

PHOTOELECTRONS KICKS BACK: RECOIL EFFECTS IN PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy is widely used for the study of electronic structure of solids. The binding energy E_B of the electron in the sample is determined from the following equation:

$$E_B = h\nu - E_{kin} - \varphi,$$

where E_{kin} is the measured electron kinetic energy, $h\nu$ is the photon energy for excitation, and φ is the work function. This procedure, however, overlooked recoil effects, i.e., the momentum (or energy) imparted to the emitting atom by the outgoing electron. This is simply because the recoil effect is not easily measurable in vacuum ultraviolet (VUV) and soft X-ray (SX) photoelectron spectra.

In the last few years, hard X-ray (HX) photoelectron spectroscopy with the excitation energy of 6-8 keV has been realized using high brilliance synchrotron radiation [1-3], resulting in useful studies on semiconductors and correlated materials. The achieved high energy resolution ($\Delta E < 80$ meV) enables us to investigate recoil effects in a solid.

In this study, we successfully observed the recoil effects in the C 1s core level photoelectron spectra of highly oriented pyrolytic graphite (HOPG). HX photoelectron spectra at the excitation energies of 5950 and 7940 eV were measured at the undulator beamline **BL29XU**. Details of the apparatus including X-ray optics are described in Refs. [2,3]. SX spectra at the excitation energy of 340, 870 eV were measured at the undulator beamline **BL17SU**. The total instrumental energy resolution (ΔE) for the SX and HX spectra were determined as 100 meV and 120 meV by fitting the Fermi-edge profiles of Au measured at 20 K.

C 1s core level spectra of HOPG measured at room temperature with SX excitation (340 and 870 eV) and HX excitation (5950 and 7940 eV) are shown in Fig. 1(a). The spectra are obtained effectively in normal emission geometry. The peak position of the spectrum obtained with $h\nu = 870$ eV shifts to lower binding energy in comparison with that of $h\nu = 340$ eV spectrum. This shift is due to the difference in the probing depth of photoelectrons between these excitation energies. With increase of the kinetic energy, the probing depth of a photoelectron becomes larger. The spectra of $h\nu = 340$ and $h\nu = 870$ eV are dominated by the surface and bulk components, respectively. With increase of the excitation energy, i.e., the kinetic energy of the C 1s photoelectron, the peak position shifts to the higher binding energy side.

It is also obvious that asymmetric broadening becomes much wider for the higher energy photoelectrons, while the total instrumental energy resolution for these spectra is almost the same.

For the possible origin of these spectral changes, the effect of associated elementary excitation such as plasmons is discarded, since the peak position itself shifts, depending on the kinetic energy. The asymmetric line shape of the C 1s core level spectra obtained with soft X-ray excitation has been discussed in relation with semimetallic character of graphite, and can be fitted by the Doniach-Sunjić function [5]. This possibility can also be excluded for the same reason. Thus, we are led to a picture based on recoil effects for explaining the observed peak shift and broadening, which depends on the kinetic energy of the photoelectron.

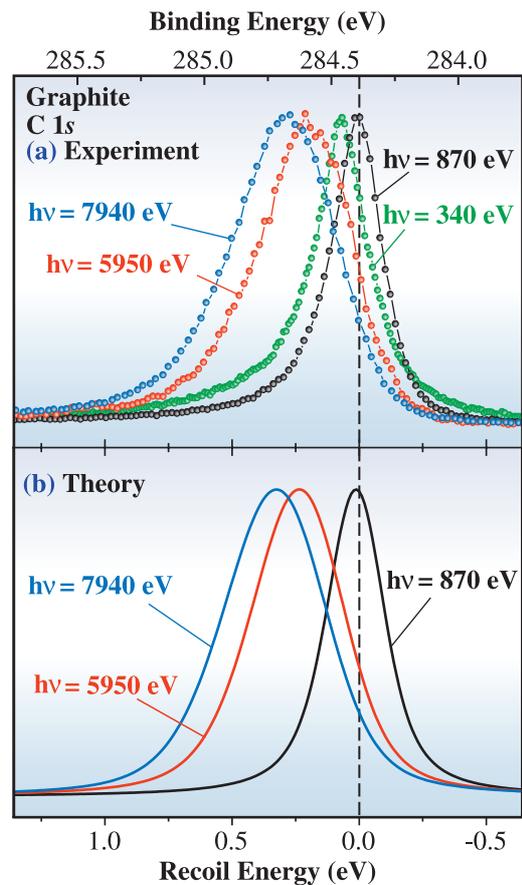


Fig. 1. (a) Photon energy dependence of C 1s core level spectra of graphite. The soft X-ray ($h\nu = 340$ and 870 eV) and hard X-ray ($h\nu = 5950$ and 7940 eV) are measured at the emission angle of 90° and 85° relative to the sample surface. (b) Theoretically obtained spectra taking into account the recoil effect in a Debye model with $\hbar\omega_b = 75$ meV.

