

Angle-Resolved Photoelectron Spectroscopy Studied Based on Plane Density of States. Application to Beryllium

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ABSTRACT

Intensity of angle-resolved photoelectron spectrum from valence bands of single crystals has been derived. It depends on properties of photon, parameters of crystals and orientation of spectrometer. Information possible from experiment and experimental conditions has been analyzed to simplify the theoretical interpretation. The important influence of the angle of acceptance on the results of X-ray photoelectron spectroscopy is in detail investigated. The plane density of states (PDOS) has been introduced as a new characteristic property of electronic structure describing the angle-resolved photoelectron spectroscopy (ARPES). Application of the derived theory to hexagonal crystal Beryllium (Be) is realized by the calculations and discussions of PDOSs for its ΓA , ΓM and ΓA directions whose results show significant anisotropy. These direction dependences of PDOSs contribute to valuating not only the number but also the energy-independence, energy-dependence, and the other properties of electronic states of the considered material taken from ARPES. The peaks of PDOSs are explained in terms of band structure.

Keywords: Angle-resolved photoelectron spectroscopy, plane density of states, band structure, orientation of crystal and spectrometer dependence, hexagonal crystal Be.

INTRODUCTION

Photoelectron spectroscopy has developed into a powerful method providing information on energy distribution or electronic structure of crystals [1-19]. Depending on the orientation of sample, the emission direction of electrons from crystal surface the angle-resolved photoelectron spectroscopy (ARPES) provides the angular distribution anisotropy of energy distribution of photoelectrons [3-19]. Here, for creation by the Röntgen light in X-ray photoelectron spectroscopy (XPS), the dominant volume effects play important role, while the ultraviolet photoelectron spectroscopy (UPS) provides information on electronic structure in the surface area. Many efforts have been made to obtain the detail information of sample taken from ARPES, for example, the photo-ionization dynamics [7], the band structures [8, 9], the spin-orbital coupling [10], the electron dynamics [11], the electronic structures in crystal layers [12] in atomic sheets [13], in surface and bulk areas [14], in magnetic materials [15], in superconductive materials [16], in nanostructures [17], in valence bands of semiconductors [18] and in compounds [19]. Unfortunately, a reliable and effective method

for describing the angle-resolved photoelectron spectra with its angular distribution anisotropy of energy distribution still represents an attractive problem, whose solution is expected to increase the amount and accuracy of information obtainable from ARPES.

The purpose of this work is to derive a method for describing the energy distribution of angle-resolved photoelectron spectra from valence bands of single crystals. In Section 2 the analytical expression of angle-resolved photoelectron spectrum has been derived. It depends on the main characters of ARPES such as properties of photon, parameters of crystals and orientation of spectrometer. The information possible from experiment and experimental conditions to be realized have been analyzed to simplify the theoretical interpretation. The important influence of the angle of acceptance on the results of XPS is in detail investigated. The plane density of states (PDOS) has been introduced as a new characteristic property of electronic structure in the ARPES. Application of the derived theory (Section 3) to hexagonal crystal Beryllium (Be) is realized by the numerical calculations and discussions of PDOSs for its ΓA , ΓM and ΓA

directions whose results show significant anisotropy describing different information of electronic states obtained from experimental ARPES. The peaks are explained in terms of band structure. The conclusions are presented in Section 4.

FORMALISM

Intensity of Angle-Resolved Photoelectron Spectra in Three-Step Model

In photoemission process electrons are created according to Fig. 2.1 from the initial state

$$H'(t) = We^{-i\omega t} + We^{i\omega t}, W = \frac{e}{m} \sqrt{\frac{\hbar}{2\epsilon_0\Omega\omega}} e^{i\mathbf{q}\cdot\mathbf{r}} \mathbf{e} \cdot \hat{\mathbf{P}}, \tag{2.2}$$

where \mathbf{e} is polarization vector and Ω is normalization volume, ω is photon frequency.

