

## EFFECT OF ELECTRON COLLISIONS OF INTERBAND TRANSITIONS IN METALS

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A kinetic equation for electrons in metals is derived and takes into account interband electron transitions and their mutual collisions with phonons. An expression for the high-frequency electric conductivity tensor is obtained. Its analysis leads to the following results, which are valid for arbitrary electron and phonon dispersion laws: 1) At optical frequencies lower than the threshold of the internal photoeffect, interband transitions affect the electric conductivity appreciably. In particular, an additional contribution to electron-phonon collisions appears which, in the far infrared region, is identical in frequency dependence and in order of magnitude with the intraband contribution of the interelectron collisions. However, the temperature dependence is different. 2) In the vicinity of the internal-photoeffect threshold, collisions modify the frequency dependence of interband electric conductivity.

A concrete calculation of interband electric conductivity is performed for metals described by the weak pseudopotential model. "Interband" effective collision frequencies are calculated for polyvalent nontransition metals and expressions are obtained for the shape and height of the internal-photoeffect peaks. The results are compared with available experimental data. Possible causes of discrepancy between the experimental values of the internal-photoeffect peak widths and those calculated here are discussed. For alkali metals it is shown that the "extra" absorption bands observed experimentally may be ascribed to indirect interband and to intraband electron transitions to regions in *p*-space which are close to the Bragg planes. The shape of the "extra" band and the value of its long-wave threshold are in good agreement with the experiments.

AS is well known, the optical properties of most typical metals in near-infrared and in the visible regions of the spectrum are determined to a considerable degree by the interband transitions of the electrons (the so-called internal (photoconductive) photoeffect)<sup>[1]</sup>. In many papers (see, for example, [2-4]), the contribution of the interband transitions to the optical characteristics of the metals is determined on the basis of various assumptions concerning the electronic spectrum. The authors of these papers did not take into account the effect of various electron collisions on the interband transitions. However, in the spectral region where the frequency of the light  $\omega$  is smaller than or is close to the threshold frequency of the direct interband transitions  $\omega_{\text{dir}}$ , it is essential to take the collisions into account.

Indeed, when  $\omega < \omega_{\text{thr}}$ , interband transitions can occur only with collisions taking part. As will be shown below, these processes play an appreciable role even at frequencies much lower than the threshold frequency. The threshold frequency  $\omega = \omega_{\text{thr}}$ , itself, the optical characteristics (we shall henceforth speak specifically of the electric conductivity  $\sigma$ ), defined without allowance for collisions, usually contain a singularity. In the general case, as shown by Kaganov and Lifshitz<sup>[3]</sup>, the first or second derivative of the electric conductivity with respect to the frequency  $\omega$  becomes infinite at  $\omega = \omega_{\text{thr}}$ . On the other hand, in metals for which the weak local pseudopotential is valid and in which the weak local pseudopotential is valid and in which the Fermi surface intersects the boundaries of the Brillouin zone, the electric conductivity itself becomes infinite at the threshold. (This circumstance was first pointed out by Harrison<sup>[4]</sup>.) Understandably, allowance

for the collisions should lead to a significant change in the behavior of  $\sigma(\omega)$  near threshold.

The present paper is devoted to an analysis of interband transitions and to the calculation of the electric conductivity tensor for different electron dispersion laws, with allowance for electron-electron and electron-phonon collisions.

## 1. KINETIC EQUATION WITH ALLOWANCE FOR INTERBAND TRANSITIONS

We derive below a quantum kinetic equation for the single-particle density matrix of electrons in a metal, with account taken of the possibility of interband transitions of the electrons and of their collisions with one another and with phonons.

The single-particle density matrix is defined, as usual, as follows<sup>1)</sup>:

$$\rho_{pp'}(t) = \langle a_p^\dagger(t) a_{p'}(t) \rangle, \quad (1)$$

where  $a_p^\dagger(t)$  and  $a_p(t)$  are the Heisenberg operators of creation and annihilation of a Bloch electron in a state with quasi-momentum *p*, and the spin indices  $\sigma$  will henceforth be omitted as a rule.

