Directional Compton Profiles, X-ray Scattering Factors and the One-Electron Density Matrix for Diamond, Silicon and Germanium

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Abstract

Experimentally determined directional Compton profiles and the X-ray scattering factors $f(2,2,2)$ of crystalline diamond, silicon and germanium are fitted by using a model for the one-electron density matrix containing only interactions between nearest neighbours. It is concluded that such a model is only capable of reproducing the anisotropic properties of the electronic ground state, whereas isotropic ground-state properties require the consideration of intraatomic hybrid–hybrid interactions as well as interatomic interactions between higher-order neighbours.

1. Introduction

Among the quantities which are fitted to bond models, X-ray scattering data play a special role because they depend on the detailed shape of the electronic ground state. Phillips (1970) reproduced the ('forbidden') elastic X-ray scattering factor $f(2,2,2)$ of tetrahedral materials related to the ground-state charge density by starting from a bond charge between neighbouring atoms. Dawson (1967) successfully assumed a non-spherical charge distribution at the atom sites. Using a nonspherical wave function at the atom sites giving the same charge distribution as in Dawson's model, Weiss & Phillips (1968) attempted to describe the anisotropy of the ground-state momentum density as measured by inelastic X-ray scattering (Compton scattering).

In this paper we attempt to reproduce both the results of measurements of the $G = 2\pi/a_0 (2,2,2)$ component of the elastic X-ray scattering factor ($a_0 =$ lattice constant),

$$f(G) = \int \rho(\mathbf{r}) \exp(i\mathbf{G}.\mathbf{r}) \, d^3 r, \tag{1}$$

and the directional Compton profile (DCP)(in atomic units; $\omega =$ energy shift, $\mathbf{K} =$ scattering vector),

$$J_\mathbf{K}(\omega) = \int n(\mathbf{p}) \, \delta(\omega - K^2/2 - \mathbf{K}.\mathbf{p}) \, d^3 p, \tag{2}$$

of diamond, Si and Ge by using a model based on the well known sp^3 hybrid orbitals. The charge density $\rho(\mathbf{r})$ and the momentum density $n(\mathbf{p})$ are related to the first-order density matrix $\Gamma(\mathbf{r}|\mathbf{r}')$ *via*

$$\rho(\mathbf{r}) = \Gamma(\mathbf{r}|\mathbf{r}) \tag{3}$$

and

$$n(\mathbf{p}) = \int\int \Gamma(\mathbf{r}|\mathbf{r}') \exp[i\mathbf{p}(\mathbf{r} - \mathbf{r}')] \, d^3r d^3r'. \tag{4}$$

II. Local decomposition of the density matrix

It is straightforward to decompose the first-order density matrix into local contributions associated with the atom sites by using a set of localized electron states (Aikala, 1975*a,b*). It is by no means clear, however, under what circumstances such a decomposition can be terminated after a finite number of terms. For tetrahedrally coordinated crystals with two atoms per unit cell the most simple but, nevertheless, nontrivial parametrization is

$$\Gamma(\mathbf{r}|\mathbf{r}') = \Gamma_A(\mathbf{r}|\mathbf{r}') + \Gamma_B(\mathbf{r}|\mathbf{r}'), \tag{5}$$

where A and B are the atoms in the unit cell and the atomic contributions are taken as

$$\Gamma_j(\mathbf{r}|\mathbf{r}') = \sum_{v=1}^{4} \alpha_1^j \, \psi_j^v(\mathbf{r}) \, \psi_j^{*v}(\mathbf{r}')$$
$$+ \alpha_2^j \, \psi_2^j(\mathbf{r}) \, \psi_{j'}^{*v'}(\mathbf{r}' - \mathbf{R}_{jj'}), \tag{6}$$
$$j,j' = A,B.$$

ψ_j^v are the usual sp^3 hybrids associated with atom j. v, v' are such that the corresponding hybrids have maximum overlap (belong to the same bond). $\mathbf{R}_{jj'}$ is the distance vector between nearest neighbours. In this expression contributions associated with intraatomic hybrid interaction are neglected as well as interatomic interactions between higher-order neighbours.