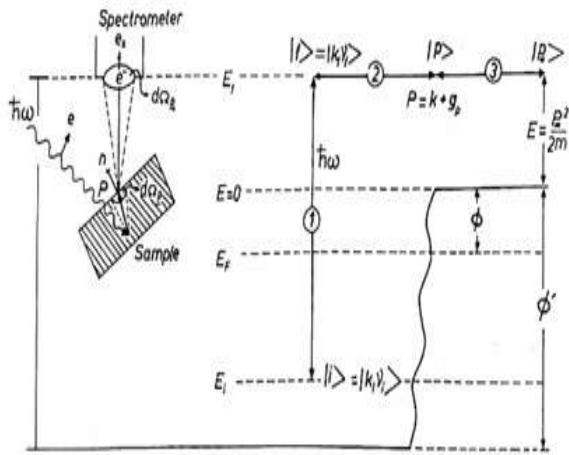


Fig2.1. Photoemission process in three-step model. 1, 2, 3 are the numbers of steps. The directions of electron momentum inside and outside sample and of polarization are indexed.

The final state in Eq. (2.1) is a scattering state which outside crystal is a penetrating wave. In three-step model (Fig. 2.1) the total transmission probability per time of emission process consists of

$$\mathbf{P}(E, \mathbf{e}_s, \mathbf{n}, \Phi') = \sqrt{2mE} \left\{ \mathbf{n} \left[\sqrt{(\mathbf{e}_s \cdot \mathbf{n})^2 + \Phi' / E} - (\mathbf{e}_s \cdot \mathbf{n}) \right] + \mathbf{e}_s \right\}, \tag{2.4}$$

which is obtained from the energy and momentum balances of photoelectron at the surface of crystal

For XPS in good approximation one can obtain $\mathbf{P} = \mathbf{P}_a$, so that the probability for transmission of electron through crystal surface will be determined as

$$\gamma_{i \rightarrow \mathbf{P}_a} = \sum_f \gamma_{i \rightarrow f} \left| \langle f | \mathbf{P} \rangle \right|^2 \delta_{E_i, E_f}. \tag{2.5}$$

$|i\rangle = |k_i, v_i\rangle$ into the final state $|f\rangle$. The transmission probability of this process in the Born approximation is given by

$$\gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | W | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \tag{2.1}$$

where the delta function shows that electron can absorb only a quantum energy $\hbar\omega$ and W is taken from the action field of one photon in the form

- Transmission probability per time from the initial state $|i\rangle$ to the Bloch state $|f\rangle = |k_f, v_f\rangle$
- Probability for transport of electron from state $|f\rangle$ to $|f'\rangle$ by scattering [8-11] where electron penetrates to the surface, and
- Probability of penetration of electron through the surface.

Consequently, the total transmission probability per time has resulted as

$$\gamma_{i \rightarrow \mathbf{P}_a} = \sum_{f, f'} \gamma_{i \rightarrow f} P_{ff'}^{scatt} \cdot P_{f' \mathbf{P}_a}^{surf}. \tag{2.3}$$

Focusing to volume effects the scattering effects are neglected so that it is given $P_{ff'}^{scatt} = \delta_{ff'}$, which is equal to 1 when the normal component of momentum of electron has sufficient value to overcome the potential wall Φ' to reach the crystal surface. Moreover, the momentum \mathbf{P} of electron before emission through crystal surface relates with its value $\mathbf{P}_a = \sqrt{2mE} \mathbf{e}_s$ outside crystal through the height of Φ' and the crystal normal \mathbf{n} by

The momentum \mathbf{P} of photoelectron can be written in the summation of reciprocal vector \mathbf{g}_p and vector \mathbf{k} in the first Brillouin zone (BZ)

$$\mathbf{P} = \mathbf{k}(\mathbf{P}, \mathbf{b}_i) + \mathbf{g}_p(\mathbf{P}, \mathbf{b}_i). \tag{2.6}$$

