Fourier-Transformed Compton Profiles: A Sensitive Probe for the Microstructure of Semiconductors

B. Kramer,* P. Krusius,† W. Schröder, and W. Schülke
Institut für Physik, Universität Dortmund, Dortmund, Federal Republic of Germany
(Received 1 April 1977)

Fourier-transformed experimentally determined valence Compton profiles of trigonal, polycrystalline, and amorphous Se are presented. For trigonal and polycrystalline Se, the experimental results are reproduced quantitatively by a self-consistent orthogonalized-plane-wave calculation. The results are discussed in terms of one- and two-electron densities. Because of the surpriseinly large differences between the amorphous and crystalline results we believe that the Fourier-transformed Compton profile is a powerful probe for the microstructure of semiconductors.

In the usual interpretation of Compton profiles (CP) of solids it is very difficult to separate valence- and core-electron contributions and to estimate multiple scattering and the influence of the resolution function. These problems can be essentially avoided by Fourier transformation of the measured CP's into r space.[1] Core electrons and multiple scattering contribute to the Fourier-transformed CP (FTCP) only at distances that are small compared to atomic distances, because the core states are localized and the multiple-scattering CP is almost constant.[1,2] The resolution function appears in the FTCP only as a multiplicative function instead of the convolution in momentum space.

In the impulse approximation the FTCP can be written in terms of the one-particle density matrix, $\gamma_1(\vec{r}\,|\,\vec{r}\,')$, of the electronic ground state as

$$B(\vec{t}) = \Omega^{-1}\int_\Omega d^3r\,\gamma_1(\vec{r}\,|\,\vec{r}+\vec{t}), \tag{1}$$

where $\vec{t}$ is a vector parallel to the direction of the momentum transfer in the inelastic x-ray scattering, and Ω is the normalization volume. For completely occupied bands we have in the one-electron approximation

$$B(\vec{t}) = \Omega^{-1}\sum_{n(\mathrm{occ})}\int d^3r\,\Phi_n(\vec{r})^*\Phi_n(\vec{r}+\vec{t}), \tag{2}$$

where $\Phi_n(\vec{r})$ is the Wannier function corresponding to the energy band n.

In this paper, we show that experimentally determined FTCP's are extremely sensitive to structural changes in a material and are therefore very useful in differentiating various structural phases with respect to their atomic and electronic structure. As an example, we use the elemental semiconductor selenium, which can easily be prepared in various crystalline and amorphous phases.

The CP's of trigonal Se were measured with the same apparatus as was used for polycrystalline and amorphous Se.[3] The trigonal and polycrystalline FTCP's are calculated using a self-consistent orthogonalized-plane-wave (OPW) procedure without any fitting parameter.[4] The results for the trigonal phase are shown in Fig. 1. Figure 1(a) shows a comparison between experiment and theory, corrected for resolution, for $\vec{t}$ parallel to the trigonal axis ($\vec{t}\parallel\vec{c}$) together with the Fourier-transformed resolution function. Figure 1(b) shows the curves for $\vec{t}\perp\vec{c}$. Figure 2 exhibits the experimental results for polycrystalline and amorphous Se together with a curve for polycrystalline Se, which was obtained by averaging the trigonal results according to $B(t) = \frac{1}{3}B_\parallel(t) + \frac{2}{3}B_\perp(t)$. Comparing the curves in Fig. 1, we notice that the agreement between theory and experiment is quite satisfactory.

A statistical accuracy of 0.6% was achieved at the center of the total CP measured in the momentum range ±10 a.u., corresponding to a resolution of 0.3 a.u. on the t axis. The zeros of the FTCP's up to 10 a.u. were found to be unaffected by these statistical errors.[5] The core states contribute only for $t \lesssim 2$ a.u. and do not affect the zeros either. Therefore, any interpretation of $B(\vec{t})$ should start from its zeros. The deviation in the positions of the zeros up to 10 a.u. in Fig. 1(a) is explained by the above reasons, and the difference in the depth of the first minimum at 5.3 a.u. may be assigned to multiple-scattering effects. The rather strong deviation in the amplitude of $B_\perp$ [Fig. 1(b)] between 8 and 12 a.u. may be of statistical origin, or partly due to an underestimation of the interchain interaction in the theory. Table I contains the calculated and experimental zeros of $B(\vec{t})$ for $\vec{t}\parallel\vec{c}$ together with the distances between the atoms along the chain. The positions

