Singularities in the energy distribution of photoelectrons

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Formulas are obtained, describing the photoelectron energy-distribution singularities connected with the structure of the crystal energy bands. It is shown that allowance for scattering leads to a strong deformation of the singularities of the internal photo-yield to such an extent that new singularity lines appear on the (E-ω) plane. The analytic relations near the symmetrical points of the Brillouin zone are considered in detail.

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INTRODUCTION

The study of the energy distribution of photoemission electrons is a convenient means of obtaining information on the electron spectra of solids.[1–7] Compared with the frequency dependence of the dielectric constant $\varepsilon(\omega)$, the electron energy distribution $N(E,\omega)$ contains an additional parameter, the energy E of the emitted electrons, which can be measured with high accuracy. To describe the electron distribution it is customary to use a three-step model,[2–6] in which the electron emission probability is determined by the product of the probabilities of single-electron photoexcitation, of reaching the surface, and of passing above the potential barrier. The first of these probabilities, for the case of direct transition, is proportional in the principal approximation to the energy distribution of the interband density of states

$$\rho(E,\omega)=\sum_{\mathbf{p}}\delta(\hbar\omega-\varepsilon_1(\mathbf{p})+\varepsilon_2(\mathbf{p}))\,\delta(E-\varepsilon_1(\mathbf{p})). \qquad (1)$$

This quantity is determined directly by the spectra $\varepsilon_2(\mathbf{p})$ and $\varepsilon_1(\mathbf{p})$ of the lower and upper bands. The summation over the quasimomenta $\mathbf{p}$ in (1) is within the limits of the Brillouin zone, and it is necessary to take into account only the occupied states in the lower band and the free states in the upper bands. As shown by Kane,[3–5] $\rho(E,\omega)$ has singularity lines on the $(E-\omega)$ plane. These singularities stem from the vicinities of those $\mathbf{p}$-space points in which the "ω plane," $\varepsilon_1(\mathbf{p})-\varepsilon_2(\mathbf{p})=\hbar\omega$ is tangent to the "E plane," $\varepsilon_1(\mathbf{p})=E$. The tangency of the surfaces can be either of the extremal or of the saddle-point type, and accordingly the singularities are either rectangular discontinuities or have a logarithmic character.

A comparison of the results of the numerical calculations of the spectra and of the experimental data on the photoemission for a number of substances[7–9] shows that the behavior of $N(E,\omega)$ corresponds in general to the structure of $\rho(E,\omega)$. However, as will be shown below, strong damping of the single-electron states, which lie far from the Fermi surface, and also scattering occurring in the course of motion towards the sample surface, lead to deformation of the singularities to the extent that new singularities appear on the $(E-\omega)$ plane. The purpose of this study is to ascertain the character of the $N(E,\omega)$ singularities in the presence of smearing. Recognizing that the more consistent theories of photoemission[10–13] are at the same time also the more cumbersome ones, we shall follow the three-step model. We assume that this can not influence significantly the position and character of the singularities. The situation is analogous here to the situation arising in the study of the surface impedance of metals in a strong magnetic field,[14] when the position and the character of the singularities are insensitive to the calculation procedure, whereas of the impedance itself is determined only qualitatively in the relaxation-time approximation.

ENERGY DISTRIBUTION OF THE PHOTOELECTRONS

To obtain the distribution of the emitted electrons, we first find the average number of electrons that land in a unit time, under the influence of the electromagnetic-wave field, in the upper band in the vicinity of the point $\mathbf{p}$ of quasimomentum space.[1)] This quantity is determined by the time-averaged derivative $\partial\rho_{\mathbf{pp}}/\partial t$, where $\rho_{\mathbf{pp}}$ is the diagonal element of the density matrix

$$\rho_{\mathbf{p}'\mathbf{p}}(t)=\langle a_{\mathbf{p}'}^{+}(t)a_{\mathbf{p}}(t)\rangle; \qquad (2)$$

here $a_{\mathbf{p}}^{+}(t)$ and $a_{\mathbf{p}}(t)$ are the Heisenberg operators for the creation and annihilation of a Bloch electron in a state with quasimomentum $\mathbf{p}$; so long as we are not interested in substances with magnetic order, each such state will be regarded as doubly degenerate in spin, and the spin index will be omitted. The angle brackets denote equilibrium statistical averaging over the grand canonical ensemble.

The total Hamiltonian of the system is written in the form

$$H=\sum_{\mathbf{p}}\xi_{\mathbf{p}}a_{\mathbf{p}}^{+}a_{\mathbf{p}}-\frac{e}{c}\mathbf{A}\sum_{\mathbf{p}_1\mathbf{p}_2}\mathbf{v}_{\mathbf{p}_1\mathbf{p}_2}a_{\mathbf{p}_1}^{+}a_{\mathbf{p}_2}+H_1,\qquad \mathbf{A}=A_0\mathbf{e}\cos\omega t, \qquad (3)$$

where $\xi_{\mathbf{p}}=\varepsilon(\mathbf{p})-\mu_0$; $\varepsilon(\mathbf{p})$ is the dispersion law, μ_0 is the chemical potential, $\mathbf{A}$ is the vector potential of the electromagnetic-field wave with frequency ω and with polarization $\mathbf{e}$, and the velocity matrix elements $\mathbf{v}_{\mathbf{p}_1\mathbf{p}_2}$ differ from zero if $\mathbf{p}_1-\mathbf{p}_2=\mathbf{g}$. The Hamiltonian H_1 describes the interaction of the electrons with one another and with the phonons. Therefore photoexcitation is essentially a resonant process, i.e., at a fixed frequency a contribution is made to all the quantities of interest to us only by a small region of **p**-space, and we take this interaction into account, just as in[16], by introducing into the spectrum an effective damping $\gamma_\mathbf{p}$ and by assuming that $\xi_\mathbf{p}$ already incorporates the corresponding renormalization. The damping $\gamma_\mathbf{p}$ was the subject to the studies[15,16].