Thus, with $p_\mathbf{K} \equiv \mathbf{p}.\mathbf{K}/K = K/2 - \omega/K$, the DCP is given by

$$J(p_\mathbf{K}) = \tfrac{1}{2} J^A(p_\mathbf{K}) + J^B(p_\mathbf{K}), \tag{7}$$

where J^A and J^B are the atomic contributions associated with Γ_A and Γ_B. The anisotropy of the Compton profile

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Table 1. *The parameters ζ_s, ζ_p, α_2, β, γ of the model density matrix of Ge, Si and diamond are optimally fitted to experimental DDCP's*

The goodness of the fit is represented by the reduced χ^2. $f(2,2,2)_{calc}$ is calculated using the left-hand model density matrix parameters.

Parameter	ζ_s	ζ_p	α_2	β	γ	χ^2	$f(2,2,2)_{calc}$	$f(2,2,2)_{exp}$
Substance (orientation)								
Ge ([100] − [110])	2·0	1·7	2·8 ± 0·6	1·64	0·66	0·7	0·14 ± 0·03	0·145 ± 0·02 (a)
([100] − [111])	2·0	1·7	2·8 ± 0·6	1·64	0·66	0·6		
Si ([100] − [110])	1·6	1·4	4·0 ± 0·8	1·61	0·68	2·4	0·18 ± 0·03	0·185 ± 0·03 (b)
([100] − [111])	1·6	1·4	4·0 ± 0·8	1·61	0·68	1·3		
diamond ([100] − [110])	1·6	1·55	4·0 ± 0·6	1·59	0·7	2·7	0·12 ± 0·02	0·144 ± 0·015 (c)
([100] − [111])	1·6	1·55	4·0 ± 0·6	1·59	0·7	1·6		

(a) Jennings (1969), (b) Fujimoto (1974), (c) Renninger (1955).

depends only on the second term in (6), since the contribution of the first (atomic) term is isotropic.

The scattering factor of the 'forbidden' reflexion of the diamond structure $f(2,2,2)$ is given by

$$f(2,2,2) = \tfrac{1}{2}[f^A(2,2,2) - f^B(2,2,2)]. \qquad (8)$$

It depends only on the second term in the decomposition of the density matrix. Thus, this term represents the effect of a 'bonding charge' on $\Gamma(\mathbf{r}|\mathbf{r}')$. For $\alpha_1^j = \alpha_2^j$, (5) and (6) yield the density matrix as obtained from the usual bond orbital model (Harrison, 1973).

III. Results

The parameters in (6) are fitted to our DCP results obtained for Si and Ge using a γ-Compton spectrometer (Bonse, Schröder & Schülke, 1979) and to the deconvoluted experimental data of Reed & Eisenberger (1972) in the case of diamond. The theoretical DCP's of Si and Ge are convoluted with the experimental resolution (Gaussian of FWHM = 0·54 a.u.),
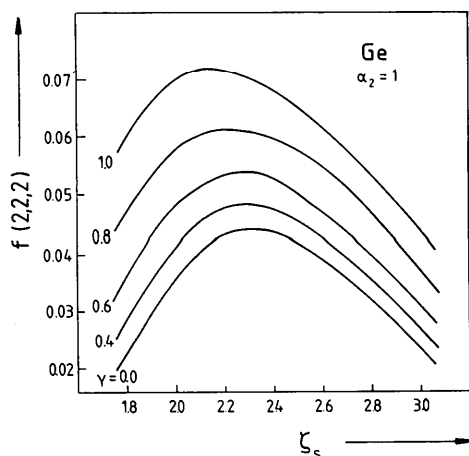
the theoretical DCP's of diamond are convoluted with a Gaussian of FWHM = 0·15 a.u. to account for residual resolution effects.

