puted on the basis of the iron atom phase contributions. Refinement was carried out by difference electron density calculations. Final coordinates are given in Table 2 where Fe(2), O(3), O(4) and B are in the 4(*c*) positions of the space group *Pnma* while Fe(1), O(1) and O(2) are in the 8(*d*) positions. A final *R* value of 0·086 was obtained for 187 observed reflections using isotropic temperature factors with $B=0{\cdot}52$ Å^2 for the iron atoms and $B=0{\cdot}90$ Å^2 for the lighter atoms. The calculated and observed values of the structure factors are given in Table 3.

The structure is an unusual one for boron compounds, as it contains the tetrahedral BO_4^{5-} anion. However, the crystals are isostructural with the mineral norbergite, $Mg_2SiO_4Mg(OH,F)_2$ (Taylor & West, 1929). Since for Fe_3BO_6 the conditions of preparation preclude the existence of divalent iron and hence of hydroxyl groups, both crystallographically independent iron atoms are octahedrally coordinated by six oxygen atoms, whereas in norbergite the octahedra coordinating the magnesium atoms contain both oxygen atoms and hydroxyl groups (or fluorine atoms). The accuracy of the coordinates and bond distances is limited by the almost exact overlap of O(1) and O(4) and the poor resolution of O(2) and O(3) in the *h0l* projection. The mean distances are 1·47 Å for the B–O bonds and 2·04 Å for the Fe–O bonds.

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The importance of the imaginary part of the scattering factor of bonded carbon.

By A. I. M. RAE and E. N. MASLEN, *Department of Physics, University of Western Australia, Nedlands, Western Australia*

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The theoretical evaluation of scattering factors for atoms in the bonded state is assuming increasing importance with the improvement in the accuracy of X-ray structure analyses. In particular, experimental evidence has been obtained for the distribution of σ-bonding electrons along the carbon–carbon bonds of the benzene ring (*e.g.* Rietveld & Maslen, 1965). A considerable amount of effort has been expended on the calculation of aspherical scattering curves (*e.g.* McWeeny, 1951, 1952, 1953, 1954; Freeman, 1959; Dawson 1961, 1964*a*, *b*). Most of this work refers to atoms in the ground or prepared valence state, which latter is spherically symmetric in the case of carbon (McWeeny, 1951) and is therefore not a sufficiently good approximation to account for the experimental observations. The only treatment of bonded carbon is that of McWeeny (1954) who derived aspherical scattering factors for the carbon atom in the diamond and graphite structures. Carbon in benzene would be expected to have a scattering factor similar to the latter to an approximation one order beyond that of spherically symmetric atoms. However, examination of the values given for the graphite scattering factor in Table 1 of McWeeny (1954) shows that, within the plane of the molecule, it is isotropic to within 0·02e. This extremely small variation is clearly not sufficient to account for the comparatively prominent σ-bond features which have been observed experimentally. Further examination of McWeeny's calculations shows that an imaginary contribution to the scattering factor has been ignored as insignificant. The present paper derives values for the imaginary contributions to the carbon scattering factor in diamond and in graphite and shows how it is related to the asymmetry arising from the σ-bonding. The practical application of complex scattering curves with particular reference to the structure of *p*-diphenylbenzene is discussed.

Diamond

The effective scattering factor for carbon in the diamond structure is given, using McWeeny's (1954) equation (5), by

$$f_0^e=f_{0c}+q_0{}^\sigma \sum_{n=1}^{4} f_0(\varrho_0{}^{\sigma n})+\tfrac{1}{2}\, q_{01}{}^\sigma \sum_{n=1}^{4} f_0(\varrho_{0_n}{}^{\sigma n})$$

where the first two terms are isotropic and the last, which is the relevant anisotropic term, may be expanded as,

$$\tfrac{1}{2}q_{01}^0 \sum_{n=1}^{4} f(\varrho_{0n}{}^{\sigma n}) \exp\,(2\pi i\, X\, R\, \hat{\mathbf{S}}\,.\,\hat{\mathbf{r}}_n)\,.$$