The equation of motion for the density matrix (2) can then be written out in the form

$$i\hbar\frac{\partial\rho_{\mathbf{p}'\mathbf{p}}}{\partial t}=(\xi_{\mathbf{p}\mathbf{p}'}+i\gamma_{\mathbf{p}\mathbf{p}'})\rho_{\mathbf{p}'\mathbf{p}}-\frac{e}{c}\mathbf{A}\mathbf{v}_{\mathbf{p}\mathbf{p}'}(n_{\mathbf{p}'}-n_\mathbf{p})$$
$$-\frac{e}{c}\mathbf{A}\Big[\sum_{\mathbf{p}_1\neq\mathbf{p}'}\mathbf{v}_{\mathbf{p}\mathbf{p}_1}\rho_{\mathbf{p}'\mathbf{p}_1}-\sum_{\mathbf{p}_1\neq\mathbf{p}}\mathbf{v}_{\mathbf{p}_1\mathbf{p}'}\rho_{\mathbf{p}_1\mathbf{p}}\Big];\tag{4}$$

here $\xi_{\mathbf{p}\mathbf{p}'}=\xi_\mathbf{p}-\xi_{\mathbf{p}'}$, $\gamma_{\mathbf{p}\mathbf{p}'}=\gamma_\mathbf{p}+\gamma_{\mathbf{p}'}$; $n_\mathbf{p}=\rho^{(0)}=\langle a_\mathbf{p}^+a_\mathbf{p}\rangle$ are the equilibrium Fermi occupation numbers, i.e., we have separated in explicit form the terms linear in **A** from the nonequilibrium part of the equations that is due to the interaction with the electromagnetic field. Recognizing that the first-order terms drop out after time averaging (designated by a superior bar), we obtain in second order in **A**

$$\overline{\frac{\partial\rho_{\mathbf{p}\mathbf{p}}}{\partial t}}=\frac{2}{\hbar}\left(\frac{eA_0}{2c}\right)^2\sum_{\mathbf{p}_1\neq\mathbf{p}}|\mathbf{e}\mathbf{v}_{\mathbf{p}\mathbf{p}_1}|^2(n_{\mathbf{p}_1}-n_\mathbf{p})\gamma_{\mathbf{p}\mathbf{p}_1}(Q_-^{-1}+Q_+^{-1}),$$
$$Q_\pm=(\xi_{\mathbf{p}\mathbf{p}_1}\pm\hbar\omega)^2+\gamma_{\mathbf{p}\mathbf{p}_1}^2,\tag{5}$$

and since we assume that the frequency is close to resonance for the band under considerations, we can neglect the term Q_+^{-1} in the parenthesis.

In accordance with the three-step model, [2,6] the probability that an electron excited to the state p will emerge from the crystal without scattering, taking into account summation over the volume of the sample, is proportional to the electron mean free path $l_\mathbf{p}=t_\mathbf{p}|\nabla_\mathbf{p}\xi_\mathbf{p}|$, where $t_\mathbf{p}\sim\gamma_\mathbf{p}^{-1}$ is the lifetime of the excited state multiplied by the cosine of the angle between the electron velocity $\mathbf{v}_\mathbf{p}=\nabla_\mathbf{p}\xi_\mathbf{p}$ and the normal n to the plane of the surface of the crystal, and also by a certain sufficiently smooth function $C(\mathbf{p})$, which reflects the properties of the potential barrier on the sample surface. Since we are interested in the energy distribution of the electrons, we must also take into account the density of states with quasimomentum p and energy E; this quantity is proportional to the imaginary part of the Green's function $G_\mathbf{p}(E)$, i.e., it takes the form[17]

$$\operatorname{Im}G_\mathbf{p}(E)=\frac{1}{\pi}\frac{\gamma_\mathbf{p}}{(\xi_\mathbf{p}-E)^2+\gamma_\mathbf{p}^2}.\tag{6}$$

The distribution of the emitted electrons is given by the sum over the quasimomenta of the excited states, but the summation must be carried out only over that part of the p space in which $\mathbf{n}\cdot\mathbf{v}_\mathbf{p}>0$, corresponding to an electron moving to the outside.

The singularities of interest to us are connected with small region of p space near the point $\mathbf{p}_0$ where the surfaces $\xi_{\mathbf{p}\mathbf{p}+\mathbf{g}}=\hbar\omega$ and $\xi_\mathbf{p}=E$ are tangent, or else near the points where the lines of intersection of these surfaces with the surface $\mathbf{n}\cdot\mathbf{v}_\mathbf{p}=0$. Changing over to integration, taking outside the integral sign the functions that will vary little in this region, and assuming that the upper band is not filled, we write down the formula for the energy distribution of the photoelectrons in the form

$$N(E,\omega)=T\int\frac{\gamma\,dy}{(E-y)^2+\gamma^2}\int\frac{\gamma'\,dx}{(x-\hbar\omega)^2+(\gamma')^2}f(x,y),\tag{7}$$

$$f(x,y)=\int d^3p|\mathbf{n}\nabla_\mathbf{p}\xi_\mathbf{p}|n_{\mathbf{p}+\mathbf{g}}\delta(\xi_\mathbf{p}-y)\delta(\xi_{\mathbf{p}\mathbf{p}+\mathbf{g}}-x);$$
$$T=\frac{1}{\pi\hbar}\left(\frac{eA_0}{2c}\right)^2C(\mathbf{p}_0)t_{\mathbf{p}_0}|\mathbf{e}\mathbf{v}_{\mathbf{p}_0\mathbf{p}_0+\mathbf{g}}|^2,\quad\gamma\equiv\gamma_{\mathbf{p}_0},\quad\gamma'\equiv\gamma_{\mathbf{p}_0\mathbf{p}_0+\mathbf{g}}.\tag{8}$$