For $f(2,2,2)$ the experimental data given in Table 1 are used. Fitting to the difference between the Compton profiles (DDCP's) corresponding to different directions of the scattering vector $\mathbf{K}$ one obtains information about α_2. Then α_1 is given by normalization. As the atomic states, s and $\mathbf{p}$, constituting the sp^3 hybrids

$$\psi^\nu = \tfrac{1}{2}(\beta s + \sqrt{3}\, \gamma \mathbf{p}^\nu), \qquad (9)$$

Slater type orbitals (STO's) with ζ_s and ζ_p Slater exponents (Clementi & Raimondi, 1963) are used, $\mathbf{p}^\nu$ pointing in the direction of the νth bond. Figs. 1 and 2

Fig. 1. X-ray scattering factor as a function of STO exponent ζ_s for different hybrid parameters (γ) calculated for a bond model with $\alpha_2 = 1$.
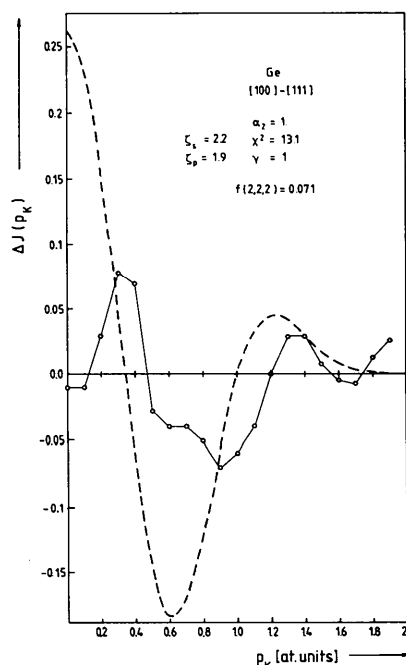

Fig. 2. Experimental DDCP ([100] − [111]) (O—O) for Ge together with a calculated DDCP ([100] − [111]) (———) with ζ_s = 2·2, ζ_p = 1·9, $\alpha_2 = 1$, $\gamma = 1$. No good fit is possible ($\chi^2 = 13\cdot1$).

show the results for $f(2,2,2)$ and the DDCP, respectively, as obtained for $\gamma = 1$ and $\alpha_2 = 1$ (limiting case of the bond orbital model, Harrison, 1973), where the ζ_s/ζ_p ratio is the same as in the free atom. It is not possible to fit the experimental data within this model simply by changing ζ_s and ζ_p even when taking into account the overlap between the hybrids along a bond, i.e. $\alpha_2 < 1$. Maintaining the simplicity of our model, the only way to improve the results is to take γ and α_2 as fitting parameters in addition to ζ_s and ζ_p. This means that the orthogonality of the hybrids at the atom sites is destroyed (Kane & Kane, 1978) and that α_2 is influenced by interactions between more than only nearest neighbours.

Figs. 3 to 6 and Table 1 show the results for the DDCP's of diamond, Si and Ge which were obtained by the following procedure. With a given value of α_2, the reduced mean-square deviations between theory and experiment, χ^2_{110}, by fitting the DDCP's ([100] − [110]) and χ^2_{111} by fitting the DDCP's ([100] − [111]), are calculated as a function of γ for various pairs of ζ_s, ζ_p, again with the same ratio ζ_s/ζ_p as in the free atoms. The reduced mean-square deviation χ^2 is defined as

$$\chi^2 = \frac{1}{N\Delta^2} \sum_{i=1}^{N} [g(p_i) - g(p_i)_{exp}]^2, \qquad (10)$$