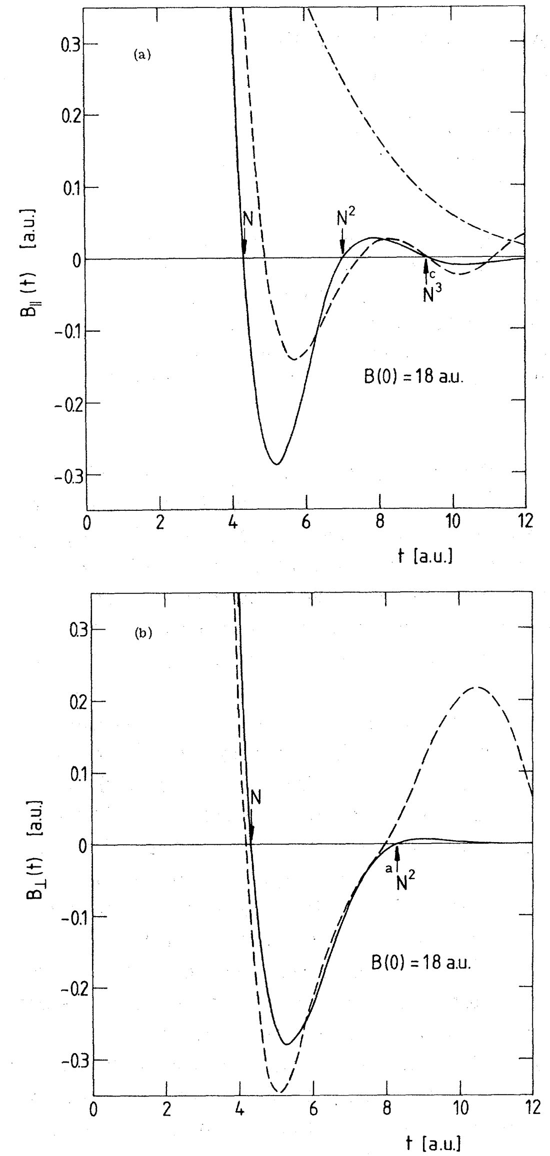

FIG. 1. FTCP's of trigonal Se for (a) $\vec{t}\parallel\vec{c}$ and (b) $\vec{t}\parallel\vec{a}\perp\vec{c}$. Dashed lines, experiment; full lines, theory. The resolution function (dash-dotted line) corresponds to a full width at half-maximum of 0.56 a.u. in momentun space. Arrows denote (a) distances between first (N), second (N^2), and third (N^3) neighbors within a chain, and (b) first neighbor (N) and interchain (N^2) distances. All curves are normalized to eighteen valence electrons per unit cell.

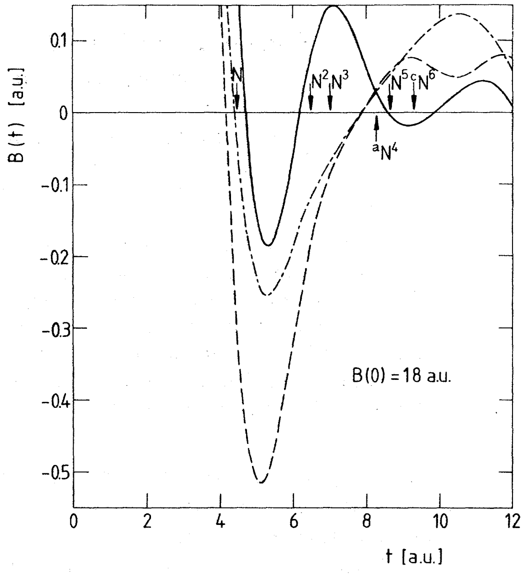

FIG. 2. Experimental FTCP's of polycrystalline (dashed line) and amorphous (full line) Se. The dash-dotted curve is obtained by directionally averaging the results for trigonal Se. Arrows labeled by N, N^2, etc., denote the distances between first, second, etc., neighbors in trigonal Se.

of the theoretical zeros up to 30 a.u. agree within less than 4% with the atomic distances, although these enter the first-principles calculation in a very indirect way via the space group. For $\vec{t}\perp\vec{c}$ a similar effect is observed.[5] For larger t's the magnitudes are beyond the computational accuracy.

From Eq. (2) the zeros occurring at lattice distances are easy to understand. According to the completeness relation, Wannier functions belonging to different elementary cells are orthogonal. Therefore $B(\vec{t}\neq 0)=0$ for vectors $\vec{t}$ of the Bravais lattice. Hence, we expect zeros at multiples of the lattice constants c and a for $\vec{t}\parallel\vec{c}$ and for $\vec{t}\perp\vec{c}$, respectively (Fig. 1 and Table I). The other ze-

TABLE I. Zeros t_j of the FTCP of trigonal Se for $\vec{t}\parallel\vec{c}$ in comparison with atomic distances, a_j, within a chain. Experimental values (first column) above $t = 10$ a.u. are not reliable because of the experimental statistical error. The atomic distances are determined by using the lattice constants of Ref. 6. All numbers are given in atomic units.

t_j(exp)	t_j(theory)	a_j
4.85	4.32	4.48
7.40	7.02	7.02
9.26	9.32	9.36
	12.98	12.89
	15.48	15.93
	18.56	18.72
	21.95	22.07
	24.20	25.17
	27.00	28.08

ros are obviously related to other properties of the Wannier functions and may indicate changes in the sign in some of them.[7] Surprisingly, these zeros agree quite well with the atomic distances. We do not yet have any unique explanation for this effect.