By virtue of the inversion symmetry of $\xi_\mathbf{p}$, we can integrate in (8) over all of space, without limits, after taking the modulus $|\mathbf{n}\cdot\nabla_\mathbf{p}\xi_\mathbf{p}|$ and dividing by two.

Formula (7) differs from (1), which was used by Kane, in two respects. First, account is taken of the damping of the energy states by the factors preceding $f(x,y)$ and by integration with respect to x and y; second, the expression for $f(x,y)$ contains a factor $(\mathbf{n}\cdot\mathbf{v}_\mathbf{p})$. which is also connected with electron scattering.

SINGULARITIES IN THE ELECTRON DISTRIBUTION

Near an analytic critical point $\mathbf{p}_0$ (i.e., one which is not a band-degeneracy point), the expansions of $\xi_\mathbf{p}$ and $\xi_{\mathbf{p}\mathbf{p}+\mathbf{g}}$, accurate to second-order terms, are given by

$$\xi_\mathbf{p}=\xi_0+\mathbf{v}\mathbf{k}+\sum_{ij=1}^{3}\mu_{ij}k_ik_j,\tag{9}$$

$$\xi_{\mathbf{p}\mathbf{p}+\mathbf{g}}=\xi_{0\mathbf{g}}+\mathbf{v}'\mathbf{k}+\sum_{ij=1}^{3}\mu_{ij}'k_ik_j,\tag{10}$$

where $\mathbf{k}=\mathbf{p}-\mathbf{p}_0$, and if $\mathbf{p}_0$ is a point of tangency of the E and ω surfaces, then the velocities v and v′ are collinear.

The singularities of $N(E,\omega)$ are connected with the singularities of $f(x,y)$ and are of the following types:

I. Lines of diffuse discontinuities. If the velocities v and v′ are not equal to zero near the point $\mathbf{p}_0$ where the E and ω surfaces are tangent, and if the line of intersection of the surfaces is an ellipse, then, directing the k_3 axis along v, we can reduce (8), after integration with respect to k_3 and rotation in the (k_1k_2) plane, to the form

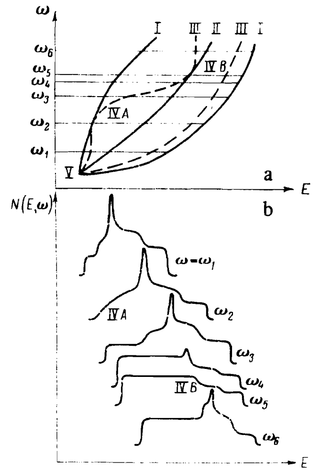
$$f(x,y)=\left|\frac{n_3}{v'}\right|\int dk_1\,dk_2\,\delta\left(\frac{\Delta y}{v}-\frac{\Delta x}{v'}-B_1k_1^2-B_2k_2^2\right),$$
$$v'=\mathbf{v}\mathbf{v}'/v,\qquad B\equiv B_1B_2>0,\tag{11}$$

here $\Delta y=y-\xi_0$, $\Delta x=x-\xi_{0\mathbf{g}}$, the constants B_1 and B_2 are the principal values of the second-rank tensor $\mu_{ij}'/v'-\mu_{ij}/v$; $i,j=1,2$.

As a result we obtain the behavior of $N(E,\omega)$ near the line of singularities:

$$N(E,\omega)=\frac{|n_3|T}{|v'|B^{1/2}}\operatorname{arcctg}\frac{B_2\Delta}{|B_2|\Gamma},$$
$$\Delta=\frac{\Delta\omega}{v'}-\frac{\Delta E}{v},\quad\Gamma=\frac{\gamma'}{|v'|}+\frac{\gamma}{v},\quad\Delta E=E-\xi_0,\quad\Delta\omega=\omega-\xi_{0\mathbf{g}}.\tag{12}$$

II. Lines of smeared logarithmic singularities. The difference from the preceding case lies in the fact that the intersection of the E and ω surfaces near the point of their tangency is now a hyperbola. In this case, formula (11) holds, with $B<0$. Then



a) Possible plots of the singularity lines on the $(E-\omega)$ plane. The Roman numbers correspond to the singularity lines and points numbered in the text. b) Schematic representation of the energy distribution of the photoelectrons at the frequencies marked on Fig. a. $N(E,\omega)$ has a square-root behavior near the points IV A and IV B.

$$N(E,\omega)=N_0(E,\omega)-\frac{|n_3|T}{|v'||B|^{1/2}}\frac{\pi}{2}\ln(\Delta^2+\Gamma^2), \tag{13}$$

where $N_0(E,\omega)$ is the regular part due to contribution of distances far from $\mathbf{p}_0$.

