Similarly the electron content N_+ of a positive lobe associated with the tetrahedral distortion is defined by the equation

$$N_+ = \tfrac{1}{8}\int_0^\infty r^2 F(r)\mathrm{d}r\,. \tag{13}$$

Evaluating equation (13) using the parameters of $F(r)$

Table 2. *Application of the significance tests of Hamilton* (1964, 1965*a*) *to the results obtained by comparing the various distortion models based on two different sets of wave functions, with the diamond powder measurements of Göttlicher & Wölfel* (1959)

The various hypotheses can be rejected at the 100α% confidence level if the computed weighted R-factor ratios R are greater than the significance points $R_{b,\,n-p,\,\alpha}$ where b is the number of parameters out of the total p parameters that are fixed during the initial refinement and n is the total number of observations.

		Results based on refinement of complete set of data		Results based on refinement of 'low-angle' data	
Wave functions used	Significance points	Computed weighted-R factor ratios	Confidence level for rejection of hypothesis	Computed weighted-R factor ratios	Confidence level for rejection of hypothesis
HF wave functions of Clementi (1965)	$R_{2,\,21,\,0\cdot005} = 1{\cdot}287$	$R_1 = R_{\text{spher}}/R_{td}$ * $= 2{\cdot}657$	$\leqslant 0{\cdot}5$ %	$R_1 = 2{\cdot}601$	$\leqslant 0{\cdot}5$ %
	$R_{1,\,20,\,0\cdot005} = 1{\cdot}224$	$R_2 = R_{td}/R_{tp}$ † $= 1{\cdot}387$	$< 0{\cdot}5$ %	$R_2 = 1{\cdot}389$	$< 0{\cdot}5$ %
HFS wave functions of Herman & Skillman (1963)	$R_{2,\,21,\,0\cdot005} = 1{\cdot}287$	$R_1 = 1{\cdot}926$	$< 0{\cdot}5$ %	$R_1 = 1{\cdot}868$	$< 0{\cdot}5$ %
	$R_{1,\,20,\,0\cdot005} = 1{\cdot}224$	$R_2 = 1{\cdot}218$	$\simeq 0{\cdot}6$ %	$R_2 = 1{\cdot}237$	$< 0{\cdot}5$ %

* *td* stands for tetrahedral distribution.

† *tp* stands for tetrahedral plus 4th order cubic distribution.

shown in equation (9), gives the result,

$$N_{+}=0{\cdot}0807\ (0{\cdot}0291)\ \text{electrons}\,. \tag{14}$$

Non-spherical analysis of diamond data using HFS wave functions

The choice of the set of basis wave functions that are to be used in these non-spherical calculations is important, since it influences the values of the differences that are finally used in these analyses [see equation (6)].

It is of interest, therefore, to consider the effect of using a different set of theoretical wave functions to approximate the spherical component of the 'bonded' atom. For this purpose the Hartree–Fock–Slater (HFS) wave functions of Hanson, Herman, Lea & Skillman (1964) were used, since these represented the first relatively complete set of wave functions for the elements $Z=1$ to $Z=100$ calculated to the same numerical accuracy. The ground state wave functions for carbon corresponding to the electronic configuration $C(1s)^2(2s)^2(2p)^2$ were used. Conventional full-matrix least-squares refinement of the complete set of diamond data using the HFS wave functions gave $B_C=0{\cdot}218$ $(0{\cdot}009)$ Å^2, with the scale factor fixed at unity, and structure factors, $\bar{F}_{\text{calc}}$(HFS), based on these parameters are included in Table 1. It is interesting to note that the spherical 'prepared' model in this case gives a better fit to the observed data than the corresponding HF results.

Least-squares refinement of the complete set of data using a model including the effects of tetrahedral distortion gave the parameters

$$\begin{aligned} A &= 9{\cdot}21\ (2{\cdot}78)\\ B &= 2{\cdot}56\ (0{\cdot}30)\\ B_C &= 0{\cdot}218\ (0{\cdot}005)\ \text{Å}^2\,. \end{aligned} \tag{15}$$

Application of the significance tests showed that introduction of the tetrahedral distortion gave a highly significant improvement in the fit to the experimental data (see Table 2).

When a 4th order cubic distortion is also included in the model the parameters

$$\begin{aligned} A &= 8{\cdot}71\ (2{\cdot}44)\\ B &= 2{\cdot}63\ (0{\cdot}25)\\ C &= -2{\cdot}36\ (0{\cdot}83)\\ B_C &= 0{\cdot}220\ (0{\cdot}004)\ \text{Å}^2 \end{aligned} \tag{16}$$

are obtained by full-matrix least-squares refinement of the complete set of diamond data. Results based on these parameters, $F_{\text{calc},\,TC}$(HFS), are included in Table 1 and the calculations summarized in Table 2 show that inclusion of the 4th order cubic distortion into the calculated structure factors has made a further significant improvement in the fit to the observed diamond data.

