CALCULATION OF PHOTOEMISSION CHARACTERISTICS OF CUBIC K_3Sb

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A three-step model of photoelectron emission is used to calculate the quantum efficiency and the energy distribution functions of emitted electrons with allowance for the scattering of the excited electrons leading to the production of electron—hole pairs. The calculated quantum efficiency is compared with experimental data in the visible part of the spectrum. The correlation between the structure of the photoemission characteristics and the density of the electron states is discussed.

It was shown in the previous [1] that the basic features of the spectral dependences of the optical characteristics of cubic K_3Sb, a representative of the group of antimony—alkali compounds, can be understood on the basis of the model of the band spectrum proposed in [1, 2]. Here, we study the photoemission properties of this compound. To calculate them, we use the band spectrum and optical characteristics calculated, as in [1], by means of an empirical pseudopotential with allowance for nonlocality and the spin—orbit interaction.

Photoelectron emission will be regarded as a three-step process [3]. The first stage of this process — the optical excitation — is accompanied by transitions of electrons from the valence to the conduction band. For compounds with narrow valence bands (such as K_3Sb), these transitions can be described on the basis of models of both direct and indirect transitions. Indeed, the energy distribution of the optically excited electrons in the model of direct transitions is described by the function

$$N_0(E,\ \omega)=\frac{\sum\limits_{n,s}\int d^3\kappa\,|M_{ns}(\boldsymbol{\kappa})|^2\delta(E-E_s(\boldsymbol{\kappa})-\hbar\omega)\,\delta(E-E_n(\boldsymbol{\kappa}))}{\sum\limits_{ns}\int d^3\kappa\,|M_{ns}(\boldsymbol{\kappa})|^2\delta(E_n(\boldsymbol{\kappa})-E_s(\boldsymbol{\kappa})-\hbar\omega)}, \tag{1}$$

where M_{ns} are the matrix elements of the optical transitions, E is the electron energy, $\hbar\omega$ is the photon energy, summation is performed over the electron states in the valence band (s) and the conduction band (n), and integration over the Brillouin zone.

Assuming that the matrix elements M_{ns} depend on $\boldsymbol{\kappa}$ only through the energies $E_n(\boldsymbol{\kappa})$, $E_s(\boldsymbol{\kappa})$ and replacing $\sum\limits_s\delta(E-\hbar\omega-E_s)$ in (1) by $\rho_v(E-\hbar\omega)$ (since for flat valence bands E_s hardly depends on $\boldsymbol{\kappa}$), we obtain for $N_0(E,\ \omega)$ the expression

$$N_0(E,\ \omega)=\frac{M^2(E,\ \omega)\,\rho_v(E-\hbar\omega)\,\rho_c(E)}{\int dE_1M^2(E_1,\ \omega)\,\rho_v(E_1-\hbar\omega)\,\rho_c(E_1)}, \tag{2}$$

which describes the energy distribution of the electrons in the model of indirect transitions. (Here, ρ_c and ρ_v are the densities of the electron states in the conduction and valence bands, respectively; M^2 are the probabilities of optical transitions averaged over the wave vectors.)

In considering the second stage of photoemission, the propagation of the excited electrons to the surface, we shall regard the electron as a randomly walking particle. We shall restrict ourselves to considering electron scattering processes in which electron—hole pairs are formed (ee scattering). In such a scattering, the electron loses an energy greater in magnitude than the gap width. Since the probability of ee scattering decreases strongly with decreasing electron energy, in the part of the spectrum in which we are interested (the visible and adjoining ultraviolet), we can ignore electrons

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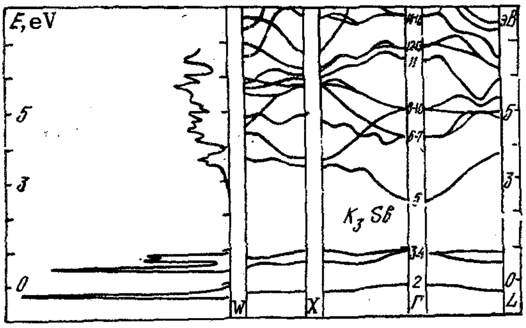

Fig. 1. Energy spectrum and density of electron states.