It follows from the above expression that the imaginary part of the scattering factor is antisymmetric with respect to $\hat{S}$ and reaches a maximum in a direction parallel to one of the bonds [the direction $\hat{S}_4$ as defined by McWeeny (1954)] where it is equal to,

$$\tfrac{1}{2}\, q_{01}{}^\sigma\, [\sin\,(2\pi\, X\, R)\, f_0'' - 3 \sin\,(2\pi\, X\, R/3)]\, f_0{}^\psi]$$

where ψ is the tetrahedral angle corresponding to $\cos\psi=-\frac{1}{3}$. (The minus sign is missing in McWeeny's paper but his results, which depend only on $\cos\,(2\pi\, X\, R \cos\psi)$ are correct.) In a direction perpendicular to the plane containing two bonds (McWeeny's $\hat{S}_3$) and in a direction bisecting the angle between two bonds (McWeeny's $\hat{S}_1$ and $\hat{S}_2$), the imaginary component falls to zero. Thus the anomaly whereby the scattering factors along $\hat{S}_3$ and $\hat{S}_4$ were almost identical is removed. The variations of the real and imaginary parts with X are illustrated in Fig. 1 and tabulated in Table 1.

Graphite

The effective scattering factor for graphite is given by McWeeny (1954) equation (7) as,

$$\begin{aligned} f_0^e=f_{0c}+q_0{}^\sigma f_{0v}+(q_0{}^\pi-q_0{}^\sigma)\, f_0(\varrho_0{}^\pi) \\ +\tfrac{1}{2}\, q_{01}{}^\sigma \sum_{n=1}^{3} f(\varrho_{0n}{}^{\sigma n}) \exp\,(2\pi i\, X\, R\, \hat{\mathbf{S}}\,.\,\hat{\mathbf{r}}_n) \\ +\tfrac{1}{2}\, q_{01}{}^\pi \sum_{n=1}^{3} f(\varrho_{0n}{}^{\pi \dot{a}}) \exp\,(2\pi i\, X\, R\, \hat{\mathbf{S}}\,.\,\hat{\mathbf{r}}_n) \end{aligned}$$

Table 1. *Effective scattering factors for carbon in the diamond and graphite structures*

The values for the real parts are taken from McWeeny (1954). The vectors $\hat{S}_i$ are defined in the text.

	X(a.u.)	0·00	0·05	0·10	0·15	0·20	0·25	0·30	0·40	0·50
Diamond (real)	$\hat{S}_1$ (S2)	6·00	5·17	3·53	2·33	1·83	1·67	1·59	1·38	1·17
	$\hat{S}_3$	6·00	5·17	3·56	2·41	1·92	1·73	1·59	1·37	1·17
	$\hat{S}_4$	6·00	5·18	3·57	2·42	1·93	1·74	1·60	1·37	1·17
(imaginary)	$\hat{S}_4$	0·00	0·06	−0·04	−0·15	−0·12	−0·04	0·01	0·00	0·00
Graphite (real)	$\hat{S}_1$	6·00	5·19	3·60	2·44	1·94	1·75	1·61	1·39	1·18
	$\hat{S}_2$	6·00	5·19	3·60	2·44	1·94	1·76	1·63	1·38	1·17
	$\hat{S}_3$	6·00	5·27	3·78	2·57	1·93	1·66	1·53	1·35	1·16
(imaginary)	$\hat{S}_1$	0·00	−0·02	−0·09	−0·14	−0·11	−0·03	0·01	0·00	0·00

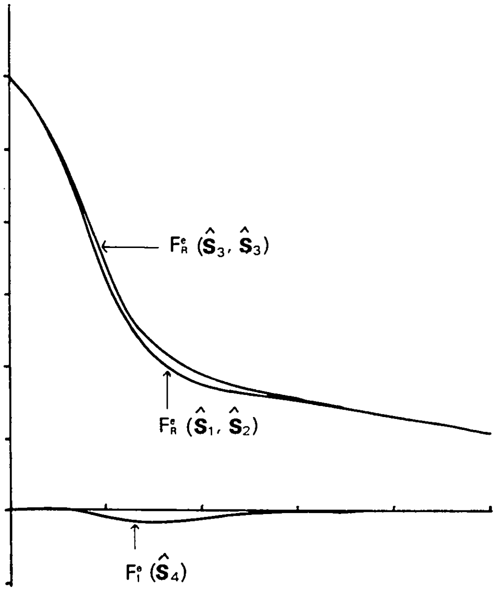

Fig. 1. The effective scattering factor for carbon in the diamond structure. $f_R{}^e$ and $f_I{}^e$ refer to the real and imaginary parts respectively. The vectors $\hat{S}_i$ are defined in the text.

