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A pseudopotential calculation for Compton profile anisotropy in GaP

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Abstract. An empirical pseudopotential calculation has been carried out to study the anisotropy of Compton profiles between [100] and [111] directions of GaP. Compared to a purely local potential an l -dependent non-local potential is seen to explain the experimental anisotropy rather well. The contributions of the first and the second bands to the total measured anisotropy are found to cancel each other. This is found to be true even for Si. This means that the measured Compton profile anisotropies in compound and elemental semiconductors cannot be viewed in terms of the differences in the nature of the lowest band. Core-orthogonalization correction was found to have negligible effect on the Compton profiles.

1. Introduction

Compton scattering experiments using x- or γ -rays yield valuable information regarding the ground state electronic wavefunction in the scatterer. Together with the data from positron annihilation experiments such as Doppler broadening and 2γ angular correlation measurements Compton profile (CP) data yield a lot of information regarding the electron momentum distribution (EMD) in any system. However, unlike the positron annihilation experiments, where the presence of the positron disturbs the electron distribution, Compton scattering offers a clean probe for studying the EMD of the ground state electronic wavefunction in various systems. As far as interpretation is concerned, one usually employs a band wavefunction for the electrons and calculates the CP or its anisotropies depending upon the experimental data. A comparison with the experimental data enables one to test the validity of the various approximations involved in the calculation of the band structure.

As far as semiconductors are concerned the empirical pseudopotential technique has been found to be quite useful [1]. The optical properties are very well explained in terms of the energy band structure calculated in this formalism. Because of its simplicity it is quite tempting to use this to calculate CP as well as EMD anisotropies in elemental and compound semiconductors. In this model one replaces the actual crystal potential by a smooth pseudopotential. Because of this, one can expand the crystal wave function in terms of a set of plane waves which generate the interstitial part very accurately. However, the solution does not have wiggles in the core region which are not generated because of the neglect of the orthogonalization with core states, but the energy band structure is accurately reproduced. Although this technique is known to be insensitive to slight changes in the potential, it has been applied to

study CP anisotropies in the case of Si and Ge [2, 3] and later on in some compound semiconductors [4-7]. The absolute individual CPs in all cases are expected to be strongly peaked ones and in each of the systems studied so far viz Si, Ge and GaAs the experimental value of $J(0)$ was found to be smaller than the theoretical one. However, the anisotropies turned out to be in reasonably good agreement with experiment. This discrepancy in the low momentum region between theory and experiment is believed to be due to the neglect of the core orthogonalization correction. At the same time the agreement of the calculated anisotropy with experiment leads one to believe that such a correction is probably isotropic in nature, a fact which simplifies the problem. On Si the effect of core orthogonalization correction on EMD was studied by Shülke [3]. Surprisingly this correction was found to result in a negligible effect. As one knows the CP is an integral of the EMD and hence it remained to be evaluated how far the individual CPs are affected by such a correction.

In an earlier work we had carried out a directional CP measurement on GaP [5]. However, there has been no theoretical result to compare with the experimental data. In two recent studies on GaAs the CP anisotropies calculated by pseudopotential theory were found to agree very well with the measured data [6, 7]. Looking at the success of the theory in GaAs it was decided to carry out such a calculation in GaP. In addition in the present work it was also decided to include the core orthogonalization correction and to see how it affects the individual CPs and to see the corresponding anisotropy.

2. Theory

In the pseudopotential formalism the wavefunction for an electron in the ν th valence band at a k point is given by

$$\Psi_{\nu k}(\mathbf{r}) = \left(\frac{1}{\Omega}\right)^{1/2} \sum_{\mathbf{G}} C_{\nu k}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (1)$$

where $C_{\nu k}(\mathbf{G})$ is the coefficient of the plane wave corresponding to a given reciprocal lattice vector \mathbf{G} and Ω is the volume of the crystal.

In such a case the momentum density of the valence electrons is given as

$$\rho(\mathbf{p}) = \frac{1}{\Omega} \sum_{\nu k} \sum_{\mathbf{G}} |C_{\nu k}(\mathbf{G})|^2 \delta_{\mathbf{p}, \mathbf{k}+\mathbf{G}} \quad (2)$$

The ν and k summations are to be carried out over the occupied states.

