Theoretical investigation of the structure of x-ray photoelectron spectra of crystals

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Some general relations determining the intensity of x-ray photoemission from single-crystal and polycrystalline solids are derived in the one-electron approximation. Plane waves (PW) and orthogonalized plane waves (OPW) are used to describe the state of the excited electron. It is shown that allowance for the orthogonalization terms are important for the computation of the cross sections for photoionization of valence electrons. The obtained results are discussed, using as examples the transition and noble metals and semiconductors and dielectrics with the diamond and zinc-blende structures. The difference between the spectra of polycrystals and single crystals of the transition metals can be appreciable, whereas for dielectrics this difference is small. The results of the calculation of the x-ray photoelectron spectra of crystals are in good agreement with the experimental data. To obtain the fine distinctive features of the structure of a spectrum, particularly in the investigation of the transition metals, the many-electron effects should be taken into account.

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I. INTRODUCTION

X-ray photoelectron spectroscopy is an effective method of investigating the electronic structure of crystals.[1,2] This is connected with the fact that it can be used to determine energy band structure, the charge state of atoms in crystals, the type of chemical bond. Also of considerable interest is the study of the process itself of x-ray photoemission in solids: the elucidation of the factors determining the electron-photoionization cross section values and of the many-electron effects which manifest themselves in x-ray photoelectron spectra. In the present paper the main attention is given to the theoretical description in the one-electron approximation of x-ray photoemission of electrons from crystals. The applicability of the one-electron approximation is due to the fact that, in the case of ionization of the valence shells of atoms, the many-electron effects do not, in the x-ray region of the spectrum, in contrast to the near-absorption-threshold region considered in Refs. 3 and 4, lead to a significant change in the structure of the spectra. For example, as was shown in Refs. 5 and 6, the hole formed upon the photoemission of electrons in the valence band gives rise to small shifts of the individual energy subbands relative to each other.

Definite progress has been made in the development of the theory of photoelectron emission in the optical and ultraviolet regions of the spectrum.[7] For crystals the form of the photoelectron spectra in the optical region is determined not only by the distribution of the valence electrons over the energy states, but also by the band structure of the free states. Besides the volume states, there can also appear surface states in the optical photoelectron spectra.

The x-ray photoelectron spectra carry information primarily about the electronic states in the volume of the crystal, since the effective escape depth of the photoelectrons in this case is several times greater than in the optical region of the spectrum. As a result of the high values of the excitation energy (~ 1500 eV) in the x-ray region, the density of free states is a monotonic function of the energy, and therefore it does not affect the form of the photoelectron spectra. A vast experimental material on x-ray photoelectron spectroscopy of metals, alloys, dielectrics, and semiconductors has already been accumulated, but there is virtually no work on the theoretical discussion of the obtained results.

In the present paper we consider a theoretical model that can be used to describe x-ray photoemission from crystals, and derive some general relations determining the structure of the x-ray photoelectron spectra of single-crystal and polycrystalline samples. A discussion of the obtained results is carried out for the transition and noble metals and for semiconductors and dielectrics with the diamond and zinc-blende structures.

II. GENERAL THEORETICAL RELATIONS FOR THE DESCRIPTION OF PHOTOELECTRON EMISSION FROM CRYSTALS

The probability of emission into the solid angle $d\Omega_P$ of a photoelectron of energy E_P from a crystal under the action of x rays of frequency ω is described by the relation

$$dI(E_P, \theta_P, \varphi_P) \sim E_P^{1/2} \sum_{n,k} |\langle \psi_v(k) | W | \psi_c(P) \rangle|^2 d\Omega_P, \tag{1}$$

where ψ_v is the wave function of the initial state of the electron in the valence band, ψ_c is the wave function of the excited electron, and W is the operator of interaction with the electromagnetic field:

$$W = -\frac{e}{mc} \exp(i\mathbf{q}\mathbf{r}) \mathbf{A} \mathbf{P}.$$

We shall describe the electromagnetic field by a linearly polarized plane wave with wave vector $\mathbf{q}$ and polarization vector $\mathbf{A}$. The summation in (1) is over all the

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k vectors satisfying the condition $E_\mathbf{P} - E_n(\mathbf{k}) = \hbar\omega$.

The work function, φ, for an electron in the sample can be taken into account by replacing $E_\mathbf{P}$ by $(E_\mathbf{P} - \varphi)$ in the preceding formulas. This does not affect the shape of the energy distribution curve of the x-ray photoelectrons and, therefore, below the work function will not be taken into consideration.