Comparison of the results given in equations (9) and (16) show that the e.s.d.'s of the distortion parameters for the HFS calculations are approximately double those for the HF calculations. The smaller e.s.d.'s for the distortion parameters and the better agreement factors obtained for the structure factors based on the 'complete' distortion model, $F_{\text{calc},\,TC}$(HF), show that the calculations based on the HF wave functions give

Table 3. *Experimental structure factors for silicon on an absolute scale*

hkl	sin θ/λ (Å^{-1})	F_{obs}(GW)	F_{obs}(DMW)	F_{obs}(HKKK)
111	0·15946	60·81 ± 0·11	60·98 ± 0·45	62·11 ± 0·28
220	0·26040	67·84 ± 0·16	68·32 ± 0·48	68·64 ± 0·40
311	0·30534	44·12 ± 0·17	44·35 ± 0·45	44·01 ± 0·06
222	0·31892	−1·36 ± 0·08*	−1·36 ± 0·08	−1·36 ± 0·08*
400	0·36826	56·16 ± 0·24	58·72 ± 0·64	56·16 ± 0·64
331	0·40130	39·26 ± 0·11	39·54 ± 0·51	38·98 ± 0·34
422	0·45102	50·72 ± 0·24	50·64 ± 0·72	49·60 ± 0·16
333 }	0·47838	{ 33·54 ± 0·34	33·71 ± 0·40	33·15
511 }	0·47838	{ 33·54 ± 0·34	34·05 ± 0·45	32·92
440	0·52079	43·12 ± 0·32	43·60 ± 0·56	43·28 ± 0·80
531	0·54466	28·91 ± 0·11	—	29·42 ± 0·57
620	0·58226	37·68 ± 0·08	—	37·68
533	0·60370	25·68 ± 0·11	—	25·40 ± 0·40
444	0·63784	33·68 ± 0·56	34·72 ± 0·56	33·76
551 }	0·65747	{ 22·40 ± 0·28	—	23·19 ± 0·11
711 }	0·65747	{ 22·40 ± 0·28	—	—
642	0·68894	29·44 ± 0·24	—	—
731 }	0·70716	{ 19·86 ± 0·23	—	—
553 }	0·70716	{ 19·86 ± 0·23	—	—
822 }	0·78119	{ 23·52 ± 0·24	—	—
660 }	0·78119	{ 23·52 ± 0·24	23·52 ± 0·40	—
751 }	0·79730	{ 15·95 ± 0·23	15·95 ± 0·28	—
555 }	0·79730	{ 15·95 ± 0·23	15·95 ± 0·28	—
880	1·04159	—	11·92 ± 0·32	—
777	1·11622	—	7·75 ± 0·23	—
888	1·27568	—	7·76 ± 0·24	—
10,10,0	1·30198	—	7·28 ± 0·24	—

* 222 reflexion of DeMarco & Weiss (1965).

a significantly better fit to the observed data. The HF wave functions are normally preferred for crystallographic calculations (Cromer, 1965*b*), especially for lighter elements, and in the refinements of the various sets of silicon data, to be described in the following sections, only a spherical 'prepared' model based on HF wave functions will be used.

X-ray data for silicon

Three different sets of X-ray data for silicon are available in the literature. Each set of data was measured at room temperature (taken to be 20°C) and was placed on an 'absolute scale' by the relevant authors. These are the powder measurements of Göttlicher & Wölfel (1959), the perfect single-crystal measurements of DeMarco & Weiss (1965) and the pendellösung fringe results of Hattori, Kuriyama, Katagawa & Kato (1965).

Structure factors for each of these three sets of silicon data are listed in Table 3, the values of $(\sin\theta)/\lambda$ in this Table being calculated using the cell parameter $a = 5{\cdot}431$ Å at 20°C (DeMarco & Weiss, 1965).

The F_{obs}(GW) data of Table 3 are obtained by converting the experimental results of Göttlicher & Wölfel (1959) to structure factors. The f(DMW) results given in Table 1 of DeMarco & Weiss (1965) represent the version for stationary atoms obtained by correcting their actual measurements for the effects of thermal vibration, using the temperature factor $B_{\text{Si}} = 0{\cdot}444$ Å^2,* and for anomalous dispersion effects ($\Delta f'_{\text{Si}} = 0{\cdot}1$) which occur when Mo $K\alpha$ radiation is used to collect the data. Reversing this procedure and then converting the resultant numbers to structure factors give the F_{obs}(DMW) values of Table 3. The F_{obs}(HKKK) data in this Table are taken from the f(HKKK) values of Hattori *et al.* (1965), with the error estimates of Dawson (1967*c*), converted to structure factors. For the 222 reflexion, no result is recorded by Göttlicher & Wölfel (1959) or Hattori *et al.* (1965). Following Dawson (1967*c*), the DeMarco & Weiss (1965) value has been taken, which is the room temperature measurement of Weiss & Middleton (1965), for which there is no dispersion correction.

