ANGLE - RESOLVED LASER - RAY PHOTOELECTRON SPECTROSCOPY OF SIMPLE METALS

Nguyen Van Hung

Faculty of Physics, College of Natural Sciences - VNU

I. INTRODUCTION

Photoelectron measured in spectrometer have energy and momentum which are connected to the ones inside the crystal. That is why photoelectron spectra provide information about electronic structure of solid states [1]. This work is the next step of our previous one [2] in which a theory of Angle - resolved Laser - ray Photoelectron Spectroscopy (LPS) has been developed. According to this theory the intensity of LPS spectra is given by:

$$I(\omega, \vec{e}, \vec{q}, \vec{b_i}, \phi, \vec{n}, E, \vec{e_s}) dE d\Omega_p \sim \int_{\Omega_a} d^3P(\Upsilon_{i\to f} + \Upsilon_{i\to f'})\theta(E_F - E_i)\delta(E - E_i - n\hbar\omega), \quad (1)$$

here the linear contribution:

$$\Upsilon_{i\to f} = \frac{2\pi}{\hbar}\left| \sum_{f_2, f_3 \cdots f_n} \frac{\langle i \mid W \mid f_2\rangle\langle f_2 \mid W \mid f_3\rangle \cdots \langle f_N \mid W \mid f_n\rangle}{(E_{f_2} - E_i - \hbar\omega)(E_{f_3} - E_i - 2\hbar\omega)\cdots(E_{f_n} - E_i - N\hbar\omega)} \right|^2, \quad (2)$$

$$\Upsilon_{i\to f'} = \frac{2\pi}{\hbar}\left| \sum_{f'_2, f'_3 \cdots f'_n} \frac{\langle i \mid W' \mid f'_2\rangle\langle f'_2 \mid W' \mid f'_3\rangle \cdots \langle f'_N \mid W' \mid f'_n\rangle}{(E_{f'_2} - E_i - 2\hbar\omega)(E_{f'_3} - E_i - 4\hbar\omega)\cdots(E_{f'_n} - E_i - 2N\hbar\omega)} \right|^2, \quad (3)$$

$$n = 2, 3, \cdots, N+1.$$

The function $\theta(E_F - E_i)$ indicates that photoelectrons have been transmitted from the state with energy E_i through the Fermi level E_F; $\mid i\rangle$ and $\mid f\rangle$ describe electronic states; $\omega, \vec{e}, \vec{q}$ are frequency, polarisation vector and momentum of photon; $\vec{b_i}, \phi, \vec{n}$ are basic vector of reciprocal vector $\vec{g}$, the height of potential barrier and surface - normal of crystal; $E, \vec{e_s}$ are kinetic energy and moving direction of photoelectron to spectrometer, respectively. W, W' are powerful radiations of laser ray. Electron is emitted to the final state in a energy interval dE and a space angle $d\Omega_p$. Ω_a is the angle of acceptance. If matrix elements are considered to be constant, the intensity of LPS spectra is characterized by Plane Density of States (PDOS)

$$D(\varepsilon, \vec{e_s}, k_o) = \sum_{\nu} \int_{BZ} d^3k \delta(\varepsilon - E(\vec{k}, \nu))\delta(\vec{e_s}.\vec{k} - k_0), \quad (4)$$

where ν is band index, $\vec{k}$ is wave vector and k_0 is distance of considered cross - section to the center of Brillouin zone (BZ).

Our purpose in this work is to calculate matrix elements in (2) and (3), that means, the intensity (1) for simple metals and through that to evaluate the angle-resolved LPS. The numerical calculation is carried out for Beryllium (Be), a typical simple metal.

