Review

Two-dimensional angle-resolved photoelectron spectroscopy using display analyzer—Atomic orbital analysis and characterization of valence band

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Abstract

The information obtained by two-dimensional angle-resolved photoelectron spectroscopy in UPS (ultraviolet photoelectron spectroscopy) region is described. A display-type spherical mirror analyzer can measure wide-angle angular distribution of photoelectrons of one particular kinetic energy (binding energy) without changing the angles of incident light and the sample. The shape of the cross section of valence band, especially of the Fermi surface can be observed directly on the screen. Three-dimensional energy band and Fermi surface are obtained by scanning the binding energy of two-dimensional band mapping. In the case of linearly polarized light excitation the symmetry relation in the photoelectron excitation process can also be displayed as “angular distribution from atomic orbital ADAO”, which is used to distinguish the atomic orbitals constituting the energy band. An example is shown for the atomic orbital analysis of Cu Fermi surface at each k point. It was successfully revealed that the Cu 4p orbitals are aligned with their axes pointing outwards. Another important angular distribution is the “photoemission structure factor PSF”, which originates from the interference among photoelectron waves from individual atoms. PSF determines the intensity inequality between Brillouin zones and reveals the bonding character of the energy band.

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1. Introduction

Photoelectron spectroscopy is a powerful technique to study both electronic and atomic structure of solid and surfaces [1]. Using the rule of the energy and momentum conservation in the photoemission process the valence band structure can be measured directly. Two-dimensional angle-resolved photoelectron spectroscopy provides a rich variety of information. In UPS (ultraviolet photoelectron spectroscopy) region the two-dimensional angular distribution of constant kinetic energy (binding energy) photoelectron reveals the shape of cross section of valence band, one application of which is the Fermi surface mapping. The electronic and chemical character of materials are determined mostly by the motion of electrons at Fermi level. The two-dimensional Fermi surface mapping reveals the electronic structure change during the phase transition such as superconductivity or CDW.

The two-dimensional photoelectron angular distribution in XPS (X-ray photoelectron spectroscopy) region is also powerful in the analysis of three-dimensional atomic structure around specific atoms by using the technique of photoelectron diffraction (PED) or photoelectron holography (PEH). Very recently a new method of taking "stereo photograph of atomic arrangements" was invented [2] utilizing the phenomenon of "rotation of forward scattering peaks" [3]. The stereoscopic photographs of atomic arrangements can be displayed directly on the screen of display-type spherical mirror analyzer [4] without any computer-aided conversion process. These developments in XPS region has been described in previous report [5], and this article only concerns on UPS region.

Recent development of high performance commercial analyzer made it easy to measure Fermi surface structure [6,7]. Usually the sample is rotated around two axes while the direction of incident light and detectors are fixed because the light source and the detector are usually large and they are difficult to rotate around the sample. The symmetry relation with respect to the electric vector of the light disappears in this "rotating-sample method". This symmetry relation in the photoelectron excitation process by using a linearly polarized light is important and can be used to distinguish the symmetry of the initial state, especially to determine the atomic orbital constituting the energy band. A display-type spherical mirror analyzer [4] can measure wide-angle angular distribution of photoelectrons of one particular kinetic energy without changing the angles of incident light and the sample.

Fig. 1 shows an example of two-dimensional energy band of graphite obtained by a display-type spherical mirror analyzer and linearly polarized light [8]. The brightness is proportional to the photoelectron intensity. Graphite has honeycomb carbon sheets (shown in Fig. 8 later), and its electronic structure has hexagonal symmetry. Hexagonal Brillouin zone is shown by white lines in Fig. 1. The center of the hexagon is the Γ point, the apex is the K point, and the midpoint of one side is the M point. We can see strong short four lines just inside the four K points.

The valence band structure of graphite is shown in Fig. 2. The valence band consists of π, σ2, σ3, and σ1 (not shown) bands. The π band is made of p_π orials, σ1 and σ2 are from p_π and p_σ orbitals, and σ3 are mainly from s orbitals. The graph shown in Fig. 2 is a...
typical presentation of band structure, where the dispersions are shown by curves only along symmetric directions. Fig. 1 is a two-dimensional cross section of this band at the binding energy of horizontal dotted line, which corresponds to the binding energy of 0.7 eV.

Comparing Figs. 1 and 2 one can recognize that Fig. 1 has much more information than Fig. 2. Fig. 1 shows the band dispersion not only along the symmetric direction but also in the whole Brillouin zone. Moreover we can see strong anisotropy in Fig. 1. Because the electronic structure has hexagonal symmetry, we expect six-fold symmetric pattern. We can see, however, only four strong short lines in Fig. 1 at near the left and right four $K$ points, and we cannot see them at near the top and bottom $K$ points. This strong anisotropy is a result of symmetric relation between the atomic orbital and the direction of electric vector of the incident light. This anisotropy in direction has a meaning that this $\pi$ band is made from $p_\pi$ orbitals, which is explained theoretically in Section 3.2.

