Theoretical study of the angular dependence of x-ray photoelectron spectra of metals

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A theoretical investigation is made of the shape of x-ray photoelectron spectra of crystals for various directions of emission of the photoelectrons. For description of the x-ray photoemission the orthogonalized plane wave model proposed by us previously [Sov. Phys. JETP **45**, 993 (1977)] is used. The effect on the shape of the photoelectron spectra of the polarization of the x rays and the spectrometer aperture angle is analyzed. The angular dependence of the cross sections for photoionization of valence electrons and the x-ray photoelectron spectra of single crystals of aluminum and copper are calculated. A method is proposed for determination of the partial density of states of electrons of various symmetry types from the experimental data obtained by the method of x-ray photoelectron spectroscopy with use of the angular dependence of the valence-electron photoionization cross sections.

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1. INTRODUCTION

Recently as a consequence of the refinement of experimental technique in x-ray photoelectron spectroscopy (XPS) the possibility has appeared of studying the energy distribution of photoelectrons emitted from a single crystal in a definite direction. Several groups[2-5] have observed a significant change in the structure of the x-ray photoelectron spectra of the valence band of single crystals of copper, silver, and gold on change of the sample position relative to the x-rays incident on it. Study of the angular dependence of x-ray photoelectron spectra permits additional information to be obtained on the electronic states in the valence band of crystals. For this purpose it is necessary to carry out a theoretical analysis of the process of x-ray photoemission and to learn what factors determine the angular dependence of x-ray photoelectron spectra. It is of interest also to analyze theoretically the experimental techniques, since in reality the experiments study photoelectrons emitted not in a strictly defined direction, but within some solid angle whose value is determined by the aperture angle of the photoelectron-analyzer entrance window. It is necessary to learn how the angular dependence of x-ray photoelectron spectra is related to the size of the analyzer aperture angle.

In a previous article[1] we proposed a theoretical model for description of x-ray photoemission from polycrystalline materials, and also from single crystals with the condition that all photoelectrons leaving the sample surface are analyzed by a spectrometer.

In the present work we use this model to consider questions related to the angular dependence of x-ray photoelectron spectra. Cross sections are calculated for photoionization of electrons of various symmetry types for different directions of photoemission. The effect of the polarization of the x rays on the angular dependence of x-ray photoelectron spectra is discussed. X-ray photoelectron spectra are calculated for aluminum and copper for various cases of polarization of the radiation and various directions of emission of photoelectrons. A method is proposed for construction of partial densities of states of valence electrons on the basis of experimental data with use of the angular dependence of the cross sections for photoionization of electrons of various symmetry types.

2. DETERMINATION OF CROSS SECTIONS FOR PHOTOIONIZATION OF VALENCE ELECTRONS

Using the description of the photoemission process the orthogonalized plane wave model proposed earlier,[1] we obtain the following formula for the energy distribution of photoelectrons emitted from a crystal into a solid angle $d\Omega_{\mathbf{P}}$:

$$dI(E_{\mathbf{P}},\theta_{\mathbf{P}},\varphi_{\mathbf{P}})\sim E_{\mathbf{P}}^{1/2}\sum_{lm}\Big\{\sum_{\alpha}N_{lm}{}^{\alpha}(E)\,|Q_{lm}{}^{\alpha}(\mathbf{P})|^2 + \sum_{\alpha}\sum_{\beta\neq\alpha}N_{lm,lm}^{\alpha\beta}\exp[i\mathbf{P}(\boldsymbol{\tau}_\alpha-\boldsymbol{\tau}_\beta)]\,Q_{lm}{}^{\alpha}(\mathbf{P})\,Q_{lm}{}^{\beta*}(\mathbf{P})\Big\}d\Omega_{\mathbf{P}}, \tag{1}$$

where

$$Q_{lm}{}^{\alpha}(\mathbf{P})=(\mathbf{AP})F_i{}^{\alpha}(\mathbf{P})+i\sum_{p}F_p{}^{\alpha}(\mathbf{P})\,(\mathbf{AG}_{ip}{}^{\alpha}), \tag{2}$$

$$N_{ij}{}^{\alpha\beta}=\sum_{n,\mathbf{k}}c_i{}^{\alpha*}(\mathbf{k})\,c_j{}^{\beta}(\mathbf{k}). \tag{3}$$

All of the remaining symbols in the formulas are identical to those used in Ref. 1.