Hence, through vector \mathbf{b}_i the orientation of crystal is determined and everywhere $\mathbf{k}_i = \mathbf{k}_f = \mathbf{k}$ due to momentum conservation. Consequently, the intensity of photoelectron spectrum for ARPES in the present derived theory has resulted as

$$\begin{aligned} \tilde{I}(\omega, \mathbf{e}, \mathbf{q}; \mathbf{b}_i, n, \Phi'; E, \mathbf{e}_s) dEd \Omega_p &= I(\omega, \mathbf{e}, \mathbf{q}; \mathbf{k}, \mathbf{g}_p, E) dEd \Omega_p \\ &= \frac{\Omega m \sqrt{2mE}}{(2\pi)^2 \hbar^4} \int d^3 \mathbf{P} \sum_{\nu_i, \nu_f}^{resol.} \left| \langle \mathbf{k} \nu_i | W | \mathbf{k} \nu_f \rangle \right|^2 \left| \langle \mathbf{k} \nu_f | \mathbf{k} + \mathbf{g}_p \rangle \right|^2 \delta(E - E(\mathbf{k}, \nu_i) - \hbar\omega) \delta_{E_f, E}. \end{aligned} \quad (2.7)$$

This intensity depends on the properties of photon ($\omega, \mathbf{e}, \mathbf{q}$), the parameters of crystal (\mathbf{b}_i, n, Φ') and the orientation of spectrometer (E, \mathbf{e}_s). They are included by Eqs. (2.1), (2.4) and (2.6), respectively. The summation over the final states is expressed by integration over the momentum- and \mathbf{k} -intervals whose values are specified by dE and $d\Omega_p$ which are indexed by the resolution of spectrometer (*resol.*). This expression of ARPES is convenient for describing rotation of spectrometer or crystal performed in experiment [4].

Plane Density of States as a Characteristic Value for ARPES

The analysis of photoelectron intensity given by Eq. (2.7) for ARPES can be performed based on the experimental conditions. In the angle of acceptance $\Delta\theta$ and energy resolution ΔE all electrons contribute to photoelectron spectra. They have momentums with the value (ΔP) and the direction (ΔP_\perp) lying in an interval around \mathbf{P}_a (Fig. 2.2). These values are presented in Table 2.1 for the normally used experimental values of $\Delta\theta$ and ΔE .

Table 2.1. Comparison of the values of ΔP and ΔP_\perp for Cu based on the normally used experimental values of ΔE and $\Delta\theta$.

Photoemission	E(ryd)	\mathbf{P}_a (a.u.)	$\Delta E(\text{eV}) \rightarrow \Delta P(\text{a.u.})$	$\Delta\theta$ (degree) $\rightarrow \Delta P_\perp$ (a.u.)
UPS	1	1	0.2 \rightarrow 0.01	3 \rightarrow 0.05
XPS	100	10	0.5 \rightarrow 0.002	3 \rightarrow 0.5

Considering the size of BZ is one atom unit (a.u.) Table 2.1 shows the following conclusions:

- For UPS the momentum interval is small compared to the size of BZ so that it is in a good approximation the contribution of one point from BZ is measured.
- For XPS the length of momentum vector is exactly fixed, but the value of ΔP_\perp is of the

size of BZ, then the contributions of electronic states with \mathbf{k} -vectors given by Eq. (2.6) on a spherical surface are measured which is approximated to a plane because the value of \mathbf{P}_a is great compared to the size of BZ. This leads to the further consideration of a cross-plane in the first BZ.

Based on the description in Fig. 2.2 and Fig. 2.3 we calculate

$$\int^{resol.} d^3 P = dP_\perp \int^{resol.} d^2 P = \frac{m \hbar^2}{p} dE \int^{resol.} d^2 k \approx \frac{m \hbar^2}{p} dE \int_{BZ} d^3 k \delta(\mathbf{e}_s \cdot \mathbf{k} - k_0), \quad (2.8)$$

where \mathbf{e}_s is normal direction of the cross-plane and k_0 is its distance to the center of BZ (Fig.2.3).

