

## Recoil effects of photoelectrons in a solid

Y. Takata,<sup>1,\*</sup> Y. Kayanuma,<sup>2,†</sup> M. Yabashi,<sup>3,4</sup> K. Tamasaku,<sup>3</sup> Y. Nishino,<sup>3</sup> D. Miwa,<sup>3</sup> Y. Harada,<sup>1</sup> K. Horiba,<sup>1</sup> S. Shin,<sup>1</sup> S. Tanaka,<sup>5</sup> E. Ikenaga,<sup>4</sup> K. Kobayashi,<sup>4</sup> Y. Senba,<sup>4</sup> H. Ohashi,<sup>4</sup> and T. Ishikawa<sup>3,4</sup>

<sup>1</sup>Soft X-ray Spectroscopy Laboratory, RIKEN SPring-8 Center, Sayo-cho, Hyogo 679-5148, Japan

<sup>2</sup>Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

<sup>3</sup>Coherent X-ray Optics Laboratory, RIKEN SPring-8 Center, Sayo-cho, Hyogo 679-5148, Japan

<sup>4</sup>JASRI, SPring-8, Sayo-cho, Hyogo 679-5198, Japan

<sup>5</sup>Graduate School of Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

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High-energy-resolution C 1s photoelectron spectra of graphite were measured at excitation energies of 340, 870, 5950, and 7940 eV using synchrotron radiation. On increasing the excitation energy, i.e., increasing kinetic energy of the photoelectron, the bulk origin C 1s peak position shifts to higher binding energies. This systematic shift is due to the kinetic-energy loss of the high-energy photoelectron by kicking the atom and is clear evidence of the recoil effect in photoelectron emission. It is also observed that the asymmetric broadening increases for the higher-energy photoelectrons. All these recoil effects can be quantified in the same manner as the Mössbauer effect for  $\gamma$ -ray emission from nuclei embedded in crystals.

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Photoelectron spectroscopy is widely used for the study of electronic structure of solids.<sup>1</sup> The binding energy  $E_B$  of the electron is often calculated from the photoelectron kinetic energy using the following equation:

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

where  $E_{kin}$  is the measured electron kinetic energy,  $h\nu$  is the photon energy for excitation, and  $\phi$  is the work function. This procedure overlooked recoil effects, which lead to part of the kinetic energy being imparted to the emitting atom. As a result, the binding energy determined in this way is greater than the true binding energy. This effect is very small for vacuum ultraviolet and soft-x-ray photoelectron spectra, so that recoil effects can be safely neglected. For photoelectrons with 1000 eV kinetic energy emitted from carbon atom, the recoil energy is estimated to be only  $\sim 45$  meV, although Kukkk *et al.* succeeded recently in observing small deviation in spectral shape of vibronic lines in gaseous methane, which have been attributed to a recoil effect.<sup>2</sup>

The momentum transfer at recoil is a fundamental process observed in experiments of neutron and x-ray scatterings,<sup>3</sup> high-energy electron backscattering,<sup>4,5</sup> etc. For photoelectron emission, Domcke and Cederbaum<sup>6</sup> predicted that the recoil effect can be observed as a spectral modification for gaseous molecules with light atoms. Quite recently, Fujikawa *et al.*<sup>7</sup> evaluated the amount of shift and broadening of core-level photoelectron spectra, as well as for electron backscattering, due to recoil effect in solids. It is noted that at keV energies, since the momentum of an electron is much larger than that of a photon of the same energy and the transferred momentum is largely that of the emitted electron, it should be possible to detect recoil effects in photoelectron emission with keV energies.

In the past few years, hard-x-ray photoelectron spectroscopy with the excitation energy of 6–8 keV has been realized using high brilliance synchrotron radiation,<sup>8–10</sup> resulting in useful studies on semiconductors and correlated materials.<sup>11,12</sup> Since the achieved energy resolution is quite good

( $\Delta E < 80$  meV), it gives us an opportunity to investigate recoil effects in a solid.