III. If a point $\mathbf{p}_0$ at which the velocity is directed parallel to the surface of the sample, i.e., $v_n=\mathbf{n}\cdot\mathbf{v}_{p0}=0$ but $\mathbf{v}_{p0}\neq 0$, first appears on the line of intersection of the E and ω surfaces, then the anomaly of $f(x,y)$ is obtained by transforming (8) into an integral along the intersection line l of the E and ω surfaces and by separating the contribution of the vicinity of the point of tangency of this line with the surface $\mathbf{n}\cdot\mathbf{v}_p=0$:

$$\begin{aligned} f(x,y)&=f_0(x,y)-\frac{4a_0}{|[\mathbf{v}_{p_0}\times\mathbf{v}'_{p_0}]|}\int_0^{(\delta_0)^{1/2}}dl\,(l^2-\delta_0)\,\theta(\delta_0)\\ &=f_0(x,y)+\frac{8}{3}\frac{a_0}{|[\mathbf{v}_{p_0}\times\mathbf{v}_{p_0}']|}(\delta_0)^{3/2}\theta(\delta_0),\\ \theta(z)&=\begin{cases}1, & z>0\\ 0, & z<0\end{cases};\quad \delta_0=\frac{(b_0\Delta x+c_0\Delta y)}{a_0}; \end{aligned}\tag{14}$$

here

$$a_0=\left(\frac{\partial^2 v_n}{\partial l^2}\right)_{l=0},\quad b_0=-\left(\frac{\partial v_n}{\partial x}\right)_{\Delta x=0},\quad c_0=-\left(\frac{\partial v_n}{\partial y}\right)_{\Delta y=0},$$

$f_0(x,y)$ is the regular part.

Thus, $f(x,y)$ has diverging second derivatives. The increment to the distribution of the photoelectrons near the line of these singularities becomes smeared out:

$$\begin{aligned} \Delta N(E,\omega)&\sim\begin{cases}(\Delta_0/a_0)^{1/2} & \text{if}\quad |\Delta_0|\gg\Gamma_0\\ (\Gamma_0/a_0)^{1/2} & \text{if}\quad |\Delta_0|\leqslant\Gamma_0\end{cases},\\ \Delta_0&=b_0\Delta\omega+c_0\Delta E,\quad \Gamma_0=|b_0|\gamma'+|c_0|\gamma. \end{aligned}\tag{15}$$

IV. The singularity line corresponding to the preceding case may be tangent to a discontinuity line or to a logarithmic-singularity line. Near such a tangency point, choosing the directions of the axes as in the derivation of (11)–(13), we represent (8) in the form

$$\begin{aligned} f(x,y)&=\int\frac{dk_1\,dk_2}{v|v'|}\left|\eta\frac{\Delta x}{v'}+A_1k_1+A_2k_2\right|\delta\left(\frac{\Delta y}{v}-\frac{\Delta x}{v'}-B_1k_1^2-B_2k_2^2\right),\\ \eta&\equiv 2\mu_{33}n_3+\mu_{23}n_2+\mu_{13}n_1; \end{aligned}\tag{16}$$

here A_1 and A_2 are linear in n_1 and n_2, and are, just as B_1 and B_2, functions of the components of the tensors μ_{ij} and μ'_{ij} and of the angle of rotation of the (k_1k_2) plane.

As the point of tangency is approached, the character of each of the singularities is altered (see the figure). The distance along the E axis on the $(E-\omega)$ plane between the singularity lines will be described by the parameter $\alpha(\Delta\omega)^2$, where

$$\alpha\equiv\frac{\eta^2Bv}{(v')^2(B_2A_1^2\pm B_1A_2^2)},$$

the plus sign is for tangency with the discontinuity line and the minus sign for tangency with logarithmic-singularity line. At $|\lambda|\ll\Gamma$, where $\lambda=\alpha(\Delta\omega)^2/v$, the function $\Delta N(E,\omega)$ has the following behavior in both cases:

$$\begin{aligned} \Delta N(E,\omega)&=\pm\frac{2^{1/2}|\eta|T}{(v')^2|v\alpha B|^{1/2}}F(\alpha,\Delta,\Gamma),\\ F(\alpha,\Delta,\Gamma)&=(\tilde\Delta+(\Delta^2+\Gamma^2)^{1/2})^{1/2},\quad \tilde\Delta=\alpha\Delta/|\alpha|. \end{aligned}\tag{17}$$

At $|\Delta\omega/v'|\gg|\lambda|\gg\Gamma$ each of the singularities exhibits an individual behavior. Near the discontinuity line (point IV A in the figure) we obtain

$$\begin{aligned} N(E,\omega)&=\frac{|\eta\Delta\omega|T}{v(v')^2}\operatorname{arcctg}\left(-\frac{\tilde\Delta}{\Gamma}\right),\quad |\Delta|\ll|\lambda|\\ N(E,\omega)&=\frac{Tv^{1/2}|\eta|(\tilde\Delta\pm\lambda)^{3/2}\theta(\tilde\Delta\pm\lambda)}{|\alpha|^{3/2}B^{1/2}(v'\Delta\omega)^2},\quad \Gamma\ll|\tilde\Delta\pm\lambda|\ll|\lambda|,\quad \tilde\Delta>0,\\ N(E,\omega)&=\frac{2|\eta|(\tilde\Delta)^{1/2}T}{(v')^2|v\alpha B|^{1/2}},\quad \tilde\Delta\gg|\lambda| \end{aligned}\tag{18}$$