For XPS there is very small difference between vectors $\mathbf{e}_s, \mathbf{P}/|\mathbf{P}|$ and $\mathbf{g}_p/|\mathbf{g}_p|$, as well as it is

possible to describe $k_0 = P - g_p$ (Fig. 2.3). Then, the intensity (2.7) for ARPES is simplified as

$$I(\omega, \mathbf{e}, \mathbf{q}; \mathbf{k}, \mathbf{g}_p, E) dEd \Omega_p = \frac{E^2 (\mathbf{e} \cdot \mathbf{P})^2}{2\pi \hbar \omega} \sum_{\nu_i} \int_{BZ} d^3 k |\varphi_i(P)|^2 \delta(E - E(k, \nu_i) - \hbar\omega) \delta(\mathbf{e}_s \cdot \mathbf{k} - k_0). \quad (2.9)$$

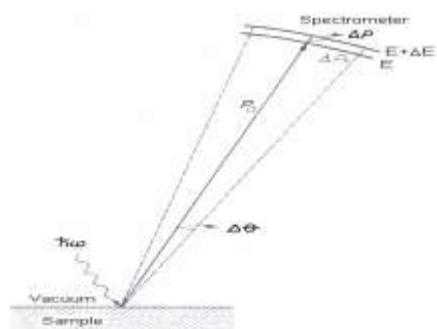


Fig.2.2. Description of electron momentum intervals included by spectrometer in ΔP and ΔP_\perp .

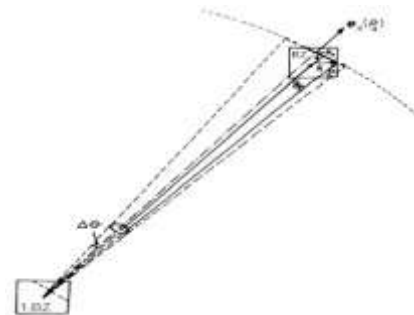


Fig.2.3. Cross-plane in BZ to which vector \mathbf{P}_a belongs (solid) and its reduction to the first BZ (1.BZ) (dashed).

It is seen from Fig. 2.3 that the cross-plane resulted from ARPES is presented in BZ which is reduced to the first BZ (1.BZ). Hence, for constant matrix element the intensity of angle-

$$n_p(\varepsilon, k_0, \mathbf{e}_s) = \sum_{\nu_i} \int_{BZ} d^3k \delta(E - E(k, \nu_i) - \hbar\omega) \delta(\mathbf{e}_s \cdot \mathbf{k} - k_0). \quad (2.10)$$

This PDOS depends on the orientation of spectrometer described by vector \mathbf{e}_s showing the angle-dependence in ARPES and characterizes the number of electronic states of energy interval dE lying in the plane. By integration over k_0 it leads to the usual density of states (DOS)

$$n(\varepsilon) = \int_{BZ} d^3k_0 n_p(\varepsilon, k_0, \mathbf{e}_s). \quad (2.11)$$

For polycrystalline materials the intensity given by Eq. (2.7) needs to be averaged over all directions of vector \mathbf{b}_i of reciprocal lattice. Based on the relation between \mathbf{P}_a and \mathbf{b}_i given by Eq. (2.6) it is the same to rotate \mathbf{b}_i or \mathbf{P}_a . By rotating \mathbf{P}_a or spectrometer (\mathbf{e}_s) this vector \mathbf{P}_a will be lying in many BZs creating there respective cross-planes as presented in Fig. 2.3

$$n_p(\varepsilon, k_0, \mathbf{e}_s) = \sum_{\nu} \int_{BZ} d^3k \delta(E - E(k, \nu) - \hbar\omega) \delta(\mathbf{e}_s \cdot \mathbf{k} - k_0) = \sum_{\nu} \int \frac{dk}{|\partial E(\mathbf{k}, \nu) / \partial \mathbf{k}|}, \quad (3.1)$$

where, after integration over delta function the linear integral will be performed over gradient of energy $E(\mathbf{k}, \nu)$ containing the considered plane. This integration is realized along a line of constant energy $E(\mathbf{k}, \nu) = E$ in the plane (\mathbf{e}_s, q_0) having distance q_0 from center of BZ and normal direction \mathbf{e}_s . Note that for free electron $E = \hbar^2 k^2 / 2m$, $dk = kd\varphi$, so that its PDOS provides a constant (energy-independent) value

$$n^{FE}(E) = \oint \frac{d\varphi}{\hbar^2 / m} = \frac{m}{\hbar^2} \cdot 2\pi. \quad (3.2)$$

The calculation of PDOS in this work is performed for Be having hexagonal structure using the band structure data calculated based on the method of Taut [20]. Fig. 3.1a illustrates 1/24 part of BZ of Be (Γ AHLMK) and Fig. 3.1b illustrates six planes parallel to plane Γ MK. Fig. 3.2 illustrates the band structure of Be for plane Γ MK including three bands where the second and third bands contribute to Fermi-surface.