In this study, we measured the C 1s core-level photoelectron spectra of highly oriented pyrolytic graphite (HOPG), using high energy resolution ( $\Delta E = 100$ – $120$  meV), with the aim of investigating recoil effects due to photoelectron emission in a solid. HOPG is a suitable material for study of the recoil effect because of the light atomic mass of carbon. Furthermore, reliable studies of surface-bulk core level shift of HOPG have already been established recently,<sup>13–16</sup> providing a very suitable reference for this study. The experimentally obtained spectra in the present study confirm the surface core-level shift. For the bulk derived feature, the spectra exhibit systematic kinetic energy loss and the anomalous asymmetric broadening on increasing the excitation energy. All these features are clear evidence of recoil effect and can be theoretically quantified in the same picture as the Mössbauer effect for  $\gamma$ -ray emission.

Measurements of C 1s photoelectron spectra of HOPG were performed at SPring-8 using synchrotron radiation. Hard-x-ray photoelectron spectra at excitation energies of 5950 and 7940 eV were measured at the undulator beamline BL29XU using a hemispherical electron energy analyzer, SCIENTA R4000-10 kV. Details of the apparatus including x-ray optics are described in Refs. 9, 17, and 18. Soft-x-ray spectra at excitation energies of 340 and 870 eV were measured at the undulator beamline BL17SU (Ref. 19) using an electron analyzer, SCIENTA SES-2002. Clean surfaces of HOPG were prepared by peeling off an adhesive tape at a pressure of  $10^{-8}$  Pa for all measurements. All the measurements on graphite reported here were carried out at room temperature. The energy scale of the spectra was calibrated very accurately ( $< 10$  meV) by measurements of the Au 4f core levels and the Fermi edge at room temperature. The total instrumental energy resolution ( $\Delta E$ ) for the soft-x-ray and hard-x-ray spectra were determined as 100 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 tem-

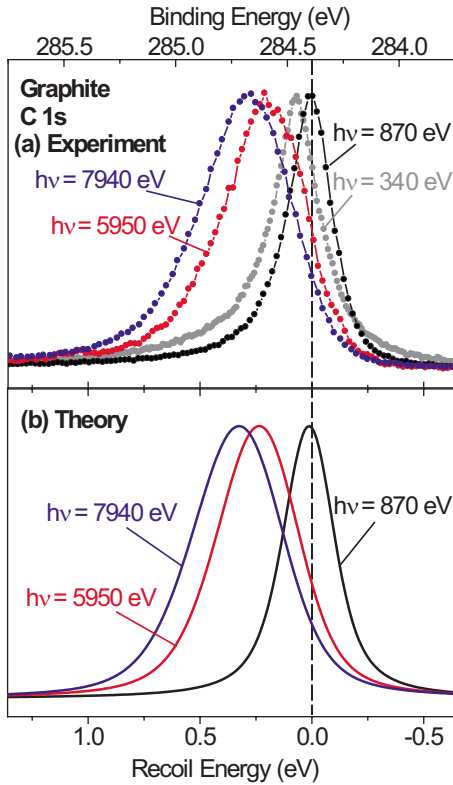


FIG. 1. (Color online) (a) Photon energy dependence of C 1s core-level spectra of graphite. The soft x ray ( $h\nu=340$  and  $870$  eV) and hard x ray ( $h\nu=5950$  and  $7940$  eV) are measured at the emission angles of  $90^\circ$  and  $85^\circ$  relative to the sample surface. (b) Theoretically obtained spectra taking into account the recoil effect in a Debye model with  $\hbar\omega_{b,D}=75$  meV.