The CP along a given direction z corresponds to an integral over the momentum density given by

$$J(q) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(\mathbf{p}) dp_x dp_y \quad (3)$$

with $q = p_z$.

Alternatively one uses a Fourier inversion scheme which allows one to work in position space. Here one first calculates the Fourier transform of $\rho(\mathbf{p})$ along a given

direction. This function which is an autocorrelation function in position space is given by

$$B(\mathbf{r}) = \int \rho(\mathbf{p}) e^{i\mathbf{p}\cdot\mathbf{r}} d^3p \quad (4)$$

One can derive the CP along a particular direction z as

$$J(p_z) = \int_{-\infty}^{\infty} B(z) e^{-ip_z z} dp_z \quad (5)$$

Using equation (3) in equation (4) one can get

$$B(\mathbf{r}) = \frac{1}{\Omega} \sum_{\nu\mathbf{k}} \sum_{\mathbf{G}} |C_{\nu\mathbf{k}}(\mathbf{G})|^2 e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (6)$$

In the present case, following [2, 3], $B(\mathbf{r})$ was first calculated for different directions of GaP and it was then Fourier transformed to obtain the required valence CP. The valence profile was normalized to eight electrons and then added to the free atom core profile [8]. In order to compare the theoretical result with the experimental data the total theoretical profile was convoluted with the residual instrumental function (RIF) of the experiment [9]. The CP thus obtained was finally normalized to a free-atom Hartree-Fock value of 19.34 electrons between 0 and 6 au. We have used both local and non-local pseudopotentials. The local pseudopotential form factors used in the present calculation are those of Cohen and Bergstresser [10]. The non-local potential parameters are taken from the data of Chelikowsky and Cohen [11]. The k -summation in equation (6) was carried out using ten special points in the Brillouin zone [12]. For each \mathbf{k} state the eigenvalue problem was solved taking 90 plane waves and treating them exactly. In order to calculate $J(p_z)$ for any direction z very accurately, the function $B(z)$ was calculated up to 30 au.

3. Results and discussion

The present theoretical valence CPs before RIF convolution corresponding to the [100] and [111] directions are given in table 1. The calculated $\Delta J_{100-111}$ anisotropy after RIF convolution is compared with experimental data in figure 1. From the figure one can notice that the local potential added to an l -dependent non-local potential results in a better agreement compared with a purely local potential. In addition, one can also notice that the theoretical anisotropy oscillates with a slightly shorter frequency compared with the experimental one. This has already been seen in Si and Ge [2]. Even our earlier results in GaAs confirms this [6].

If one looks at the valence bands in elemental and compound semiconductors one sees that unlike the elemental ones, in the compound semiconductors the lowest valence band is isolated from the remaining three. The partial contribution of this band to the total anisotropy was examined by Nara et al [3] and they found that in the low-momentum region the contribution of this band is very different in compound semiconductors. In order to have a close look at this we have carried out such a calculation in Si and GaP. In order to compare the individual band contributions with the experimental data, each band contribution to $B(\mathbf{r})$ along each direction was

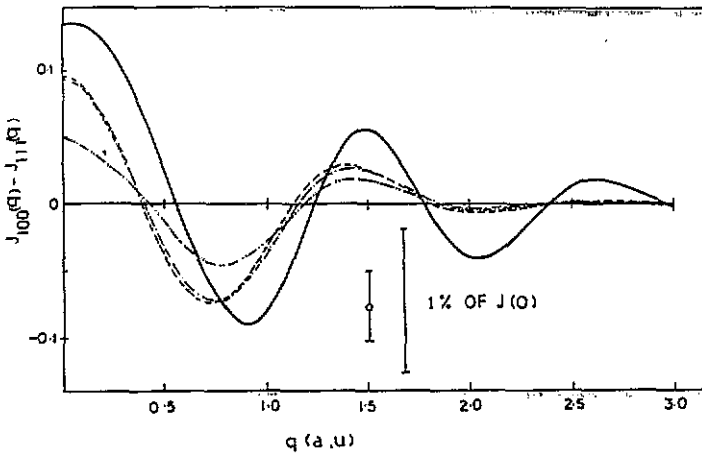


Figure 1. Experimental and theoretical CP anisotropy of GaP local (---), non-local (---), core-orthogonalized non-local (- · -) and experimental (—) CP anisotropy $\Delta J(g)_{100-111}$ of GaP.