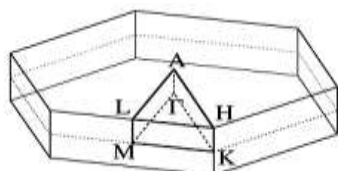


Fig.3.1 (a). 1/24 part of BZ of Be (Γ AHLMK)

resolved spectrum given by Eq. (2.9) is characterized by the plane density of states (PDOS) as a new characteristic property of electronic structure

which are reduced to the first BZ. Suggesting these planes fill the BZ fully, then an average over the whole first BZ is necessary. Therefore, for constant matrix element the intensity of photoelectron spectrum from a polycrystalline material is proportional to the usual DOS.

APPLICATION TO BERYLLIUM

Application of the derived theory to crystal Be is realized by the numerical calculations of PDOSs for Be in different directions and discussions of the results.

For analyzing XP-spectrum the expression of PDOS given by Eq. (2.10) is further transformed into the following form

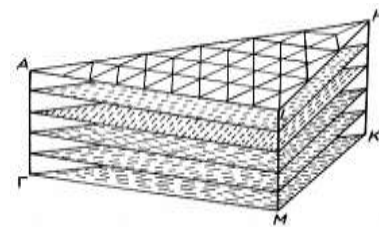


Fig.3.1 (b). Six planes parallel to plane Γ MK.

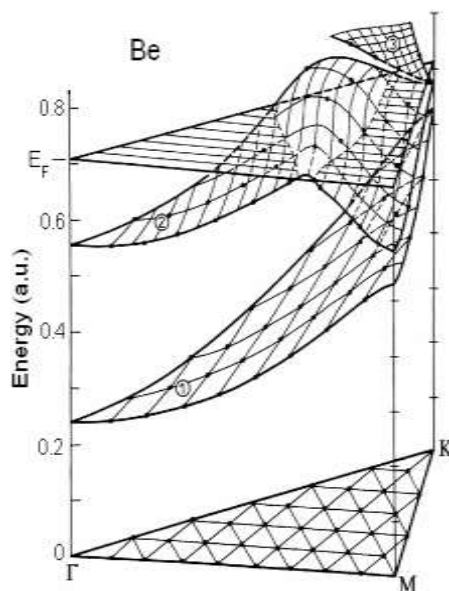


Fig.3.2. Band structure of Be in plane Γ MK where the second and third bands contribute to Fermi-surface.

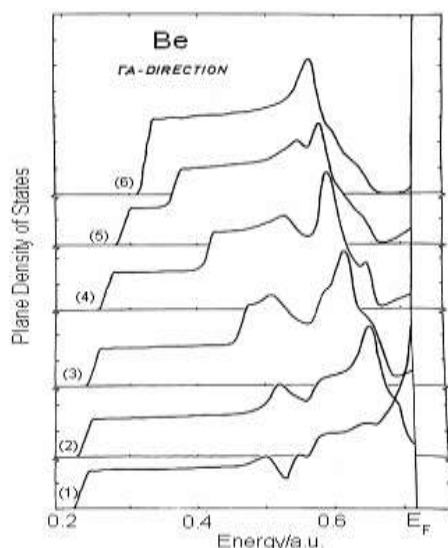


Fig.3.3. PDOSs of Be for 6 planes from Γ MK to ALH having normal direction Γ A presented in Fig. 3.1b calculated using the present theory where the number of each plane is indicated