To describe the electronic states in the valence band, let us use linear combinations of Bloch functions constructed on the atomic orbitals $\chi_i(\mathbf{r})$:

$$\psi_v = \sum_i c_i(\mathbf{k}) \frac{1}{\sqrt{N}} \sum_\nu \exp(i\mathbf{k}\mathbf{R}_\nu)\chi_i(\mathbf{r}-\mathbf{R}_\nu), \tag{2}$$

and, as the wave functions of the excited electrons, let us use plane waves orthogonalized to all the valence and ground states:

$$\psi_c = \langle \mathbf{r}|\mathbf{P}\rangle - \sum_i \langle \mathbf{r}|u_i\rangle\langle u_i|\mathbf{P}\rangle$$
$$= \frac{1}{\sqrt{N\Omega_0}}\exp i\mathbf{P}\mathbf{r} - \frac{1}{\sqrt{N}}\sum_i \sum_\nu \exp(i\mathbf{k}\mathbf{R}_\nu)u_i(\mathbf{r}-\mathbf{R}_\nu)F_i(\mathbf{P}),$$
$$\tag{3}$$

where

$$F_i(\mathbf{P}) = \frac{1}{\sqrt{\Omega_0}}\int d^3r\, u_i^*(\mathbf{r})\exp i\mathbf{P}\mathbf{r}, \tag{4}$$

while the $u_i(\mathbf{r})$ are wave functions of the valence (χ_i) or core electrons of the atoms.

Notice that the index i in (2) and (3), which specifies the i-th electronic state, is a combination of the three quantum numbers $\{n_i,\ l_i,\ m_i\}$, and that the sum over i is, in fact, a triple sum over n_i, l_i, and m_i.

Let us compute the transition-probability matrix element $\langle\psi_v|W|\psi_c\rangle$ in the dipole approximation, which is permissible at excitation energies $\hbar\omega \sim 1500$ eV. In doing this we neglect the overlap of the atomic orbitals localized at the various lattice sites. Summing over all the lattice sides ν, we obtain an equation expressing the law of conservation of electron momentum in the photoemission process:

$$\mathbf{P} = \mathbf{k} + \mathbf{Q},$$

where $\mathbf{Q}$ is a reciprocal-lattice vector. However, for angular spectrometer apertures greater than 6–8° and excitation energies $\hbar\omega \sim 1500$ eV, the momentum conservation law does not lead to additional limitations in the analysis of electronic states with different $\mathbf{k}$ vectors lying inside the Brillouin zone. Therefore, it is sufficient to restrict ourselves, when performing the summation over $\mathbf{k}$ in the expression (1), to the terms determined by the condition

$$E_\mathbf{P} \leqslant E_n(\mathbf{k}) + \hbar\omega < E_\mathbf{P} + \Delta E_\mathbf{P},$$

which expresses the law of conservation of energy in the photoemission process.

The transition probability matrix element can be written in the form

$$\langle\psi_v|W|\psi_c\rangle \sim (\mathbf{A}\mathbf{P})\sum_i c_i^* F_i(\mathbf{P}) + i\sum_i c_i^* \sum_p F_p(\mathbf{P})\,(\mathbf{A}\mathbf{G}_{ip}),$$

where

$$\mathbf{G}_{ip} = \int d^3r\,\chi_i^*(\mathbf{r})\nabla u_p(\mathbf{r}).$$

For greater simplicity of form of the obtained expressions, we shall assume that the summation in these expressions always includes all the occupied states, but that $c_i \equiv 0$ if i does not pertain to states of the valence band. Let us introduce the notation

$$\gamma_p = \sum_i c_i^*(\mathbf{A}\mathbf{G}_{ip}). \tag{5}$$

Then, using the identity $f - f^* = 2i\,\mathrm{Im}(f)$, we obtain

$$|\langle\psi_v|W|\psi_c\rangle|^2 \sim \sum_i \sum_j [F_i^* F_j\{c_i c_j^* P^2 \cos^2\vartheta + \gamma_i^*\gamma_j\} - 2P\cos\vartheta\,\mathrm{Im}(F_i^* c_i F_j\gamma_j)]$$

