 Fullerite C\textsubscript{60} optical constants in the C 1s NEXAFS region

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Abstract. Using data on the absorption cross sections the refraction coefficient spectral dependence \( n(E) \) and the spectra of the remaining optical coefficients (reflection coefficient, phase shift, and atomic form factor) in the fullerite C\textsubscript{60} C 1s near edge X-ray absorption fine structure (NEXAFS) region (280–350 eV) were determined. For the \( n(E) \) calculations the Kramers-Kronig integral relations (KKRs) were used. The KKR computations were performed using data on atomic carbon absorption cross sections in the 10–30000 eV range and on solid and gaseous C\textsubscript{60} – in the 0–120 eV. Absorption cross section spectrum in the fullerite C\textsubscript{60} C 1s NEXAFS region were measured.

1. Introduction

The resonant nature of the X-ray radiation interaction with certain chemical elements in the region of the ionization thresholds of core electrons leads to the appearance of a near edge X-ray absorption fine structure (NEXAFS) in the absorption spectrum in the vicinity of which an anomalous refraction is observed. The X-ray refraction coefficient \( n \) and other optical constants (absorption and reflection coefficients and atomic form factors) are fundamental spectral characteristic that contains unique information about the material. The determination of optical constants spectral dependencies for a wide range of materials and chemical compounds in the resonant absorption regions is an actual task in modern material science. It was demonstrated in works [1-3] that data about a sample obtained from absorption and reflection spectra can contain independent and complementary information. The spectral dependencies of optical constants in resonant absorption region demonstrate a complex non monotonic behavior that lead to difficulties in their experimental determination.

It is known that the real and imaginary parts of the complex permittivity, refraction and reflection coefficients, and atomic form factor are related to each other in a wide energy range by the Kramers-Kronig integral relations (KKRs) [4, 5]. KKR are general in nature and do not depend on the state of aggregation, structure, and atomic composition of the studied matter. These relations make it possible to obtain the numerical value of one optical constant (real/imaginary) for a given energy \( E \), through the full spectrum of another optical constant (imaginary/real), determined by integrating over the entire spectral range. In particular, spectral dependencies of the absorption cross sections \( \sigma(E) \) and the refraction coefficient \( n(E) \) are related by the KKR and can be calculated through each other if they were measured in an entire (wide) energy range. Spectra of all other optical constants can be obtained from the \( \sigma(E) \) and \( n(E) \).

The currently available methods for obtaining data on refraction coefficients in the NEXAFS region are indirect and aimed at obtaining the values of the dispersion corrections for the atomic form
factor [6-8]. In the work [9] simultaneous implementation of the total electron yield (TEY) method and X-ray reflection spectroscopy using the KKRs allowed the authors to obtain the absorption coefficients and to deduce the optical constants for HfO$_2$. It was shown that this technique required small grazing incidence angles (less then ~4°) and is extremely surface-sensitive. Moreover, in our previous works [10, 11] it was demonstrated that TEY method can be successfully used for spectral dependence cross section measurements near the C 1s absorption edge of carbon-containing compounds with correct consideration of the non-monochromatic background and instrumental distortions. In the current study using the TEY method a detailed set of optical constants at photon energies in the vicinity of the fullerite C$_{60}$ C 1s NEXAFS region was determined.

2. Methods
To study the spectral dependencies of the absorption cross sections in NEXAFS region, a 99.98% pure fullerite powder with a crystallite size of 0.05–0.5 mm (produced by Fullerene-Center, Nizhniy Novgorod, Russia) was used.

To obtain the n(E) spectral dependence, it is necessary to have data on the $\sigma(E)$ in the entire energy range, which are uniquely determined through the absorption cross sections. The calculations were based on the spectra of the absorption cross sections in a wide energy range (10–30000 eV) outside the absorption edges [12], in the 0–120 eV energy region [13-16] and near the C 1s absorption edge.

The absorption cross sections in the C$_{60}$ C 1s near edge X-ray absorption fine structure region (280–350 eV) were measured in Russian-German beamline at BESSY II [17, 18] in the total electron yield (TEY) mode with the correct registration of the nonmonochromatic background and higher orders radiation from diffraction grating. For energy calibration the energy positions of the first- and second-order light-excited Au 4f$_{7/2}$ lines were used. The flux in arbitrary units was measured by the Au plate. The photon energy resolution was less than 0.05 eV. The studied samples were prepared by pressing the C$_{60}$ powder into the Cu-plate surface. The resulting spectrum was reduced to an absolute scale according to the Henke tables [12] for atomic C by the cross section values under and above the C 1s absorption edge.

Figure 1 shows the spectral dependence of the C$_{60}$ absorption cross section on the absolute scale (in Mb), obtained by dividing the fullerite TEY signal by the monochromatized synchrotron radiation (SR) intensity, followed by dividing the fullerite TEY signal by the certain coefficient using the spectral dependence of the carbon atom [12] according to the method given in [11] and with correct account of the background radiation using Ti-film filter. It should be noted that in the case of the TEY method, the influence of the instrumental distortions is minimized due to the small photoelectron escape depth. The figure shows that the experimentally obtained dependence of the fullerite absorption cross section in a wide range of photon energies agrees well outside the C 1s NEXAFS spectrum with the data on the absorption cross sections of the carbon atom. The observed oscillations in the O 1s edge region are related to the additional structure in the incident SR beam due to the presence of an oxide layer on the surface of the optical elements in the beamline.