Full-matrix least-squares refinement of each complete set of silicon data, allowing an isotropic temperature factor to vary while the scale factor was fixed at unity, gave the results:

$$\begin{aligned} &F_{\text{obs}}(\text{HKKK})\ \text{data:}\ B_{\text{Si}} = 0{\cdot}449\ (0{\cdot}028)\ \text{Å}^2\\ &F_{\text{obs}}(\text{DMW})\ \text{data:}\ B_{\text{Si}} = 0{\cdot}455\ (0{\cdot}036)\ \text{Å}^2 \qquad (17)\\ &F_{\text{obs}}(\text{GW})\ \ \text{data:}\ B_{\text{Si}} = 0{\cdot}471\ (0{\cdot}020)\ \text{Å}^2\,. \end{aligned}$$

Allowance was made for the effects of anomalous dispersion by using the real part of the dispersion correction, where $\Delta f'_{Si} = 0{\cdot}09$ for the F_{obs}(DMW)† and F_{obs}(GW)† data (Cromer, 1965*a*) and $\Delta f'_{Si} = 0{\cdot}075$ for the F_{obs}(HKKK)‡ data.

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* This value corresponds to the Debye temperature $\Theta_M = 543$°K determined by Batterman & Chipman (1962).

† Data collected using Mo $K\alpha$ radiation.

‡ Data collected using both Mo and Ag $K\alpha$ radiations, the value 0·075 being the mean of the values of Δf_{Si} for the separate radiations.

Table 4. *Calculated structure factors for silicon on an absolute scale*

Results to be compared with F_{obs}(HKKK)			Results to be compared with F_{obs}(DMW)			Results to be compared with F_{obs}(GW)		
hkl	$\bar{F}_{\text{calc}}$(HF)	$F_{\text{calc},\,TC}$(HF)	*hkl*	$\bar{F}_{\text{calc}}$(HF)	$F_{\text{calc},\,T}$(HF)	*hkl*	$\bar{F}_{\text{calc}}$(HF)	$F_{\text{calc},\,TC}$(HF)
111	59·398	62·088	111	59·473	60·957	111	59·449	60·613
220	68·162	68·656	220	68·250	68·249	220	68·176	68·549
311	44·686	43·933	311	44·742	44·307	311	44·675	43·986
222	0·000	−1·420	222	0·000	−1·363	222	0·000	−1·477
400	57·075	56·071	400	57·141	57·139	400	57·017	55·702
331	38·197	38·574	331	38·239	38·414	331	38·140	38·686
422	49·495	49·607	422	49·544	49·540	422	49·382	49·567
333	33·260	33·302	333	33·291	33·175	333	33·169	33·260
511	33·260	33·131	511	33·291	33·310	511	33·169	32·916
440	43·289	43·346	440	43·325	43·321	440	43·137	43·237
531	29·151	29·139	444	33·659	33·655	531	29·035	29·009
620	38·064	37·997	660	23·976	23·971	620	37·883	37·732
533	25·681	25·742	555	16·303	16·298	533	25·547	25·649
444	33·641	33·698	751	16·303	16·306	444	33·441	33·541
551	22·742	22·766	880	12·813	12·809	551	22·596	22·630
			777	7·635	7·631	711	22·596	22·505
			888	7·629	7·625	642	29·676	29·694
			10,10,0	7·220	7·216	553	20·092	20·070
						731	20·092	20·105
						660	23·742	23·703
						822	23·742	23·747
						555	16·138	16·133
						751	16·138	16·167
Agreement factors	$R_u = 0{\cdot}0155$ $R_w = 0{\cdot}0260$	$R_u = 0{\cdot}0044$ $R_w = 0{\cdot}0053$		$R_u = 0{\cdot}0217$ $R_w = 0{\cdot}0566$	$R_u = 0{\cdot}0159$ $R_w = 0{\cdot}0181$		$R_u = 0{\cdot}0137$ $R_w = 0{\cdot}0224$	$R_u = 0{\cdot}0087$ $R_w = 0{\cdot}0086$

In these refinements the spherical 'prepared' model was based on the HF wave functions of Clementi (1965) for the ground state of silicon, Si(^3P). Batterman & Chipman (1962) give the value $\Theta_M=543\,^\circ\mathrm{K}$ for the Debye temperature of silicon with an 'error' of $\pm 8\,^\circ\mathrm{K}$. If this 'error' is taken to be the e.s.d. for Θ_M then each of the isotropic temperature factors given in equation (17) agrees with the value $B_{\mathrm{Si}}=0{\cdot}444$ Å^2 calculated from Θ_M.