In addition to the directional asymmetry, we can see Brillouin zone inequivalence. In Fig. 1 we can see strong features only inside the first Brillouin zone. This inequivalence of Brillouin zone has a meaning that this band is a "bonding band", which will be explained in Section 3.3. Thus the combination of a display analyzer and a linearly polarized light enables analysis of atomic orbitals and bonding character in a very short time.

Even a three-dimensional energy band can be obtained by scanning the binding energy of two-dimensional band mapping. Fig. 3 is a result of three-dimensional construction of graphite valence band by stacking many two-dimensional patterns [9]. The three-dimensional energy band enables the quantitative analysis of electric behavior. The group velocity of electron is obtained by differentiating the three-dimensional surface as shown in Fig. 4 [9]. The quantity concerning to electric conductivity or cohesive energy are also obtained by integrating the curved surface. In this way the photoelectron spectroscopy using a display analyzer opened new fields of photoelectron spectroscopy. In the following sections the apparatus, theory with some examples, and its recent application are described.

2. Display-type spherical mirror analyzer

A display-type spherical mirror analyzer (DIANA) (Fig. 5) [4,10-13] is a different type of display analyzer than Eastman-type display analyzer [14,15]. Compared to the Eastman-type display analyzer, this analyzer has two advantages. One is that the emission and detection angles of photoelectrons are exactly parallel; hence the pattern displayed on its screen is not distorted. The other is that the acceptance angle can be made infinitely

Fig. 3. Three-dimensional band structure of graphite.

Fig. 4. Group velocity of graphite $\pi$ band.

Fig. 5. Display-type spherical mirror analyzer (DIANA).
wide, because the convergence to the exit aperture is exact irrespective of the angle, and has no spherical aberration. Therefore, one can measure the angular distribution of particles of one particular kinetic energy up to about 2π steradians at a time. The energy analysis principle has been changed from “focus-defocus” [4] to “high-pass and low-pass filtering’’ [10,11]. The energy resolution of the latest DIANA [12,13] is about 0.3% of the pass energy.

Fig. 5 shows a schematic view of the new DIANA [13]. It consists of a hemispherical main grid (G1), outer spherical grid, and guard rings (Gd). There are 160 obstacle grids (Ob) on the inner surface of the outer sphere. The Ob’s are axially symmetric with respect to the axis connecting the sample and the center (O) of the hemisphere. G is grounded. The potentials V(r) [V] of Ob’s and guard rings are biased according to their radii r from O by the formula V(r) = −2Ed(1 − a/r), where Ed [eV] is the pass energy and a is the radius of the main grid G. The electrostatic field in the space surrounded by the electrodes G, Ob and Gd is thus made spherically symmetric with respect to the center O. The trajectories of the emitted electrons from the sample are subjected to this field after passing through G, and their loci are ellipsoidal orbits obeying the Kepler’s law. Their trajectories inside G are straight lines.

The electrons of energy Ed converge exactly to the exit aperture A, which is located at the symmetric position of S with respect to O. Their incident angles are exactly parallel to their emission angles. The Ob’s play essential roles in energy analysis by cutting unnecessary electrons that have higher kinetic energies than the pass energy Ed [10,11]; an electron having slightly higher energy travels slightly outside focus, collides with the electrodes and is absorbed or scattered. The scattered electrons are unlikely to pass through the small exit aperture A. Thus the Ob works as a “low-pass filter”. On the other hand, the retarding grid R works as a “high-pass filter”, which retards the electrons that have lower kinetic energies than the applied potential.

The electrons, having passed through the retarding grid, are amplified by a pair of microchannel plates (MCP), M, and are converted by a phosphor screen (P) to light pulses which are detected from outside the vacuum chamber by a cooled CCD camera. The two-dimensional photoelectron intensity angular distribution (2D-PIAD) on the screen is the same as the original 2D-PIAD in front of the sample. An electron gun is mounted for the purpose of LEED measurement. Synchrotron radiation (SR) or excitation light is introduced through a hole. The acceptance angle is limited by the solid angle of the plane MCP, and is ±60°. The energy resolution (ΔEd/Ed) of the present analyzer has been estimated to be 0.3% of the pass energy.

3. Theory of two-dimensional angle-resolved photoelectron spectroscopy of valence band

3.1. Two-dimensional angle-resolved photoelectron spectroscopy of valence band

Angle-resolved photoelectron spectroscopy is a method to analyze electronic structure of solid by measuring the kinetic energy of photoelectrons excited by ultraviolet light. Fig. 6 summarizes the parameters used in angle-resolved photoelectron spectroscopy. The incident photon is a monochromatic vacuum ultraviolet light of energy ℏν. E is its electric vector. The incident direction of light is denoted by polar coordinate (θi, φi). The direction of the photoelectron is denoted by polar coordinate (θ, φ). Ed and k are the kinetic energy and the wave vector of the photoelectron, respectively. Its spin σ is not described in this article. σ of photoelectron does not change from that of the initial state in usual photoemission process.