The fullerite C$_{60}$ C 1s NEXAFS spectrum was decomposed into the absorption bands and the edge. Each band was approximated by a dispersion (Lorentz) curve, for which the KKR solution can be found analytically [19]. The absorption edge was modeled by an arctangentoid. This representation allows to obtain a solution for optical constants separately for the edge and absorption bands. In the regions outside the absorption edges (120–280 eV and 0.39–30 keV) power law approximation was used. For the calculation the absorption cross sections data in the energy range above 30 keV were obtained by power law extrapolating of the spectrum in the 10–30 keV range [12]. All calculations were performed in Wolfram Mathematica.
Figure 1. Absorption cross sections spectra of atomic C taken from the Henke tables (blue dashed line) [12] and fullerite C$_{60}$ (black solid line) normalized per carbon atom.

The calculated integral sum of C$_{60}$ absorption cross sections per carbon atom in the energy range of 0–100 keV was 6.4, which is in good agreement with the Thomas-Reich-Kuhn sum rule, close to the number of electrons in the carbon atom $Z=6$. This indicates high reliability and accuracy of the data on the absorption cross sections in a wide range of the fullerite absorption spectrum.

Then, using the KKR [4,5],

$$n(E_0) = 1 + C \frac{2}{\pi} V.p. \int_0^\infty \frac{\sigma(E)}{E^2-E_0^2} dE,$$

where $C=(N_A \rho c \hbar/(2A))=0.83$ eV/cm$^2$, $N_A$ is Avogadro number, $\rho=1.68$ g/cm$^3$ is the fullerite C$_{60}$ density, $A=720.696$ g/mol is the C$_{60}$ molecular weight, $c$ is the speed of light in a vacuum, $\hbar$ is Planck’s constant, V.p. denotes the Cauchy principal value, the $n(E)$ dependence was calculated.

3. Results

The $n(E)$ spectral dependence was calculated by numerical integration. The remaining optical coefficients are uniquely determined from the spectral dependences of $n(E)$ and $\sigma(E)$. The expressions for the real and imaginary parts of the atomic form factor ($f_1, f_2$) are [20]:

$$f_1 = \frac{\delta}{x}, f_2 = \frac{-\gamma}{x},$$

where $x = \frac{4\pi e^2 h^2}{m \beta^2} \cdot N_f = \frac{116.299}{E^2(eV)}, \delta = 1 - n^2 + k^2, \gamma = 2kn, k = \sigma N \lambda/4\pi$ is extinction coefficient, $m$ is electron mass, $e$ is electron charge, $N$ is the concentration of atoms, $N_f$ is the number of dipoles per unit volume. The measured $\sigma(E)$ spectrum and calculated results of $n(E)$ in the C 1s absorption edge region using (1) showed in Figure 2.
Figure 2. The spectra of (a) the measured absorption cross section and (b) the calculated refraction coefficient of the C$_{60}$ in the region near the C 1s absorption edge.

The expressions for reflection coefficient $R_s$ and phase shift $\psi_s$ are [21]:

$$R_s = \sqrt{R_s e^{i\psi_s}}, \quad R_s = \frac{(a - \sin \theta)^2 + b^2}{(a + \sin \theta)^2 + b^2}, \quad \psi_s = \arctan \left( \frac{-2 \sin \theta}{\sin^2 \theta - a^2 - b^2} \right).$$

where $a^2 = \frac{1}{2} \left[ \sqrt{(\sin^2 \theta - \delta)^2 + \gamma^2} + (\sin^2 \theta - \delta) \right], \quad b^2 = \frac{1}{2} \left[ \sqrt{(\sin^2 \theta - \delta)^2 + \gamma^2} - (\sin^2 \theta - \delta) \right], \quad \theta$ is the X-ray grazing incidence angle, $R_s$ is complex reflection coefficient.

Data on the spectra of the real and imaginary parts of the atomic form factor are presented in Figure 3, and Figure 4 shows the calculated spectra of the reflection coefficient and the phase shift during reflection for different X-ray grazing incidence angles.

4. Conclusions

In this work the optical coefficients (refraction and reflection coefficients, phase shift, and atomic form factor) of the fullerite C$_{60}$ near the C 1s absorption edge region was determined by KKRs using the absorption cross section data. The presented method of fullerite C$_{60}$ optical constant determinations also can be applicable not only to carbon allotropes, but to a wide range of monoatomic and polyatomic compounds. It can provide reliable determination of optical constants in the NEXAFS regions, where they are difficult to measure, but such information is needed.
Figure 3. The C\textsubscript{60} spectra of (a) the real and (b) imaginary parts of the atomic form factor in the region near the C 1s absorption edge.

Figure 4. C\textsubscript{60} spectral dependences of (a) the reflection coefficient and (b) the phase shift during reflection in the region near the C 1s absorption edge for different X-ray grazing incidence angles (in miliradians).
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