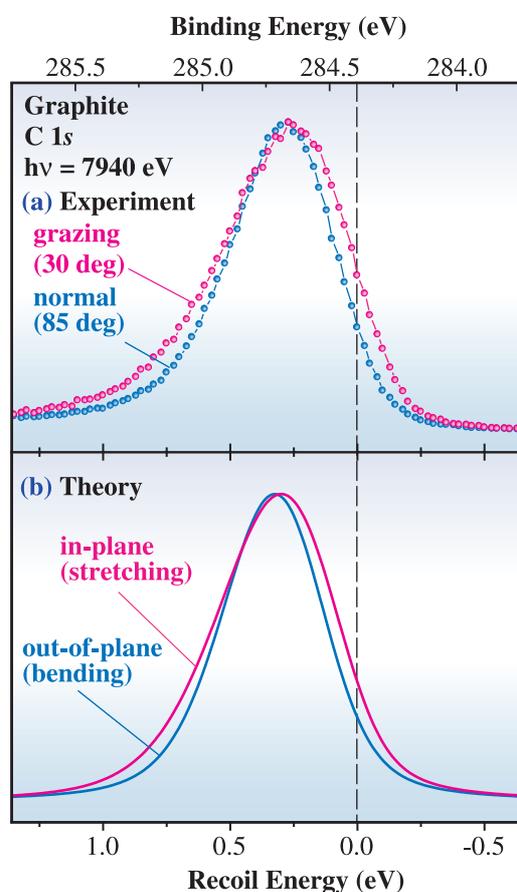


Fig. 2. (a) C 1s core level spectra of graphite measured at the photon energy of 7940 eV at the emission angles of 85° (normal) and 30° (grazing) relative to the sample surface. (b) Theoretically obtained spectra with the Debye energies $\hbar\omega_b = 75$ meV and $\hbar\omega_s = 150$ meV for the bending and stretching modes, respectively.

For an atom with mass M in free space, the recoil energy δE is simply estimated from the momentum conservation as $\delta E = (m/M)E_{kin}$, where m is the electron mass. For a carbon atom with the mass ratio $m/M = 1/22000$, δE becomes as large as 0.36 eV for $E_{kin} = 8$ keV. In the solid, this recoil energy is absorbed by the phonon bath, resulting in the excitation of phonons. The zero-phonon transition corresponds to the event in which the recoil energy is transferred to the center of mass motion of the total crystal. This is essentially the same as the Mössbauer effect in the γ -ray emission from nuclei embedded in crystals.

Based on these considerations, a full quantum calculation with adiabatic approximation and an anisotropic Debye model for graphite was carried out. Details are described in Ref. [4]. The theoretical spectra of the C 1s normal emission photoelectrons of graphite are plotted as a function of the recoil energy

in Fig. 1(b). The lifetime broadening (full width at half maximum) is taken to be 160 meV as is known for graphite [5]. The spectra are then convoluted with a Gaussian function corresponding to the experimental resolution of 120 meV. Theoretical spectra reproduce the experimental spectra fairly well without any adjustable parameters. Note that, at 870 eV excitation, the peak shift is quite small, but phonon excitations cause the asymmetric broadening.

Figure 2 (a) shows the experimental C 1s core level spectra of HOPG measured with 7940 eV excitation at the emission angle of 85° (the same as that in Fig. 1(a)) and 30° relative to the sample surface. The peak slightly shifts to lower binding energy and becomes broader for the grazing emission spectrum. Theoretical spectra are shown in Fig. 2(b). The theoretical spectra reproduce well the observed emission angle dependence. The larger spectral width in the grazing angle emission, relative to the normal one, is attributed essentially to the large Debye cut-off frequency for the stretching mode, which is roughly twice that for the bending mode.

The experimental and theoretical results confirm the recoil effects of photoelectrons in solids, making it an important aspect of high-energy photoelectron spectroscopy. We are investigating recoil effects in valence band photoelectron spectra. Such studies using high energy photoelectron spectroscopy will give us new insights on the dynamics of chemical bonding.

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References

- [1] K. Kobayashi *et al.*: Appl. Phys. Lett. **83** (2003) 1005.
- [2] Y. Takata *et al.*: Nucl. Instrum. Meth. A **547** (2005) 50.
- [3] T. Ishikawa *et al.*: Nucl. Instrum. Meth. A **547** (2005) 42.
- [4] Y. Takata, Y. Kayanuma, M. Yabashi, K. Tamasaku, Y. Nishino, D. Miwa, Y. Harada, K. Horiba, S. Shin, S. Tanaka, E. Ikenaga, K. Kobayashi, Y. Senba, H. Ohashi and T. Ishikawa: Phys. Rev. B **75** (2007) 233404, *cond-mat/0609241*.
- [5] T. Balasubramanian *et al.*: Phys. Rev. B **64** (2001) 205420.