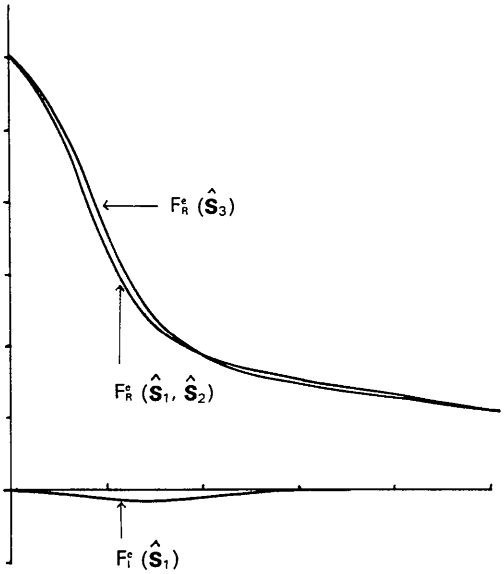

Fig. 2. The effective scattering factor for carbon in the graphite structure. $f_R{}^e$ and $f_I{}^e$ refer to the real and imaginary parts respectively. The vectors $\hat{S}_i$ are defined in the text.

where the last two are the relevant anisotropic terms. It again follows that the imaginary part is antisymmetric and reaches a maximum in a direction parallel to the bond (McWeeny's $\mathbf{S}_1$), where it is given by

$$\tfrac{1}{2}\sin(2\pi X R)\,(q_{01}{}^{\sigma} f_0'' + q_{01}{}^{\pi} f_\pi'')$$
$$-2\sin(\pi X R)\,(q_{01}{}^{\sigma} f_0{}^{\beta} + q_{01}{}^{\pi} f_\pi{}^{\beta\pi/2})$$

where $\beta = 120°$, *i.e.* $\cos\beta = -\tfrac{1}{2}$. McWeeny states that $\cos\beta = \tfrac{1}{2}$, but again this affects the imaginary and not the real component for the same reasons as stated above for the tetrahedral case.

The imaginary part falls to zero in the other two directions considered by McWeeny; *i.e.* in the plane of the molecule, perpendicular to the bond ($\hat{S}_2$) and perpendicular to the molecular plane ($\hat{S}_3$). The variation of the imaginary contribution with X is shown, along with the real parts in the three directions, in Fig. 2 and Table 1. The fact that

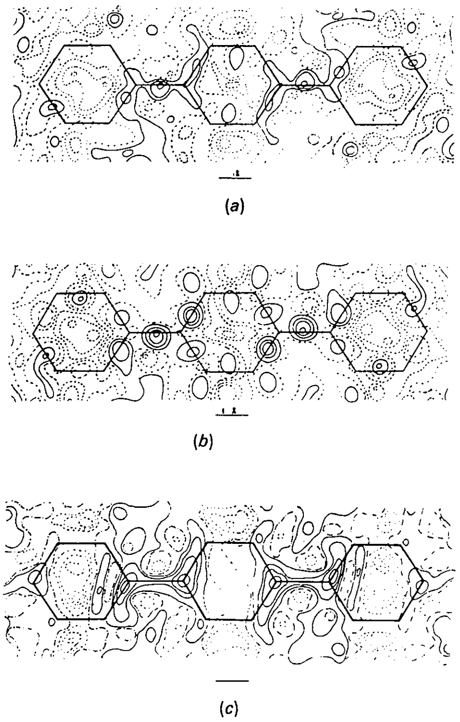

Fig. 3. Section through the difference synthesis of *p*-diphenylbenzene evaluated on structure factors which were calculated with (*a*) spherical scattering factors, (*b*) real aspherical scattering factors and (*c*) complex aspherical scattering factors. Negative contours broken, zero contour chain dotted, contour interval 0·05 e.Å^{-3}.

anisotropic component is finite along $\hat{S}_1$ and zero along $\hat{S}_2$ removes the almost complete isotropy of the atom in the plane of the molecule. The entire anisotropy due to σ bonding is then reflected in the imaginary contribution. Moreover, if the imaginary part is ignored, the electron density represented by the scattering factor is centrosymmetric, which is clearly incorrect. The point group symmetry of the graphite atom is $P3m$, but if the real part alone were used, the symmetry would be $P6m$.

