Recoil Effect of Photoelectrons in the Fermi Edge of Simple Metals

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High energy resolution photoelectron spectroscopy of conduction electrons in the vicinity of the Fermi edge in Al and Au at excitation energies of 880 and 7940 eV was carried out using synchrotron radiation. For the excitation energy of 7940 eV, the observed Fermi energy of Al shows a remarkable shift to higher binding energy as compared with that of Au, with accompanying broadening. This is due to the recoil effect of the emitted photoelectrons. The observed spectra are well reproduced by a simple model of Bloch electrons based on the isotropic Debye model.

In x-ray photoelectron spectroscopy (XPS), the emitted electron kicks the atom from which it is ejected in accordance with the conservation of momentum [1–3]. This gives rise to a loss of the kinetic energy of the emitted photoelectron. This effect is usually negligible because of the enormous mass difference between the atom and the electron, as long as the excitation energy is not very large. Quite recently, however, clear evidence of recoil effects has been found in the hard x-ray photoelectron spectra of graphite [4]. Under the excitation of the core level by x-ray photons with an energy of several keV, the photoelectron spectra show a remarkable shift and broadening as compared to the case of excitation by soft x rays. Recoil effects of carbon $1s$ photoelectrons have also been reported in CH_4 molecules [5] and CF_4 molecules [6], in this case as a recoil induced modification of vibrational structures.

Based on a simple picture of an atom at rest in vacuum, the recoil energy ΔE imparted to the atom with mass M by a photoelectron with mass m and kinetic energy E_K is estimated as

$$\Delta E = E_K(m/M). \tag{1}$$

This recoil energy ΔE is observed as an apparent increase of the binding energy of the core electron. In solids, the recoil energy is absorbed by the phonon bath, resulting in the excitation of phonons. Actually, the observed photoelectron spectra for C $1s$ in graphite have been well reproduced by an anisotropic Debye model [4], which takes into account solid state effects appropriate to graphite [7]. The recoil effects of the core electrons are characterized by the peak shift and the asymmetric broadening depending on the incident x-ray energy. Subsequently, such characteristic features have been observed in the core level XPS not only for $1s$ of graphite but also in other materials such as Be $1s$ in Be metal, B $1s$ in MgB_2 and $2p$ level in Al metal [8]. The existence of remarkable recoil effects in the hard x-ray

photoelectron spectra is now well established as far as the core level is concerned.

Similar spectroscopic features of recoil effects have been observed in other fundamental processes such as elastic electron scattering [9,10] and neutron scattering [11,12]. These spectra can be understood essentially by the same principle of momentum conservation [13]. In contrast to the electron scattering and the neutron scattering, however, the photoelectron spectra tell us information on the specific electronic state from which the electron is ejected. A natural question then arises: Are there any recoil effects in the photoelectron spectra for valence levels? Since the Bloch electrons in the valence bands are delocalized all over the crystal, it may be considered at first sight that the recoil momentum is shared by all the atoms of the crystal so that there would be no observable recoil effect, just like the recoilless transition in the Mössbauer effect [14]. In the present Letter, we show, for the first time, a clear evidence of the recoil effect for conduction electrons in a simple metal. The experimental data for XPS in the vicinity of the Fermi edge of Al indicate a remarkable shift and broadening depending on the excitation energy. The observed spectra are well reproduced by a theory which takes into account the momentum conservation of the Bloch electrons expanded in a Wannier function basis.

High resolution photoelectron spectroscopy of conduction electrons in the vicinity of the Fermi edge was performed at SPring-8 using synchrotron radiation. Hard x-ray spectra at the excitation energy of 7940 eV and soft x-ray spectra of 880 eV were measured at the undulator beam lines BL29XU [15,16] and BL17SU [17], respectively, using hemispherical electron energy analyzers. The thick films of Au and Al on Cu substrates were prepared by evaporation in the UHV preparation chamber, and were directly transferred into the measurement chamber. No signal from the substrate Cu or surface contamination

was observed in both hard and soft x-ray photoelectron spectra. The energy scale of the spectra were calibrated very accurately (<5 meV) by fitting the Fermi edge spectra of Au.