$$= S_1 + S_2 + S_3 + S_4 + S_5,$$

where

$$S_1 = P^2 \cos^2\vartheta \sum_i F_i^* F_i c_i c_i^*,$$

$$S_2 = 2P^2 \cos^2\vartheta \sum_i \sum_{j>i} \mathrm{Re}(F_i^* F_j c_i c_j^*), \tag{6}$$

$$S_3 = \sum_i F_i^* F_i \gamma_i^* \gamma_i, \quad S_4 = 2\sum_i \sum_{j>i}\mathrm{Re}(F_i^* F_j\gamma_i^*\gamma_j),$$

$$S_5 = -2P\cos\vartheta \sum_i \sum_j \mathrm{Im}(F_i^* c_i F_j\gamma_j),$$

while ϑ is the angle between the directions of $\mathbf{A}$ and $\mathbf{P}$.

The first two terms, S_1 and S_2, correspond to the plane-wave approximation, while S_3, S_4, and S_5 are corrections resulting from the orthogonalization terms.

To determine the quantities F_i, (4), and γ_i, (5), let us introduce two coordinate systems: the laboratory system (r, θ, φ) whose polar axis coincides with the direction of the vector $\mathbf{A}$ and the system (r', θ', φ') connected with the crystal. The orientation of the coordinate system of the crystal relative to the laboratory system is characterized by the Euler angles (α, β, γ), which we shall henceforth denote by the abbreviated form (β). Spherical harmonics written in one coordinate system are expressible in terms of linear combinations of spherical harmonics written in the other coordinate system:

$$Y_{lm'}(\theta',\varphi') = \sum_m D_{m,m'}^l(\beta)Y_{lm}(\theta,\varphi),$$

$$Y_{lm}(\theta,\varphi) = \sum_{m'} D_{m,m'}^l(\beta)Y_{lm'}(\theta',\varphi'),$$

where the $D_{m,m'}^l(\beta)$ are the matrix elements of the rotations.

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Writing in the integral (4) the atomic orbital $u_i(r)$ in the form of a product of the radial and angular parts, and expanding the plane wave in a series in terms of the spherical harmonics and the spherical Bessel functions, we obtain

$$F_i(\mathbf{P}) = \frac{4\pi}{\sqrt{\Omega_0}} T_i(P) i^{l_i} Y^*_{l_i m_i}(\theta_P{}', \varphi_P{}'),$$

where

$$T_i(P) = \int_0^\infty r^2 R_{n_i l_i}(r) j_{l_i}(Pr)\, dr. \qquad (7)$$

Using the relation[8]

$$\langle s | \nabla | t \rangle = m\hbar^{-2}(E_i - E_s)\langle s | \mathbf{r} | t \rangle,$$

we obtain for γ_i the following expression:

$$\gamma_i = \sum_p c_p{}^* U_{pi} \frac{1}{3}(-1)^{m_p} \left[\frac{4\pi}{3}(2l_p+1)(2l_i+1) \right]^{1/2}$$
$$\times Y_{1,-m_p+m_i}(\theta_A{}', \varphi_A{}') c(l_p l_i 1; -m_p, m_i) c(l_p l_i 1; 0, 0),$$

where

$$U_{pi} = \frac{m}{\hbar^2}(E_{n_i l_i} - E_{n_p l_p}) \int_0^\infty r^3 R_{n_p l_p}(r) R_{n_i l_i}(r)\, dr, \qquad (8)$$

while the $c(l_i l_j L; m_i, m_j)$ are Clebsch-Gordan coefficients.[9]

1. *X-ray photoelectron spectra of polycrystals.* To describe the photoelectron emission from polycrystalline samples, let us write the formulas (6) in the coordinate system connected with the crystal, and then transfer the vectors **A** and **P** into the laboratory system of coordinates and average over all values of the Euler angles, which is equivalent to averaging over all possible positions of the crystal relative to the laboratory system of coordinates. In this case the expression for the angular distribution of the photoemission can be reduced to the form

$$I \sim A + B \cos^2 \vartheta,$$

which agrees with the result obtained in Ref. 10 for a gas of multi-atomic molecules.

2. *X-ray photoelectron spectra of single crystals.* In deriving the corresponding expressions for the intensity of x-ray photoemission from single-crystal samples, it is necessary to take into account the specific position of the sample relative to the x rays incident on it. In this case the photoemission is characterized by a strong anisotropy, and the various directions of emission of the photoelectrons will differ not only in the flux intensity, but also in the distribution of the photoelectrons over energy.