perature with soft-x-ray excitation ( $340$  and  $870$  eV) and hard-x-ray excitation ( $5950$  and  $7940$  eV) are shown in Fig. 1(a). The spectra are obtained effectively in normal-emission geometry. The photoelectron detection angles relative to the sample surface for the soft-x-ray and hard-x-ray spectra were  $90^\circ$  and  $85^\circ$ , respectively. The peak position of the spectrum obtained with  $h\nu=870$  eV shifts to lower binding energy ( $284.39$  eV) in comparison with that of  $h\nu=340$  eV spectrum ( $284.47$  eV). 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. The observed surface-bulk core-level shift is consistent with the results reported by Balasubramanian *et al.*<sup>15</sup> using photon energies of  $300$ – $348$  eV and a total energy resolution of about  $50$  meV. It was shown that surface-bulk core-level splitting results in a weak bulk feature at a lower binding energy compared to the surface derived feature. In the present study, our  $h\nu=340$  eV spectrum is similar to that reported by Balasubramanian *et al.*<sup>15</sup> while the  $h\nu=870$  eV spectrum is dominated by the bulk derived feature.

With increase of the excitation energy, i.e., the kinetic energy of the C 1s photoelectron, the peak position shifts to higher-binding-energy side. It is also obvious that asymmet-

ric 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.<sup>13–16</sup> 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 depend on the kinetic energy of the photoelectron.

For an atom with mass  $M$  in free space, the recoil energy  $\delta E$  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  $m/M=1/22\,000$ ,  $\delta E$  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  $\gamma$ -ray emission from nuclei embedded in crystals.<sup>20</sup>

Without loss of generality, we assume that a core electron of the carbon atom located at the lattice point  $\vec{R}^0$  is ejected by the x-ray irradiation. The actual nuclear position  $\vec{R}$  may deviate from its equilibrium value  $\vec{R}^0$  as  $\vec{R}=\vec{R}^0+\vec{u}$  because of the thermal and zero-point vibrations. The interaction Hamiltonian with the x ray is given by  $H_I=(a+a^\dagger)\vec{\epsilon}\cdot\vec{p}$ , aside from irrelevant factors, where  $a$  is the annihilation operator for the x ray with energy  $h\nu$  and the polarization vector  $\vec{\epsilon}$ . The momentum of photon is neglected here, since it is an order of magnitude smaller than the that of the emitted electron in this x-ray energy region. The initial state of transition is given by  $|\Psi_i\rangle=|h\nu\rangle\otimes|\psi_c\rangle\otimes|i\rangle$ , where  $|h\nu\rangle$  is the one-photon state,  $|\psi_c\rangle$  is the core electron state with energy  $\epsilon_c$ , and  $|i\rangle$  is a phonon state of the crystal. The crucial point of the theory is that the wave function of the core electron is given by the form  $\langle\vec{r}|\psi_c\rangle=\psi_c(\vec{r}-\vec{R})$ . This is the adiabatic approximation, and the recoil effect results directly from this functional form. On the other hand, the final state of the transition is given by  $|\Psi_f\rangle=|0\rangle\otimes|\psi_k\rangle\otimes|f\rangle$ , in which  $|0\rangle$  is the vacuum of the photon,  $|\psi_k\rangle$  is the plane wave of the electron,  $\langle\vec{r}|\psi_k\rangle=(2\pi)^{-3/2}\exp(i\vec{k}\cdot\vec{r})$ , with energy  $\hbar^2\vec{k}^2/2m$ , and  $|f\rangle$  is a phonon state.

Using the functional forms for  $|\Psi_i\rangle$  and  $|\Psi_f\rangle$  and changing the integration variable from  $\vec{r}$  to  $\vec{r}-\vec{R}$ , we find

$$\langle\Psi_f|H_I|\Psi_i\rangle=\vec{\epsilon}\cdot\vec{\mu}\langle f|e^{-i\vec{k}\cdot\vec{R}}|i\rangle,$$

in which

$$\vec{\mu}=(2\pi)^{-3/2}\int d^3r e^{-i\vec{k}\cdot\vec{r}}\left(-i\hbar\frac{\partial}{\partial\vec{r}}\right)\psi_c(r).$$