The summation in Eq. (3) is carried out over the entire Brillouin zone in accordance with the results of Shevchik,[6] who showed that even at room temperature the vibrations of the atoms in the crystal lattice lead to the necessity of taking into account in x-ray photoelectron spectra all **k** states inside the Brillouin zone even in the case of limitingly small aperture angles.

The second term in the right-hand side of Eq. (1) describes the interference of electron waves from different sublattices of the crystal. In the case of a crystal containing only one atom per unit cell, this term disappears and the x-ray photoelectron spectra is a superposition of local partial densities of states taken with weighting factors whose value depends on the energy and direction of emission of the photoelectrons (in this case the index α designating the number of the atom in the unit cell can be dropped):

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$$dI(E_P,\theta_P,\varphi_P)\sim\sum_{lm}N_{lm}(E)\sigma_{lm}(\mathbf{P})\,d\Omega_P. \tag{4}$$

Thus, the angular dependence of x-ray photoelectron spectra is determined by the angular dependence of the cross sections for photoionization of electrons of various symmetry types:

$$\sigma_i(\mathbf{P})=E_P^{1/2}|Q_i(\mathbf{P})|^2. \tag{5}$$

Separating the atomic functions into a radial and an angular part, carrying out the integration over angles, and taking into account the properties of Clebsch-Gordan coefficients, we obtain

$$\begin{aligned}Q_i(\mathbf{P})=i^{l_i}\Big\{&E_P^{1/2}T_{nl_i}\cos\vartheta Y^*_{l_im_i}(\hat{\mathbf{P}}')-\Big(\sum_{n'}T_{n',l_i+1}U_{n',l_i+1;\,nl_i}\Big)\\&\times\sum_m Y^*_{l_i+1,m}(\hat{\mathbf{P}}')Y^*_{1,m_i-m}(\hat{\mathbf{A}}')\left[\frac{4\pi(2l_i+3)}{3(2l_i+1)}\right]^{1/2}\\&\times c(1(l_i+1)l_i;\,m_i-m,m)\,c(1(l_i+1)l_i;\,0,0)+\\&+\Big(\sum_{n'}T_{n',l_i-1}U_{n',l_i-1;\,nl_i}\Big)\sum_m Y^*_{l_i-1,m}(\hat{\mathbf{P}}')Y^*_{1,m_i-m}(\hat{\mathbf{A}}')\left[\frac{4\pi(2l_i-1)}{3(2l_i+1)}\right]^{1/2}\\&\times c(1(l_i-1)l_i;\,m_i-m,m)\,c(1(l_i-1)l_i;\,0,0)\Big\}.\end{aligned} \tag{6}$$

All of the factors in Eq. (6) have been written in the system of coordinates fixed to the crystal. The laboratory system we specify in such a way that the z axis (the polar axis) is parallel to the direction of propagation of the electromagnetic radiation. Defining the location of the laboratory system relative to the crystal system by the Euler angles, we can express the spherical harmonics contained in Eq. (6) in terms of a linear combination of spherical harmonics in the laboratory system[7]:

$$Y_{lm_1}(\theta',\varphi')=\sum_{m_2}Y_{lm_2}(\theta,\varphi)D^{l*}_{m_1m_2}(\alpha,\beta,\gamma). \tag{7}$$

Equations (5) and (7) provide the possibility of calculating cross sections for photoionization of electrons for any position of the single-crystal sample with respect to the x rays incident on it. For specific calculations the final formulas are conveniently expressed in terms of real combinations of spherical harmonics.

In the present work we discuss theoretically the geometry of the experiments carried out in Refs. 2–5 on study of the angular dependence of x-ray photoelectron spectra.

In Fig. 1 we have shown the position of the sample in the HP 5950A electron spectrometer in which the principal experimental results were obtained on the angular dependence of x-ray photoelectron spectra. The vectors determining the direction of propagation of the electromagnetic radiation and the flux of photoelectrons lie in a plane perpendicular to the sample surface. In the spectrometer there is the possibility of rotation of the sample around the axes 1 (perpendicular to the plane of incidence of the radiation) and 2 (perpendicular to the sample surface). The angle δ between the photon flux and the photoelectron flux is fixed and in the HP 5950A spectrometer is 72°. The sample is a single crystal whose surface coincides with a definite crystallographic plane. By rotation around axis 2 it is possible to establish the necessary position of the plane of incidence of the radiation with respect to the crystal, and then by rotating the sample around axis 1, x-ray photoelectron spectra are obtained for various values of the angle of incidence of the radiation ψ.