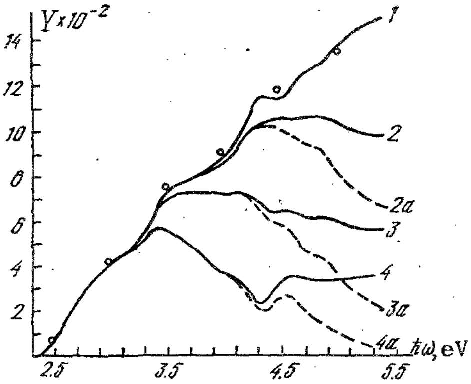

Fig. 2. Quantum efficiency Y(ω) calculated with (curve 1) and without (curves 2-4) allowance for the ee interaction; the broken curves show Y(ω) without the contribution of secondary electrons.

that undergo two or more ee scatterings. Following [3], we assume that the distribution with respect to the directions of motion of the excited and scattered electrons is isotropic, and that the only electrons which reach the vacuum are those that arrive at the surface within an exit cone with energy exceeding the vacuum level. (The exit cone is defined by the condition $\theta < \theta_0$, where θ is the angle between the normal to the surface and the direction of motion of the electron; θ_0 is the critical angle for which emission is still possible.) In such an approach, the energy distribution function N(E, ω) of the emitted electrons and the quantum efficiency Y(ω) are each a product of probabilities integrated over the intermediate states:

a) the probability P(x, ω)dx of absorption of a photon by an electron at depth x from the surface in a layer of thickness dx;

b) the probability N_0(E', ω)dE' of optical excitation of the electron to a state with energy between E' and E' + dE';

c) the probability f(E', E; x) of the photoelectron's getting from the depth x to the surface with energy E in the exit cone. Thus

$$N(E, \omega) = \int dE' N_0(E', \omega) \int_0^\infty dx P(x, \omega) f(E', E; x), \tag{3}$$

$$Y(\omega) = \int dE N(E, \omega). \tag{4}$$

In the framework of the quasiclassical random-walk model, the probability f(E', E: x) for a semi-infinite sample has the form [3]

$$f(E', E; x) = \left\{ \delta(E' - E) T(E, x) + \frac{1}{l'} \left[\int_0^1 dy \int_0^{x/y} dr + \int_{-1}^0 dy \int_0^\infty dr \right] e^{-r/l'} S(E', E) T(E, x - ry) \right\}. \tag{5}$$

Here, $T(E, x) = \frac{1}{2} \int_K^1 dz e^{-x/lz}$; $l = l(E)$ is the mean free path of an electron with energy E between ee scatterings; $l' = l(E')$; $K = \cos\theta_0$; $S(E', E)$ is the probability that the electron goes over in the ee scattering from a state with energy E' to one with energy E.

Substituting (5) in (3) and assuming that the light propagates in accordance with the exponential law $P(x, \omega) = \alpha(\omega) e^{-\alpha x}$ (where α(ω) is the coefficient of optical absorption), we obtain

$$N(E, \omega) = \frac{1}{2} \int dE' N_0(E', \omega) \left[1 - K \frac{1}{\alpha l} \ln \left(\frac{1 + \alpha l}{1 + \alpha l K} \right) \right] \left\{ \delta(E' - E) + \right.$$

$$\frac{1}{2} S(E', E)\left[\frac{1}{\alpha l'}\ln(1+\alpha l') + \frac{l}{2l'}\ln\left(1+\frac{l'}{l}\right) + \frac{lK}{2l'}\ln\left(1+\frac{l'}{lK}\right)\right]\Bigg\}. \tag{6}$$

In our model, the main parameter, which determines the probability of scattering of the excited electron, is the mean free path $l(E)$. It is intimately related to the band structure and can be expressed in terms of the mean group velocity V(E) of the electron and the lifetime τ(E) of a state with the given energy: $l(E) = V(E) \cdot \tau(E)$. The mean group velocity V(E) and the coefficient of optical absorption $\alpha(\omega)$ are calculated on the basis of the band spectrum shown in Fig. 1. The energy dependence of the parameter K was chosen in the simple form

$$K = \begin{cases} \sqrt{\dfrac{W}{E}}, & E > W \\ 1, & E \leqslant W \end{cases},$$

where W is the work function (for cubic K_3Sb, W = 2.3 eV). This expression is obtained if the electrons at the surface are treated as a gas of free electrons and one requires conservation of the tangential component of the electron quasimomentum on the transition through the interface of the media. We calculated the lifetime τ(E) and the probability S(E', E) in Kane's approximation of "random" $\boldsymbol{\kappa}$ [4]:

$$\tau^{-1}(E) = A \int_{E_g}^{E-E_g} dE_1 \rho_c(E_1) \int_{E_g-E+E_1}^{0} dE_0 \rho_v(E_0)\, \rho_c(E_0 + E - E_1), \tag{7}$$

$$S(E', E) = \frac{2\rho_c(E) \int_{E_g-E'+E}^{0} dE_0 \rho_v(E_0)\, \rho_c(E_0 + E' - E)}{A^{-1}\tau(E')}. \tag{8}$$

In this approximation, the conservation of the quasimomentum in the process of ee scattering is ignored, and the matrix elements of the ee interaction are assumed independent of the wave vectors of the initial and final states. The calculation of τ(E) then results in the appearance of a parameter A, which can be determined if we know the mean free path at some energy. Since we do not, we varied the unknown A in a wide range.