We write the Hamiltonian of the system in the form

$$H = H_0 + H_f + H_{ee} + H_{ep},$$

$$H_0 = \sum_p \xi_p a_p^\dagger a_p + \sum_q \hbar \omega_q b_q^\dagger b_q.$$

Here  $\xi_p = \epsilon_p - \mu$  is the excitation energy. We assume

<sup>1)</sup>We use the scheme of "expanded bands." The single-particle state is specified by a quasimomentum *p*, which varies over all of reciprocal space. The interband transition in such a scheme is the transition in *p*-space with change of the quasimomentum by a certain reciprocal-lattice vector *g*.

that the renormalization of the energy and of the chemical potential as a result of the interactions is already taken into account in  $\xi_p$ . The quantities  $b_q^+$  and  $b_q$  are the operators of creation and annihilation of a phonon with momentum  $q$ .

The Hamiltonian of the interaction with the electromagnetic field is

$$H_f = -\frac{e}{c} \mathbf{A} \mathbf{v} = -\frac{e}{c} \mathbf{A} \sum_{\mathbf{p}_1, \mathbf{p}_2} \mathbf{v}_{\mathbf{p}_1, \mathbf{p}_2} a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2},$$

$$\mathbf{A} = \mathbf{A}_0 e^{i(\omega + \delta)t}, \quad \delta \rightarrow +0,$$

where  $\mathbf{v}_{\mathbf{p}_1, \mathbf{p}_2}$  are the matrix elements of the velocity, which do not vanish if  $\mathbf{p}_1 - \mathbf{p}_2 = \mathbf{g}$ . When  $H_f$  is written in this form, no account is taken of the inhomogeneity of the magnetic field, which is of no importance in the analysis of effects connected with interband transitions.

The electron-electron and electron-phonon interactions are written in the form

$$H_{ee} = -\frac{1}{2} \sum_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \mathbf{p}_4} W_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \mathbf{p}_4} a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2}^+ a_{\mathbf{p}_3} a_{\mathbf{p}_4},$$

$$H_{ep} = \sum_{\mathbf{p}, \mathbf{p}_1, \mathbf{q}} \mathcal{B}_{\mathbf{p}, \mathbf{p}_1, \mathbf{q}} a_{\mathbf{p}_1}^+ a_{\mathbf{p}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+),$$

$$W_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \mathbf{p}_4} = \frac{1}{2\Omega} \sum_{(\mathbf{p}' = \mathbf{p} + \mathbf{g})} c_{\mathbf{p}_1, \mathbf{p}'}^* c_{\mathbf{p}_2, \mathbf{p}'} c_{\mathbf{p}_3, \mathbf{p}'} c_{\mathbf{p}_4, \mathbf{p}'},$$

$$\times (u_{\mathbf{p}_2, -\mathbf{p}_1} \delta_{\sigma_1, \sigma_2} \delta_{\sigma_3, \sigma_4} - u_{\mathbf{p}_3, -\mathbf{p}_1} \delta_{\sigma_1, \sigma_3} \delta_{\sigma_2, \sigma_4}) \delta_{\mathbf{p}_4, \mathbf{p}'} - \mathbf{p}_2' - \mathbf{p}_3' = \mathbf{p}_1',$$

$$\mathcal{B}_{\mathbf{p}, \mathbf{p}_1, \mathbf{q}} = \Delta \Omega^{-1/2} q^{1/2} \sum_{(\mathbf{p}' = \mathbf{p} + \mathbf{g})} c_{\mathbf{p}_1, \mathbf{p}'}^* c_{\mathbf{p}, \mathbf{p}'} \delta_{\sigma_1, \sigma_2} \delta_{\mathbf{p}_2' - \mathbf{p}_1 + \mathbf{q}}.$$

In these formulas  $\Omega$  is the volume of the system,  $u_p$  is the Fourier transform of the potential energy of the interaction of two electrons,  $\Delta$  is the ep interaction constant, and  $c_{\mathbf{p}, \mathbf{p} + \mathbf{g}}$  are the coefficients of expansion of the Bloch wave function  $\psi_p$  in plane waves:

$$\psi_p = \sum_{\mathbf{g}} c_{\mathbf{p}, \mathbf{p} + \mathbf{g}} e^{i(\mathbf{p} + \mathbf{g})\mathbf{r}/\hbar}.$$