Figure 1 shows the photoelectron spectra around the Fermi edge of Au (squares) and Al (circles) measured at 20 K with the excitation energy of 7940 eV. The total instrumental energy resolution for both the spectra, as determined by the beam line crystal monochromator and the electron energy analyzer, is the same. The binding energy scale is calibrated by assuming that the recoil energy in Au ($M = 197$) is negligible. It is clear that the Fermi edge of Al ($M = 27$) is shifted to higher binding energy. This shift is due to the kinetic energy loss of photoelectron from the Fermi level in Al because of its lighter atomic mass compared to Au, and is an evidence of the recoil effect of Bloch electrons. Furthermore, the edge profile has a slightly larger slope for Al than for Au. Conventional fitting analysis of these Fermi edge profiles using the Fermi-Dirac function (not shown) elucidates an energy shift of 120 meV in Al relative to Au, and Gaussian widths of 160 meV for Al and 124 meV for Au. The broadening of the width in Al is also a sign of the recoil effect because the contribution of the instrumental energy resolution to the width is the same in these spectra.

Soft x-ray spectra of Au (squares) and Al (circles) measured at 50 K with the excitation energy of 880 eV are shown in Fig. 2. In the wide range spectra [Fig. 2(a)], it is difficult to recognize the difference between the Au and Al. However, in the expanded spectra [Fig. 2(b)], the energy shift and the broadening of Fermi edge profile is certainly observed. A fitting analysis clarifies a energy shift of 12 meV in Al relative to Au, and Gaussian width of 140 meV in Al and 118 meV in Au.

Consider the transition probability $I(\vec{k}, \vec{K})$ in which a Bloch electron with wave vector $\vec{k}$ is emitted to the free-electron state with wave vector $\vec{K}$ by an x-ray photon with energy $h\nu$. We neglect the momentum of the incident photon since it is an order of magnitude smaller than that of the emitted electron in this energy region. Without recoil effect, the component of the wave vector parallel to the surface is conserved in the periodic zone scheme. The perpendicular component is not conserved, but is determined by the conservation of energy. In the presence of recoil effect, it is written as

$$\epsilon_k + h\nu + \epsilon_m = E_K + \epsilon_n,$$

in which ϵ_k is the energy of the Bloch electron measured from the vacuum level and ϵ_m and ϵ_n are the energies of the lattice vibrations in the initial state and the final state, respectively. The interaction Hamiltonian with the x-ray photon is given by $H_I = (a + a^\dagger)\vec{\kappa} \cdot \vec{p}$, aside from irrelevant factors, where a is the annihilation operator for the x
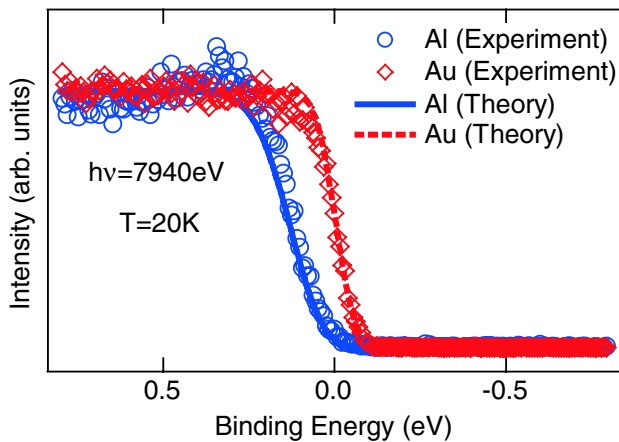

FIG. 1 (color online). Photoelectron spectra near Fermi edge of Al (circles) and Au (squares) with excitation energy 7940 eV. The zero point of the binding energy is chosen at the observed value of the chemical potential of Au. The solid line and the dotted line indicate the theoretical curves calculated by the Debye model.
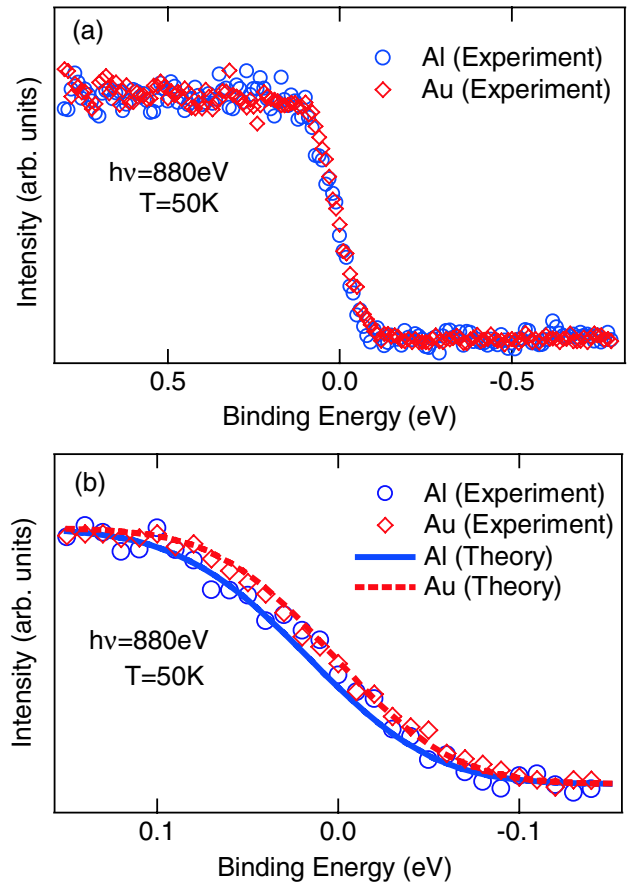