Comparing the experimental FTCP for the polycrystal with the directionally averaged curve (Fig. 2), we observe good agreement for the positions of the zeros. However, the depth of the minimum at 5 a.u. is a factor of 2 smaller in the averaged curve. This results from the rather crude averaging procedure, statistics, and residual multiple-scattering effects originating from different geometries of the crystalline and polycrystalline samples.[5]

The amplitude of the amorphous FTCP is considerably reduced compared to the polycrystalline curve. The first zero is clearly shifted to larger $\vec{t}$, whereas the second zero appears already at 6.2 a.u. in amorphous Se instead of at 7.8 a.u. as in polycrystalline Se. The same zeros within less than 2% and the same behavior of the amplitudes, within the statistical accuracy, were obtained in two independent measurements using the same sample geometry.[3]

The connection of the zeros in FTCP with properties of the ground state can be discussed using the density matrix. The probability for having two electrons simultaneously at positions $\vec{r}_1$ and $\vec{r}_2$ is given by the diagonal part of the two-particle density operator $\gamma_2(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)$. In the Hartree-Fock approximation

$$\gamma_2(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)=\gamma_1(\vec{r}_1|\vec{r}_1)\gamma_1(\vec{r}_2|\vec{r}_2)-\gamma_1(\vec{r}_1|\vec{r}_2)\gamma_1(\vec{r}_2|\vec{r}_1). \tag{3}$$

For macroscopically homogeneous systems Eqs. (1) and (3) yield

$$\gamma_2(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)=|B(0)|^2-|B(\vec{r}_2-\vec{r}_1)|^2. \tag{4}$$

If $\gamma_2(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)=|B(0)|^2$, the two electrons are not correlated. Therefore, from the OPW results in Fig. 1, one would conclude that electrons in two adjacent chains are almost uncorrelated, because $B_\perp \approx 0$ above $t=a$, the interchain distance. In the experiment $B_\perp$ and $B_\parallel$ are of the same order of magnitude for these t values, when taking into account the statistical inaccuracy. This indicates a correlation interaction beyond the Hartree-Fock approximation for electrons located at different chains.

At the zeros of FTCP γ_2 has maxima and $\gamma_2 = B(0)^2$. At these distances two electrons may be interpreted as being uncorrelated. This is similar to the behavior of the noninteracting Fermi gas, where the oscillations in γ_2 (Friedel oscillations) are related to the Fermi momentum. Comparing the decrease with t in the amplitudes of the measured FTCP's we observe that in amorphous Se FTCP decreases more rapidly than in the polycrystal. Thus, electrons in the amorphous phase are less correlated than in the polycrystal. It is intuitively clear that this may be attributed to the lack of long-range order.

At the present stage of our investigations we understand the features of $B(t)$ only qualitatively. Also, the experimental technique may be improved to obtain better resolution and statistics. Nevertheless, even with our present experimental accuracy, it is evident that the differences between the FTCP's of amorphous Se and its polycrystalline and trigonal counterparts are tremendous. Comparing our results with those obtained by using other experimental techniques (radial distribution function, optical absorption, photoemission, etc.) we must conclude that the inelastic x-ray scattering technique provides the most sensitive probe for testing the electronic and atomic structure of crystalline and amorphous systems. This is due to the fact that to a good approximation, the differential cross section is directly related to the nondiagonal part of the ground-state density matrix, whereas in other experiments transition probabilities and energy differences between the ground state and excited states play an important role.

This work was supported by the Deutsche Forschungsgemeinschaft. Stimulating discussions with Professor U. Bonse, Professor J. Treusch, and Dr. H. Leschke are gratefully acknowledged.

---

*Present address: Fachbereich Physik, Universität Essen, Gesamthochschule, Federal Republic of Germany.

†On leave of absence from Electron Physics Laboratory, Helsinki University of Technology, Helsinki SF-02150 ESPOO 15, Finland.

[1] P. Pattison and B. Williams, Solid State Commun. 20, 585 (1976); P. Pattison, W. Weyrich, and B. Williams, to be published.

[2] V. Halonen, B. Williams, and T. Paakkari, Phys. Fenn. 10, 107 (1975).

[3] U. Bonse, W. Schröder, and W. Schülke, Solid State Commun. 21, 807 (1977).

[4] P. Krusius, to be published.

[5] B. Kramer, P. Krusius, W. Schröder, and W. Schülke, to be published.

[6] P. Unger and P. Cherin, in *The Physics of Selenium and Tellurium*, edited by C. Cooper (Pergamon, New York, 1967), pp. 223–229.

[7] For Wannier functions, which do not change sign within in the unit cell, one would expect only lattice zeros in $B(\vec{t})$.

ERRATUM

MUON AND ELECTRON NUMBER NONCONSERVATION IN A $V-A$ GAUGE MODEL. B. W. Lee, S. Pakvasa, R. E. Shrock, and H. Sugawara [Phys. Rev. Lett. 38, 937 (1977)].

There is a misprint in the last sentence of p. 937; "$m_{L^0} \simeq 12$–30 GeV for $B = 10^{-9}$" should read "$m_{L^0} \simeq 12$ GeV for $B = 10^{-9}$." Also, in Ref. 1, "J. Ellis, M. M. Gaillard, and D. V. Nanopoulos, to be published" should read "J. Ellis, M. K. Gaillard, and D. V. Nanopoulos, Nucl. Phys. B109, 213 (1976)."