NEXAFS C1s-spectra apparatus distortion study

A E Mingaleva1,2, O V Petrova1,2, D V Sivkov1,3, N N Shomysov1, S V Nekipelov1,2, R N Skandakov1, V N Sivkov1

1Komi Science Centre of Urals Branch, RAS, 167982, Syktyvkar, Russia
2Pitirim Sorokin Syktyvkar State University, 167001, Syktyvkar, Russia
3Immanuel Kant Baltic Federal University, 236041, Kaliningrad, Russia

Abstract. The results of the comparison of TEY and transmission methods of X-ray absorption spectra measurements as well as “thickness effect” modeling in the linear absorption coefficient spectral dependences of the C60-films in the NEXAFS C1s-spectra are represented. The calculations were performed with using linear absorption coefficient spectra obtained in TEY mode as the true (undistorted) data. The modelling results are in good agreement with the experiment. All NEXAFS C1s-spectra was carried out at the BESSY II using synchrotron radiation from the Russian-German dipole beamline.

Introduction

Absorption spectroscopy with soft X-ray (25-1500 eV) analyzes the near edge X-ray absorption fine structure (NEXAFS) for identification of condensed mater atomic and chemical composition and electron structure. NEXAFS is formed by electron excitation from core to unoccupied states of mater structural unit (atom, molecule, cluster or quasimolecule) and investigate mater in nanosize scale.

Traditionally, the X-ray absorption coefficient \( \mu(E) \) is determined in transmission mode using the sample of known thickness \( d \) by measuring the intensities of incident \( I_0 \) and transmitted \( I \) through a sample monochromatic X-ray beam:

\[
\mu(E) = \frac{1}{d} \ln \left( \frac{I_0}{I} \right),
\]

where the intensities \( I_0 \) and \( I \) are measured with correct evaluation of background radiations. This method requires the sample in the form of very thin film because of the radiation’s short absorption length. More over it is well known that the intensities and form of X-ray absorption \( \mu(E) \) thin structure is distorted together with sample thickness \( d \) growth [1-3]. Such spectra distortions results from spectrometer apparatus function are known in literature as “thickness effect” [1, 4]. “Thickness effect” distortion express in intensity reduction and broadening of sharp resonances within contrasts structure and unification of smaller peaks.

Due to apparatus function \( \phi(E-E') \) which is normalized per unit the experimentally measured \( I_0, I \) and \( \mu \) would differ from their true values \( I_0', I' \) and \( \mu' \)[2,3]:

\[
\mu(E) = \frac{1}{d} \ln \left[ k \int e^{-\mu(E)d} \cdot \phi(E-E')dE \right],
\]

where \( k \) - normalization constant. Due to thin lines absence in soft X-ray emission spectra the form of apparatus function in this region as well as \( \mu(E) \) true value can’t be identified. Therefore, in modeling, this function is chosen as the dispersion.

At present time the absorption coefficient measurements are commonly carried out by registration of total electron yield (TEY) from the investigated sample. NEXAFS realized in TEY mode probe only thin near-surface layer up to 50 \( \AA \) [5]. This fact allows neglecting the “thickness
effect” distortion influence for NEXAFS-spectra measured in TEY mode which is proportional to linear absorption coefficient and incident radiation intensity [6].

In current research a comparison between NEXAFS C1s-spectra measured as in transmission and in TEY mode and correct evaluation of background radiation is represented on the example of nanostructured carbon material – fullerene C$_{60}$. Moreover the modelling of NEXAFS C1s-spectra “thickness effect” distortion for thin C$_{60}$-layers using as the true value $\sigma'$ in equation (2) the TEY-spectra was made. This modelling allow to estimate the optimal C$_{60}$-layers thickness for better correlation between transmission and TEY spectra.

The choice of polycrystalline fullerite C$_{60}$ as a test compound for current resource is limited by following factors: (i) the fullerite C$_{60}$ has one absorption edge and narrow multi-peaks contrasts fine structure and (ii) it can be prepared as thin film for transmission method and fine crystalline powder for TEY method.

**Experimental and simulation details**

All NEXAFS C1s-spectra of fullerene C$_{60}$ measured in TEY and transmission mode was carried out at the Berliner Elektronenspeicherring fur Synchrotronstrahlung II (BESSY II) using radiation from the Russian-German dipole beamline (RGBL).

For suppression and estimation of background radiation in incident and transmitted through thin sample film synchrotron radiation and measured TEY-signal the specific absorption 220 nm Ti-film filter was used [7,8]. In TEY-experiment, Ti-filter was fixed on gold mesh with a small cell and placed between exit slit and analytical chamber. In transmission the Ti-filter was used as a film for C$_{60}$-layers deposition. The photon energy was calibrated by first narrow peak (285.38 eV) in NEXAFS C1s-spectra of HOPG [9].

![Image](image_url)

**Figure 1.** Transmitted intensities of Ti-film with thickness $d=220$ nm (curve 1) and deposited on it C$_{60}$-layers with thickness $d=60$ nm (curve 2), $d=145$ nm (curve 3), $d=260$ nm (curve 4).

