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A study of the electronic structure of polyethylene with Compton scattering experiments

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Abstract

In the present study, we present results for the electronic momentum density of polyethylene obtained by Compton scattering of X- and γ-ray radiation. Measurements taken along *c*-axis, which is the axis of the primary carbon chain of an oriented polymer macromolecule, are compared to measurements taken perpendicular to it (a, b direction). The analysis is based on the examination of differential Compton profiles between two crystallographic directions, and on the autocorrelation function $B(\vec{r})$, aiming to derive information for the spatial charge distribution. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

For many years, the technique of Compton scattering of X- and γ-ray radiation has been applied in different materials such as metals, alloys, magnetic materials [1–3] and even superconductors [4,5], yielding unique information on their electronic structure. Recently [6], there has been an attempt to extend such experiments to the study of polymers, a vast category of materials with much interest because of their applications.

In the present work, we employ Compton scattering spectroscopy to polyethylene (PE), one of the simplest macromolecules, in order to probe experimentally, the electronic momentum density (EMD).

In a Compton scattering experiment an incident monochromatic beam of X- or γ-ray photons is scattered by the sample. The inelastically scattered radiation, deflected through a fixed scattering angle, is measured as a function of energy. By converting this spectrum to a momentum scale, the so-called Compton profile (CP) is obtained. The CP is the projection of the EMD, $n(\vec{p})$, of the scatterer on the scattering vector $\vec{k}$, which is the vector difference between the wave vectors of the scattered, $\vec{k}_s$, and incident, $\vec{k}_i$, beams,

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respectively. With $\vec{k}$ chosen along the z-axis, and using the impulse approximation (IA), the CP is given by the expression [1,2]:

$$J(p_z) = \int_{p_x}\int_{p_y} n(p_x, p_y, p_z)\,\mathrm{d}p_x\,\mathrm{d}p_y. \tag{1}$$

Since $n(\vec{p})$ is a probability density, the CP obeys a normalization rule $\int_{-\infty}^{+\infty} J(p_z)\,\mathrm{d}p_z = \int_{-\infty}^{+\infty} J(q)\,\mathrm{d}q = Z$, with Z the total number of electrons, while q is related to $\vec{p}$ and $\vec{k}$ by $q = \vec{k}\cdot\vec{p}/|\vec{k}|$. The CP is symmetric with respect to the so-called Compton peak $J(0)$ at the recoil energy [2]. The EMD is related to the momentum wave function $\chi(\vec{p})$, by $n(\vec{p}) = |\chi(\vec{p})|^2$, which, by Fourier transform, yields the real-space wave function $\psi(\vec{r})$. In this way, Compton scattering experiments provide experimental data that can be compared to theoretical calculations.

By aligning a characteristic crystallographic direction of the sample parallel to the scattering vector, it is possible to investigate the EMD in this direction through the so-called Directional CP (DCP). DCPs have been extensively used in the past in the study of various materials in order to reveal the differences of EMD in different directions [3]. Data processing includes background subtraction, correction for absorption and Compton cross-section, followed by a conversion to atomic units of momentum and normalization to the total number of electrons. Most of these corrections as well as the usual correction for absolute CPs (e.g. multiple scattering, etc.) barely affect the ultimate $\Delta J'$s, as they cancel out in the subtraction process.

For the purposes of this study DCPs of high oriented PE have been measured, at room temperature, for two directions, parallel to c-axis, $J\|$, which is the axis of the primary carbon chain, and perpendicular to it $J_\perp$, aiming to investigate differences of EMD between these two directions.

2. Experimental procedures

In the present work two independent experimental setups have been used. We had the first confirmation of the validity of the method carrying out DCP measurements on polymeric material at the synchrotron beam line DW31A of the Laboratoire d'Utilization du Rayonnement Electromagnétique in Orsay, France. We have observed differences in CPs taken in two different directions although without having very good statistical accuracy. In order to increase the statistical accuracy and the transferred momentum in the measured DCPs, measurements on the same sample have been repeated using a γ-ray (59.54 keV) Compton spectrometer at the Solid State Physics Laboratory of the Patras University, Greece.

The synchrotron radiation beam is monochromatized by Bragg reflection from a double [2 2 0] silicon monochromator to produce an energy of 21 keV [7]. The beam is focused on the PE sample which is a rectangular bar $6\times6\times22\,\mathrm{mm}^3$ (see fw. sample preparation). A high resolution focusing spectrometer is used to energy analyze photons deflected from the sample through an angle 135°. Photons of the same energy are focused at a single point on the Rowland circle and detected by a position-sensitive detector (PSD). The resolution function, deduced from the FWHM of the thermal diffuse scattering peak, was 0.17 a.u. of momentum.