Structure factors, $F_{\mathrm{calc}}(\mathrm{HF})$, for the spherical 'prepared' model, calculated using the temperature factors of equation (17), are listed in Table 4 for each of the three sets of silicon data.

Non-spherical analysis of the silicon data of Hattori *et al.* (1965) using HF wave functions

Full-matrix least-squares refinement of the complete set of silicon data of Hattori *et al.* (1965), using a model including the effects of tetrahedral distortion only, gave the results:

$$\begin{aligned} A &= 1{\cdot}045\ (0{\cdot}318)\\ B &= 0{\cdot}796\ (0{\cdot}096)\\ B_{\mathrm{Si}} &= 0{\cdot}452\ (0{\cdot}013)\ \text{Å}^2 \end{aligned} \qquad (18)$$

(note that unit weights were used in this analysis because of the uncertainty in the e.s.d. of some of the Hattori *et al.* (1965) data). Once again, the model including the effects of tetrahedral distortion can be shown to give a highly significant improvement in the fit to the observed data (see Table 5).

Inclusion of a 4th order cubic distortion also gives a highly significant improvement to the spherical 'prepared' plus tetrahedral distortion model, see Table 5, and the least squares fitted parameters in this case are:

$$\begin{aligned} A &= 1{\cdot}037\ (0{\cdot}208)\\ B &= 0{\cdot}863\ (0{\cdot}059)\\ C &= -0{\cdot}398\ (0{\cdot}097)\\ B_{\mathrm{Si}} &= 0{\cdot}449\ (0{\cdot}008)\ \text{Å}^2\,. \end{aligned} \qquad (19)$$

Results, $F_{\mathrm{calc},\,TC}(\mathrm{HF})$, based on these parameters are included in Table 4. Using the values of the distortion parameters given in equation (19) the quantities N_+ and n_-, the amount of charge redistributed per bond by the tetrahedral and 4th order cubic distortions respectively, are found to be

$$\begin{aligned} N_+ &= 0{\cdot}1245\ (0{\cdot}0463)\ \text{electrons}\\ n_- &= 0{\cdot}0439\ (0{\cdot}0182)\ \text{electrons}\,. \end{aligned} \qquad (20)$$

The details of this type of calculation for silicon have already been described by Dawson (1967*c*) who also presents a calculation of the total non-spherical distribution in the $(1\bar{1}0)$ plane of silicon; the main feature of this calculation shows that the electron density associated with the bonding features is smaller in magnitude in silicon than it was in diamond. This seems strange at first, since a comparison of the results given in equations (12), (14) and (20) show that the extent of electron redistribution is slightly greater in silicon than in diamond; however, the lattice parameter for silicon is larger than that for diamond so that the redistribution occurs over a larger volume and thus the electron density everywhere is lower.

Non-spherical analysis of the silicon data of Göttlicher & Wölfel (1959) using HF wave functions

Analysis of the complete set of silicon data of Göttlicher & Wölfel (1959) shows that a model including the effects of tetrahedral distortion gives a highly significant improvement in the fit to the observed data, and

Table 5. *Application of the significance tests of Hamilton* (1964, 1965*a*) *to the results obtained by comparing the various distortion models, based on the* HF *wave functions of Clementi* (1965), *with the three different sets of silicon data at present available in the literature*

		Results based on refinement of complete set of data		Results based on refinement of 'low-angle' data	
Silicon measurements	Significance points	Computed weighted-R factor ratios	Confidence level for rejection of hypothesis	Computed weighted-R factor ratios	Confidence level for rejection of hypothesis
Single crystal data of Hattori *et al.* (1965)	$R_{2,\,12,0\cdot005}=1\cdot555$	$R_1=2\cdot889$	$\leqslant 0\cdot5\,\%$	$R_1=2\cdot378$	$\leqslant 0\cdot5\,\%$
	$R_{1,\,11,0\cdot005}=1\cdot453$	$R_2=1\cdot697$	$<0\cdot5\,\%$	$R_2=1\cdot697$	$<0\cdot5\,\%$
Powder data of Göttlicher & Wölfel (1959)	$R_{2,\,20,0\cdot005}=1\cdot303$	$R_1=2\cdot133$	$\leqslant 0\cdot5\,\%$	$R_1=2\cdot112$	$\leqslant 0\cdot5\,\%$
	$R_{1,\,19,0\cdot010}=1\cdot196$	$R_2=1\cdot221$	$\simeq 0\cdot7\,\%$	$R_2=1\cdot190$	$\simeq 1\cdot2\,\%$
Single crystal data of DeMarco & Weiss (1965)	$R_{2,\,15,0\cdot005}=1\cdot424$	$R_1=3\cdot127$	$\leqslant 0\cdot5\,\%$	$R_1=3\cdot065$	$\leqslant 0\cdot5\,\%$
	$R_{1,\,14,0\cdot250}=1\cdot050$	$R_2=1\cdot023$	$\sim 45\,\%$	$R_2=1\cdot022$	$\sim 45\,\%$
	$R_{1,\,14,0\cdot500}=1\cdot017$				