II. INTENSITY OF LPS SPECTRA OF SIMPLE METALS

The most important simple metals with configurations of the outer electronic shell are presented in Tab. 1. The positive ions in these simple metals are small. The conducting electrons which are not strongly influenced by positive ions can move near freely. Therefore, these near free electrons can be described by Orthogonal Plane Wave (OPW)

Monovalent	Li	Na	K	Rb	Cs	
Alkalimetals	2s	3s	4s	5s	6s	
Bivalent	Be	Mg	Ca	Sr	Zn	Cd
metals	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$4s^2$	$5s^2$
Threevalent	Al	Ga	In			
metals	$3s^23p$	$4s^24p$	$5s^25p$			

Tab. 1. Most important simple metals
with configurations of outer electronic shell in neutral atoms

$$\left.\begin{matrix} \mid i\rangle \\ \mid f\rangle \end{matrix}\right. \sim \mid \psi^{OPW}\rangle = F\left\{\mid \varphi_j^{PS}\rangle - \sum_c \mid \psi_c\rangle\langle\psi_c \mid \varphi_j^{PS}\rangle\right\}; j = 1, 2, \cdots, N+1, \tag{5}$$

where the core - function is given by

$$\mid \psi_c(\vec{r})\rangle = \frac{1}{\sqrt{N_c}}\sum_{\vec{R}}\sum_l A_l e^{i\vec{k_a}.\vec{R}}\varphi_a(\vec{r} - \vec{R} - \vec{d_l}), \tag{6}$$

and pseude-functions have the form

$$\mid \varphi_j^{PS}(\vec{r})\rangle = \frac{1}{\sqrt{\Omega}}\sum_{g_j} C g_j(\vec{k}, \nu_j) e^{i(\vec{k}+\vec{g_j}).\vec{r}}. \tag{7}$$

In these functions $\vec{k_a}$ is wave vector core - state and Ω is normalizing volume. The OPW (5) describe the following electronic states

- Initial state, if $j = 1(\nu_1 = \nu, g_1 = g)$,
- Intermediate states, if $j = 2, 3, \cdots, N$,
- Final state, if $j = N + 1$ which is reduced to one OPW, it means that

$$\mid \varphi_{N+1}^{PS}\rangle = \mid \varphi_f^{PS}\rangle = \frac{1}{\sqrt{\Omega}} e^{i(\vec{k}+\vec{g_p}).\vec{r}}; \vec{P} = \vec{P}_{N+1}, \vec{g_p} = \vec{g}_{N+1}. \tag{8}$$

The function (6) is normalized according to the number N_c of basic cells at $\vec{R}$ and each cell has N_a atoms at $\vec{d}_l$. In the above expressions the momentum conversation $\vec{k}_i = \vec{k}_f = \vec{k}$ for transition from initial state to intermediate and final one is satisfied.

The core-function ψ_c appears only in a combination which is calculated as follows

$$\sum_c \mid \psi_c\rangle\langle\psi_c \mid = \sum_{\vec{R}}[\varphi_a(\vec{r}-\vec{R}-\vec{d}_1)\varphi_a^*(\vec{r}-\vec{R}-\vec{d}_1) + \varphi_a(\vec{r}-\vec{R}-\vec{d}_2)\varphi_a^*(\vec{r}-\vec{R}-\vec{d}_2)+$$
$$+\cdots+\varphi_a(\vec{r}-\vec{R}-\vec{d}_l)\varphi_a^*(\vec{r}-\vec{R}-\vec{d}_l)]. \tag{9}$$

From the orthogonalization of OPW (5)

$$\langle\psi_{\vec{k}}^{OPW} \mid \psi_{\vec{k}}^{OPW}\rangle = F^2\sum_{g,g'}C_gC_g^*\left\{\delta_{\vec{P},\vec{P}'} - N_a\sum_{g''}\delta_{\vec{P}-\vec{P}',\vec{g''}}\varphi_a(\vec{P})\varphi_a^*(\vec{P}')S(\vec{P}-\vec{P}')\right\}, \tag{10}$$

in our case we received

$$F^2 \approx 1 + N_a\sum_{g,g'}C_gC_{g'}^*\varphi_a(\vec{k}+\vec{g})\varphi_a^*(\vec{k}+\vec{g}')S(\vec{g}-\vec{g}'). \tag{11}$$

In the calculation we have used the expressions of structure factor

$$S(\vec{q}-\vec{q}') = \frac{1}{Na}\sum_l e^{-i(\vec{q}-\vec{q}')\cdot\vec{d}_l}. \tag{12}$$