The above expression of the interaction Hamiltonian coincides with that for the Mössbauer effect,<sup>21</sup> so that we readily

obtain the following expression for the photoelectron spectrum as a function of the relative binding energy  $E$  measured from the recoilless value:

$$I(E) = \frac{|\vec{\varepsilon} \cdot \vec{\mu}|^2}{2\pi} \int_{-\infty}^{\infty} dt e^{-iEt/\hbar - \Gamma|t|/\hbar} F(t),$$

in which the generating function  $F(t)$  is given by the canonical average,

$$F(t) = \langle e^{i\vec{k} \cdot \vec{u}(t)} e^{-i\vec{k} \cdot \vec{u}} \rangle,$$

with  $\vec{u}(t)$  being the Heisenberg representation of  $\vec{u}$  at time  $t$ , and  $\Gamma$  is the lifetime broadening factor. For harmonic crystals,  $F(t)$  can be written in the closed form,  $F(t) = \exp[G(t)]$ , where

$$G(t) = \sum_q \alpha_q^2 \{ [2n(\omega_q) + 1] (\cos \omega_q t - 1) - i \sin \omega_q t \},$$

with

$$\alpha_q^2 = \left( \frac{\hbar}{2N\tilde{M}\omega_q} \right) |\vec{k} \cdot \vec{\eta}_q|^2$$

and

$$n(\omega_q) = 1/(e^{\hbar\omega_q/k_B T} - 1),$$

in which  $q$  is the abbreviation for the wave vector and the branch index of phonons,  $\tilde{M}$  is the mass of unit cell,  $N$  is the number of unit cells, and  $\vec{\eta}_q$  is the polarization vector of the phonon. The photoelectron spectrum  $I(E)$  is the convolution of a structure function with the Lorentz function. The former consists of the recoilless line (the zero-phonon line) and its phonon sidebands. Unlike the Mössbauer effect, one can control the so-called Debye-Waller factor continuously from almost recoilless to strong coupling by changing the energy of the x ray. The spectrum may depend also on the relative angle of the  $\vec{k}$  vector of the emitted electron because of the anisotropy of the phonon spectrum.

In actual calculation, we adopt an anisotropic Debye model for graphite. The stretching (in-plane) mode and the bending (out-of-plane) mode are assumed to be independent. The surfaces of constant frequency for each mode have a prolate spheroidal form in  $\vec{q}$  space reflecting the highly anisotropic dispersion relation for the in-plane propagation and the out-of-plane propagation.<sup>22</sup> Then,  $G(t)$  is given by

$$G(t) = \int_{-\infty}^{\infty} d\omega (e^{i\omega t} - 1) \{ J_s(\omega) \cos^2 \theta + J_b(\omega) \sin^2 \theta \} \quad (1)$$

for the emission angle  $\theta$  relative to the surface, where  $J_\lambda(\omega)$  ( $\lambda = s, b$ ) are given by

$$J_\lambda(\omega) = \frac{\delta E}{\hbar \omega} \{ [n(\omega) + 1] D_\lambda(\omega) \Theta(\omega) + n(|\omega|) D_\lambda(|\omega|) \Theta(-\omega) \},$$

with the step function  $\Theta(\omega)$ . Here,  $D_\lambda(\omega)$  is the density of state per atom,