To derive the kinetic equation, we use a method similar to the Bogolyubov method as applied to systems subjected to second quantization (see, for example, [5]). Differentiating the density matrix (1) with respect to time and using the equation of motion of the Heisenberg operators  $i\hbar \partial a(t)/\partial t = [a(t), H]$ , we obtain

$$\left( i\hbar \frac{\partial}{\partial t} + \xi_{\mathbf{p}'\mathbf{p}} \right) \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}} \rangle + \frac{e}{c} \mathbf{A} \sum_{\mathbf{p}_1, \mathbf{p}_2} \mathbf{v}_{\mathbf{p}_1, \mathbf{p}_2} \langle [a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}, a_{\mathbf{p}_2}^+ a_{\mathbf{p}}] \rangle$$

$$= \sum_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3} (W_{\mathbf{p}, \mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2} a_{\mathbf{p}_3} \rangle - W_{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \mathbf{p}'} \langle a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2}^+ a_{\mathbf{p}_3} a_{\mathbf{p}} \rangle)$$

$$+ \sum_{\mathbf{p}_1, \mathbf{q}} (\mathcal{B}_{\mathbf{p}, \mathbf{p}_1, \mathbf{q}} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+) \rangle - \mathcal{B}_{\mathbf{p}_1, \mathbf{p}, \mathbf{q}} \langle a_{\mathbf{p}_1}^+ a_{\mathbf{p}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+) \rangle), \quad (2)$$

$$\xi_{\mathbf{p}'\mathbf{p}} = \xi_{\mathbf{p}'} - \xi_{\mathbf{p}}$$

The time argument of the creation and annihilation operator will henceforth be omitted.

It is now necessary to write equations of the same type for the mean values of the four electron operators and of the two electron and one phonon operators in the right side of (2). For example,

$$\left( i\hbar \frac{\partial}{\partial t} + \xi_{\mathbf{p}'\mathbf{p}_1} + \hbar\omega_q \right) \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1} a_{\mathbf{p}_2} a_{\mathbf{p}_3} \rangle + \frac{e}{c} \mathbf{A} \sum_{\mathbf{p}_4} (\mathbf{v}_{\mathbf{p}, \mathbf{p}_4} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2} a_{\mathbf{p}_4} \rangle$$

$$+ \mathbf{v}_{\mathbf{p}, \mathbf{p}_4} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2} a_{\mathbf{p}_4} \rangle - \mathbf{v}_{\mathbf{p}_4, \mathbf{p}_1} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2} a_{\mathbf{p}_4} \rangle - \mathbf{v}_{\mathbf{p}_4, \mathbf{p}} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2} a_{\mathbf{p}_4} \rangle)$$

$$= -\frac{1}{2} \sum_{\mathbf{p}_4, \mathbf{p}_5, \mathbf{p}_6, \mathbf{p}_7} W_{\mathbf{p}, \mathbf{p}_4, \mathbf{p}_5, \mathbf{p}_6, \mathbf{p}_7} \langle [a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}^+ a_{\mathbf{p}_2} a_{\mathbf{p}_3}, a_{\mathbf{p}_4}^+ a_{\mathbf{p}_5}^+ a_{\mathbf{p}_6} a_{\mathbf{p}_7}] \rangle, \quad (3)$$

$$\left( i\hbar \frac{\partial}{\partial t} + \xi_{\mathbf{p}'\mathbf{p}_1} + \hbar\omega_q \right) \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1} b_{\mathbf{q}} \rangle + \frac{e}{c} \mathbf{A} \sum_{\mathbf{p}_2} (\mathbf{v}_{\mathbf{p}, \mathbf{p}_2} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1} b_{\mathbf{q}} \rangle$$

$$- \mathbf{v}_{\mathbf{p}, \mathbf{p}'} \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1} b_{\mathbf{q}} \rangle) = \sum_{\mathbf{p}_2, \mathbf{p}_3, \mathbf{q}_1} \mathcal{B}_{\mathbf{p}, \mathbf{p}_2, \mathbf{p}_3, \mathbf{q}_1} \langle [a_{\mathbf{p}'}^+ a_{\mathbf{p}_2} b_{\mathbf{q}_1}, a_{\mathbf{p}_3}^+ a_{\mathbf{p}_1} (b_{\mathbf{q}_1} + b_{-\mathbf{q}_1}^+)] \rangle. \quad (4)$$