Table 1. The calculated profiles along [100] and [111] directions of GaP with local and non-local pseudo-potentials. The profiles are not convoluted with RIF.

g (au)	Local [100]	Local [111]	Non-local [100]	Non-local [111]
0.0	5.613	5.634	5.706	5.658
0.1	5.598	5.622	5.698	5.626
0.2	5.487	5.456	5.515	5.453
0.3	5.302	5.187	5.334	5.227
0.4	4.933	4.836	4.985	4.898
0.5	4.377	4.303	4.363	4.369
0.6	3.606	3.685	3.581	3.731
0.7	2.710	2.906	2.662	2.902
0.8	1.982	2.057	1.939	2.040
0.9	1.307	1.361	1.272	1.324
1.0	0.803	0.804	0.784	0.745
1.1	0.470	0.408	0.449	0.370
1.2	0.253	0.217	0.230	0.194
1.3	0.151	0.131	0.145	0.133
1.4	0.079	0.077	0.068	0.066
1.5	0.059	0.052	0.059	0.046
1.6	0.027	0.034	0.021	0.029
1.7	0.024	0.022	0.022	0.020
1.8	0.012	0.013	0.009	0.011
1.9	0.006	0.007	0.005	0.006
2.0	0.005	0.004	0.003	0.003

calculated including the residual autocorrelation function (RAF) which is the Fourier transform of the RIF. The partial anisotropies of all four bands calculated this way for both Si and GaP are shown in figures 2 and 3 respectively. One can notice that the contribution of the first band for GaP starts from a positive value and that for Si starts from a negative value quite similar to the earlier results on GaAs and Sn [4]. However, it is interesting to notice that the second band contribution to CP anisotropy

in both GaP and Si is almost exactly opposite to that of the first band. In both GaP and Si the observed anisotropy is practically due to the third and the fourth bands, the major contribution coming from the fourth. This is quite similar to what one finds in metals where the nature of the profile is decided by the band close to the Fermi level [13].

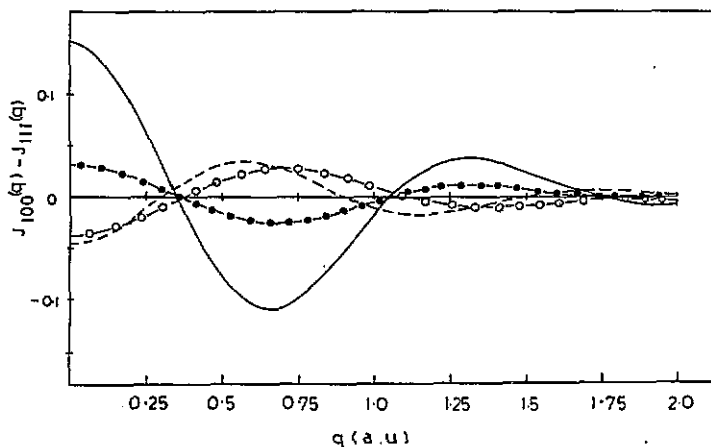


Figure 2. Band-by-band theoretical CP anisotropy $\Delta J(q)_{100-111}$ of Si. first band (—○—), second band (—●—), third band (---) and fourth band (—).

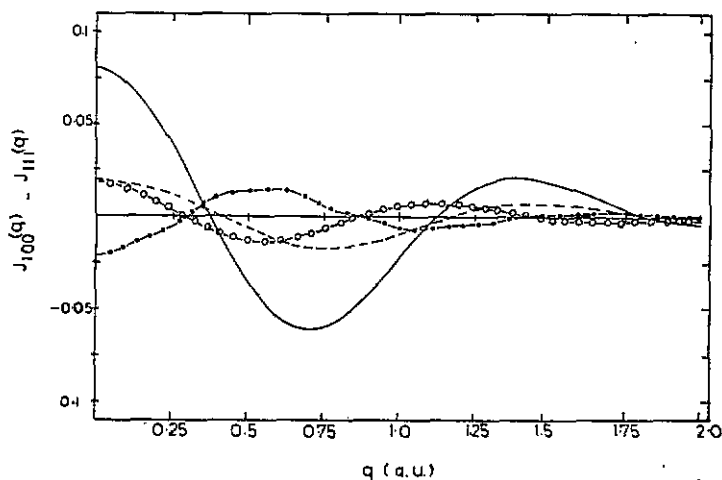


Figure 3. Band by band theoretical CP anisotropy $\Delta J(q)_{100-111}$ of GaP. The notations the same as in figure 2.