The γ-rays spectrometer utilizes a 300 mCi ^{241}Am disc source in a 160° scattering angle geometry, insuring also a well-fixed scattering vector, $\vec{k}$, which is indispensable for DCP measurements. The scattered radiation was measured with a HPGe detector cooled by a LN_2 cryostat. The spectrometer has a relatively good total resolution of 352 eV FWHM at 59.54 keV, corresponding to 0.54 a.u. of momentum near the peak of the CP.

Thin rectangular slices of semicrystalline PE ($6\times6\times2\,\mathrm{mm}^3$) have been stretched in order to produce oriented samples. They have been stretched to about twice their original length and the degree of orientation has been checked by X-ray diffraction. Fig. 1 is a typical X-ray diffractogram showing characteristic peaks of unoriented (before stretching) and oriented samples taken along c-axis and perpendicularly to it. The peaks from ab-planes of semicrystalline sample are vanishing in the case of the stretched one, when XRD is taken along c-axis. Similarly, peaks from planes parallel to c-axis are diminished in the

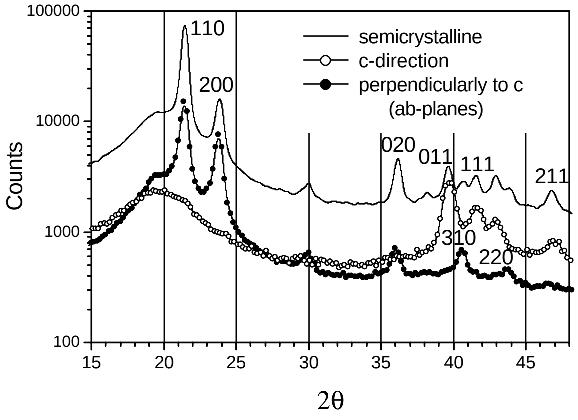

Fig. 1. XRDs from semicrystalline and oriented polyethylene for estimation of the orientation degree. Lines [0 1 1], [1 1 1], [2 1 1] from *ab*-planes are vanishing in the stretched samples whereas [1 1 0], [2 0 0], [0 2 0], [3 1 0], [2 2 0] from planes in *c*-direction remain indicating high orientation along the *c*-axis.

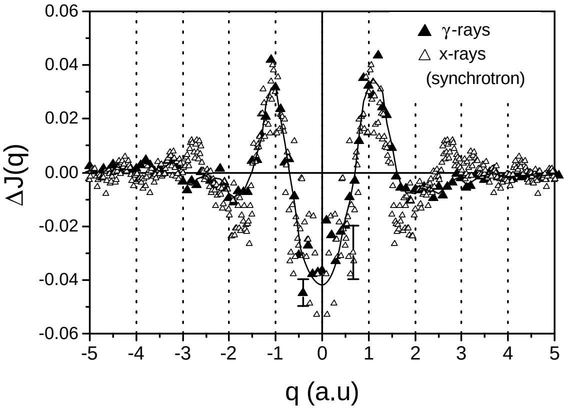

Fig. 2. Anisotropy of the Compton profile $\Delta J(q)$, measured along the *c*-axis and perpendicular to *c*, with γ-rays and X-rays synchrotron radiation shown in the range of −5–5 a.u. Error bars indicate the statistical error. For clarity, solid lines have been drawn through the experimental points from the γ-rays experiment.

XRD perpendicularly to it, implying a high degree of orientation. Several slices prepared and checked in this way have been put together to form a sample of $6 \times 6 \times 22\,\mathrm{mm}^3$ used in both the experimental setups. The orthogonal shape of the sample, with the long side coinciding with *c*-axis facilitates the alignment of the sample with respect to the scattering vector in order to take measurements in certain crystallographic directions and this applies to both XRD and inelastic scattering experiments.

3. Results and discussion

In the case of γ-rays measurements, more than 3×10^7 counts were accumulated under the CP for each spectrum (8×10^5 at the Compton peak), in order to obtain high statistical accuracy, whilst in the case of synchrotron measurements there was an average of 5×10^7 counts under the CPs (2.5×10^5 at the Compton peak). In all the cases, the CPs were normalized to a total of 16 electrons, which is the sum of all electrons in a (–CH_2–CH_2–) polymer unit, between −7 and 7 a.u. of momentum, corresponding to the number of electrons of the sample that can be excited from the incident photons.

In Fig. 2, the obtained difference of CPs (ΔJ) from X-rays synchrotron radiation and γ-ray are shown together for comparison. In each set of measurements ΔJ is the difference of CPs taken along *c*-axis minus that taken perpendicularly to it (along *ab*-planes).