Near the logarithmic-singularity line (point IV B in the figure) we have

$$\begin{aligned} N(E,\omega)&=-\frac{\pi|\eta\Delta\omega|T}{4v(v')^2}\ln(\Delta^2+\Gamma^2),\quad |\Delta|\ll|\lambda|\\ N(E,\omega)&=\frac{2Tv^{1/2}|\eta|(\tilde\Delta\pm\lambda)^{3/2}\theta(\tilde\Delta\pm\lambda)}{3|\alpha|^{3/2}|B|^{1/2}(v'\Delta\omega)^2},\quad \Gamma\ll|\tilde\Delta\pm\lambda|\ll|\lambda|,\quad \tilde\Delta<0\\ N(E,\omega)&=-\frac{2|\eta|(\tilde\Delta)^{1/2}T}{(v')^2|v\alpha B|^{1/2}},\quad \tilde\Delta\gg|\lambda|. \end{aligned}\tag{19}$$

V. The singularity lines of types I–III terminate in symmetrical critical points.[3] The point of the tangency of the E and ω surfaces lands in this case on a high-symmetry point of the Brillouin zone, and then $\mathbf{v}=\mathbf{v}'=0$ in the expansions (9) and (10), while μ_{ij} and μ'_{ij} have similarly-directed principal axes. The character of the anomalies in the distribution of the electrons will depend of the type of the crystal symmetry and on the orientation of the surface of the sample relative to the principal axes of the crystal:

$$f(x,y)=2\int d^3k\left|\sum_{i=1}^3\mu_in_ik_i\right|\delta\left(\Delta y-\sum_{i=1}^3\mu_ik_i^2\right)\delta\left(\Delta x-\sum_{i=1}^3\mu_i'k_i^2\right).\tag{20}$$

It is easy to verify that at arbitrary μ_i, μ_i', and n_i the singularity lines of all three types should converge at different angles to a symmetrical point on the $(\Delta E-\Delta\omega)$ plane. If the E and ω surfaces are both ellipsoids, then their tangency takes place in succession on the principal axes, and the singularity lines meet in a symmetrical critical point inside one of the quadrants. At $|\Delta\omega| \ll \gamma'$, the $N(E, \omega)$ distribution has a smeared maximum of width $\sim\gamma$ with respect to E, and at $|\Delta\omega| \gg \gamma'$ smeared discontinuities appear near the values $\Delta E/\mu_i - \Delta\omega/\mu_i' = 0$ for the largest and the smallest of the μ_i/μ_i', as well as a logarithmic peak for the axis with the intermediate value of this ratio. If at least one of the E and ω surfaces is a hyperboloid, then the singularity lines lie in two adjacent quadrants and, in particular, if the hyperboloid is the ω surface, then $N(E, \omega) \sim F(\mu, \Delta E, \gamma+\gamma')$ at $|\Delta\omega| \ll \gamma'$. At $|\Delta\omega| \gg \gamma'$ the behavior of $N(E, \omega)$ is different on the right and on the left of the intersection point. Both the smeared-discontinuity line and the smeared-logarithms line approach from one side, but only the line of smeared discontinuities from the other. They are separated by a singularity line of type III.

In all these cases, if the plane

$$\sum_{i=1}^{3} \mu_i n_i k_i = 0$$

passes through the principal axis along which the E and the ω surfaces are tangent, then the line of singularity of type I or II corresponding to this tangency may merge with the line of singularities of type III, and the the singularity acquires a square-root character. If this plane passes through two points of tangency of the E and ω surfaces, then two of the singularity lines of type I and II merge with the singularity lines of type III, and as a result they also become of the square-root type.

If the effective masses in both directions are equal to each other, i.e., $\mu_2 = \mu_3 \equiv \mu \neq \mu_1$, and simultaneously $\mu_2' = \mu_3' \equiv \mu' \neq \mu_1'$ (this situation can be encountered, for example, in crystals of hexagonal and tetragonal symmetry), then it is necessary to retain the terms of next order in k in the expansions (9) and (10) near the plane $k_1 = 0$. For symmetry considerations, this increment can be expressed in the form

$$\delta\xi_p = a(k_2^2+k_3^2)^2 + bk_2^2k_3^2, \quad \delta\xi_{pp-g} = a'(k_2^2+k_3^2)^2 + b'k_2^2k_3^2. \tag{21}$$

In the plane $k_1 = 0$ there appear then four identical extrema, symmetrically arranged, with a saddle point midway between each two extrema.

We introduce cylindrical coordinates with the z axis directed along k_1 and integrate with respect to $\rho^2 = k_2^2 + k_3^2$; then

$$j(x, y) = \int_0^{2\pi} d\varphi \int_{-\infty}^{\infty} \frac{dk_1}{|\mu\mu'|} \left| \mu_1 n_1 k_1 + \mu \left(\frac{1}{\mu}(\Delta y - \mu_1 k_1^2) \right)^{1/2} (n_2 \sin\varphi + n_3 \cos\varphi) \right|$$
$$\times \delta\left(\frac{\Delta x}{\mu'} - \frac{\Delta y}{\mu} - \frac{M}{\mu\mu'} k_1^2 + (\Delta x)^2 (\beta' + \alpha' \cos 4\varphi) \right) \theta\left(\frac{\Delta y - \mu_1 k_1^2}{\mu} \right),$$
$$\alpha' = (b'/\mu' - b/\mu)/(\mu')^2, \quad \beta' = ((a'+b')/\mu' - (a+b)/\mu)/(\mu')^2, \tag{22}$$

where $M \equiv \mu\mu_1' - \mu_1'\mu'$, and the axes k_2 and k_3 pass through the tangency point of the E and ω surfaces. For the sake of argument we shall assume that the singularity lines approach the symmetrical point at $\Delta\omega > 0$.