Figure 2 shows the calculated quantum efficiencies Y(ω).

The upper curve 1 describes Y(ω) without allowance for ee interaction in the model of indirect transitions. The dependence Y(ω) with allowance for ee interaction is shown by curves 2-4 for three different values of A. The chosen values correspond to a mean free path l at E = 5 eV equal to 100, 10, and 1 Å, respectively. The broken curves show the quantum efficiency without the contribution of secondary electrons. It is normalized to one absorbed photon. The energy distribution functions N(E, ω), calculated for three different photon energies ($\hbar\omega$ = 3.38, 4.65, 5.5 eV) with l = 10 Å at E = 5 eV, are plotted in Fig. 3. The finite lifetime of the excited states is taken into account semiphenomenologically by the introduction of an effective level width. This is achieved by going over from N(E, ω) to the function $\int E_1 L(E, E_1) N(E_1, \omega)$ by means of the δ-like function $L(E, E_1) = \pi^{-1} \cdot \Gamma / [\Gamma^2 + (E - E_1)^2]$, where the broadening parameter Γ is taken equal to 0.04 eV. To interpret the features of the N(E, ω) curves, it is convenient to use the correspondence between the structure of the density of electron states and the structure of the optical electron energy distribution $N_0(E, \omega)$. The density of the electron states in the valence band of cubic K_3Sb has a well-defined δ-like nature, while the density of the states in the conduction band oscillates in a wide range. Since $N_0(E, \omega) \sim \rho_v(E - \hbar\omega)\rho_c(E)$, the structure of $N_0(E, \omega)$ as a whole must repeat the structure of the density of the electron states in the valence band (presence of three sharp peaks) shifted through the energy scale by $\hbar\omega$. The same peaks must also be present in the distribution of the emitted electrons, though, of course, the scattering processes and conditions of leaving the material distort the initial energy distribution. At large $\hbar\omega$, the spectrum of emitted electrons contains secondary electrons (the broad peak at low energies in the curves in Figs. 3b and 3c). There are only two peaks in the N(E, ω) curve at $\hbar\omega$ = 3.38 eV (Fig. 3a) because the transitions from the lower valence band take place to states below the vacuum level.

Figure 2 shows that in the investigated spectral region ee scattering plays an

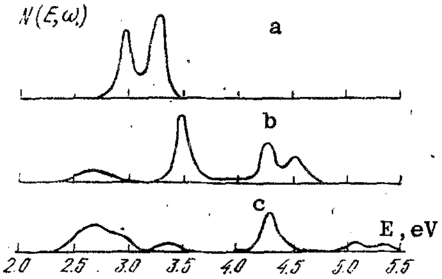

Fig. 3. Energy distribution functions of emitted electrons calculated for photon energies 3.38 eV (a), 4.65 eV (b), 5.5 eV (c).

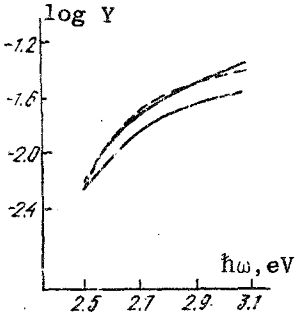

Fig. 4. Theoretical (broken) and experimental (continuous) curves of the quantum efficiency.

important part. Variation of the parameter A in a fairly wide range leads to a certain change in the structure of the Y(ω) curve, and also to a displacement of the threshold of electron—hole pair production (from 3.1 to 3.7 eV). It can be seen in Fig. 2 that the secondary electrons appear in the emission spectrum at photon energies $\hbar\omega \approx 4.2$ eV. It is characteristic that this energy and the number of secondary electrons are almost insensitive to variation of A. To illustrate the equivalence we noted above between the models of direct and indirect transitions in the case of compounds with narrow valence bands, we have plotted in Fig. 2 the results of calculating Y(ω) in the former model.

For comparison with the experimental data [5], we also calculated the quantum efficiency normalized to an incident photon: $Y'(\omega) = (1 - R(\omega))Y(\omega)$. The coefficient of optical reflection R was calculated on the basis of the complex permittivity function calculated in [1]. Comparison of the theoretical Y(ω) with the experimental values (for two different samples) at photon energies up to 3.1 eV (Fig. 4) reveals good agreement. When this agreement is considered in the light of the equivalence of the models just mentioned, it serves as an indirect proof that the valence bands in cubic K_3Sb have small dispersion. Unfortunately, the literature does not contain data on measurements of the quantum efficiency of cubic K_3Sb at higher photon energies, so that we cannot make a more complete and detailed comparison with experiment or determine more accurately quantities such as the threshold for the production of electron—hole pairs or the electron mean free path at a given energy.

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