Here we consider the photoemission process from the initial state |i〉 having the wave vector q and energy Ei to the final state |f〉 with the wave vector k and energy Ef using a method described in Ref. [8,16]. The photoelectron intensity I(θ, φ) is expressed by so-called Fermi’s golden rule as

\[ I(\theta, \phi) \propto D^*(E_{\text{f}}, k)|M_{q1}|^2 \delta(E_{\text{f}} - E_{\text{i}} - h\nu). \]  

(1)

The delta function \( \delta(E_{\text{f}} - E_{\text{i}} - h\nu) \) expresses the law of energy conservation. The momentum conservation \( \delta(k - q - G_{1}) \) also holds because of the periodicity along the crystal surface, where \( k, q \), and \( G_{1} \) are wave vectors of the photoelectron, the initial state, and the reciprocal lattice unit vector parallel to the surface, respectively. When the potential change is not sharp the initial state wave number perpendicular to the surface \( q_{z} \) can be calculated from \( k_{z} \), in vacuum considering their potential difference. This \( q_{z} \) dependence produces three-dimensional \( (k_{x}, k_{y}, k_{z}) \) band structure, which will be shown later. \( D^*(E_{\text{f}}, k_{1}) \) is the one-dimensional density of state 1D-DOS, which is the sum of density of state in a Brillouin zone at \( E_{\text{f}} \) and \( k_{1} \). The distribution of \( D^*(E_{\text{f}}, k_{1}) \) in the Brillouin zone represents the shape of cross section of the band structure at \( E_{\text{f}} \) in the case of an ideal two-dimensional system.

\( M_{q1} \) is the transition matrix from the initial state to the final state. In the dipole approximation \( M_{q1} \) is expressed as

\[ |M_{q1}|^2 = [(\hat{r} \cdot \mathbf{r})(\mathbf{q} \cdot (k_{1} - k))], \]  

(2)

where \( \hat{r} \) is the polarization unit vector of the incident light, which is parallel to \( \mathbf{E} \), and \( \mathbf{r} \) is the dipole operator.

The initial state |i〉 having the wave vector q is written here by a Bloch state in tight-binding approximation as

\[ |i⟩ = \sum_{n} c_{n} |\psi_{n}(r)⟩, \]

where \( c_{n} \) is the Bloch coefficient and \( |\psi_{n}(r)⟩ \) is the Bloch state with wave vector \( q \) and energy \( E_{n} \). The wave number perpendicular to the surface \( q_{z} \) does not conserve strictly due to the force from sudden change of potential perpendicular to the surface, and also from the uncertainty principle considering the small escape depth.
\[ |\psi\rangle = \frac{1}{\sqrt{N}} \sum_j \sum_{\mu} e^{iR_j \cdot \mathbf{e}_\mu} \psi_\mu \phi_\mu (r - R_j - \tau_\mu), \]

where \( N \) is the total number of atoms, \( \tau_\mu \) is the position vector of the \( \mu \)th atom in the \( j \)th unit cell at \( R_j \), \( \phi_\mu (r) \) is the \( \mu \)th orbital of the \( \mu \)th atom, which is expressed using a spherical harmonics \( Y_{\ell \mu}(\theta, \phi) \) as

\[ \phi_\mu (r) = R(r) Y_{\ell \mu}(\theta, \phi). \]

\( R(r) \) is its radial function, while \( \ell \) and \( \mu \) are the quantum number of the orbital angular momentum and its \( \ell \)-component of orbital angular, respectively. Note that in many cases the atomic orbital is the sum of different \( m \)’s, for example \( p_\mu \) orbital is the sum of \( m = -1 \) and \( 1 \).

The final state \( |\psi\rangle \) with the wave vector \( \mathbf{k} \), which is a plane wave at the detector and is also a Bloch state in bulk, is written as

\[ |\psi\rangle = 4\pi \sum_{\ell \mu} (i)^\ell e^{-i\mathbf{k} \cdot \mathbf{R}_j} Y_{\ell \mu}(\theta, \phi) Y_{\ell \mu}(\theta, \phi) R_j (r). \]

Using the above formula for \( |\psi\rangle \), \( M \) is written as

\[ M = \frac{1}{\sqrt{N}} \sum_j \sum_{\mu} e^{i(R_j \cdot \mathbf{e}_\mu)} \langle f' | \mathbf{e} \cdot \mathbf{r} | \phi_\mu (r - R_j - \tau_\mu) \rangle \]

\[ \times \frac{1}{\sqrt{N}} \sum_j \sum_{\mu} e^{i(R_j \cdot \mathbf{e}_\mu)} \langle f' \mathbf{r} + R_j + \tau_\mu | \mathbf{e} \cdot \mathbf{r} | \phi_\mu (r') \rangle. \]

Here, \( \mathbf{r} \) in the bracket was replaced by \( \mathbf{r}' = \mathbf{r} + \mathbf{R}_j + \mathbf{\tau}_\mu \).