The results appear to be in general agreement and the most prominent characteristic is an oscillatory behaviour in ΔJ. This oscillatory behaviour cannot be attributed to the CP taken perpendicularly to *c*-axis, where it is expected to be smooth due to the uniform distribution of carbon and hydrogen atoms on the *ab*-planes. On the contrary, in the direction along the *c*-axis in which the carbon atoms chain is stretched, the CP is expected to reflect the distinct periodicity of C–C bond coming along this direction, and hence be responsible for the oscillations.

The observed oscillatory behaviour can be further analyzed using the autocorrelation function $B(\vec{r})$, in order to extract more information concerning the real space. $B(\vec{r})$ is the Fourier transform of the momentum density

$$B(\vec{r}) = \int n(\vec{p})\mathrm{e}^{-\mathrm{i}\vec{p}\vec{r}}\,\mathrm{d}\vec{p}, \tag{2}$$

where

$$n(\vec{p}) = \sum_i \chi_i(\vec{p})\chi_i^*(\vec{p}) \quad \text{and} \quad \chi(\vec{p}) = \int \psi(\vec{r})\mathrm{e}^{-\mathrm{i}\vec{p}\vec{r}}\,\mathrm{d}\vec{r}.$$

It can easily be shown [8] that $B(\vec{r})$ is the sum of autocorrelation functions of the one-electron configuration space wave functions $\psi_i(\vec{r})$, along one specific direction:

$$B(\vec{r}) = \sum_i B_i(\vec{r}) = \sum_i \iiint \psi_i(\vec{s})\psi_i^*(\vec{s}+\vec{r})\,\mathrm{d}\vec{s}.$$

From Eqs. (1) and (2) it follows that

$$B(z) = \int J(p_z)\mathrm{e}^{-\mathrm{i}p_z z}\,\mathrm{d}p_z.$$

Positive or negative signs of $B(\vec{r})$ are related to the correlation of the electron wave functions and when combined with theoretical models, one can reach useful conclusions for their character.

Fig. 3 show the autocorrelation function $B(z)$ deduced by Fourier transform of the experimental CPs. In both cases (i.e. along *c*-axis and perpendicularly to it), we observe some common characteristics. Both $B(z)$s are of the "one node" type which is known to represent overlapping of p-type bonding molecular orbitals, (2p,2p)σ-MOs. The positive sign area which extends up to about 2.2 Å represents bonding area of MOs, i.e. bond lengths up to this limit [8], while the negative sign area represents the antibonding contributions.

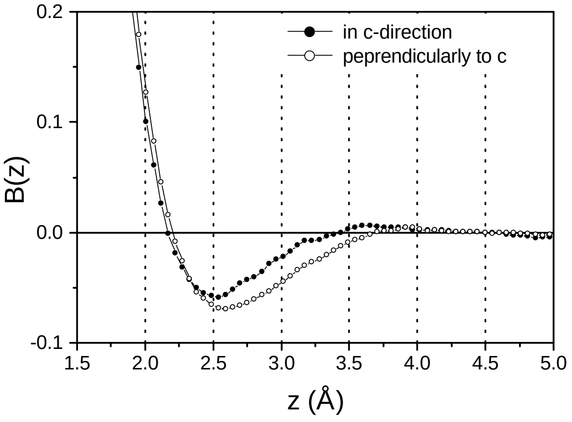

Fig. 3. $B(z)$ function as deduced from the experimental CPs, shown in the area of interest i.e. around its zero values.

In order to investigate the observed differences in $B(z)$ in two directions, we use the Fourier transform of CP anisotropy, ΔJ, to obtain $\Delta B(z)$, which according to the bond oscillation principle [1], reveals the frequency components in the anisotropy oscillations. Since the reciprocal space of the momentum space is the real space, from $\Delta B(z)$, the involved bond lengths can be deduced.

The experimental result is shown in Fig. 4, from which we observe an anisotropic behaviour with two areas of opposite sign. The negative sign area up to 2.2 Å implies that, the charge distribution in the *c*-direction is smaller than the one perpendicular to it, and the positive area between 2.2 and 3.9 Å, corresponds to the reverse situation.