We consider now the region $\Delta\omega \gg \gamma'$. First, the symmetrical critical point is approached by the smeared-discontinuity line stemming from the tangency of the E and ω surfaces on the k_1 axis. At $n_1 \neq 0$ we have near it

$$N(E, \omega) = 2\pi T \left| \frac{\mu_1 n_1}{M} \right| \operatorname{arcctg} \frac{M\Delta_1}{|M|\Gamma_1}.$$
$$\Delta_1 = \Delta E/\mu_1 - \Delta\omega/\mu_1', \quad \Gamma_1 = \gamma/|\mu_1| + \gamma'/|\mu_1'|. \tag{23}$$

At $n_1 = 0$ this line merges with a singularity line of type III, and then at $|\Delta_2| \gg |\Delta_1|$, where $\Delta_2 = \Delta\omega/\mu' - \Delta E/\mu$, we have

$$N(E, \omega) = \frac{4(n_2^2+n_3^2)^{1/2}|\mu||\mu_1\mu_1'|^{1/2}}{|\mu\mu'|^{3/2}|\Delta_2|^{1/2}} TF(M, \Delta_1, \Gamma_1). \tag{24}$$

Second, singularity lines of types I and II, coming from points of tangency of the E and ω surfaces lying in the plane $k_1 = 0$, reach this line at a finite angle. At $|\alpha'|(\Delta\omega)^2 \ll \Gamma_2$, where $\Gamma_2 = \gamma/|\mu| + \gamma'/|\mu'|$, these two lines merge. Then we obtain at $n_2^2 + n_3^2 \neq 0$ near such a threshold, i.e., when $|\Delta_1| \gg |\Delta_2|$,

$$N(E, \omega) = \frac{\pi T(2(n_2^2+n_3^2))^{1/2}|\mu_1\mu_1'|^{1/2}|\Delta_1|^{1/2}\Gamma_2}{|\mu\mu'|^{1/2}|M|(\Delta_2^2+\Gamma_2^2)^{1/2}F(M, \Delta_2, \Gamma_2)}. \tag{25}$$

Thus, $N(E, \omega)$ has near the threshold $\Delta_2 = 0$ a sharp maximum at $\Delta_2 = 3^{-1/2}\Gamma_2$, and decreases at $|\Delta_2| \gg \Gamma_2$ on one side of this maximum like $\Gamma_2|\Delta_2|^{-3/2}$, and on the other side like $|\Delta_2|^{-1/2}$. At $n_2^2 + n_3^2 = 0$ and $n_1 = 1$, these lines are merged also with a singularity line of type III, and then $N(E, \omega)$ is described in this region by formula (23), except that Δ_1 is replaced by Δ_2.

At $|\alpha'|(\Delta\omega)^2 \gg \Gamma_2$ we can distinguish between diverging lines of the smeared discontinuity and of the logarithmic singularity. One of them is located at $\Delta_2' = 0$ and the other at $\Delta_2'' = 0$, where $\Delta_2' = \Delta_2 + (\beta' - \alpha')(\Delta\omega)^2$, $\Delta_2'' = \Delta_2 + (\beta' + \alpha')(\Delta\omega)^2$, and the singularities on these lines take the form

$$N(E, \omega) = \frac{\pi T|n_0||\mu|^{1/2}f(z)}{2^{1/2}|\mu'||\alpha' M\Delta\omega|^{1/2}}; \tag{26}$$

Here n_0 is the projection of the vector $\mathbf{n}$ in the direction of the tangency point responsible for the singularity, the function $f(z)$ is equal to $\tan^{-1}(z/\Gamma_2)$ or to $\pi\ln(z^2 + \Gamma_2^2)$, while $z = \Delta_2'$ or Δ_2''. Between these lines lie singularity lines of type III, which can be tangent to these lines at a particular direction of the vector $\mathbf{n}$, and by the same token alter significantly the form of the singularities (26). Thus, at $n = n_1$ they are tangent to each of the lines and the singularities assume the following character:

$$\Delta N(E, \omega) = \pm \frac{|\mu|T}{|\alpha'|^{1/2}|M\Delta\omega|} F(\alpha', z, \Gamma_2). \tag{27}$$

Inasmuch as there are four identical singular points on the $k_1 = 0$ plane in p space, it follows that if $n \neq n_1$ and two of the vectors $n_0 = \pm n_3$ are equal to zero while the other two are not equal to zero ($n_0 = \pm n_2 \neq 0$), then for one and the same value of Δ_2' (or Δ_2'') the singularities of the type (26) become superimposed on singularities whose form differs from (27) by the presence of the factor

$$\frac{|\mu_1|}{|M|^{1/2}}\left(\frac{n_1^2}{|M|}+\frac{n_2^2}{4|\alpha'\mu(\mu')^2\Delta\omega|}\right). \qquad (28)$$

In the region $|\Delta\omega| \ll \gamma'$ there is a smeared peak of width γ with respect to E. At $\Delta\omega < 0$ and $|\Delta\omega| \gg \gamma'$, the width of the peak increases like $|\Delta\omega|$, and the height decreases like $|\Delta\omega|^{-2}$.