where $g(p_i)$ and $g(p_i)_{exp}$ are the theoretical and experimental points, respectively, and Δ is the estimated experimental statistical error as indicated in Figs. 4 to 6. By changing also α_2, that set of α_2 and γ giving the
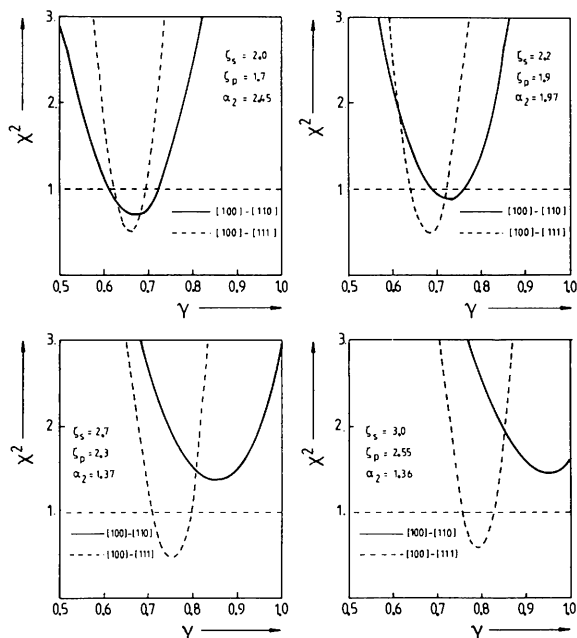
minimum value of $\chi^2_{110} + \chi^2_{111}$ was taken as the best fit. The appropriate pair of ζ_s, ζ_p was selected so as to give the minimum of both χ^2_{110} and χ^2_{111} at the same γ. In all cases such a pair could be found, which can be seen as a consistency test for our model, as far as anisotropic properties are concerned. In Fig. 3, as an example of such a fitting procedure χ^2_{110} and χ^2_{111} as functions of γ are shown for different ζ_s. In each case the situation of the best fit (minimum of $\chi^2_{110} + \chi^2_{111}$ by changing α_2) is shown.
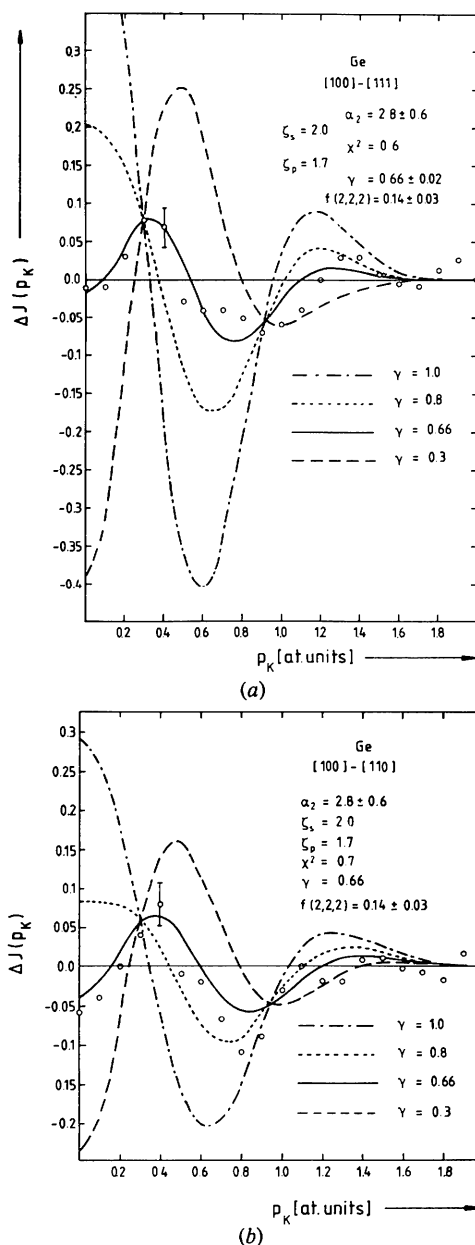

Fig. 4. Experimental and calculated DDCP's ([100] − [111]) (a) and ([100] − [110]) (b) of Ge with optimal fit obtained by $\alpha_2 = 2\cdot8 \pm 0\cdot6$, $\zeta_s = 2\cdot0$ ($\zeta_p = 1\cdot7$), $\gamma = 0\cdot66$ (solid line). Calculated DDCP's with same α_2 and ζ_s but $\gamma = 1\cdot0, 0\cdot8, 0\cdot3$ (broken lines).