We have considered the case when the polarization vector, **A**, of the electromagnetic wave incident on the single-crystal sample is directed along the z axis of the crystal. In this case the laboratory system of coordi-

nates coincides with the coordinate system of the crystal and, consequently, the D rotation matrix is a unit matrix, i.e.,

$$D^l_{m,m'}(0,0,0) = \delta_{mm'}.$$

The corresponding expressions for $S_1, \ldots, S_5$ are obtained from (6) with allowance for the fact that $\vartheta = \theta_P$.

If we assume that roughly all the electrons leaving the sample surface are registered by the spectrometer (this practically corresponds to the experimental technique used at present in x-ray photoelectron spectroscopy), then it is necessary to average the expression for the intensity over the hemisphere bounded by the sample surface. In the general case it is difficult to carry out this averaging. The problem gets simplified if the vector **A** is directed along the z axis and the surface of the sample coincides with the xy plane of the coordinate system, since then, neglecting the interference between the electronic states of different symmetry classes, we can replace the integral over the hemisphere by half the integral over the entire sphere. However, in this case the x rays should propagate parallel to the sample surface, which does not correspond to any specific experimental situation. We can, in other cases in which the vector **A** is not perpendicular to the crystal surface, also go over to integration over the whole sphere, which will entail some approximation. This approximation will, apparently, not lead to appreciable errors, since the photoemission intensity is highest in the direction of the vector **A**.

III. THE TRANSITION AND NOBLE METALS

Let us apply the relations obtained in Sec. II to crystals of the transition and noble metals. Their valence band has quite a complex structure, produced as a result of the hybridization of the electronic states of the s-p and d symmetry classes; the s-p states are distributed over the whole width of the valence band, while the d states are localized in a comparatively narrow energy region. In the case of transition metals at the end of a period and the noble metals, the density of valence d states in the region of their localization significantly exceeds the density of the s-p states. Because of this, as was shown in Refs. 11 and 12, mainly the d states are reflected in the x-ray photoelectron spectra of the valence band of these crystals. To construct the wave function ψ_V, (2), let us apply the Hodges-Ehrenreich interpolation scheme,[13] in which, as the basis, one uses plane waves for the s-p states and atomic orbitals for the d states. In this case the contribution of the s-p states to the transition-probability matrix element is small and can be neglected.

Going over to real combinations of the spherical harmonics, we obtain the following expression for the energy distribution of the photoelectrons in the case of polycrystalline samples of copper:

$$I^{Cu}(\omega, E) \sim \sum_{n,k} \{ |c_{xy}{}^n|^2 + |c_{yz}{}^n|^2 + |c_{xz}{}^n|^2 + |c_{x^2-y^2}{}^n|^2 + |c_{3z^2}{}^n|^2 \}$$
$$\times [E^{1/2} T_{3d}{}^2 \cos^2 \vartheta + E^{1/2}(T_{2p} U_{2p;3d} + T_{sp} U_{sp;3d})^2 \cdot {}^1/_{25}(3 + \cos^2 \vartheta)$$
$$+ E T_{3d}(T_{2p} U_{2p;3d} + T_{sp} U_{sp;3d}) \cdot {}^4/_5 \cos^2 \vartheta].$$

Thus, up to a factor that insignificantly changes its magnitude along the width of the valence band, the x-ray photoelectron spectrum reproduces the density of states of the valence d electrons.

However, the experimental x-ray photoelectron spectra of polycrystalline samples of transition metals at the end of a period and the noble metals differ from the computed density-of-states curves. This difference consists, first and foremost, in different intensity ratios for the individual features of the spectrum, although the positions of these features along the energy axis coincide with the positions of the corresponding features in the density-of-states curves.[14] A possible cause of the observed difference is the neglect in the theoretical model used of the relaxation effects. In particular, if the relaxation-induced energy shifts have different magnitudes for states with different energies, then this leads to a change in the shape of the spectrum.