also that inclusion of a 4th order cubic distortion into the model produces a further significant improvement in the fit to the observed data. The parameters for the 'complete' distortion model are:

$$\begin{aligned} A &= 1{\cdot}474\ (0{\cdot}355) \\ B &= 1{\cdot}271\ (0{\cdot}145) \\ C &= -0{\cdot}825\ (0{\cdot}324) \\ B_{\mathrm{Si}} &= 0{\cdot}472\ (0{\cdot}008)\ \text{Å}^2 \end{aligned} \tag{21}$$

and structure factors, $F_{\mathrm{calc},\,TC}$(HF), based on these parameters are listed in Table 4, the details of the significance testing again being given in Table 5.

Non-spherical analysis of the silicon data of Demarco & Weiss (1965) using HF wave functions

When the complete set of silicon data of DeMarco & Weiss (1965) are analysed for non-spherical effects, a model including the effects of tetrahedral distortion alone is found to give a better fit to the experimental data than that obtained by using the spherical 'prepared' model. The relevant parameters are:

$$\begin{aligned} A &= 0{\cdot}972\ (0{\cdot}198) \\ B &= 0{\cdot}950\ (0{\cdot}193) \\ B_{\mathrm{Si}} &= 0{\cdot}455\ (0{\cdot}012)\ \text{Å}^2 \end{aligned} \tag{22}$$

and structure factors, $F_{\mathrm{calc},\,T}$(HF), based on these parameters are given in Table 4. The appropriate significance tests are listed in Table 5 which also shows that the inclusion of the effects of a 4th order cubic distortion in this case does not produce any further significant improvement in the fit to the observed data.

A second approach

All of the non-spherical analyses described in the preceding sections have been carried out on the complete set of experimental data available. The full-matrix least-squares refinements used in these analyses allowed for the simultaneous variation of an isotropic temperature factor, a scale factor and the relevant distortion parameters; however, as mentioned before, the scale factor could be taken to be unity in all cases. These results are conveniently summarized in Table 6.

A second approach to these non-spherical analyses is to refine the 'high-angle' data for an isotropic temperature factor (with the scale factor fixed at unity), and subsequently refine the 'low-angle' data (with the scale factor fixed at unity and the isotropic temperature factor fixed at the value found from the 'high-angle' data) for bonding features. The basis of this approach is that the bonding features are predominantly an outer-electron phenomena and must primarily affect the 'low-angle' data whereas the reverse is true for thermal vibration effects. Beyond a certain limit, then, the numerical uncertainties associated with the random errors that are present in all experiments could be considered to be of the same magnitude as any genuine features of non-sphericity that the data could possibly contain. The inclusion of these 'high-angle' data in any

Table 6. *Results obtained by analysing the various complete sets of diamond and silicon data for bonding features using the distortion models described in the text*