From Bloch’s theorem for the complex band structure,

\[ \langle f' \mathbf{r} + \mathbf{R}_j + \mathbf{\tau}_\mu | \mathbf{e} \cdot \mathbf{r} | \phi_\mu (r') \rangle = e^{-i\mathbf{k} \cdot \mathbf{R}_j} \langle f' | \mathbf{r} | \phi_\mu (r') \rangle. \]

Then

\[ M = \frac{1}{\sqrt{N}} \sum_j \sum_{\mu} e^{-i\mathbf{k} \cdot \mathbf{R}_j} \langle f' | \mathbf{r} | \phi_\mu (r') \rangle. \]

We define the “angular distribution from atomic orbital ADAO” \( A_{\mu} \) as

\[ A_{\mu} \equiv \langle f' | \mathbf{r} | \phi_\mu (r') \rangle. \]

The dipole operator can be expressed by the spherical harmonics as

\[ \mathbf{e} \cdot \mathbf{r} = \sum_{\ell \mu} \sqrt{\frac{2\ell}{\ell + 1}} Y_{\ell \mu}(\theta, \phi) Y_{\ell \mu}^*(\theta, \phi), \]

where \( \mathbf{e}_z = (\mathbf{e}_x + i \mathbf{e}_y) / \sqrt{2}, \mathbf{e}_\phi = \mathbf{e}_z \).

The integral for the angular part can be expressed by Gaunt coefficient \( c^l(m', l, m) \).

\[ c^l(m', l, m) = \frac{4\pi}{3} \int \int Y_{l \mu}^*(\theta, \phi) Y_{l \mu \nu}^*(\theta, \phi) Y_{l \mu}(\theta, \phi) \sin \theta \phi d\theta d\phi. \]

This \( c^l(m', l, m) \) is not zero only when \( m = m' \pm 1 \).

Using the above formula, \( M_{\mathbf{k}} \) is written as

\[ M_{\mathbf{k}} \propto \frac{1}{\sqrt{N}} \sum_{j \mu} e^{-i\mathbf{k} \cdot \mathbf{R}_j} \sum_{\nu} c_j Y_{\ell \mu}^*(\theta_\nu, \phi_\nu) c^l(f, m + \mu, l, \nu), \]

where \( \mathbf{R}_j \) is the integral of the radial part, which is a constant complex number depending on \( l, \ell, \) and \( \nu \), and tabulated by Goldberg et al. [17].

Then ADAO \( A_{\mu} (\mathbf{k}, \phi_\nu) \) can be written as

\[ A_{\mu} (\mathbf{k}, \phi_\nu) = \sum_{\ell \mu} R_{\ell} \sum_{\nu} c_j Y_{\ell \mu}^*(\theta_\nu, \phi_\nu) c^l(f, m + \mu, l, \nu). \]

The range of the sum over \( j \) in Eq. (13) is unlimited for parallel component \( j_2 \) and semi-infinity for perpendicular component \( j_1 \).

\[ \frac{1}{\sqrt{N}} \sum_{j \mu} c_j^l \sum_{\nu} \sum_{\ell \mu} e^{-i\mathbf{k} \cdot \mathbf{R}_j} \sum_{\nu} \delta_{\ell \nu} \delta_{\mu \nu} \frac{1}{1 - e^{-i\mathbf{k} \cdot \mathbf{R}_j}}. \]

Here \( \mathbf{k} \) is the lattice vector between the equivalent layers parallel to the surface, and \( \mathbf{k}^* \) has an imaginary part to consider absorption. The idea of “weighted-indirect-transition”, which is the combination of 1D-DOS and this factor was introduced by Grandke et al. [18]. The second term in Eq. (15) is very close to the delta symbol \( \delta_{\ell \nu} \delta_{\mu \nu} \). Hence, it can be written as \( \delta_{\mathbf{k} \cdot \mathbf{R}_j} \), and \( M_{\mathbf{k}} \) is written as

\[ M_{\mathbf{k}} \propto \sum_{\mu} e^{-i\mathbf{k} \cdot \mathbf{R}_j} A_{\mu}, \]

and

\[ \mathbf{k} = \mathbf{q} + \mathbf{G}. \]

Hence the intensity distribution is expressed as

\[ I(\theta, \phi) \propto D^2(E_\nu, \mathbf{k}) \sum_{\nu} e^{-i\mathbf{k} \cdot \mathbf{R}_j} A_{\mu}^2 \delta(E_{\nu} - E_i - h\nu). \]