For a copper single crystal we can derive the following expression for the photoelectron-flux intensity;

$$I^{Cu}(\omega, E) \sim E^{\nu_1} T_{3d}^2 \sum_{n,k} \{3|c_{xy}{}^n|^2 + (9+3M)(|c_{yz}{}^n|^2+|c_{xz}{}^n|^2)$$

$$+3|c_{x^2-y^2}^n|^2 + (11+4M)|c_{3z^2}^n|^2\},$$

where

$$M = \frac{7[(T_{2p}U_{2p;3d}+T_{3p}U_{3p;3d})^2 + 2\sqrt{E}\,T_{3d}(T_{2p}U_{2p;3d}+T_{3p}U_{3p;3d})]}{5ET_{3d}^2}.$$

In this case the contributions of the individual d orbitals to the intensity enter with different coefficients. In particular, the contribution of the orbitals having a z component is enhanced, which is due to the choice of the position of the single crystal relative to the x rays incident on it. This fact can lead to some changes in the structure of the photoelectron spectrum and to some difference between the spectrum and the partial density of the valence d states.

Additional information about the electron structure of crystals can be obtained by investigating the angular dependence of the x-ray photoemission from single-crystal samples. We can distinguish those directions of photoelectron emission for which the form of the spectrum is largely determined by electronic states of a definite symmetry class. This allows us to determine the energy and spatial localization of the various electronic states. The problem of devising experiments for investigations of this type in the x-ray region of the spectrum is a complex one, but attempts have already been made in this direction.[15,16]

IV. CRYSTALS WITH THE DIAMOND AND ZINC-BLENDE STRUCTURES

The analysis of the x-ray photoelectron spectra of dielectrics and semiconductors of the A^{IV}, $A^{III}B^V$, and $A^{II}B^{VI}$ types is of special interest. For the transition and noble metals the contribution of the valence d electrons to the photoelectron spectrum by far exceeds the contribution of the s-p electrons. In dielectrics and semiconductors the contributions to the spectrum of

states of the s- and p-symmetry classes are comparable in magnitude, and the structure of the photoelectron spectrum is largely determined by the ratio of these contributions.

In interpreting the x-ray photoelectron spectra of compounds, we must take into account the fact that, even when electrons of the different kinds of atoms in the crystal form a chemical bond, they nonetheless preserve some individuality of the atomic states, as a result of which the cross sections for photoionization of the s and p electrons of the various constituents differ from each other.

To describe the valence electron states in the semiconductors and dielectrics, we used the tight-binding method in the form proposed by Chadi and Cohen.[17] In deriving the relations determining the form of the photoelectron spectrum, we neglected the interference between the electronic waves from the various sublattices of the diamond or zinc-blende structure.

In the general case the expression for the intensity of the photoemission from polycrystals can be written in the form

$$I(\omega, E) \sim \sum_i \sum_{l(i)} \sigma_l{}^i(\vartheta, E) N_l{}^i(E), \tag{9}$$

where

$$N_l{}^i(E) = \sum_k \sum_m |c_{lm}{}^i(k)|^2$$

is the local partial density of the i-th atom's electronic states having a symmetry of the l-th class. The summation in the expression (9) is performed over the atoms located in a unit cell of the crystal and over the valence electron states with orbital moments l.

For silicon, the quantities $\sigma_l^i(\vartheta, E)$ for the two atoms in the unit cell are equal, and are determined by the formulas

$$\sigma_s{}^{Si}(\vartheta, E) = E^{\nu_1}T_{3s}{}^2 \cos^2\vartheta + E^{\nu_2}(T_{2p}U_{2p;\,3s}+T_{3p}U_{3p;\,3s})^2 \cos^2\vartheta$$
$$-ET_{3s}(T_{2p}U_{2p;\,3s}+T_{3p}U_{3p;\,3s})2\cos^2\vartheta, \tag{10}$$

$$\sigma_p{}^{Si}(\vartheta, E) = E^{\nu_2}T_{3p}{}^2 \cos^2\vartheta + E^{\nu_1}(T_{1s}U_{1s;\,3p}+T_{2s}U_{2s;\,3p}$$
$$+T_{3s}U_{3s;\,p})^2+ET_{3p}(T_{1s}U_{1s;\,3p}+T_{2s}U_{2s;\,3p}+T_{3s}U_{3s;\,3p})\cdot{}^2/_3\cos^2\vartheta. \tag{11}$$

Notice that

$$\sum_{i=1,2} N_l{}^i(E) = N_l(E),$$

where $N_l(E)$ is the partial density of states of the l-th symmetry class.

In the case of Si, $N_l^1(E) = N_l^2(E)$.