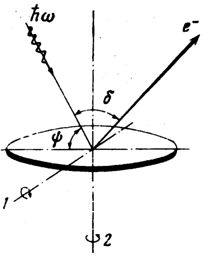

FIG. 1. Position of sample in HP 5959A spectrometer.

In the laboratory system introduced here the direction of the polarization vector **A** is determined by the angles $\theta_{\mathbf{A}}$ and $\varphi_{\mathbf{A}}$, where $\theta_{\mathbf{A}}=\pi/2$ since **A** is perpendicular to the direction of propagation of the radiation.

We shall consider three cases of polarization:

(1) the vector **A** lies in the plane of incidence of the electro-magnetic radiation ($\sigma_i^{(1)}=\sigma_i$ for $\varphi_{\mathbf{A}}=\varphi_{\mathbf{P}}$);

(2) the vector **A** is perpendicular to the plane of incidence of the radiation and parallel to the sample surface ($\sigma_i^{(2)}=\sigma_i$ for $\varphi_{\mathbf{A}}=\varphi_{\mathbf{P}}+\pi/2$);

(3) unpolarized radiation:

$$\sigma_i^{(0)}=\frac{1}{2\pi}\int_0^{2\pi}\sigma_i\,d\varphi_{\mathbf{A}}.$$

It can be shown that from the formulas for the photoionization cross section (5) and (6) in the case of unpolarized radiation it follows that

$$\sigma_i^{(0)}={}^1/_2(\sigma_i^{(1)}+\sigma_i^{(2)}).$$

We note that for the experimental geometry considered, in the plane-wave (PW) approximation we have always $\sigma_i^{(2)}=0$, since $\mathbf{A}\perp\mathbf{P}$, and the angular dependence of the photoionization cross section $\sigma_i^{(0)}$ for unpolarized radiation is the same as for $\sigma_i^{(1)}$. We shall discuss the angular dependence of the photoionization cross sections in the orthogonalized plane wave (OPW) approximation.

3. ELECTRONS OF *s* AND *p* SYMMETRY. ANGULAR DEPENDENCE OF X-RAY PHOTOELECTRON SPECTRA OF ALUMINUM

Since σ_s depends only on the angle between **A** and **P**, its value will not change with change of the angle ψ, but σ_s will be different for different polarizations of the radiation.

For a crystal with cubic symmetry of the lattice the orbitals p_x, p_y, and p_z are equivalent. Therefore the value of σ_p also will not change with change of ψ, but will depend on the direction of polarization of the radiation. For crystals with a lower symmetry of the lattice, in particular, for layered structures, a more complicated angular dependence of σ_p is possible.

Since the ratio of the contributions of s and p states to x-ray photoelectron spectra will be different for different directions of polarization of the radiation, use of polarized radiation to excite possibility of separating the contributions of electrons of different symmetry types in x-ray photoelectron spectra of elements containing *s* and *p* electrons in the valence band.

We have considered this case for the example of aluminum, for which the x-ray photoelectron spectra can be represented in the form

$$dI(E,\mathbf{P})=\{\sigma_s(\mathbf{P})N_s(E)+\sigma_p(\mathbf{P})N_p(E)\}d\Omega_{\mathbf{P}}.$$

The partial densities of states of valence *s* and *p* electrons of aluminum were taken from Ref. 8, where they were calculated by means of the augmented plane wave (APW) method. The insignificant contribution of electron states of *d*-type symmetry was not taken into account by us. In calculation of the photoionization cross sections the quantities T_{nl} and $U_{n'l;nl}$ were determined with use of the Clementi wave functions.[9] As a result we obtain for the different polarization cases

$$\sigma_s^{(1)}/\sigma_p^{(1)}=11.88,\quad \sigma_s^{(2)}/\sigma_p^{(2)}=0,\quad \sigma_s^{(0)}/\sigma_p^{(0)}=6.98.$$

Thus, for polarization in the plane of incidence the x-ray photoelectron spectra should reflect mainly the density of states of *s*-type symmetry, and for polarization perpendicular to the plane of incidence—the density of states of *p*-type symmetry. The calculated x-ray photoelectron spectra are given in Fig. 2. It can be seen that for the two polarization directions considered the shape of the x-ray photoelectron spectra should differ substantially. The calculated spectra for the case of natural radiation are close in shape to curve 1. Unfortunately, there are no corresponding experimental data.