A beautiful band-by-band decomposition of the total charge density in GaAs and Si has been done by Cohen and Chelikowsky [1]. If one looks at the data on GaAs one notices that the first-band contribution is completely ionic and that that for the second band is completely covalent. The same is expected to be true for GaP. However, the contributions of these two bands to the experimental anisotropy are found to cancel

each other. Compared to this the third and the fourth band contributions are mixed in the sense that they have both ionic and covalent character. The presence of some amount of ionicity is expected to result in a reduced anisotropy. If one compares the CP anisotropy data in Si or Ge with that in GaP one actually notices a reduction in the same. Furthermore, because the anisotropy is primarily due to structure, one finds similar results in all semiconductors. In all tetrahedral semiconductors there is a strong σ -bond along the (111) direction. In case of diamond the $\Delta B_{111-100}(r)$ anisotropy has a dip at the first bond length. This is due to the $(2p, 2p)\sigma$ bond contribution. This has been shown by Pattison et al [14] in their analysis of the reconstructed three dimensional anisotropic autocorrelation functions. This has also been seen in GaAs [6, 7]. Since the situation in GaP is not far from this here also one gets a similar result (figure 4).

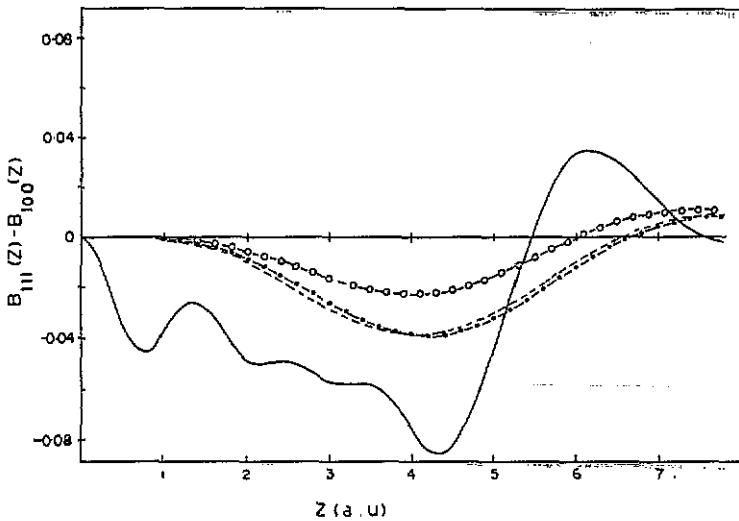


Figure 4. Theoretical local (—○—), non-local (— —), core-orthogonalized non-local (—●—) and experimental (—) $\Delta B(z)_{111-100}$ anisotropy of GaP.

Now let us proceed to evaluate the effect of core-orthogonalization on the CPs and the corresponding anisotropy. Inclusion of core-orthogonalization correction within a pseudopotential formalism is rather straight forward. The scheme has earlier been discussed elsewhere [3]. However a brief discussion on the relevant equations is presented in the appendix. The core orbitals used for this correction were taken from the tables of Clementi and Roetti [15]. The CP anisotropy obtained after applying this correction is also shown in figure 1. As has been found in case of valence EMD in Si, the CPs and $B(r)$ s for GaP did not change much after applying this correction. This means, within the pseudopotential formalism, although it is possible to explain the CP anisotropy rather well, it is not possible to explain the absolute CPs themselves even with the core-orthogonalization correction. The reason behind the failure could be the finiteness of the basis. In principle one should take an infinite number of plane-waves in the linear superposition which when orthogonalized to the core states is expected to produce the required oscillations in the core. The finiteness of the basis which is decided by convergence in energy eigenvalues is the culprit. We hope that a scheme such as the OPW method where orthogonalization with respect to core states

is included from the beginning would improve the results.