When the initial state is composed of only one \( \nu \)th atomic orbital, we can pull ADAO term out of the absolute value as

\[ I(\theta, \phi) \propto D^2(E_\nu, \mathbf{k}) \sum_{\nu} e^{-i\mathbf{k} \cdot \mathbf{R}_j} |A_{\mu}(\theta, \phi)|^2 \delta(E_{\nu} - E_i - h\nu) \]

\[ = D^2(E_\nu, \mathbf{k}) |F(\mathbf{k})|^2 |A_{\mu}(\theta, \phi)|^2 \delta(E_{\nu} - E_i - h\nu). \]

We introduced here a “photoemission structure factor PSF” \( F(\mathbf{k}) \) as

\[ F(\mathbf{k}) = \sum_{\nu} e^{-i\mathbf{k} \cdot \mathbf{R}_j} A_{\nu}. \]

The term |\( F(\mathbf{k}) |^2 \) is an intensity distribution in a reciprocal \( \mathbf{k} \) space, which is independent of the kinetic energy of photoelectrons or incident angle of photons. This factor originates from the interference of the waves from different groups of atoms in a unit cell and is
similar to the structure factors in X-ray or electron diffraction replacing the scattering factors by the coefficients for each atomic orbital in the LCAO wavefunction.

Here we showed that the photoelectron intensity angular distribution (PIAD) from valence band can be understood in simple cases as a product of 1D-DOS, "photoemission structure factor PSF", and "angular distribution from atomic orbital ADAO". From next section we will see how these terms act in real systems using the data for single crystal graphite.

3.2. Angular distribution from atomic orbital ADAO

The formula for the "angular distribution from atomic orbital ADAO" is shown in Eq. (14). In the case of x band of graphite as shown in Fig. 1, initial (l, m) is (1, 0). The electric vector of the incident light is along x direction, and only e_x is not zero. Therefore e_1 = -1/\sqrt{2}, e_2 = 0, and e_z = 1/\sqrt{2}. In dipole selection rule, l' can be either 2 or 0. In the present case, however, only l' = 2 state is realized because the final state has m' values of either +1 or -1. Hence Eq. (14) becomes

\[ A_{p_x} = R_2 \left( -Y_{1,1}(\theta_x, \phi_x)\psi_{11}(2,1,1,0) + Y_{2,-1}(\theta_x, \phi_x)\psi_{21}(2,-1,1,0) \right) / \sqrt{2}. \]  

(21)

Because these two Gaunt coefficients have the same value, the intensity distribution from this p_x atomic orbital \( I_{p_x}(\theta, \phi) \) becomes

\[ I_{p_x}(\theta, \phi) = |A_{p_x}|^2 \propto \left| -Y_{1,1}(\theta, \phi) + Y_{2,-1}(\theta, \phi) \right|^2 = |\sin \theta \cos \phi|^2. \]  

(22)

Similarly the intensity distribution from p_y and p_z, atomic orbitals become

\[ I_{p_y}(\theta, \phi) \propto |\sin \theta \sin \phi|^2 \]  

(23)

\[ I_{p_z}(\theta, \phi) \propto R_2 \left( \frac{3}{4\pi} \sin^3 \theta \cos \phi - \sqrt{\frac{1}{12\pi} - 3 \cos^2 \theta - 1} \right) + e^{-i\phi} \frac{R_2}{\sqrt{3}n} \]  

(24)

When the kinetic energy of photoelectron is 50 eV the values in Eq. (24) are \( R_2 = 0.645, R_0 = 0.185, \delta_2 = 2.996, \) and \( \delta_0 = 6.160 \) [17].

The angular distributions thus calculated are shown in Fig. 7. The direction of the electric vector E of the incident light is horizontal. The two-dimension density plot can be compared to the experimental distribution. The three-dimensional presentations are also shown in the column [f]. Note that the shape of the ADAO from s orbital is the same as the orbital shape of p_x, and those from p orbital are the same as one of d orbitals, and so on. This is the result of multiplicity of Eq. (11) in the photoexcitation process. Thus the ADAOs from different atomic orbitals are almost orthogonal to each other. Hence we can easily distinguish initial state atomic orbital when we observe two-dimension angular distribution pattern in whole angles in principle. The method of atomic orbital analysis from two-dimensional angular distribution bases on this phenomenon of orthogonality. The actual application of this method is not so straightforward as described below.

Consider the assignment of atomic orbital constituting the band shown in Fig. 1. Even if we observe full-solid-angles, we can observe only a part of angular distribution because the band exists only at particular region as shown in Fig. 1. This is the effect of delta function in Eq. (1), which shows a cross section of the band. The characteristic of Fig. 1 is the lack of intensity on the central vertical line as well as on the central horizontal line. Several intensity angular distributions in Fig. 7, such as s, p_x, p_y, p_z, do not contradict with the pattern in Fig. 1. We can get whole intensity angular distribution when we scan the binding energy. The bright color of the π band in the lower picture in Fig. 3 shows the place where the intensity is high. The important information is that the intensity at M point parallel to E is strong and not zero. From this fact we can deny the possibility of p_z, d_z orbitals. From this qualitative analysis it is impossible to distinguish s and p_x orbitals because both of them do not have intensity on the central vertical line. For the quantitative analysis we proposed a rotation method [20], where the sample is rotated around the sample normal axis, and the intensity variation is examined with respect to the rotation angle. Using this rotation method we can distinguish all orbitals in principle. In most cases, however, this method is not necessary because we know the orbital groups constituting the band. In case of graphite, the energy of s band is much (about 20 eV) lower than p bands and the band observed in Fig. 1 should be one of the p bands. Then we can conclude that the band in Fig. 1 is composed of p_orbitals.