There is a minimum at 1.4 Å in $\Delta B(z)$, that should correspond to the projection of the C–C bond length of PE along the direction of the scattering vector which is the direction of the *c*-axis. In the case of PE, the geometry of the C–C bond with a length of 1.54 Å and an angle of 109.8° between successive carbon atoms, implies a projection of 1.26 Å along the *c*-axis. This value is in very good agreement with the measured position of 1.4 Å for the negative peak. The positive peak at 2.8 Å corresponds to a multiple

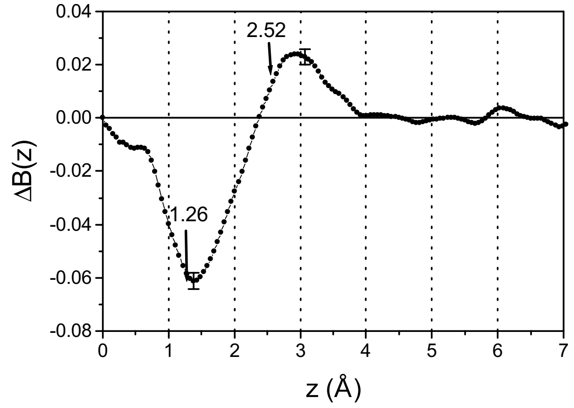

Fig. 4. $\Delta B(z)$ as deduced from CPs anisotropy (*c* minus *ab*-direction). The minimum corresponds to the projection of the C–C bond along the *c*-axis, and the maximum is a multiple of this value. Arrows indicate the theoretically expected positions of minimum and maximum.

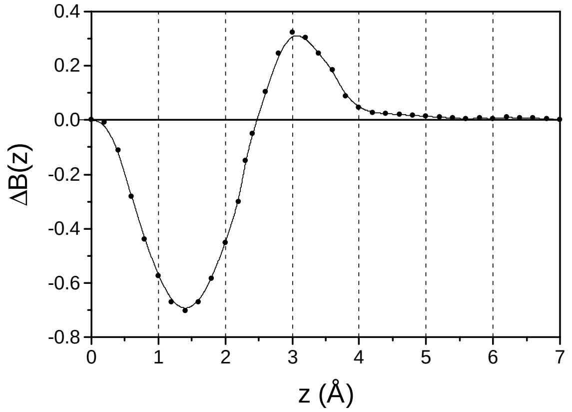

Fig. 5. The result of a simple calculation for $\Delta B(z)$ that is described in Section 3. The basic behaviour of the experimental results is reproduced (see Fig. 4).

of this characteristic length. The small differences observed in the experimental results are due to a finite accuracy in the orientation of the scattering vector, but mainly due to the non-perfect orientation of the sample, which is an inherent situation in most polymeric materials.

As further confirmation of the character of the involved MOs, we performed a simplified calculation taking the overlap of two p-type atomic orbitals (AOs), in a σ-bonding state as representing two different carbon atoms, considering for simplicity the remaining p-type AOs in antibonding state. The AOs are Slater type orbitals (STO), using as minimum basis set three Gaussian functions (STO-3G, single ζ) in the framework of linear combination of atomic orbitals (LCAO).

Two directions of overlapping have been chosen in order to simulate the experimental measurements taking into account the geometry of PE molecule. The result is shown in Fig. 5, where it can be seen that in spite of the simplicity of the model, the basic behaviour of the experimental results is reproduced. A more detailed ab initio calculation using STOs in more accurate primitive basis set (STO-NG), in comparison with these experimental results, should reveal the most appropriate electron wave functions described either in the frame of valence bond (VB) theory (hybridization) or molecular orbital (MO) theory (LCAO) for the description of the homopolar bond.

4. Conclusions

The results of this study produce strong experimental evidence that Compton scattering spectroscopy, which has been used successfully for many years in the study of electronic structure of a variety of materials, is equally useful in the study of polymeric materials.

The basic character of the involved molecular orbitals has been confirmed to be of p-type, (2p,2p)σ-MO, and the C–C bond length has been estimated to the expected value of 1.54 Å.

Accurate theoretical calculations are needed in order to reveal the exact electronic momentum density within the polymeric bond.

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References

[1] B.G. Williams (Ed.), Compton Scattering, McGraw-Hill, New York, 1977.
[2] M.J. Cooper, Rep. Prog. Phys. 48 (1985) 415.
[3] S.W. Lovesey, S.P. Collins, X-ray Scattering and Absorption by Magnetic Materials, Clarendon Press, Oxford, 1996.
[4] D.L. Anastassopoulos, G.D. Priftis, A.A. Vradis, J.G. Noudem, R. Tournier, Physica C 321 (1999) 231.
[5] M. Marangolo, et al., Phys. Rev. B 58(12) (1998-II) 7593.
[6] D.L. Anastassopoulos, G.D. Priftis, C. Toprakcioglu, A.A. Vradis, Phys. Rev. Lett. 81 (4) (1998) 830.
[7] J. Frouin, Y. Garreau, G. Loupias, D. Raoux, J. Tarbès, Nucl. Instrum. Methods A 266 (1988) 484.
[8] W. Weyrich, P. Pattison, B.G. Williams, Chem. Phys. 41 (1979) 271.