Observed data Wave functions used		Diamond GW (1959) HF	Diamond GW (1959) HFS	Silicon HKKK (1965) HF	Silicon GW (1959) HF	Silicon DMW (1965) HF
Parameters for spherical 'prepared' model alone		$B_{\mathrm{C}}=0{\cdot}204$ (0·011) Å^2	$B_{\mathrm{C}}=0{\cdot}218$ (0·009) Å^2	$B_{\mathrm{Si}}=0{\cdot}449$ (0·028) Å^2	$B_{\mathrm{Si}}=0{\cdot}471$ (0·020) Å^2	$B_{\mathrm{Si}}=0{\cdot}455$ (0·036) Å^2
No. of reflexions used		24	24	15	23	18
Agreement factors	R_u	0·0325	0·0327	0·0155	0·0137	0·0217
	R_w	0·0372	0·0312	0·0260	0·0224	0·0566
Parameters for tetrahedral distortion model	A	7·78 (1·87)	9·21 (2·78)	1·045 (0·318)	1·169 (0·286)	0·972 (0·198)
	B	2·15 (0·19)	2·56 (0·30)	0·796 (0·096)	1·053 (0·131)	0·950 (0·193)
	$^*B_T$ (Å^2)	0·205 (0·004)	0·218 (0·005)	0·452 (0·013)	0·474 (0·010)	0·455 (0·012)
No. of reflexions used		24	24	15	23	18
Agreement factors	R_u	0·0140	0·0176	0·0075	0·0092	0·0159
	R_w	0·0140	0·0162	0·0090	0·0105	0·0181
Improvement obtained by using this model		Highly significant	Highly significant	Highly significant	Highly significant	Highly significant
Parameters for tetrahedral plus 4th order cubic distortion model	A	7·05 (1·43)	8·71 (2·44)	1·037 (0·208)	1·474 (0·355)	0·922 (0·169)
	B	2·21 (0·14)	2·63 (0·25)	0·863 (0·59)	1·271 (0·145)	0·877 (0·201)
	C	−2·11 (0·52)	−2·36 (0·83)	−0·398 (0·097)	−0·825 (0·324)	0·240 (0·275)
	$^*B_T$ (Å^2)	0·206 (0·003)	0·220 (0·004)	0·449 (0·008)	0·472 (0·008)	0·455 (0·012)
No. of reflexions used		24	24	15	23	18
Agreement factors	R_u	0·0097	0·0147	0·0044	0·0087	0·0159
	R_w	0·0101	0·0133	0·0053	0·0086	0·0177
Improvement obtained by using this model		Highly significant	Significant	Highly significant	Significant	Not significant

* B_T is the appropriate isotropic temperature factor allowed to vary in the refinement (*i.e.* B_{C} for the diamond data, and B_{Si} for the silicon data).

non-spherical analysis could then be expected to degrade the physical meaning of the parameters thus obtained, and could also lead to unduly high e.s.d.'s for the corresponding distortion parameters.

This second approach is essentially that used by Dawson (1967*b*,*c*) in his analysis of diamond and silicon, and for the purposes of his calculations the 'low-angle' limit was taken to be $(\sin\theta)/\lambda=0{\cdot}7$ Å^{-1} for diamond and $(\sin\theta)/\lambda=0{\cdot}5$ Å^{-1} for silicon. However, Dawson (1967*b*,*c*) fitted his distortion parameters by a trial-and-error process and obtained the parameters $A=7{\cdot}5$, $B=2{\cdot}2$, $C=-2{\cdot}0$ for diamond using the data of Göttlicher & Wölfel (1959), and $A=1{\cdot}11$, $B=0{\cdot}88$, $C=-0{\cdot}321$ for silicon using the data of Hattori *et al.* (1965); all calculations being based on HF wave functions.

In order to examine the consequences of this second approach in the present calculations, the various sets of data for diamond and silicon have been analysed a second time using this second approach, the required calculations again being carried out by full-matrix least-squares refinement. The same 'low-angle' limits $(\sin\theta)/\lambda=0{\cdot}7$ Å^{-1} for diamond and $(\sin\theta)/\lambda=0{\cdot}5$ Å^{-1} for silicon were used in these calculations. Although the non-spherical analyses, in this case, are carried out on the 'low-angle' data, the success of the appropriate distortion model should still be judged by its fit to the complete set of data; consequently all agreement factors should be calculated for the complete set of the relevant data. It is also important to note that when the 'low-angle' data are to be refined using a model that includes only the effects of tetrahedral distortion with the scale factor and temperature factor fixed, the reflexions of type $h+k+l=4n$ must be removed from the refinement and this places a further restriction on the number of reflexions used to define the tetrahedral distortion parameters (*e.g.* in diamond only four 'low-angle' reflexions can be used to define the tetrahedral distortion parameters).

The results obtained by using this second approach are summarized in Table 7. Comparison of the results given in Tables 6 and 7 show that the general conclusions based on the significance tests of Hamilton (1964, 1965*a*) are the same for the two approaches, with the value of R_w being identical or slightly lower if the complete set of data is used in the refinements. It is rather difficult to compare the e.s.d.'s of the distortion parameters from these two sets of calculations since different numbers of reflexions have been used for the various models in the second approach. However, taking the e.s.d.'s at their face value, it is interesting to note that the second approach produces smaller e.s.d.'s for the distortion parameters associated with the best refinements: – that is, for the diamond data of Göttlicher & Wölfel (1959) and the silicon data of Hattori *et al.* (1965), when HF wave functions are used. On the other hand, the second approach produces larger e.s.d.'s for the distortion parameters for the refinement of the diamond data of Göttlicher & Wölfel (1959) using HFS wave functions, and for the silicon data of Göttlicher & Wölfel (1959) and DeMarco & Weiss (1965) using HF wave functions.