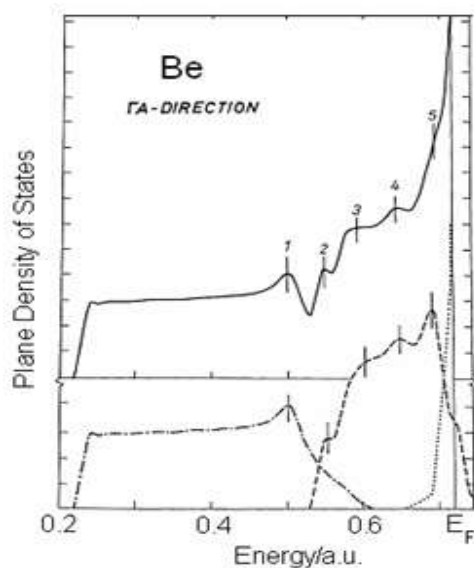


Fig.3.4. (b) Contributions of first band (---), second band (—) and third band (····) to PDOS for plane Γ MK (Γ A-direction) calculated using the present theory where the used energy bands are taken from Fig. 3.2.

Fig. 3.3 illustrates PDOSs of Be for 6 planes having normal direction Γ A presented in Fig. 3.1b from plane Γ MK to plane Γ LH calculated using the present theory. These PDOSs are different for different planes. Here the constant values of PDOS describe those for free electrons, i.e., energy-independent, and the other values having peaks obtained from contributions of energy bands (Fig. 3.2). These results provide information on electronic states in different planes having the same emission direction. The contributions of energy bands to PDOS for plane Γ MK (Γ A-direction) can be seen in Fig.

3.4. It contains peak 1 taken from the first band and the others 2, 3, 4, 5 from the second band, the contribution of the third band is shown in the last part of this curve. Such considerations can be useful for studying electronic states in crystal sheets or layers using ARPES as it was performed in experiments [12, 13].

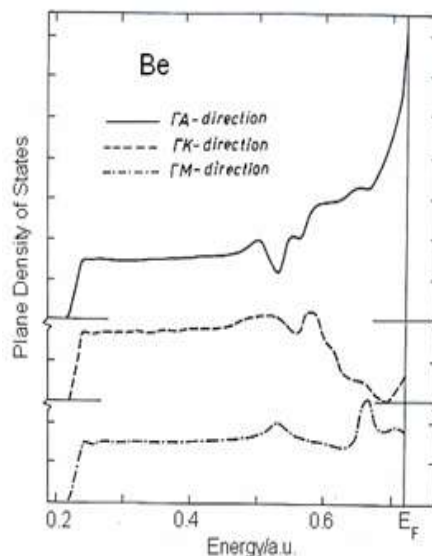


Fig.3.5. Comparison of PDOSs for planes Γ MK (Γ A-direction), Γ MLA (Γ K-direction) and Γ KHA (Γ M-direction) of Be calculated using the present theory.

The results of PDOSs of Be for three directions Γ A, Γ K and Γ M calculated using the present theory are presented in Fig. 3.5. Their anisotropic values for these directions describe the differences of electronic states in different planes perpendicular to different directions of the considered crystal. These results contribute to valuating not only the number but also the energy-independence and energy-dependence, as well the other properties of electronic states of the considered material taken from ARPES.

CONCLUSIONS

In this work the intensity of angle-resolved photoelectron spectrum from valence bands of single crystals has been derived based on three-step model and the analysis of normally used experimental conditions. The theory is applied to hexagonal Beryllium (Be) but it can also be generalized to other crystal structures including semiconductors.

The derived intensity depends on the main characters of ARPES such as properties of photon, parameters of crystals and orientation of spectrometer. The information possible from experiment and experimental conditions to be realized have been analyzed to simplify the theoretical interpretation.

The important influence of the angle of acceptance on the results of XPS is in detail investigated. The plane density of states (PDOS) is introduced as a new characteristic property of electronic structure described by the ARPES.

The PDOSs for ΓA , ΓM and ΓA directions of hexagonal crystal Be have been calculated. They show significant anisotropy characterizing the direction dependence of ARPES. The peaks are explained in terms of band structure.

The main characters of PDOSs are direction dependences which contribute to valuating not only the number but also the energy-independence and energy-dependence, as well as the other properties of electronic states of the considered material taken from ARPES.

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