4. ELECTRONS OF *d* SYMMETRY. ANGULAR DEPENDENCE OF X-RAY PHOTOELECTRON SPECTRA OF COPPER

For electron states of *d*-type symmetry there is a strong angular dependence of the values of the photoionization cross section, which is different for t_{2g} and e_g states. In the plane wave approximation $\sigma_{t_{2g}}$ and σ_{e_g} reached their extreme values in photoemission along the symmetry directions [001], [101], and [111]; in particular, $\sigma_{t_{2g}}=0$ for the [001] direction and $\sigma_{e_g}=0$ for the [111] direction. In the OPW approximation the directions in which $\sigma_{t_{2g}}$ and σ_{e_g} reach their extreme values do not in the general case coincide with symmetry directions. The magnitude of the deviation is determined by the contribution of the orthogonalization terms and also by the angle between the vectors **P** and **A**. The directions of the extrema of $\sigma_{t_{2g}}$ and σ_{e_g} and the symmetry directions coincide for $\mathbf{P}\|\mathbf{A}$. The greatest anisotropy in the OPW approximation is for $\sigma_i^{(1)}$, but $\sigma_i^{(2)}\neq 0$ and also depends on the direction of photoemission. In addition $\sigma_i^{(0)}$ does not vanish, and consequently in the case of natural radiation the x-ray photoelectron spectra will always contain contributions of electron states of both t_{2g} and e_g symmetry.

We have calculated the angular dependence of the photoionization cross sections and the x-ray photoelectron spectra of valence electrons of copper single crystals. Since the shape of the x-ray photoelectron spectra is determined mainly by *d* states, we did not take into account *s* and *p* states in the calculation, and the spectrum was represented in the form

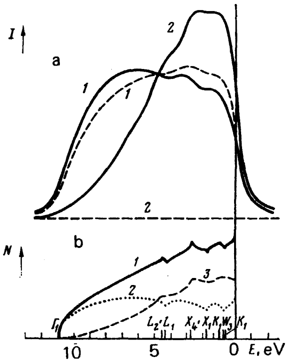

FIG. 2. Density of states and x-ray photoelectron spectra of valence electrons of aluminum (in arbitrary units). a) X-ray photoelectron spectra for polarization of the radiation parallel (1) and perpendicular (2) to the plane of incidence, calculated in the OPW spproximation (solid curves) and in the plane-wave approximation (dashed curve); b) total density of states (1) and partial densities of states of *s* electrons (2) and *p* electrons (3).

$$dI(E,\mathbf{P})=\{\sigma_{t_{2g}}(\mathbf{P})N_{t_{2g}}(E)+\sigma_{e_g}(\mathbf{P})N_{e_g}(E)\}d\Omega_{\mathbf{P}}.\tag{8}$$

The partial density of states of electrons of t_{2g} and e_g symmetry types were calculated on the basis of 5230 points in 1/48 of the Brillouin zone with use of the Hodges-Ehrenreich interpolation scheme.[10] The parameters describing the energy-band structure of copper were determined from the results of a calculation using the augmented plane wave approximations,[11] and the values of T_{nl} and $U_{n'l';nl}$ were calculated with use of the Clementi wave functions.[9]

We considered a copper single crystal whose surface coincides with the (001) plane, and the plane of incidence of the radiation was parallel 1) to the (100) plane and 2) to the (110) plane. Figures 3 and 4 show the results of calculation of the angular dependence of the photoionization cross section $\sigma_{t_{2g}}$ and σ_{e_g} for these two sample positions. For comparison we have shown also $\sigma_{t_{2g}}^{(0)}$ and $\sigma_{e_g}^{(0)}$ calculated in the plane wave approximation. It can be seen that inclusion of the orthogonalization terms can

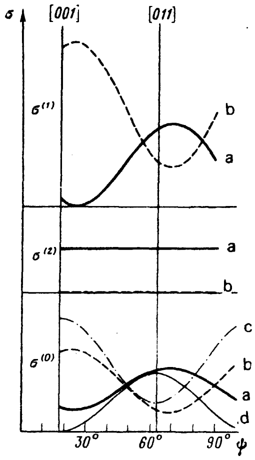

FIG. 3. Angular dependence of photoionization cross sections of valence electrons of a copper single crystal in position 1 (see Fig. 1): a—$\sigma_{t_{2g}}$ in the OPW approximation, b—σ_{e_g} in the OPW approximation, c—σ_{e_g} in the plane-wave approximation, d—$\sigma_{t_{2g}}$ in the plane-wave approximation.