Examination of Figs. 1 and 2 shows that the magnitude of the imaginary component of the scattering factor is as great as the total variation in the real part. This result is similar to those obtained by Dawson (1964*b*) for the prepared valence state scattering factors of a number of light elements. The asphericity of bonded carbon is about 30% of that of the prepared state of nitrogen. However, when an atom is symmetrically bonded, as in the case of diamond or graphite, the use of spherical scattering factors does not give rise to errors in position such as those resulting in the case of nitrogen (Dawson 1964*a*). Nevertheless, the use of aspherical scattering factors would be necessary for highly accurate measurements of thermal parameters or the detailed investigation of other features of the electron density.

Experimental application

The refinement of the structure of diphenylbenzene is described by Rietveld & Maslen (1965). Using the scattering curve for the isolated carbon atom evaluated by Freeman (1959), an R index of 9·2% was obtained. A section through the molecular plane of the final difference synthesis is shown in Fig. 3(*a*). Inspection of the distribution of electron density over the molecule shows that there are positive areas on all the carbon–carbon bonds, which are consistent with the evidence of σ-bonding electrons. It was decided to test the effect of using anisotropic scattering factors on the structure accuracy and the appearance of the difference synthesis.

Complex anisotropic scattering factors were evaluated for each reflexion using equation (7) of McWeeny (1954). Structure factors were calculated using first only the real part and then the total complex scattering factor. The R values, after scaling so that $\Sigma|F_o|=\Sigma|F_c|$, were 10·0% and 9·8% respectively. The difference syntheses evaluated using the two sets of structure factors are shown in Figs. 3(*b*) and 3(*c*). Where the real parts only were used, the effects due to σ-bonding have been, if anything, enhanced while, with the use of complex scattering factors, these features have been largely eliminated. There is still some residual electron density on and around the atoms forming the bond between the two rings, and the hollows in the middle of the end rings persist.

Similar calculations were made using the data by Cox, Cruickshank & Smith (1958) for benzene. In this case the structures were actually refined by least-squares using complex, real anisotropic and isotropic curves. The sum of the residuals was slightly lower for the complex than the real anisotropic case, but both refinements were inferior to that using the isotropic curve.

The failure of the use of complex scattering factors to lower the R index and the persistence of some of the anomalous features in the difference map indicate that the scattering factors are still not correct. In some respects the use of the isolated atom scattering factor of Freeman (1959) leads to better results than the use of the complex bonded atom curve. This may be due to the fact that the scattering factors for aromatic compounds are different from those of graphite, owing to the replacement of C by H. In particular there is no π-charge on the C–H bond and the σ-charges may also be affected. However, these would be expected to be second order effects which would, if anything, enhance the asphericity and acentricity of the atoms and it is difficult to see why spherically symmetric scattering factors should then give better values. It is more likely that the results are due to the higher accuracy of the isotropic form factors which were evaluated more recently, and it is clearly necessary for the bonded atom scattering factor to be recalculated before serious attempts are made to apply it to structure analysis.

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Notes and News

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International Union of Crystallography

Seventh General Assembly and International Congress Moscow, U.S.S.R., 12–21 July 1966

Exhibition of Photographs of Crystallographic Interest

The Commission on Crystallographic Apparatus of the Union is organizing an 'Exhibition of Photographs of Crystallographic Interest' at the Congress. This exhibition will be divided into two sections:

(*a*) Photographs of crystals; and

(*b*) Photographs of diffraction patterns from crystals.

Crystallographers and others are invited to participate actively in this exhibition by submitting suitable prints for display. The prints should be mounted on standard photographic mounting board (no glass or wooden framing) and