For a single crystal of silicon, the expression determining the flux intensity of the valence photoelectrons has the form

$$I(\omega, E) \sim E^{\nu_1} \sum_{n,k} \{|c_s{}^n|^2[{}^1/_3(E^{\nu_1}T_{3s}-(T_{2p}U_{2p;3s}+T_{3p}U_{3p;s}))^2]$$
$$+(|c_x{}^n|^2+|c_y{}^n|^2)[{}^1/_5ET_{3p}{}^2]+|c_z{}^n|^2[{}^1/_3(E^{\nu_1}T_{3p}+(T_{1s}U_{1s;3p}+T_{2s}U_{2s;3p}$$
$$+T_{3s}U_{3s;3p}))^2+{}^4/_{15}ET_{3p}{}^2]\}. \tag{12}$$

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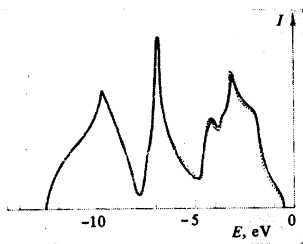FIG. 1. X-ray photoelectron spectra of single-crystal (continuous curve) and polycrystalline (points) silicon.

Crystal	σ_s/σ_p	
	PW approximation	OPW approximation
Diamond	25.0	13.6
Silicon	1.7	2.4
Germanium	5.1	0.9

If we assume that

$$\sum_{n,k} |c_x{}^n|^2 = \sum_{n,k} |c_y{}^n|^2 = \sum_{n,k} |c_z{}^n|^2 = \frac{1}{3} N_p(E), \tag{13}$$

then the formula (12) can be written in the form

$$I(\omega, E) \sim \sigma_s N_s(E) + \sigma_p N_p(E),$$

which coincides with the result (9), obtained for polycrystals. The quantities σ_s and σ_p in this case coincide with the photoionization cross section values obtained from the formulas (10) and (11) by integrating them over the upper hemisphere.

Calculations show that the equality (13) is fulfilled with sufficient accuracy in a wide energy range. Consequently, the x-ray photoelectron spectra of single-crystal and polycrystalline Si samples virtually coincide (Fig. 1).

We have carried out a computation of the x-ray photoelectron spectra of diamond, silicon, germanium, and gallium arsenide. The parameters of the tight-binding model were taken from Ref. 17. The quantities T_{nl} and $U_{nl;n'l'}$ were computed with the use of Clementi's atomic wave functions.[18] The calculation was performed over 5230 points in $\frac{1}{48}$-th part of the Brillouin zone. As can be seen from Fig. 2, the computed x-ray photoelectron spectra of diamond, silicon, and germanium are in good agreement with the experimental results.[19]

It should be noted that allowance for the orthogonalization terms does not lead to a significant change in the form of the x-ray photoelectron spectra of diamond and silicon, although the magnitudes of the cross sections for photoionization of the valence s and p electrons can change appreciably (Table I). For germanium the effect connected with the orthogonalization terms is quite substantial.

In the x-ray region of the spectrum, at excitation energies close to 1500 eV, the magnitude of the orthogonalization corrections is determined largely by the core states. The integrals $T_{nl}(E)$ in diamond, silicon, and germanium for the core functions are, on the average, ten times greater than for the valence functions. Therefore, the quantity $E^{3/2} T_{nl}^2$ (val.), which determines the contribution to the photoelectron flux intensity from the plane wave, has the same order of magnitude as $E^{1/2} T_{nl}^2$ (core). A numerical analysis shows that the orthogonalization corrections in this case exceed the contribution from the plane wave. A different

relation obtains between the contributions to the photoelectron flux intensity in the presence in the valence band of highly localized electronic states of the d-symmetry class. Thus, in the case of the noble metals the integrals $T_{nl}(E)$ for the core p states and for the valence d states are close in magnitude. Therefore, $E^{3/2} T_{nd}^2$ (val.) $\gg E^{1/2} T_{np}^2$ (core), and the orthogonalization corrections are small.