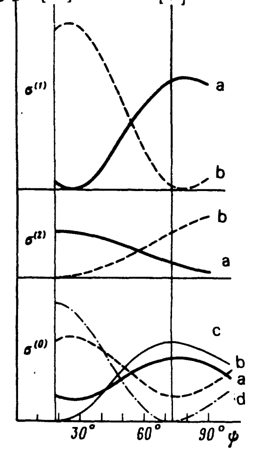

FIG. 4. Angular dependence of photoionization cross sections of valence electrons of a copper single crystal in position 2: a—$\sigma_{t_{2g}}$ in the OPW approximation, b—σ_{e_g} in the OPW approximation, c—$\sigma_{t_{2g}}$ in the plane-wave approximation, d—σ_{e_g} in the plane-wave approximation.

produce an appreciable change in the ratio of the contributions to x-ray photoelectron spectra of electron states of t_{2g} and e_g symmetry.

5. DEPENDENCE OF SHAPE OF X-RAY PHOTOELECTRON SPECTRA ON APERTURE ANGLE

The results presented above were obtained for the case of limitingly small aperture angles. However, in contemporary photoelectron spectrometers in order to achieve sufficient fluxes of photoelectrons the measurements are made with aperture angles of at least 6–8°.

It has been established by Wagner et al.[4] that the shape of x-ray photoelectron spectra calculated in terms of the direct transition model depends strongly on the value of the spectrometer aperture angle. We have considered the dependence of the photoionization cross sections on the value of the aperture angle for photoelectron emission along the [001], [110], and [111] axes. In this case by direction of emission of photoelectrons we understand the direction of the axis of the cone limiting the solid angle Ω_{ap}. The photoionization cross sections were determined from the formula

$$\sigma_i=\frac{1}{\Omega_{ap}}\int\limits_{\Omega_{ap}}\sigma_i(\theta_p,\varphi_p)\,d\Omega_p.$$

The results of the calculations are given in Fig. 5. It is evident that with increase of the aperture angle the difference in the values of σt_{2g} and σ_{e_g} decreases and for sufficiently large angles ($\varphi>\pm 30°$) they become practically equal. This result agrees with the formula from Ref. 1, which was obtained for a single crystal of copper on averaging over the total solid angle. In addition a change of the angle φ from $\varphi=0$ to $\varphi=\pm 7°$ changes the ratio $\sigma_{t_{2g}}/\sigma_{e_g}$ so insignificantly that the corresponding change in shape of the x-ray photoelectron spectra cannot be observed by means of existing experimental techniques. Thus, on increase of the aperture angle to ~14° the x-ray photoelectron spectra are practically unchanged and for the aperture angles at which the experimental study of the angular dependence of x-ray photoemission is carried out the shape of the spectra does not depend on the value of the angle. Indeed, the x-ray photoelectron spectra obtained in Refs. 4 and 5 for the same photoelectron emission directions coincide, in spite of the fact that the aperture angles differed by ~1.5 times. This result confirms the conclusion drawn by Shevchik[6] that the direct-transition model does not give a correct description of the angular dependence of the shape of the photoelectron spectra in the x-ray region.

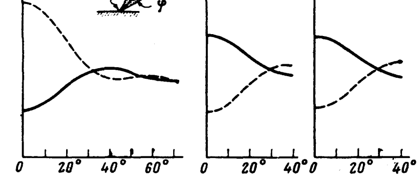

FIG. 5. Photoionization cross sections $\sigma_{t_{2g}}$ (solid curves) and σ_{e_g} (dashed curves) as a function of the aperature angle.