For transmission experiments the samples were prepared in the form of 60, 145 and 260 nm C$_{60}$-layers deposited by vacuum thermal evaporation to 220 nm free Ti-films and then fixed on Cu-holder with round slits, which linear sizes considerably exceeding the diameter of the radiation beam on the sample. The linear absorption coefficient was determined by expression (1). For measurement of incident radiation the 220 nm free Ti-films was used. Incident and transmitted radiation intensities were measured by TEY-signal registration from clear Au-photocathode. In Fig.1 the spectral dependencies of monochromatic (i.e. without background) intensities of transmitted throw 220 nm free
Ti-films ($I_0$) and throw 60, 145 and 260 nm $C_{60}$ layers deposited on Ti-films in wide energy range and in C1s-edge (the inset) are presented.

The samples for the investigation by TEY method were prepared by fullerite $C_{60}$ pressing on the surface of Cu-holder. The incident photon flux was measured using the clean Au-photoelectrode. The incident monochromatic intensity in arbitrary units was obtained by means of the division the TEY monochromatic signal of Au plate by the Au atomic cross section [8].

The modelling of NEXAFS C1s-spectra “thickness effect” was carried out by the formula (2) using the TEY-spectra as true (undistorted) value and a dispersion apparatus function:

$$
\varphi(E - E') = A_0 \left[ \frac{1}{(E - E')^2 + \left(\frac{\Delta E}{2}\right)^2} \right],
$$

where $\Delta E$ – spectrometer energy resolution, which was chosen to be $\Delta E = 0.15eV$, $A_0 = \Delta E / 2\pi$ – normalization factor.

Result and discussion

Figure 2 include the results of the comparison study of $\mu(E)$ spectral dependences of $C_{60}$ in NEXAFS C1s-spectra, measured by transmission methods for $C_{60}$-film thickness $d=260$ nm and in TEY mode. In Figure 3 partial C1s $\mu(E)$ spectral dependencies in arbitrary units and after normalization to unity at 315 eV are shown. The figure demonstrates well correlation of TEY and transmitted spectra in numbers of peaks and its energy position within discrete area before the C1s-edge (a-d peaks). However in this area the clear differences in the relative peak intensities are observed. In the transmission spectra, the structure located above the absorption edge (e-k) is low-contrast and has a significantly lower intensity in comparison with similar structure in TEY-spectra.

![Figure 2](image-url)

**Figure 2.** Linear absorption coefficient spectral dependences of $C_{60}$ in NEXAFS C1s-spectra, measured by TEY (curve 1) and transmission methods for $C_{60}$-film thickness $d=260$ nm (curve 2). The C1s-edge is indicated by the arrow.

The results of “thickness effect” modeling for series of sample thickness $d=60$ nm (curve 2), $d=145$ nm (curve 3) and $d=260$ nm (curve 4) are shown in figure 3. Figure 3 demonstrates the strong influence of the thickness effect in the spectrum of fullerite in the NEXAFS C1s-absorption edge, which is expressed in the decreasing of the area of narrow peaks and its intensity in the maximum with an increase of the sample thickness. The developed modeling program allows evaluating the optimal sample thickness for studying it by the photoabsorption method. This program can be adapted for the study of thickness effect in other samples spectra. Calculation results are in good agreement with NEXAFS C1s-absorption spectra of fullerite $C_{60}$ obtained by the transmission method.
Figure 3. Linear absorption coefficient spectral dependences of $C_{60}$ in NEXAFS $C_{1s}$-spectra, measured by TEY method (true spectrum) (curve 1) and calculated for different $C_{60}$-film thickness $d=60$ nm (curve 2), $d=145$ nm (curve 3) and $d=260$ nm (curve 4). The $C_{1s}$-edge is indicated by the arrow.

Conclusion

The current study allows us to conclude that transmission method cannot be used for correct X-ray linear absorption coefficient $\mu(E)$ measurements especially for the NEXAFS included narrow selective peaks and contrast structure, since apparatus distortions arise even at sample thickness of several tens nm. The modelling results indicate that due to “thickness effect” the narrow peaks are reduced in intensity and broadening while the continuum peaks undistorted. The modelling show the good agreement between simulating and experimental spectra measured in transmission mode for $C_{60}$-film thickness $d=260$ nm.

Acknowledgments

This work was supported by Program of UB RAS №18-10-2-23; grants RFBR and Komi Republic 16-42-110610 p-a, 16-43-110350 p-a; the Bilateral Program of the Russian-German Laboratory at BESSY II and the Russian Academic Excellence Project at the Immanuel Kant Baltic Federal University.

References

[1] Parrat L G, Hempstead C F, Jossem E L 1957 Phys. Rev. 105 1228
[2] Sivkov V N, Vinogradov A S, Nekipelov S V, Sivkov D V, Vyalikh D V, Molodtsov S L 2006 Opt. Spectrosc. 101 724
[3] Sivkov V N, Vinogradov A S 2002 Opt. Spectrosc. 93 395
[4] Lukirskii A P, Zimkina T M 1963 Izv. Akad. Nauk SSSR 27 324
[5] Stöhr J 1992 NEXAFS Spectroscopy (Berlin: Springer Verlag) p 403
[6] Gudat W, Kunz C 1972 Phys. Rev. 29 169
[7] Kummer K, Sivkov V N, Vyalikh D V, Maslyuk V V, Bliuer A, Nekipelov S V, Bredow T, Mertig I, Mertig M, Molodtsov S L 2009 Phys. Rev. B 80 155433
[8] Sivkov V N, Ob’edkov A M, Petrova O V, Nekipelov S V, Kremlev K V, Kaverin B S, Semenov N M, Gusev S A 2015 Physics of the Solid State 57 197
[9] Batson P E 1993 Phys. Rev. 48 2608