For some cases this rotation-sample method is necessary to analyze atomic orbitals. Especially in the atomic orbital analysis at Fermi surface we cannot use scanning-binding-energy method to increase the information. So far the atomic orbitals constituting the Fermi surface of Bi_Sr_Ca_Cu_O_{6+x} [19], Sr_RuO_4 [20], 2H-TaSe_2 [21] have been analyzed using this rotating-sample method. The most effective angle to distinguish various kinds of atomic orbitals is described in Ref. [22]. Recent example will be shown in Section 4.

3.3. Photoemission structure factor PSF

In order to consider "photoemission structure factor PSF" the wavefunction of the initial state must be known. The eigenfunction of π band of one-layer graphite in tight-binding approximation is obtained as
\[ W(q, r) = \frac{1}{\sqrt{N}} \sum_{\alpha} \frac{e^{i\mathbf{g} \cdot \mathbf{r}}}{\sqrt{2(1 + s_{\alpha}(|\mathbf{g}|))}} \left( \frac{\mathbf{g}}{|\mathbf{g}|} p_{\alpha}^\pi(r - \mathbf{R}_a) + e^{i\mathbf{d}_{\pi}} p_{\alpha}^\pi(r - \mathbf{R}_a - \mathbf{d}_{\pi}) \right), \]  
where \( \mathbf{g} = e^{i\mathbf{e}_{\pi}} + e^{i\mathbf{e}_{\pi}} + e^{i\mathbf{e}_{\pi}}. \)

\[ \mathbf{d}_1, \mathbf{d}_2, \text{and} \mathbf{d}_3 \text{ are position vectors of nearest neighbor carbon atoms shown in Fig. 8.} \]
\[ \mathbf{d}_1 \text{ is (d,0,0). Unit cell is shown by broken lines and two kinds of carbon atoms A and B are labeled in Fig. 8.} \]
\[ p_{\alpha}^\pi(r - \mathbf{R}_a) \text{ is a } p_{\alpha} \text{ atomic orbital of A atom in nth unit cell.} \]
\[ s_{\alpha} \text{ is the overlap integral between two adjacent } p_{\alpha} \text{ atomic orbitals.} \]

In this case the photoemission structure factor of Eq. (20) becomes

\[ |F(k)|^2 = \frac{1}{2(1 + s_{\alpha}(|r|))} \left( \frac{\mathbf{g}}{|\mathbf{g}|} + e^{-i\mathbf{g} \cdot \mathbf{q}} \right)^2. \]

The angular distribution \( |F(k_x, k_y, 0)|^2 \) of this function is plotted in Fig. 9. \( \mathbf{k} \) \( \mathbf{q} \) are connected by the delta symbol as \( \mathbf{k} = \mathbf{q} + \mathbf{G}. \) Some of \( \mathbf{G} \) are \( \mathbf{G}_0 = (0,0,0), \mathbf{G}_1 = (\frac{1}{2}, 0), \mathbf{G}_2 = (\frac{1}{2}, 0, 0) \). \( \mathbf{G}_1 \) and \( \mathbf{G}_2 \) are shown by broken arrows in Fig. 9. When we calculate the intensity of \( |F(k_x, k_y, 0)|^2 \) at certain \( \mathbf{k} \) point in Fig. 9, the combination of \( \mathbf{q} \) and \( \mathbf{G} \) is not unique, but all combination gives the same result because of the periodicity of the Bloch function.

The white line in Fig. 9 shows the first Brillouin zone (BZ). The intensity in the first BZ is high and in the next BZ is low. Hence this photoemission structure factor clearly explains the fact that we observed intensity only within the first BZ in Fig. 1.

The intensity in second nearest BZ is high, and repeats with a period of \( \sqrt{3} \times \sqrt{3} \times 2\pi \) of the reciprocal lattice. The photoemission structure factor is an intensity distribution in a reciprocal space. The difference of the intensity in different BZs originates from the interference of the photoelectron wave from different atoms in a unit cell. When the unit cell of the crystal contains more than or equal to two atoms, this difference always occurs.

When the intensity in the first BZ is high the signs of the two atomic orbitals are the same and it means that the character of the band is "bonding", whereas when the intensity in the first BZ is low the signs of the two atomic orbitals are opposite and the character of the band is "antibonding". In this way we can reveal the character of the band by observing anisotropy of the photoemission intensity among the BZs.