Table 7. *Results obtained by using a second approach to analyse the various sets of diamond and silicon data for bonding effects*

Observed data		Diamond GW (1959)	Diamond GW (1959)	Silicon HKKK (1965)	Silicon GW (1959)	Silicon DMW (1965)
Wave functions used		HF	HFS	HF	HF	HF
Parameters for spherical 'prepared' model		$B_{\rm C}=0{\cdot}207$ (0·003) Å^2	$B_{\rm C}=0{\cdot}219$ (0·003) Å^2	$B_{\rm Si}=0{\cdot}448$ (0·012) Å^2	$B_{\rm Si}=0{\cdot}483$ (0·003) Å^2	$B_{\rm Si}=0{\cdot}465$ (0·012) Å^2
No. of reflexions used		17	17	6	14	9
Agreement factors	R_u	0·0324	0·0327	0·0156	0·0125	0·0227
	R_w	0·0372	0·0312	0·0214	0·0226	0·0567
Parameters for tetrahedral distortion model	A	9·00 (1·96)	11·92 (4·04)	1·054 (0·275)	1·162 (0·502)	0·969 (0·213)
	B	2·26 (0·18)	2·80 (0·37)	0·799 (0·083)	1·048 (0·229)	0·946 (0·209)
No. of reflexions used		4	4	6	6	6
Agreement factors	R_u	0·0143	0·0181	0·0074	0·0083	0·0169
	R_w	0·0143	0·0167	0·0090	0·0107	0·0185
Improvement obtained by using this model		Highly significant	Highly significant	Highly significant	Highly significant	Highly significant
Parameters for tetrahedral plus 4th cubic order distortion model	A	7·50 (0·90)	9·91 (4·28)	1·043 (0·164)	1·450 (0·635)	0·919 (0·190)
	B	2·27 (0·08)	2·76 (0·40)	0·864 (0·046)	1·256 (0·263)	0·871 (0·230)
	C	−2·46 (0·35)	−2·83 (1·48)	−0·393 (0·076)	−0·797 (0·608)	0·254 (0·313)
No. of reflexions used		7	7	9	9	9
Agreement factors	R_u	0·0093	0·0149	0·0044	0·0079	0·0168
	R_w	0·0103	0·0135	0·0053	0·0090	0·0181
Improvement obtained by using this model		Highly significant	Highly significant	Highly significant	Significant	Not significant

In this approach the 'high-angle' data have been refined for an isotropic temperature factor, with the scale factor fixed at unity. The 'low-angle' data were subsequently refined using the distortion models described in the text. The agreement factors quoted below have been calculated for the complete set of data, although the various refinements were carried out using different parts of the complete set of data.

While the present calculations do not 'prove' that one approach is better than the other, we prefer to base our conclusions on the more conventional approach of carrying out full-matrix least-squares refinement of the complete set of data at our disposal, allowing simultaneous variation of all the parameters that describe the calculated model used to fit the observed data. This conventional approach avoids any possibility of biasing the results obtained for any bonding or other features by a subjective restriction of the analysis to consider only a certain range of data.

Discussion

In the above refinements, the two sets of powder data of Göttlicher & Wölfel (1959) have virtually been treated as though they were single-crystal data, in that equivalent reflexions have been included as separate reflexions in the refinement. In the case of powder experiments, equivalent reflexions are measured as a combined intensity and divided, using the appropriate multiplicity, on the basis of a common structure factor for each of the individual reflexions in the equivalent set. When the non-spherical model is introduced, reflexions occurring at the same value of $(\sin\theta)/\lambda$ are not necessarily equivalent and the combined intensity should be divided in a different way. One way of avoiding the problems of equivalent reflexions is to treat the 'overlapped' and 'equivalent' reflexions as a group measurement and to make special allowance for this in the least-squares refinement. This suggestion is similar to the method used by McDonald (1967) to refine his neutron powder measurements on aluminum. However, this procedure could not be adopted here since only the structure factors of the various reflexions were reported in the literature. Fortunately, in the case of diamond and silicon the 'equivalent' reflexions occur mainly at high angles and would have a small effect on bonding studies; only the 'low-angle' pair 511–333 could possibly produce a significant effect on the present calculations.