The effective masses can be equal in all three directions: $\mu_1 = \mu_2 = \mu_3 \equiv \mu$ and $\mu_1' = \mu_2' = \mu_3' \equiv \mu'$; this case is encountered with largest probability in cubic crystals, and we shall therefore assume that the fourth-order increment in (9) is of the form

$$c(k_1^2+k_2^2+k_3^2)^2+d(k_1^2k_2^2+k_1^2k_3^2+k_2^2k_3^2), \qquad (29)$$

and in (10) it differs in that the constants are interchanged $c \to c'$ and $d \to d'$. After integration with respect to k^2 we obtain in spherical coordinates

$$f(x,y)=\frac{|\Delta x|}{(\mu')^2}\int d\varphi\, d\cos\theta\,|n_1\cos\theta+\sin\theta\,(n_2\cos\varphi+n_3\sin\varphi)|$$
$$\times\delta\left(\frac{\Delta x}{\mu'}-\frac{\Delta y}{\mu}+(\Delta x)^2\left(\beta''-\frac{\alpha''}{8}g(\theta,\varphi)\right)\right), \qquad (30)$$
$$g(\theta,\varphi)=\sin^2\theta[8\cos^2\theta+\sin^2\theta(1-\cos 4\varphi)],$$
$$\alpha''=\frac{d/\mu-d'/\mu'}{(\mu')^2},\qquad \beta''=\frac{c/\mu-c'/\mu'}{(\mu')^2}.$$

The function $g(\theta, \varphi)$ has six minima ($g = 0$), eight maxima ($g = \frac{1}{3}$), and twelve saddle points ($g = \frac{1}{4}$). In each of the directions (θ, φ) determined by these extrema and saddle points there is a point of tangency of the E and ω surfaces of the corresponding type. It is easy to verify that at $|\alpha''|(\Delta\omega)^2 \gg \Gamma_2$ three singularity lines diverge, on which

$$\Delta N(E,\omega)=\frac{|n_0|Tf(\alpha''\Delta_3^{(i)}/|\alpha''|)}{(\mu')^2|\alpha''\Delta\omega|}, \qquad (31)$$

where $\Delta_3^{(i)}$ is equal to one of the quantities

$$\Delta_3'=\Delta_2-(\alpha''+\beta'')(\Delta\omega)^2,\quad \Delta_3''=\Delta_3'+(2/3)\alpha''(\Delta\omega)^2,$$
$$\Delta_3'''=\Delta_3'+(3/4)\alpha''(\Delta\omega)^2.$$

Between them lie singularity lines of type III, and for three directions of the vector $\mathbf{n}$, such that the plane

$$\sum_{i=1}^{3}\mu_i n_i k_i=0$$

passes through the point of tangency of the E and ω surfaces, the lines of type III can merge with the lines of type I and II. The corresponding singularity then acquires a square-root character

$$N(E,\omega)=\frac{TF(\alpha'',\Delta_3^{(i)},\Gamma_2)}{|\alpha''|^{1/2}|\mu'\Delta\omega|^2}, \qquad (32)$$

and by virtue of the symmetry there is always an equivalent tangency point of the E and ω surfaces through which this plane does not pass, and in such cases the singularities of the type (31) and (32) are additive.

When $|\alpha''|(\Delta\omega)^2 \ll \Gamma_2$, the singularity lines merge into one. The behavior of the distribution near this line is a smeared δ function, and at $|\Delta\omega| \gg \gamma'$ we have

$$N(E,\omega)=\frac{4\pi^2T|\Delta\omega|\Gamma_2}{(\mu')^2(\Delta_2^2+\Gamma_2^2)}. \qquad (33)$$

At $|\Delta\omega| \ll \gamma'$ the function $N(E, \omega)$ has a maximum at $\Delta E \lesssim \gamma$. In the region $\Delta\omega < 0$, $|\Delta\omega| \gg \gamma'$, this maximum located at the line $\Delta_2 = 0$, its height decreases like $|\Delta\omega|^{-2}$, and its width increases like $(\Delta\omega)^2$.

CONCLUSION

The character of the singularities in the energy distribution $N(E, \omega)$ of the photoelectrons is thus determined essentially by the topology of the equal-energy surfaces in $\mathbf{p}$ space. Formulas (12)–(33), obtained with the smearing taken into account, provide an analytic description of these singularities and may be useful for the interpretation of crystal spectra from photoemission data. Of course, all the results, as well as the employed three-step model are valid only when the smearing of the energy levels γ is sufficiently small in comparison with the band width $\Delta\xi$. The smearing γ is determined by the interaction of the Bloch electrons with one another, with the phonons, with the lattice defects, with the spins, etc. Inasmuch as usually $\Delta\xi \sim 1$ eV and $\Delta\gamma \sim 10^{-1}$–$10^{-2}$ eV, the experimentally required resolution should in practice be not worse than 10^{-3} eV, which lies within the limits of modern experimental capabilities.

For the temperature and the frequency dependences of the contribution to γ from the electron-electron and electron-phonon interaction, the results of Kopeliovich[15] are valid. If a phase transition takes place in the spin system, then the electron scattering by the spin fluctuations leads to a temperature anomaly of γ, which can be observed by studying the smearing of the singularities in the photoelectron distribution. The character of the temperature anomaly, just as for the high-frequency conductivity, is determined by the structure of the spectrum near the characteristic point $\mathbf{p}_0$. In particular, if an expansion (9) with $\mathbf{v}_{\mathbf{p}_0} \neq 0$ takes place in the vicinity of such a point, then, as shown in our earlier paper,[16]

$$\Delta\gamma\sim|T-T_c|^{-\mu(1-\nu_1)},$$

where T_c is the magnetic-ordering temperature, ν_1 is the critical exponent of the spin correlator, and μ is the exponent of the correlation radius. The numerical value of ν_1 is close to unity, resulting in a singularity of small degree in the function $\Delta\nu(T - T_c)$. It appears that this kind of anomaly was observed experimentally by Rowe and Tracey,[18] who investigate the energy distribution of the photoelectrons from nickel near T_c.