6. COMPARISON OF X-RAY PHOTOELECTRON SPECTRA CALCULATED FOR COPPER WITH EXPERIMENT

In Ref. 1 it was noted that small energy shifts of the electron states of t_{2g} and e_g symmetry type can lead to some change in the shape of x-ray photoelectron spectra of valence electrons of the transition and noble metals. Such shifts can be produced by multielectron processes, in particular by relaxation effects. However, at the present time multielectron methods of band theory have not been developed to the point where they can give quantitative results with sufficient accuracy. Therefore we introduced into the calculation an empirical parameter—a shift of the partial density of e_g states relative to t_{2g} states. The basis for introduction of this parameter is the comparison of the x-ray photoelectron spectra of photoelectrons emitted along the [111] direction (which reflect mainly t_{2g} states) and the [001] direction (which reflect mainly e_g states), and the corresponding partial densities of states. From Fig. 2 of Ref. 5 it is evident that the maximum of the x-ray photoelectron spectra of e_g states of copper is shifted with respect to the maxima of the spectra of t_{2g} states by 0.3 eV toward the Fermi level in comparison with the partial density of states of e_g symmetry calculated without taking into account multielectron effects.

In the present work the x-ray photoelectron spectra of single crystals of copper were calculated on the basis of Eq. (8) but with inclusion of a shift of e_g states of 0.3 eV toward the Fermi level. This leads to improvement of the agreement of the theoretical results with experiment in all cases when the contributions of t_{2g} and e_g states to the x-ray photoelectron spectra are close in value. In all remaining cases, when the shape of the spectrum is determined primarily by electron states of one symmetry type, the displacement introduced does not affect the results of the calculations.

The calculated x-ray photoelectron spectra are shown

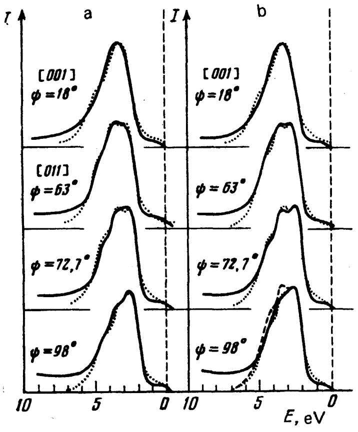

FIG. 6. X-ray photoelectron spectra of valence electrons of a copper single crystal (a) in position 1, b) in position 2, obtained for various directions of emission of photoelectrons (in case b the spectra at $\psi = 72.7$ and 98° are for emission of electrons along [111]); the dotted curves were calculated in the OPW approximation and the dashed curves in the plane-wave approximation; the solid curves are the experimental data of Ref. 4.

in Fig. 6 in comparison with the experimental spectra obtained by Wagner *et al.*[4] The theoretical curves have been spread out by a dispersion curve with half-width 0.4 eV, which corresponds to a spectrometer resolution 0.8 eV. In reality the resolution depends on the angle of emission of the photoelectrons from the sample and for the experimental x-ray photoelectron spectra shown, according to estimates made in Refs. 4 and 12, lies in the range 0.5–1.2 eV. It is evident that the theoretical x-ray photoelectron spectra calculated in the OPW approximation are in good agreement with the experimental results both on the width of the band and on the energy position and the ratio of the intensities of individual features of the spectrum. These results describe the dependence of the x-ray photoelectron spectra structure on the direction of photoelectron emission significantly better than the results of a calculation in terms of the direct-transition model given by Wagner *et al.*[4]

Wehner *et al.*[12] have calculated x-ray photoelectron spectra for copper single crystals in the plane wave approximation. In the particular cases considered, agreement with the experimental data[4] was obtained. We note that the plane wave approximation does not always give a satisfactory description of the structure of x-ray photoelectron spectra. For example, for a sample in position 2 for $\psi = 98°$ (this case is not given in Ref. 12) the x-ray photoelectron spectrum calculated in the plane wave approximation (see Fig. 6) has two peaks, since according to the calculation electron states of t_{2g} symmetry type dominate in the spectrum. The calculation in the OPW gives equal contributions of t_{2g} and e_g states to the spectrum, as a result of which the shape of the spectra is in good agreement with the experimental result.

As can be seen from Figs. 3 and 4, there are photoemission directions for which in the OPW approximation $\sigma_{t_{2g}} < \sigma_{e_g}$, or the reverse. For such directions the x-ray photoelectron spectra calculated in the OPW and plane wave approximations will differ substantially. It follows from this that for a deeper analysis of the problem it is necessary to obtain experimental data over a wide range of directions.