A possible source of error in the non-spherical analyses involves the degree to which the criterion of 'absolute' measurements applied to the various sets of diamond and silicon data. In this respect the silicon measurements of Hattori *et al.* (1965) were slightly more favourable since the results of the fringe-spacing study must be 'absolutely absolute' (Kato, 1965) although the quality of measurements still depends on the degree to which technical difficulties in the pendellösung experiment can be overcome and on the extent to which the underlying theory is adequate. Each group of authors claimed that its data were on an 'absolute' scale, and the analyses described here support these claims in that any attempt to use a scale factor different from unity is without significance. The necessity to add the value of the structure factor of the 222 reflexion, as determined in a separate experiment, to each set of data requires additional consideration. However, there appear to be no grounds to doubt the 'absoluteness' of the figures used. Moreover the low value of the 222 structure factor ensures that any reasonable scaling error in relation to the rest of the data would have had little effect on the present calculations.

The set of wave functions chosen to approximate the spherical component of the 'bonded' atom influences the final differences that are to be fitted by non-spherical distortions, and hence the distortion parameters and the final description of the bonding redistribution obtained by the fitting process. This point is illustrated by the non-spherical analyses of the complete set of diamond data of Göttlicher & Wölfel (1959) carried out using HF and HFS wave functions. The HFS wave functions gave a better spherical 'prepared' model but the distortion models for the HF calculations gave a much better fit to the diamond powder and this was also indicated by the smaller values of the e.s.d.'s of the distortion parameters obtained from the HF calculations.

Non-spherical analysis of each complete set of silicon data shows that introduction of a tetrahedral distortion of the HF spherical 'prepared' distribution produces a highly significant improvement in the fit to the observed data. Subsequent introduction of a 4th order cubic distortion produces a highly significant improvement in the fit to the observed measurements only in the case of the Hattori *et al.* (1965) silicon data; while a significant improvement is obtained for the silicon data of Göttlicher & Wölfel (1959).

It is interesting to note that the tetrahedral plus 4th order cubic distortion of an HF spherical 'prepared' charge distribution gives a much better fit to the diamond than to the silicon powder measurements of Göttlicher & Wölfel (1959).

In the full-matrix least-squares refinements carried out here, there was found to be large correlation between the distortion parameters, and this was reflected by their large e.s.d.'s.

It is important to realize that the expression of a confidence level using the significance tests of Hamilton (1964, 1965*a*) refers to the fitting of the calculated and observed structure factors only and does not necessarily imply a similar confidence in the correctness or uniqueness of the original model. In the present context, such confidence will follow the successful application of these methods to other crystals. However, the recent success of the use of anharmonic temperature factors in the analysis of neutron diffraction data on various compounds with the fluorite lattice [*e.g.* CaF_2, Dawson, Hurley & Maslen (1967); UO_2, Rouse, Willis & Pryor (1968); BaF_2, Cooper, Rouse & Willis (1968)] in which a spectacular improvement in agreement is effected by the introduction of a single parameter, confirms the correctness of one essential part of the bonding models used here, namely the necessity to satisfy the point group symmetry at the atom site.

Conclusions

Calculated structure factors based on a model that includes the effects of a tetrahedral and a fourth order cubic distortion of the spherical 'prepared' charge distribution have given a highly significant improvement in the fit to the diamond powder measurements of Göttlicher & Wölfel (1959) and to the silicon single crystal data of Hattori *et al.* (1965), when the HF wave functions of Clementi (1965) are used to describe the spherical 'prepared' distribution.

It is maintained that it is preferable to use full-matrix least-squares, combined with the significance tests of Hamilton (1964, 1965*a*) to analyse the complete set of experimental data for bonding features since in this way more information is obtained about the parameters that define the more complicated structure factor model. This point is becoming well recognized and has been used by Rouse, Willis & Pryor (1968) to analyse their neutron diffraction data on UO_2.

The necessity for placing restrictions on the form of the radial functions associated with the non-spherical distortions, the large e.s.d.'s of the distortion parameters and the dependence of the parameter values on the basis wave functions chosen to describe the spherical 'prepared' charge distribution indicate the need for exercising caution in analysing the experimental measurements for bonding features.

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The Effect of Absorption in the Small Angle Diffraction of X-rays from Stacked Lamellae

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An expression for the scattering from a regular stack of lamellae is developed, maintaining an absorption term in the calculation. The effect of the absorption is to broaden peaks at small Bragg angles. The peaks sharpen with increasing order of diffraction. An expression for the lower angular limit of observable diffraction is evolved.

Introduction

The use of X-ray small angle scattering is widespread in the study of stacked lamellar polymer systems (see Geil, 1963, for a review) and has recently been used to study lamellar spinodal decomposition in an Al–Zn alloy (Rundman & Hilliard, 1967). The scattering by such systems yields peaks at small angles. In polymeric systems several orders are sometimes observed. Taking the stacking to be regular, the small angle peaks are conveniently treated as a diffraction phenomenon. The

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