Neglecting the interference between the sublattices in the crystal, the formula for the x-ray photoemission intensity in the case of a GaAs single crystal can be represented in the form

$$I(\omega, E) = I^{Ga} + I^{As},$$

where

$$I^{Ga(As)}(\omega, E) \sim E^{1/2} \sum_{n,k} \left\{ |c_x{}^n|^2 \left[\frac{1}{3} \left(E^{1/2} T_{4s} - \sum_{n=1}^{4} T_{np} U_{pn;4s} \right)^2 \right] \right.$$
$$+ (|c_x{}^n|^2 + |c_y{}^n|^2) [\frac{1}{3}(E^{1/2}T_{4p} - T_{3d}U_{3d;4p})^2]$$
$$\left. + |c_z{}^n|^2 \left[\frac{1}{3} \left(E^{1/2} T_{4p} + \sum_{n=1}^{3} T_{ns} U_{ns;4p} \right)^2 + \frac{4}{15}(E^{1/2}T_{4p} - T_{3d}U_{3d;4p})^2 \right] \right\}.$$

The results of the computation of the density of states and the x-ray photoelectron spectra of the valence electrons of gallium arsenide are presented in Fig. 3.
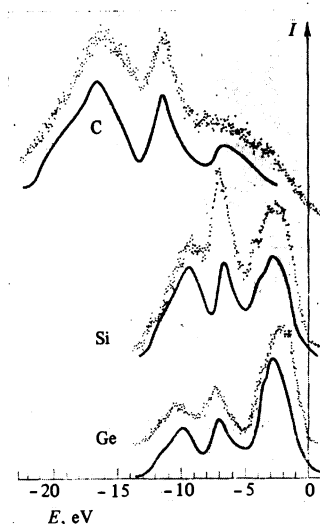

FIG. 2. Experimental and theoretical x-ray photoelectron spectra of diamond, silicon, and germanium.

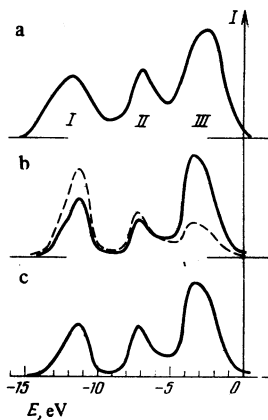V. G. Aleshin and Yu. N. Kucherenko   997

FIG. 3. The x-ray photoelectron spectrum and the density of states of the valence electrons of gallium arsenide: a) the experimentally obtained spectrum; b) the spectrum computed in the OPW approximation (continuous curve) and in the PW approximation (dashed curve); c) density of states. The theoretical lines are broadened by a dispersion line of halfwidth 0.3 eV.

TABLE II. Ratio of the peak III to the peak I in the curves of the x-ray photoelectron spectra (XPS) and of the density of states of gallium arsenide.

Compared quantities	I^{III}/I^{I}
Density of valence states	1.79
XPS (PW approximation)	0.39
XPS (OPW approximation)	1.75
XPS (experiment)	1.74

The peak I is determined largely by the $4s$ states of As, the peak II by the $4s$ states of Ga and partly by the $4p$ states of As, and the peak III by the $4p$ states of Ga and As. In Table II we present the ratio of the magnitude of the peak III to the magnitude of the peak I for all the curves shown in Fig. 3.

The presence in the system of relaxation effects for the semiconductors and dielectrics was implicitly taken into account in that the parameters with which the computation was carried out were determined by the empirical-pseudopotential method.[17]

V. CONCLUSION

In the paper we have proposed the use of plane waves orthogonalized to the valence and core states in a crystal for the description of photoelectron states. We have shown that, in the case of the transition and noble metals, polycrystalline and single-crystal samples may have different x-ray photoelectron spectra, whereas in the case of dielectrics this difference is small. This is due to the presence in metals of a complex band structure connected with the hybridization of the s-p and d electrons. By investigating the x-ray photoelectron spectra in spectrometers with small angular apertures for the collection of the photoelectrons, we can hope to establish this difference for dielectrics as well.

For polycrystalline samples the intensity of the x-ray photoelectron spectra is represented in the form of a sum of products of the partial densities of valence-electron states and the corresponding photoionization cross sections. Allowance for the orthogonalization terms in the expression for the excited-electron wave function leads to a significant change in the magnitudes of the photoionization cross sections, an effect which improves the agreement with experiment.

Notice that we have not in the present paper considered the questions connected with the passage of an excited electron through the sample surface. At electron energies ~1500 eV the diffraction phenomena are weak; therefore, they can be neglected. We also neglected the contribution of the multiply scattered electrons, a contribution which was subtracted from the experimental

spectra with which the results of the calculations were compared.

The present paper shows that a fairly good idea about the x-ray photoelectron spectra of solids can be obtained in the one-electron approximation. But to obtain the detailed features of the structure of a spectrum, especially in the investigation of transition metals, we must take the many-electron effects into account.

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