Fourier transform of atomic function $\varphi_a(\vec{r})$

$$\varphi_a(\vec{q}) = \frac{1}{\sqrt{\Omega}}\int\varphi_a(\vec{r})e^{-i\vec{q}\cdot\vec{r}}d\vec{r}, \tag{13}$$

and the relation

$$\sum_{\vec{R}}e^{i(\vec{q}-\vec{q}')\vec{R}} = N_a\sum_{\vec{g}}\delta_{\vec{q}-\vec{q}',\vec{g}}. \tag{14}$$

For simple metals the orthogonalizing component in OPW is small, we can neglect the second part in the right of equation(11), that means $F^2 \approx 1$. Moreover, free electron does not absorb electromagnetic waves. Therefore we received

$$\sum_f \mid f\rangle\langle f \mid \rightarrow \sum_f\sum_c \mid \psi_c\rangle\langle\psi_c \mid \varphi_f^{PS}\rangle\langle\varphi_f^{PS} \mid . \tag{15}$$

Using the above results, we calculated the matrix elements for one transition and received

$$\langle i \mid W \mid f\rangle \sim \sum_g C_g(\vec{k}-\vec{q},\nu)\varphi_a(\vec{k}-\vec{q}+\vec{g})S(\vec{g}-\vec{g_p}-\vec{q}). \tag{16}$$

After detailing calculation of matrix elements (2) and (3) we received the intensity of angle - resolved LPS spectra (1) for simple metals in the following form

$$I(w,\vec{e};\vec{n},\vec{b_i},\phi;E,\vec{e_s})dEd\Omega_p \sim \int_{\Omega a}d^3k\sum_{\nu,\nu_j,\nu_j'}\{\mid M(\vec{k},\nu_j,\vec{e},w,\vec{P_j})\mid^2$$
$$+\mid M'(\vec{k},\nu_j',2w,\vec{P_j'})\mid^2\}\theta(E_F-E(\vec{k},\nu))\delta(E-E(\vec{k},\nu)-n\hbar\omega), \tag{17}$$

where the matrix elements for the linear contributions are given

$$M = \sum_g C_g(\vec{k},\nu)\varphi_a(\vec{P}_1)\prod_{j=2}^{N}\mu_j(\vec{k},\vec{e},\nu_j,\omega,\vec{P}_j)S(\vec{g}-\vec{g}_j-\vec{q})(\vec{e}.\vec{P}_j) \ ,$$
$$\mu_j = \sum_{g_{j+1}} \frac{C_{g_{j+1}}(\vec{k},\nu_{j+1})\varphi_a(\vec{k}+\vec{g}_{j+1})}{E(\vec{k},\nu_{j+1})-E(\vec{k},\nu)-(j-1)\hbar\omega} \ , \tag{18}$$

and for the unlinear contributions

$$M' = \sum_{g'} C_{g'}(\vec{k},\nu')\varphi_a(\vec{P}'_1)\prod_{j=2}^{N}\mu'_j(\vec{k},\nu'_j,2\omega,P'_j)S(\vec{g'}-\vec{g}'_j-\vec{q}) \ ,$$
$$\mu'_j = \sum_{g'_{j+1}} \frac{C_{g'_{j+1}}(\vec{k},\nu'_{j+1})\varphi_a(\vec{k}+\vec{g}'_{j+1})}{E(\vec{k},\nu_{j+1})-E(\vec{k},\nu)-2(j-1)\hbar\omega} \ . \tag{19}$$

If the number of absorbed photons is defined we can calculate the intensity of angle-resolved LPS spectra of simple metals according to equations (17-19). The linear contribution to LPS is dependent on polarisation of laser ray, but the unlinear one is independent on it.