Indeed this photoemission structure factor effect is widely observed. Here, another example is given. The Si(111) \( \sqrt{3} \times \sqrt{3} - \text{Ag} \) surface is a typical metal-adsorbate induced superstructure. Three Ag atoms are included in a unit cell. So-called S\(_1\) surface state at Fermi level can be detected in the second surface Brillouin zones but not in the first surface Brillouin zone. Hirahara et al. [23] have reproduced the observed photoemission structure factors by assuming that the \( S_1 \) surface state is constituted of Ag\(_5p_\uparrow\) and \( 5p_\uparrow\) atomic orbitals in a bonding relation.

3.4. Other factors

The angular distribution is mainly described by above two factors \( A \) and \( F \), but affected by scattering process. Umklapp process, which transfer photoelectron intensity by the amount of reciprocal unit vector \( \mathbf{G} \), is often observed. The missing spot in Fig. 1 at the top and bottom K points appears at different photon energies. When the photoelectron was excited by a circularly polarized light, the angular distribution becomes different [24].

4. Application to Fermi surface of Cu single crystal

In this section a recent application of atomic orbital analysis of the Fermi surface of Cu [25] from two-dimensional photoelectron intensity angular distribution (2D-PIAD) using a polarized synchrotron radiation (SR) and a hemispherical display-type analyzer is described. As shown in Fig. 5, SR is introduced through a hole in the analyzer and perpendicularly incident on the sample surface. The polarization direction is horizontal. The 2D-PIAD at a particular kinetic energy is projected to a fluorescent planar screen with the emission angle preserved. Thus the emission angle \( \theta, \phi \) of the photoelectrons can be deduced directly from the position of the PIAD pattern on the screen. The wave number parallel to the surface \( (k_x, k_y) \) can be calculated from its kinetic energy \( E_k \) as
\[ k_x = \frac{\sqrt{2mE_h}}{h} \sin \theta \cos \phi, \]
\[ k_y = \frac{\sqrt{2mE_h}}{h} \sin \theta \sin \phi. \] (28)

The energy resolution \( \Delta E/E \) of this old-type analyzer is 1\% and the angular resolution is 1\°. The experiment was performed at the linearly polarized soft X-ray beam-line BL-7 of Ritsumeikan SR Center in Shiga, Japan [9]. The range of photon energy (\( h\nu \)) covered by a modified Rowland mount spherical grating monochromator is 35–130 eV. The chamber base pressure was \( 7 \times 10^{-10} \) Torr. The Cu(001) single crystal sample was cleaned in situ by Ar ion bombardment and subsequent annealing at 600 °C. The surface quality was checked by low energy electron diffraction.

The PIAD patterns were obtained by dividing the raw images by the analyzer transmittance pattern measured by averaging secondary electron angular distributions. Typical acquisition time for one PIAD measurement was 5 min.

A series of two-dimensional PIAD patterns at Fermi energy are shown in Fig. 10. The photon energy was from 41.5 to 77.5 eV as shown in the figure. The periphery corresponds to the emission angle of ±40° from the surface normal. The [110] direction of the Cu surface coincides with the electric vector of the incident light indicated as a horizontal arrow in the figure. These PIAD patterns are Fermi surface mapping \((k_x, k_z)\) at different \(k_z\) values.

Fig. 10. Fermi surface mapping of Cu single crystal at various photon energies.

All the PIAD patterns show two-fold symmetry due to the linear polarization of the incident light. For instance, PIAD at photon energy of 41.5 eV, four bright features appear along sides of a diamond. As the photon energy increases, they move inward. The PIAD pattern at photon energy around 50 eV shows nearly circular feature with breaks at upper and lower directions, while it gradually turns into a square-like shape at around 60 eV. Photoelectron intensities seen at outside the square-like feature excited with a photon around 70 eV correspond to the ‘necks’ between neighboring Brillouin zone (BZ) [26]. Qu et al. have reported PIADs with light incidence at an angle of 45° to the surface normal. In their configuration the asymmetry shown in Fig. 10 could not be observed. This asymmetry contains information on atomic orbitals as discussed above.

We have calculated the Cu Fermi surface using an \textit{ab initio} code [27]. The curved surface in Fig. 11 shows the calculated Cu Fermi surface. The polygon is the BZ, which arranges in a bee lattice, as shown in Fig. 12. Neighboring Cu Fermi surfaces are connected by a ‘neck’ along the \(\Gamma\)–\(L\) direction. There are protrusions in the \(\Gamma\)–\(X\) directions [28].