Fig. 3. χ^2 for fitting Ge DDCP's ([100] − [111]) and ([100] − [110]) as a function of the hybrid parameter γ for different ζ_s (ζ_p) after minimizing $\chi^2_{110} + \chi^2_{111}$.

Table 1 contains the parameters resulting from the best fit of the DDCP data. The values of $f(2,2,2)$ as calculated using the same parameters are also given. The agreement with the corresponding experimental data is reasonable within the error bars.

It is important to note at this point that an attempt to reproduce the isotropic part of the DCP's by using this simple model for the one-electron density matrix was not successful for any set of the parameters ($\chi^2 \gg 1$).

IV. Discussion

We conclude that our model, although quite successful in describing the anisotropic ground-state properties, needs to be corrected when dealing with other ground-state properties such as the density of states, the total charge density and the total momentum density. It is well known that sp^3 hybridization is a good first-order

representation of the properties of the chemical bond in diamond, Si and Ge (Harrison, 1973; McFeely et al., 1974; Harrison & Ciraci, 1974). The actual values of the parameters γ and α_2 which we obtained by our fitting procedure indicate that, starting from the usual sp^3 hybrids, interactions between more than only nearest neighbours have to be taken into account explicitly, leading to contributions to the one-electron density matrix, which are related to second, third etc. nearest neighbours as well as interhybrid interactions at a given atom. In the tight-binding picture the sources of these interactions are twofold. On the one hand there are the 'real' interatomic interactions as described by the matrix elements of the Hamiltonian between the various ansatz functions. On the other hand there are effective interactions originating in the overlap matrix elements between the ansatz functions (nonorthogo-
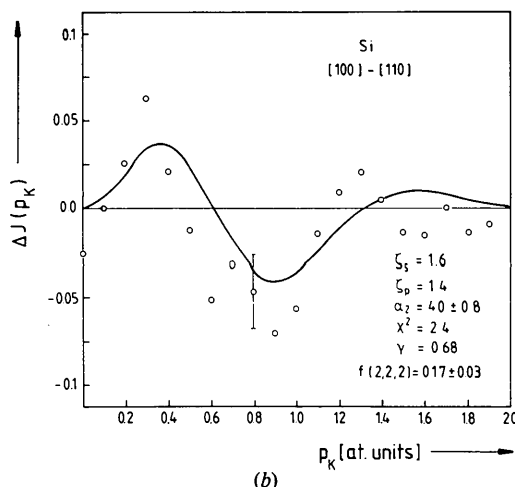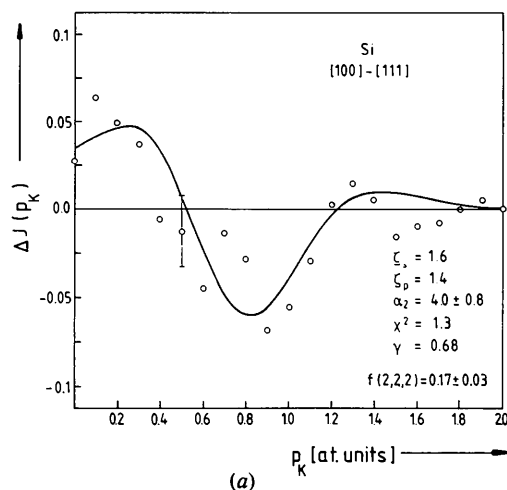

(a)

(b)