FIG. 2 (color online). (a) Photoelectron spectra near Fermi edge of Al (circles) and Au (squares) with excitation energy 880 eV. The zero point of the binding energy is chosen at the observed value of the chemical potential of Au. (b) Expanded scale plots of the spectra. The solid line and the dotted line indicate the theoretical curves calculated by the Debye model.

ray and $\vec{p}$ is the momentum of the electron, and $\vec{\kappa}$ is the polarization vector of the photon.

The initial state of the transition is given by $|\Psi_i\rangle = |h\nu\rangle \otimes |\psi_k\rangle \otimes |m\rangle$, where $|h\nu\rangle$ is the one photon state, $|\psi_k\rangle$ is the Bloch state (we suppress the band index here), and $|m\rangle$ is a phonon state. The Bloch state $\langle\vec{r}|\psi_k\rangle \equiv \psi_k(\vec{r})$ is expanded by the Wannier functions as

$$\psi_k(\vec{r}) = N^{-1/2}\sum_i e^{i\vec{k}\cdot\vec{R}_i}w(\vec{r} - \vec{R}_i), \qquad (2)$$

where $\vec{R}_i$ is the lattice vector and N is the number of atoms. In the above equation, $\vec{R}_i$ is usually regarded as a parameter fixed at the equilibrium point of the lattice $\vec{R}_i^0$. In order to describe the recoil effect, we consider it as a dynamical variable fluctuating around $\vec{R}_i^0$ as $\vec{R}_i = \vec{R}_i^0 + \vec{u}_i$, where $\vec{u}_i$ is the displacement vector. The Wannier function is assumed to follow this lattice displacement adiabatically. The lattice fluctuation gives rise to the local change of the band energy, which is nothing but the electron-phonon interaction represented by the deformation potential interaction. We neglect here the electron-lattice interaction for simplicity. The final state of the transition is given by $|\Psi_f\rangle = |0\rangle \otimes |\varphi_K\rangle \otimes |n\rangle$, in which $|0\rangle$ is the vacuum of the photon, $|\varphi_K\rangle$ is the plane wave of the electron $\langle\vec{r}|\varphi_K\rangle = (2\pi)^{-3/2}\exp(i\vec{K}\cdot\vec{r})$ with energy $E_K = \hbar^2\vec{K}^2/2m$ and $|n\rangle$ is a phonon state of the crystal.

By Fermi's golden rule, we have

$$I(\vec{k}, \vec{K}) = \left\langle\sum_f |\langle\Psi_f|H_I|\Psi_i\rangle|^2\delta(E_K + \epsilon_n - h\nu - \epsilon_k - \epsilon_m)\right\rangle, \qquad (3)$$

in which the summation $\sum_f$ runs over the final phonon states and $\langle\cdots\rangle$ means the canonical average over the initial phonon states. By using the representation of the Bloch function (1), the transition matrix element is given by

$$\langle\varphi_K|H_I|\psi_k\rangle = \vec{\zeta}\cdot\vec{\kappa}\frac{1}{\sqrt{N}}\sum_i e^{-i(\vec{K}-\vec{k})\cdot\vec{R}_i^0}e^{-i\vec{K}\cdot\vec{u}_i}, \qquad (4)$$

where we have changed the integration variable from $\vec{r}$ to $\vec{r} - \vec{R}_i$ in the evaluation of ith term, and set

$$\vec{\zeta} = (2\pi)^{-3/2}\int d^3r\, e^{-i\vec{K}\cdot\vec{r}}\left(-i\hbar\frac{\partial}{\partial\vec{r}}\right)w(\vec{r}).$$