III. NUMERICAL RESULTS OF PDOS FOR Be

It was shown that for evaluation of LPS spectra we can consider the matrix elements to be constant and the intensity of angle-resolved LPS spectra is proportional and the to the PDOS [1-3]. Beryllium (Be) is a typical simple metal, that is why it is selected for calculation of PDOS. We investigate the valence band of Be and for laser ray $n\hbar\omega \geq 1000eV$. In this case the, intensity of angle- resolved LPS spectra of Be is given by

$$I(\varepsilon,\vec{e_s},k_0)d\Omega_p \sim \sum_\nu \int_{BZ} d^3k\delta(\varepsilon-E(\vec{k},\nu))\delta(\vec{e_s}.\vec{k}-k_0)$$
$$= \sum_\nu \int\limits_{E(\vec{k},\nu)=\varepsilon} \frac{d^2k\delta(\vec{e}_s.\vec{k}-k_0)}{\mid grad_{\vec{k}}E(\vec{k},\nu)\mid} \ . \tag{20}$$

Be has hexagonal closed packing (hcp) structure. Its BZ is shown in Fig. 1. The energy band structure of Be has been calculated before [4,5]. Using these energies we calculated the contributions of a cross- section of BZ which is perpendicular to the outgoing direction $\vec{e_s}$ of photoelectron. Figs. 2 and 3 show PDOS for the directions $\vec{e_s}//\Gamma M$ (contribution from ΓAHK plane of Fig. 1) and $\vec{e_s}//\Gamma K$ (contribution from ΓALM of Fig.1), respectively. They contain the contributions of the 1st, the 2nd and the 3rd band. Therefore, they contain the detailing information of electronic structure of the considered direction. We can see in Figs. 2 and 3 that from BZ center to the energy of 0.4a.u. the electron behaves as free, that is why we receive the PDOS of free electron. They are about constant and isotropy. But at higher energies the PDOS are anisotropy and no more constant. Therefore, the PDOS can characterize the angle-resolved LPS of Be.