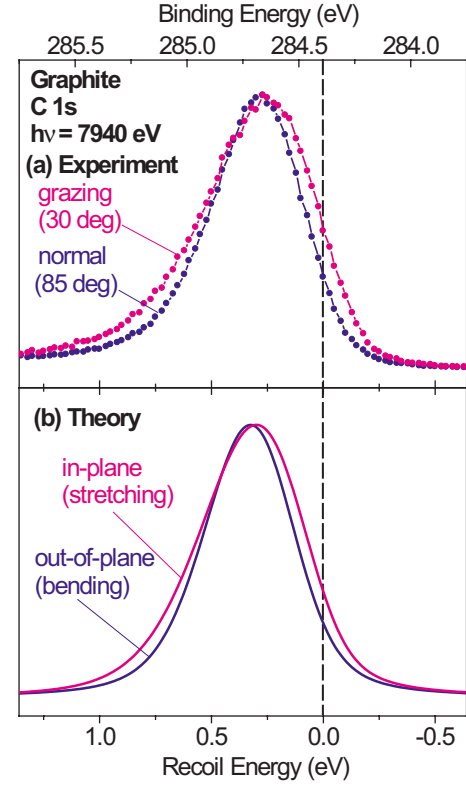


FIG. 2. (Color online) (a) C 1s core-level spectra of graphite measured at the photon energy of 7940 eV at the emission angles of 85° (normal) and 30° (grazing) relative to the sample surface. (b) Theoretically obtained spectra with the Debye energies  $\hbar\omega_{s,D} = 75$  meV and  $\hbar\omega_{b,D} = 150$  meV for the bending and the stretching mode, respectively.

$$D_\lambda(\omega) = \frac{6}{3\omega_{\lambda,D}^2 - \omega_{\lambda,C}^2} \begin{cases} \frac{\omega^2}{\omega_{\lambda,C}}, & 0 < \omega < \omega_{\lambda,C} \\ \omega, & \omega_{\lambda,C} < \omega < \omega_{\lambda,D} \\ 0, & \text{otherwise.} \end{cases} \quad (2)$$

The density of state has a characteristic of three-dimensional Debye model in low frequency ( $\omega < \omega_{\lambda,C}$ ) but of two-dimensional one at high frequency, where only the in-plane propagating modes contributes to  $D_\lambda(\omega)$ . The Debye cutoff frequencies for the stretching mode  $\hbar\omega_{s,D}$  and the bending mode  $\hbar\omega_{b,D}$  are estimated from the frequency at  $K$  point of LA mode and ZA mode, respectively. From the experimental dispersion curves,<sup>23</sup> we fix  $\hbar\omega_{s,D} = 150$  meV,  $\hbar\omega_{b,D} = 75$  meV,  $\hbar\omega_{s,C} = 6.3$  meV, and  $\hbar\omega_{b,C} = 12.5$  meV.

The theoretical spectra of the C 1s normal-emission photoelectrons of graphite were calculated and 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.<sup>14,15</sup> 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 spec-

tra of HOPG measured with 7940 eV excitation at the emission angle of  $85^\circ$  [the same as that in Fig. 1(a)] and  $30^\circ$  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 than the normal one is attributed essentially to the large Debye cutoff frequency  $\omega_{s,D}$  for the stretching mode, which is roughly twice that for the bending mode  $\omega_{b,D}$ .

It is remarkable that the gross spectral features in Fig. 1 can be understood by a semiclassical approximation.<sup>7</sup> We have checked that the spectra can be approximately fitted by a Gaussian line shape using an atomic value for the shift  $\delta E$  and a width given by the second moment due to the Doppler broadening of  $2\delta E k_B T$ . However, the semiclassical picture fails in reproducing the asymmetries of the observed line shapes, which are signatures of the quantum nature of

phonons. The anisotropic line shape shown in Fig. 2 also indicates the necessity of a full quantum-mechanical analysis taking into account the solid-state effect for such a high-resolution spectroscopy. Furthermore, the good agreement between the experimental data and the theoretical calculation tells us that the multiple-scattering effect is small.

In conclusion, recoil effects in photoelectron emission from solid were observed in the high-energy C 1s core-level spectra of graphite. The observed spectral shapes are successfully quantified in the same manner as the Mössbauer effect for  $\gamma$ -ray emission from nuclei embedded in crystals. The recoil effect exists and is measurable, making it an important aspect of high-energy photoelectron spectroscopy.

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\*Electronic address: takatay@spring8.or.jp

†Electronic address: kayanuma@ms.osakafu-u.ac.jp

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