Putting Eq. (4) into (3), and using the translational symmetry, we find after some exercise,

$$I(\vec{k}, \vec{K}) = \frac{|\vec{\zeta}\cdot\vec{\kappa}|^2}{2\pi\hbar}\int_{-\infty}^{\infty}dt\, e^{-i(E_K-h\nu-\epsilon_k)t/\hbar}\sum_i e^{i(\vec{K}-\vec{k})\cdot\vec{R}_i^0}F_i(t) \qquad (5)$$

with the spatiotemporal generating function

$$F_i(t) = \langle e^{i\vec{K}\cdot\vec{u}_i(t)}e^{-i\vec{K}\cdot\vec{u}_0}\rangle,$$

where $\vec{u}_i(t)$ is the Heisenberg representation of $\vec{u}_i$ at time t, and we have chosen $\vec{R}_0^0 = 0$. The generating function can be calculated by expanding $\vec{u}_i$ with the phonon operators as in Ref. [4],

$$F_i(t) = \exp\left[\int_{-\infty}^{\infty}\{J_i(\omega)e^{-i\omega t} - J_0(\omega)\}d\omega\right]$$

in which the spectral function $J_i(\omega)$ is given by

$$J_i(\omega) = \sum_q \alpha_q^2[\{n(\omega_q) + 1\}e^{i\vec{q}\cdot\vec{R}_i^0}\delta(\omega - \omega_q)$$
$$+ n(\omega_q)e^{-i\vec{q}\cdot\vec{R}_i^0}\delta(\omega + \omega_q)],$$

with

$$\alpha_q^2 = \left(\frac{\hbar}{2NM\omega_q}\right)|\vec{K}\cdot\vec{\eta}_q|^2,$$

and

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

where q is the abbreviation for the wave vector and the branch index of phonons, and $\vec{\eta}_q$ is the polarization vector of the phonon.

The actual calculation was done by assuming the Debye model for the phonons. The spectral function is given by

$$J_i(\omega) = \begin{cases} \frac{3g}{\omega_D^2}\{n(\omega) + 1\}\frac{c}{R_i^0}\sin(\frac{\omega R_i^0}{c}), & (0 < \omega < \omega_D) \\ \frac{3g}{\omega_D^2}n(|\omega|)\frac{c}{R_i^0}\sin(\frac{\omega R_i^0}{c}), & (-\omega_D < \omega < 0) \end{cases} \qquad (6)$$

in which $g \equiv E_K/\hbar\omega_D$ is the effective coupling constant, ω_D is the Debye frequency, and c is the sound velocity.

In the absence of the recoil effect $F_i(t) = 1$ so that Eq. (5) results in the conservation of the wave vector modulus a reciprocal lattice vector. The recoil effect, however, destroys the spatial coherence. The relative magnitude of the contribution to the total intensity of the term $i \neq 0$ to that $i = 0$ is estimated much smaller than unity even for the terms corresponding to the nearest-neighbor atoms in the region of hard x ray. We can thus safely neglect those terms as $i \neq 0$ in accordance with the incoherent scattering approximation [18]. The angular dependence both for $\vec{k}$ and $\vec{K}$ disappears in the photoelectron spectrum. By introducing the binding energy ϵ for the initial state $\epsilon = -\epsilon_k - \phi$ with ϕ being the work function, and the apparent binding energy E defined by $E = h\nu - E_K - \phi$, the photoemission spectrum is written as

$$I(\epsilon, E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\, e^{i(E-\epsilon)t/\hbar}F_0(t),$$

where the angular dependence of the emitted electrons is averaged in accordance with the experiment. The actual spectrum is given by taking the average over the initial distribution of the electrons,

$$I(E) = \int I(\epsilon, E) f(\mu - \epsilon) D(\epsilon) d\epsilon,$$

where $f(\epsilon) = 1/(e^{(\epsilon-\mu)/k_B T} + 1)$ is the Fermi distribution function with the chemical potential μ, and $D(\epsilon)$ is the density of state near the Fermi edge which is approximated constant. Finally, we take into account the Gaussian broadening due to the resolution of the apparatus.

The theoretical curves for the XPS with excitation energy 7940 eV are plotted in Fig. 1 for Au (dotted line) and Al (solid line). The Debye energies are $\hbar\omega_D(\text{Al}) = 36.8$ meV and $\hbar\omega_D(\text{Au}) = 14.2$ meV [19]. The broadening of the observed Fermi edge profile originates from three factors: the temperature dependence of the Fermi-Dirac function, the experimental resolution, and the recoil effect. The broadening due to the experimental resolution is fixed to be 108 meV (FWHM) by fitting the line shape for Au. The effective coupling constant for Al and Au are $g = 4.3$ and 1.5, respectively. In this figure, the zero of the binding energy is chosen at the experimental value of the chemical potential of Au. As shown in Fig. 1, the agreement with the theoretical curves is good. The observed Fermi energy of Al is shifted by 120 meV as compared with that of Au due to the recoil effect. A simple estimation by using Eq. (1) gives the value of this shift to be 138 meV. The quantum mechanical calculation based on the Debye model correctly reproduces the experimental value. The reduction from 138 to 120 meV is due to the quantum effect of phonons [4,14]. It should be noted that, in the case of hard x-ray excitation with energy as high as 7940 eV, even the observed Fermi energy of Au is shifted about 24 meV from the true value.