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Appendix

The pseudo-wavefunctions are orthogonalized to the core states according to

$$\Psi_{\nu\mathbf{k}}(\mathbf{r}) = N_{\nu\mathbf{k}} \left(\frac{1}{\Omega} \right)^{1/2} \sum_{\mathbf{G}} C_{\nu\mathbf{k}}(\mathbf{G}) \chi_{\mathbf{k}+\mathbf{G}} \quad (\text{A1})$$

where

$$\chi_{\mathbf{k}+\mathbf{G}} = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} - \sum_{\mathbf{c},\alpha} \mu_{\mathbf{k}+\mathbf{G}}^{\mathbf{c},\alpha} \Phi_{\alpha\mathbf{c}\mathbf{k}}(\mathbf{r}) \quad (\text{A2})$$

and

$$\mu_{\mathbf{k}+\mathbf{G}}^{\mathbf{c},\alpha} = \int \Phi_{\alpha\mathbf{c}\mathbf{k}}^*(\mathbf{r}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} d^3r. \quad (\text{A3})$$

Here $\Phi_{\alpha\mathbf{c}\mathbf{k}}(\mathbf{r})$ is a Bloch sum of tightly bound core orbitals of α th type $\phi_{\alpha\mathbf{c}}(\mathbf{r})$ centred about the atom site \mathbf{R} .

$$\Phi_{\alpha\mathbf{c}\mathbf{k}} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_{\alpha\mathbf{c}}(\mathbf{r} - \mathbf{R}) \quad (\text{A4})$$

The normalization constant $N_{\nu\mathbf{k}}$ is given by

$$N_{\nu\mathbf{k}} = \left[\sum_{\mathbf{G}} |C_{\nu\mathbf{k}}(\mathbf{G})|^2 - \sum_{\mathbf{G}} \sum_{\mathbf{G}'} \sum_{\mathbf{c},\alpha} C_{\nu\mathbf{k}}^*(\mathbf{G}) C_{\nu\mathbf{k}}(\mathbf{G}') \mu_{\mathbf{k}+\mathbf{G}}^{\mathbf{c},\alpha} \mu_{\mathbf{k}+\mathbf{G}'}^{\mathbf{c},\alpha} \right]^{-1/2} \quad (\text{A5})$$

The momentum density corresponding to (A1) is given by

$$\rho(\mathbf{p}) = \frac{1}{\Omega} \sum_{\nu\mathbf{k}} N_{\nu\mathbf{k}}^2 \sum_{\mathbf{G}} |D_{\nu\mathbf{k}}(\mathbf{G})|^2 \delta_{\mathbf{p},\mathbf{k}+\mathbf{G}} \quad (\text{A6})$$

where

$$\begin{aligned} D_{\nu\mathbf{k}}(\mathbf{G}) &= C_{\nu\mathbf{k}}(\mathbf{G}) - \frac{4\pi}{\Omega_0} \sum_{\mathbf{G}'} \sum_{nl} \sum_{\alpha} S^{\alpha}(\mathbf{G}' - \mathbf{G}) C_{\nu\mathbf{k}}(\mathbf{G}') \\ &\quad \times (2l+1) P_l(\cos\theta) R_{nl}^{\alpha}(|\mathbf{k} + \mathbf{G}|) R_{nl}^{\alpha}(|\mathbf{k} + \mathbf{G}'|) \end{aligned} \quad (\text{A7})$$

where

$$R_{nl}^{\alpha}(|\mathbf{k} + \mathbf{G}|) = \int_0^{\infty} R_{nl}^{\alpha}(r) j_l(|\mathbf{k} + \mathbf{G}|r) r^2 dr \quad (\text{A8})$$

and

$$\cos \theta = \frac{(\mathbf{k} + \mathbf{G}) \cdot (\mathbf{k} + \mathbf{G}')}{|\mathbf{k} + \mathbf{G}| |\mathbf{k} + \mathbf{G}'|}. \quad (\text{A9})$$

The autocorrelation function corresponding to (A5) is given by

$$B(\tau) = \frac{1}{\Omega} \sum_{\nu \mathbf{k}} N_{\nu \mathbf{k}}^2 |D_{\nu \mathbf{k}}(\mathbf{G})|^2 e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}. \quad (\text{A10})$$

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