7. DETERMINATION OF PARTIAL DENSITIES OF STATES OF VALENCE ELECTRONS FROM THE ANGULAR DEPENDENCE OF X-RAY PHOTOELECTRON SPECTRA

The calculated angular dependence of the photoionization cross sections for electrons of different symmetry type provide the possibility of determining from the experimentally obtained x-ray photoelectron spectra the partial densities of states of the valence electrons. The basis of the technique proposed is the ratio between the intensity of the photoelectron fluxes and the partial densities of states. Each x-ray photoelectron spectrum is characterized by a quite definite value of excitation energy and direction of emission of photoelectrons. We shall designate the combination of these parameters by the index j, and the explicit indication of the dependence on P we shall drop. Then

$$I^j(E_0)/I^j(E_1) = \Big(\sum_i N_i(E_0)\sigma_i^j\Big)\Big/\Big(\sum_i N_i(E_1)\sigma_i^j\Big),$$

from which follows the equation

$$\sum_i \sigma_i^j[I^j(E_1)N_i(E_0) - I^j(E_0)N_i(E_1)] = 0.$$

Thus, if n electron states of different symmetry type ($i = 1, \ldots, n$) contribute to the x-ray photoelectron spectra, then, for example, setting $N_1(E_0) = 1$ and using $2n - 1$ photoelectron spectra ($j = 1, \ldots, 2n-1$), we form system of linear equations for determination of the unknowns

$$N_2(E_0), \ldots, N_n(E_0),\ N_1(E_1),\ N_2(E_1), \ldots, N_n(E_1).$$

Holding E_0 constant and changing the value of E_1, we solve the system of linear equations for each new value of the energy E_1. The functions $N_i(E)$ obtained in this way are normalized to the total number of electrons in the valence band:

$$\int \sum_{i=1}^{n} N_i(E)\, dE = N.$$

As a result, in addition to the partial densities of states, we determine also the occupation numbers of electron states of various symmetry types.

For example, the x-ray photoelectron spectra of valence electrons of copper is determined by states of the t_{2g} and e_g symmetry types and to find the partial densities of these states three experimental photoelectron spectra are necessary.

With use of the experimental x-ray photoelectron spectra we obtained the partial densities of t_{2g} and e_g states of copper which are shown in Fig. 7. It can be seen that the curves obtained reflect the main features of the density of states.

If the total density of states is normalized to ten valence d electrons, we obtain 6.4 electrons for states of t_{2g} symmetry type and 3.6 for e_g-type symmetry.

Instead of the angular dependence of the photoioniza-

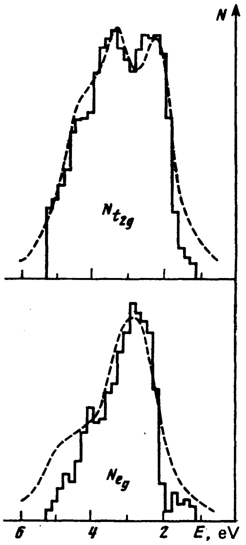

FIG. 7. Partial densities of states of valence *d* electrons of copper: the solid curves were obtained semiempirically, with use of the angular dependence of the photoionization cross sections; the dashed curves were calculated according to the Hodges-Ehrenreich interpolation scheme (the curves have been spread out by a dispersion curve with half-width 0.3 eV).

tion cross sections, in calculation of the partial densities of states it is possible to use their dependence on excitation energy. However, at the present time in the x-ray region of the spectrum the experimental possibilities of this procedure are limited. The most promising method is probably the use of synchrotron radiation for excitation of photoemission.

8. CONCLUSION

The theoretical discussion carried out in this article of the dependence of the photoelectron energy distribution on their direction of emission from single crystals and the comparison of the results with existing experimental data provide a basis for asserting that the OPW approximation is a good model for description of the angular dependence of x-ray photoemission. The photoionization cross sections calculated in terms of this model permit evaluation of the contribution to x-ray photoelectron spectra of electron states of different symmetry types, and this provides the possibility, using experimental spectra obtained for different photoelectron emission directions, of determining the region of energy localization of various electron states. A method is proposed for determination of the partial densities of states of valence electrons from the experimentally obtained angular dependence of the x-ray photoelectron spectra of single crystals. Particularly promising for this purpose is the use of polarized electromagnetic radiation for the excitation of photoemission.

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