Fig. 5. Experimental and calculated DDCP's ([100] − [111]) (a) and ([100] − [110]) (b) of Si with optimal fit obtained by $\alpha_2 = 4\cdot0 \pm 0\cdot8$, $\zeta_s = 1\cdot6$ ($\zeta_p = 1\cdot4$), $\gamma = 0\cdot68$.
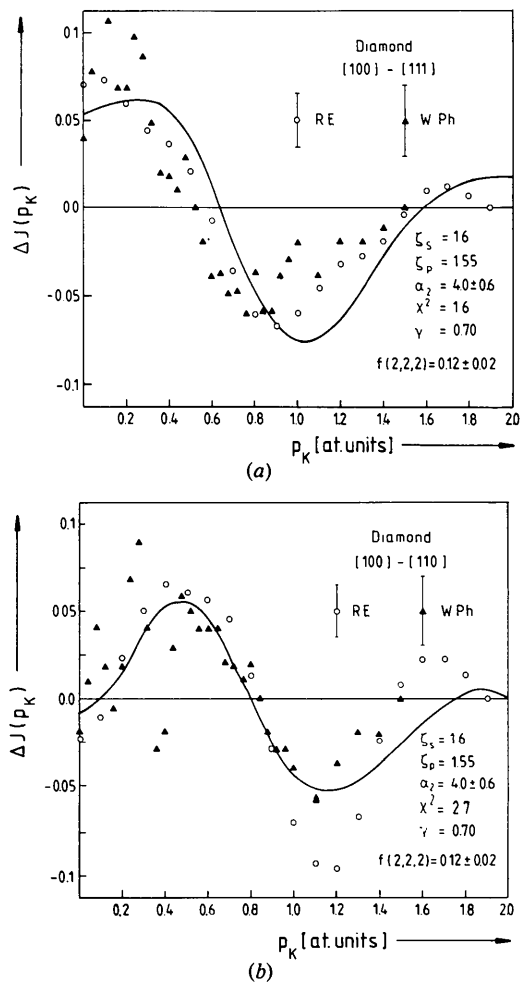

(a)

(b)

Fig. 6. Experimental (O: Reed & Eisenberger, 1972; ▲: Weiss & Phillips, 1968) and calculated DDCP's ([100] − [111]) (a) and ([100] − [110]) (b) of diamond with optimal fit obtained by $\alpha_2 = 4\cdot0 \pm 0\cdot6$, $\zeta_s = 1\cdot6$ ($\zeta_p = 1\cdot55$), $\gamma = 0\cdot70$. The fit was done only with the Reed & Eisenberger results.

nality). It is not obvious which of the two classes plays the major part in determining the properties of the electronic ground state.

For a quantitative description of the density of states of the diamond-structure semiconductors, starting from an sp^3 hybrid based tight-binding model, interatomic interactions between at least first and second nearest-neighbours have to be taken into account (Shevchik, Tejeda & Cardona, 1974).

Nonorthogonality effects yield further improvements of the resulting energy spectrum (Tejeda & Shevchik, 1976). For the charge density, it seems that the properties of the Hamiltonian are most important. Inclusion of d orbitals, $i.e.$ deviations from the sp^3 hybrid model, yields only small quantitative corrections (Kane & Kane, 1978).

For the total momentum density, orthogonalization effects seem to dominate, as has been shown in a recent model calculation (MacKinnon & Kramer, 1979). Starting from the usual sp^3 hybrid model with a Hamiltonian containing only intraatomic and first-neighbour interactions, the Fourier-transformed total momentum density has been shown to be quite insensitive to changes of the interaction parameters in the Hamiltonian. On the other hand, it turned out to be crucial for a quantitative description to take into account correctly the orthogonalization between the hybrids centred at different atoms.

The results of the present fitting procedure may be interpreted as pointing in the same direction. This is suggested from the relatively small values of γ ($\simeq 0.7$) indicating the importance of orthogonalization terms and the rather large values of α_2 ($\simeq 4.0$), showing the importance of higher neighbours.

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Ein einfacher Weg, Strukturinformation aus den diffusen Reflexen von Kristallen mit eindimensionaler Lagenfehlordnung zu erhalten

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Abstract

One-dimensionally disordered crystals consisting of layers that are equal with one another but stacked with displacement faults show sharp reflexions and diffuse streaks on their diffraction patterns. From the sharp reflexions alone an averaged structure (with fractional site-occupation factors) can be deduced. To obtain the real layer structure, the diffuse streaks have to be considered. A simple experimental and mathematical procedure is described which enables their use without the need of measuring integrated streak intensities or analysing the diffuse intensity profiles. Essentially, one has to measure the intensities of equal portions $\Delta\zeta$ at