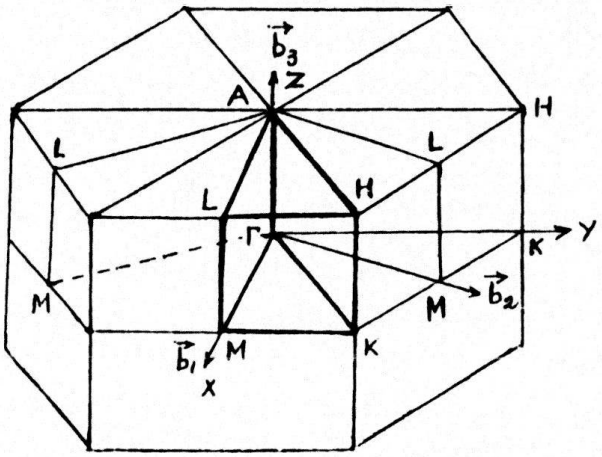

Fig. 1. BZ of Be with hcp structure

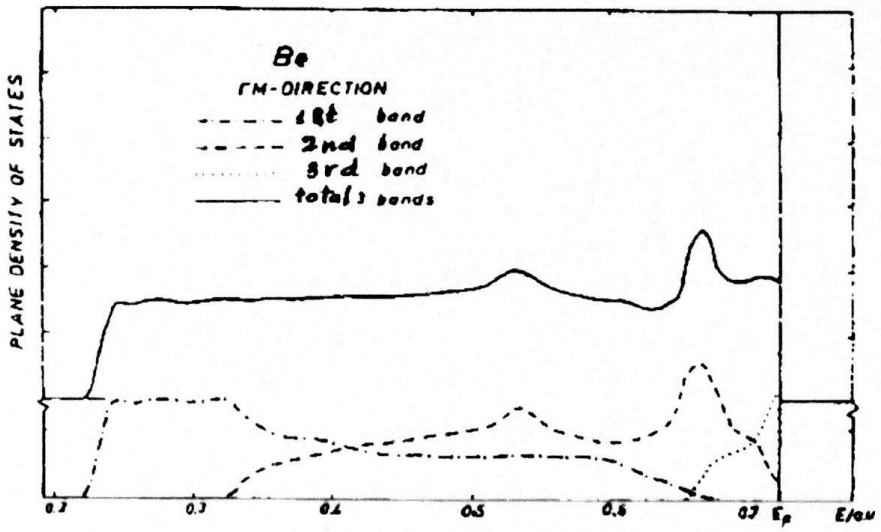

Fig. 2. PDOS of Be for ΓM direction

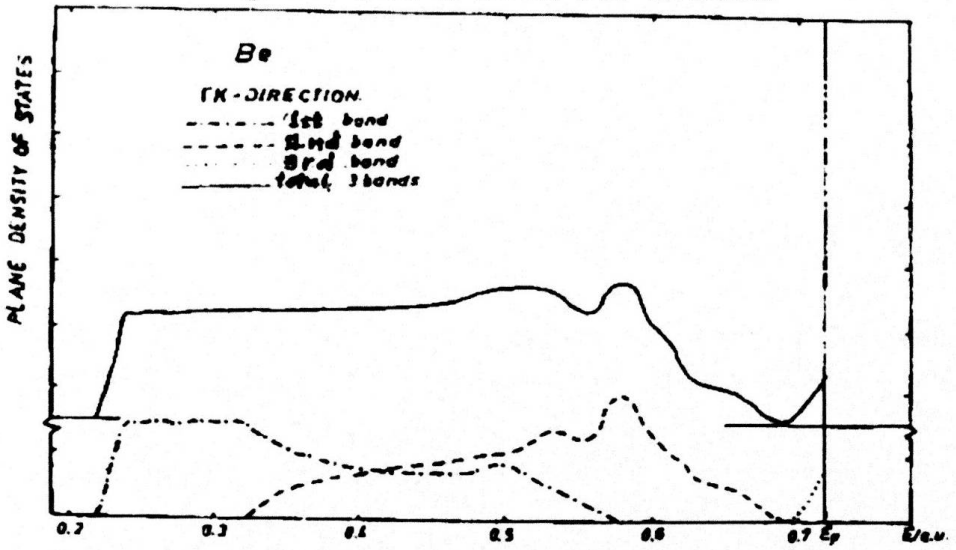

Fig. 3. PDOS of Be for ΓK direction

IV. CONCLUSIONS

Electrons in this case behave as near free ones, that is why their states are described by OPW. The matrix elements describing transitions through intermediate states and then to spectrometer due to multiphoton absorption has been calculated for linear and unlinear contributions. They contain the contributions of atomic functions, structure factor and coefficients of Bloch functions for different energy bands and reciprocal vectors. The energy of photoelectron is contained in momentum P. These values are important for analysis of electronic structure of the crystal. The linear contribution to LPS is dependent on polarisation of laser ray, but the unlinear one is independent on it. PDOS of Be for different outgoing directions of photoelectron have been calculated.

PDOS of Be for different outgoing directions of photoelectron have been calculated. They show the near free behavior of electrons in simple metals and their clear anisotropy in different directions. Therefore, they characterize the angle-resolved LPS providing detailing information of electronic structure of Be.

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PHỔ QUANG ĐIỆN TỬ DÙNG LASER PHỤ THUỘC GÓC CỦA KIM LOẠI ĐƠN GIẢN

Nguyễn Văn Hùng
Khoa Vật lý, Đại học Khoa học Tự Nhiên, ĐHQG Hà Nội

Trong bài này cường độ các phổ quang điện tử dùng laser (LPS) phụ thuộc góc của kim loại đơn giản đã được đánh giá. Các trạng trạng thái của điện tử được biểu diễn bằng sóng phẳng trực giao (OPW). Các yếu tố ma trận đối với các chuyển dịch qua các trạng thái tuyến tính và phi tuyến. Chúng bao chứa những đại lượng quan trọng đặc trưng cho cấu trúc điện tử của vật thể như hàm nguyên tử, hệ số cấu trúc và các thông số vùng năng lượng. Phần tính số mật độ trạng thái phẳng (PDOS) đã thực hiện cho Be. Chúng đã thể hiện các đặc tính cơ bản của điện tử trong kim loại đơn giản và không đẳng hướng khi quang điện tử phát ra theo các hướng khác nhau. Do đó PDOS cung cấp các thông tin chi tiết về cấu trúc điện tử của Be nhận từ các phổ LPS phụ thuộc góc.