Fig. 11. The Cu FS with AOs constituting each \(k\) point. The direction of the \(p\) orbital axes is derived experimentally. Blue, red and green colors shows the calculated orbital ratio between \(4p_x\), \(4p_y\) and \(4p_z\) orbitals, respectively. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Fig. 12. Cu FS together with the spheres corresponding to the wave vector of photoelectrons at various photon energies.
The radii of the four spherical curved surfaces drawn around the BZ labeled B in Fig. 12 represent the wave number \( k \) of the photoelectrons excited from the Fermi level with photons of 41.5, 51.5, 61.5 and 71.5 eV. The origin of the vector is set at the center of the BZ labeled A. A work function \( \Phi \) of 4.7 eV and an inner potential \( V_0 \) of 8.5 eV are assumed for calculating the wave numbers as

\[
k = \frac{\sqrt{2m(E_k + \Phi + V_0)}}{\hbar}
\]  

(29)

Intersection of these spheres and the FS indicates the direction of the observed features in Fig. 10. Note that the sphere representing the excitation by photons of 71.5 eV touches the FS in the BZ labeled D.

Figures shown in Fig. 13 are the combination of above calculation and actual PIADs. The FS labeled B and C in Fig. 12 are shown in the upper two figures, while the FS labeled B and D are shown in the lower two figures.

The sphere for photoelectrons excited by photons of 41.5 eV crosses FS near the \( \Gamma X W K \) plane. The cross section in the BZ labeled B shows a diamond-like shape. The maxima in the PIAD correspond to the cross section at the \( \Gamma K \) direction. In the case of excitation by photons of 51.5 eV, the cross section becomes more circular shape showing good agreement with observed PIAD.

The sphere for photoelectrons excited by photons of 61.5 eV crosses the FS near L points. The cross section of the FS at the BZ labeled B shrinks and become square-like. Finally, the sphere for photoelectrons excited by photons of 71.5 eV crosses also the FS in the neighboring BZ. An inner potential of 13.5 eV had to be used to reproduce the cross sections that appear in the neighboring BZs in the simulated PIAD of down-right in Fig. 13. This difference of the inner potential should be due to its energy dependence. This “neck” structure has also been reported by Aebi et al. [6]. They used He I (21.2 eV) for excitation. Their “neck” structure corresponds to the lower part of the FS in the same BZ.

As shown in Fig. 7, the ADAO from the \( p_\alpha \) orbital has zero intensity line along the vertical direction (\( \phi = \pm 90^\circ \)) and maxima in two directions of \( \phi = 0^\circ \) and \( 180^\circ \). These features are observed in the PIADs excited by photons of 61.5 eV or higher in Fig. 10. These PIADs correspond to the cross section of the FS around the X point. On the other hand, \( p_\gamma \) has its maxima in four directions of \( \phi = 45^\circ \), \( 135^\circ \), \( 225^\circ \) and \( 315^\circ \). The PIADs excited by 40–50 eV photons corresponding to the cross section of the FS near \( \Gamma X W K \) plane have such characteristic features. However, we can not simply conclude that the constituting atomic orbital at the FS within the \( \Gamma X W K \) plane is \( p_\alpha \), since the \( \text{Cu}(001) \) surface has four-fold symmetry.

To determine the constituting atomic orbitals at each \( k \) point, we have measured the PIADs using rotating-sample method with rotating azimuthal angles \( \phi_\psi \). Photons of 45 eV are used to excite the FS just in the \( \Gamma X W K \) plane. Fig. 14(a) shows the PIADs with rotating \( \phi_\psi \) from 0° to 45° in 5° steps from left to right in counterclockwise direction. The \( p_\gamma \)-like pattern (maxima in four directions) observed at the angle of \( \phi_\psi = 0^\circ \) becomes a \( p_\gamma \)-like pattern (maxima in two directions) at the angle of \( \phi_\psi = 45^\circ \).

The photoelectron intensity for the [110] and [110] directions is weak at \( \phi_\psi = 0^\circ \), and becomes strong at \( \phi_\psi = 45^\circ \) while the photoelectron intensity for the [110] and [110] directions diminish at \( \phi_\psi = 45^\circ \). The photoelectron intensity for the [100], [100], [010] and [010] directions remains weak at all angles.

Several conformations of atomic orbitals had been tested but only one of them showed good agreement with the observed PIADs. Fig. 14(c) is the calculated cross section of the FS. Fig. 14(d) shows the derived arrangements of \( p \) orbitals together with the contour map of ADAO calculated using the following equation:

\[
\rho = \frac{\rho_0}{\cosh^2 \left( \frac{r - r_0}{a} \right)}
\]

Fig. 14. Experimental FS in the \( \Gamma X W K \) plane at various azimuthal rotation angles. \( \hbar \) is 45 eV. (a) and (d) Simulated PIADs and ADAO from \( p \) orbitals with their axes pointing radially, respectively. (c) Cross section of the FS at the \( \Gamma X W K \) plane.
Moreover this gun can take SEM (scanning electron microscopy) images. We hope this new DIANA will be widely used to develop many fields of photoelectron spectroscopy.

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