In Fig. 2(b), the results for the case with excitation energy 880 eV are shown. The effective coupling constants for Al and Au are $g = 0.48$ and 0.17, respectively, in this case. Although the difference of the spectrum between Al and Au is small in this excitation energy, it does exist.

In this Letter, we have reported the modification of the photoelectron spectra at the Fermi edge due to the recoil effect in simple metals. The existence of the photoelectron recoil effect means that the electron is coupled with the crystal lattice, and the wave function of the electron follows adiabatically the atomic motion. Therefore, it is a little surprising that the Bloch electron in the valence band of Al, which is a typical material where the nearly free-electron picture works well [20], shows remarkable recoil effects. As shown above, Bloch's theorem itself guarantees the dependence of the wave function on the lattice coordinates. The recoil effect directly follows from this fact as a kinematic effect. The finding of recoil effects in the Bloch electrons indicates a new spectroscopic aspect in the XPS, and due care must be taken to interpret changes at and near the Fermi level when using hard x rays. The magnitude of the recoil effect depends essentially on the mass of the

component atoms, as shown in Fig. 1. Since the photoelctron spectra reflect also the nature of the electronic state in the initial state, the XPS recoil effect in the valence levels of *composite materials* poses an interesting problem. If the material is composed of atoms with big mass differences, and if the valence levels are made of hybridized orbitals originating in specific atomic species, the modification of the photoelectron spectra will depend on the local density of state of the level. The experimental and the theoretical study of such effects is left for future works.

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[1] C. P. Flynn, Phys. Rev. Lett. **37,** 1445 (1976).
[2] W. Domcke and L. Cederbaum, J. Electron Spectrosc. Relat. Phenom. **13,** 161 (1978).
[3] M. Cini, Phys. Rev. B **29,** 547 (1984).
[4] Y. Takata, Y. Kayanuma, M. Yabashi, K. Tamasaku, Y. Nishino, D. Miwa, Y. Harada, K. Horiba, S. Shin, S. Tanaka, K. Ikenaga, K. Kobayashi, Y. Senba, H. Ohashi, and T. Ishikawa, Phys. Rev. B **75,** 233404 (2007).
[5] E. Kukk, K. Ueda, H. Hergenhahn, X.-J. Liu, G. Prümper, H. Yoshida, Y. Tamenori, C. Makochekanwa, T. Tanaka, M. Kitajima, and H. Tanaka, Phys. Rev. Lett. **95,** 133001 (2005).
[6] T. D. Thomas, E. Kukk, R. Sankari, H. Fukuzawa, G. Prümper, K. Ueda, R. Püttner, J. Harries, Y. Tamenori, T. Tanaka, M. Hoshino, and H. Tanaka, J. Chem. Phys. **128,** 144311 (2008).
[7] See, for example, L. Wirtz and A. Rubio, Solid State Commun. **131,** 141 (2004).
[8] Y. Takata *et al.* (to be published).
[9] M. Vos and M. R. Went, Phys. Rev. B **74,** 205407 (2006).
[10] M. R. Went and M. Vos, Nucl. Instrum. Methods Phys. Res., Sect. B **266,** 998 (2008).
[11] H. Rauh and N. Watanabe, Phys. Lett. A **100,** 244 (1984).
[12] A. L. Fielding, D. N. Timms, and J. Mayers, Europhys. Lett. **44,** 255 (1998).
[13] M. Vos, M. R. Went, Y. Kayanuma, S. Tanaka, Y. Takata, and J. Mayer, Phys. Rev. B (to be published).
[14] R. L. Mössbauer, Z. Phys. **151,** 124 (1958).
[15] K. Tamasaku *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **467/468,** 686 (2001).
[16] T. Ishikawa, K. Tamasaku, and M. Yabashi, Nucl. Instrum. Methods Phys. Res., Sect. A **547,** 42 (2005).
[17] H. Ohashi *et al.*, AIP Conf. Proc. **879,** 523 (2007).
[18] L. Van Hove, Phys. Rev. **95,** 249 (1954).
[19] See, for example, C. Kittel, *Quantum Theory of Solids* (John Wiley and Sons, New York, 1963), Chap. 5.
[20] W. A. Harrison, *Solid State Theory* (McGraw-Hill, New York, 1970), Chap. 2.