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[1)]Just as in[15,16], we use the "expanded band" scheme, i.e., we assume that the quasimomentum vector changes in all of reciprocal space, and the interband transition is a transition in $\mathbf{p}$ space with change of quasimomentum by a certain reciprocal-lattice vector $\mathbf{g}$.

[1]J. Phillips, Optical Spectra of Solids (Russ. Transl., Mir. 1968); A. M. Brodskiĭ and Yu. Ya. Gurevich, Teoriya élektronnoĭ emissii iz metallov (Theory of Electron Emis-

sion from Metals), Nauka, 1973.
[2]C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030, A1040 (1964).
[3]E. O. Kane, Phys. Rev. 175, 1039 (1968).
[4]W. D. Grobman and D. E. Eastman, Surf. Sci. 37, 355 (1973).
[5]D. Brust, Phys. Rev. 139, A489 (1965).
[6]P. J. Feibelman and D. E. Eastman, Phys. Rev. B10, 4932 (1974).
[7]N. V. Smith and L. F. Mattheiss, Phys. Rev. B9, 1341 (1974); M. M. Traum and N. V. Smith, *ibid.*, 1353; N. V. Smith, ibid., 1365.
[8]F. R. Shepherd and P. M. Williams, J. Phys. C 7, 4416 (1974).
[9]J. E. Rowe and N. V. Smith, Phys. Rev. B10, 3207 (1974).
[10]G. D. Mahan, Phys. Rev. B2, 4334 (1970).
[11]W. L. Schaich and N. W. Ashcroft, Phys. Rev. B3, 2452 (1971).
[12]C. Caroli, D. Laderer-Rozenblatt, B. Roulett, and D. Saint-James, Phys. Rev. B8, 4552 (1973).
[13]H. Hermeking, J. Phys. C 6, 2898 (1973).
[14]I. M. Lifshitz, M. Ya. Azbel', and M. I. Kaganov, Élektronnaya teoriya metallov (Electron Theory of Metals), Nauka, 1971.
[15]A. I. Kopeliovich, Zh. Eksp. Teor. Fiz. 58, 601 (1970) [Sov. Phys. JETP 31, 323 (1970)].
[16]V. M. Nabutovskiĭ and Yu. G. Peĭsakhovich, Zh. Eksp. Teor. Fiz. 68, 164 (1975) [Sov. Phys. JETP 41, 80].
[17]D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys. Usp. 3, 320 (1960)].
[18]J. E. Rowe and J. C. Tracy, Phys. Rev. Lett. 27, 799 (1971).

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Spectrum and polarization of the luminescence emitted from GaAs in the energy range $E_g+\Delta$

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An investigation was made of the spectrum and polarization of the 1.48–1.94 eV photoluminescence emitted from *n*-type GaAs crystals excited with linearly and circularly polarized He-Ne laser radiation (1.48–1.94 eV). A detailed study was made of the luminescence band located near 1.86 eV, which was due to transitions between the conduction band and the split-off (by the spin-orbit interaction) valence band Γ_7. The short lifetime of holes in the band Γ_7, due to the relatively high probability of transitions between the valence subbands, resulted in a considerable deviation of the hole distribution function from the Boltzmann form (the holes did not become thermalized during their lifetime). For this reason the degree of circular polarization of the luminescence excited by circularly polarized laser radiation was close to unity. This result was evidence of almost complete optical orientation of nonequilibrium holes in the split-off band (the holes maintained the initial spin direction during their lifetime). The principal quantitative relationships obtained in the present investigation were explained satisfactorily by assuming the dominant role of electron-hole collisions in the energy relaxation of holes.

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In contrast to the optical absorption spectra, studies of the photoluminescence spectra of semiconductors have been limited mainly to the range of frequencies near the fundamental absorption edge. The "edge" luminescence in the range $\hbar\omega \lesssim E_g$ may be related to the radiative recombination of free or bound excitons, interband electron transitions, impurity–band transitions, etc. (see, for example,[1]).

An analysis of the luminescence line profile in the range $\hbar\omega > E_g$ made it possible to obtain information on the distribution function $f(\varepsilon)$ of the energy of nonequilibrium carriers. In this way it has been possible to determine the effective temperature of nonequilibrium electrons, which—under certain conditions—may exceed the lattice temperature,[2] and also to detect the deviation of the function $f(\varepsilon)$ from the Boltzmann distribution in the high-energy range.[3,4]

An investigation of the polarization of recombination radiation makes it possible to investigate, in particular, the optical orientation of free carriers in semiconductors. The phenomenon of optical orientation, i. e., the establishment of a preferential orientation of carrier spins on absorption of circularly polarized light, has been used successfully in studies of the kinetics of recombination and spin relaxation of electrons in semiconductors (see, for example,[5]).

The cited investigations were concerned with the luminescence due to electron transitions between two nearest bands (in the case of GaAs between the conduction band Γ_6 and the quadruply degenerate, at $\mathbf{k}=0$, valence band Γ_8). An investigation of the Raman scattering in *n*-type GaAs crystals, carried out by Burstein *et al.*,[6] revealed a weak luminescence band in the energy range 1.86 eV, which complicated an analysis of the scattered-light spectra. It was shown in[6] and also in[7], where the preliminary results of the present study were reported, that this band was due to transitions between the conduction band Γ_6 and the va-