We assume the interaction to be small, in which connection we uncouple the correlation functions in the right sides of (3) and (4), i.e., we express them in terms of the single-particle density matrix, for example

$$\langle [a_{\mathbf{p}'}^+ a_{\mathbf{p}_1} b_{\mathbf{q}_1}, a_{\mathbf{p}_2}^+ a_{\mathbf{p}_3} (b_{\mathbf{q}_1} + b_{-\mathbf{q}_1}^+)] \rangle = \delta_{-\mathbf{q}_1, \mathbf{q}} \{ \delta_{\mathbf{p}_1, \mathbf{p}_2} (\bar{n}_{\mathbf{p}_2} \bar{N}_{\mathbf{q}} + n_{\mathbf{p}_1} N_{\mathbf{q}}) \langle a_{\mathbf{p}'}^+ a_{\mathbf{p}_1} \rangle - \delta_{\mathbf{p}', \mathbf{p}_2} (n_{\mathbf{p}'} \bar{N}_{\mathbf{q}} + \bar{n}_{\mathbf{p}'} N_{\mathbf{q}}) \langle a_{\mathbf{p}_1}^+ a_{\mathbf{p}_3} \rangle \},$$

$$\bar{n}_{\mathbf{p}} = 1 - n_{\mathbf{p}}, \quad \bar{N}_{\mathbf{q}} = 1 - N_{\mathbf{q}}.$$

Here  $n_p$  and  $N_p$  are the equilibrium distribution functions of the electrons and phonons.

We note that we did not write out a term corresponding to ep interaction in the right side of (3) or to ee interaction in (4), for upon uncoupling they lead to mean values  $\langle b_q \rangle$  of higher order in terms of the interactions.

As a result of the uncoupling, Eqs. (2) and (4) form a closed system of equations for the density matrix.

We use the smallness of the electromagnetic field. In the approximation linear in the field, the mean values in the coefficients of the vector potential must be calculated over the equilibrium distribution. These mean values are conveniently obtained from the same equations (2)–(4), from which we discard the field terms and the time derivatives. Calculation shows that for the term

$$\frac{e}{c} \mathbf{A} \sum_{\mathbf{p}_1, \mathbf{p}_2} \mathbf{v}_{\mathbf{p}_1, \mathbf{p}_2} \langle [a_{\mathbf{p}'}^+ a_{\mathbf{p}_1}, a_{\mathbf{p}_2}^+ a_{\mathbf{p}_3}] \rangle$$

it suffices to confine oneself in (2) to the zeroth approximations in the interaction and to write it in the form  $(e/c) \mathbf{A} \cdot \mathbf{v}_{\mathbf{p}\mathbf{p}'} (n_p - n_{p'})$ .

Substituting the solutions of (3) and (4) in (2) and taking the Fourier transform with respect to time, we ultimately obtain in the approximation linear in the field<sup>2)</sup>

$$(\xi_{\mathbf{p}'\mathbf{p}} - \hbar\omega) \rho_{\mathbf{p}\mathbf{p}'}^{(1)} + \frac{ie}{\omega} \mathbf{E} \left\{ 2(n_{\mathbf{p}'} - n_{\mathbf{p}}) \mathbf{v}_{\mathbf{p}\mathbf{p}'} + \sum_{\mathbf{k}\mathbf{k}'} \frac{\mathbf{v}_{\mathbf{k}\mathbf{k}'}}{\xi_{\mathbf{k}'\mathbf{k}} - \hbar\omega} D_{\mathbf{k}\mathbf{k}'}^{pp'} \right\}$$

$$= \sum_{\mathbf{k}\mathbf{k}'} I_{\mathbf{k}\mathbf{k}'}^{pp'} \rho_{\mathbf{k}\mathbf{k}'}^{(1)}, \quad (5)$$

$$D = D_{ee} + D_{ep}, \quad I = I_{ee} + I_{ep},$$

$$D_{\mathbf{k}\mathbf{k}'}^{pp'}(\omega) = \bar{D}_{\mathbf{k}\mathbf{k}'}^{pp'}(\omega) + {}^I D_{\mathbf{k}\mathbf{k}'}^{p'p}(-\omega)^*,$$

$$I_{\mathbf{k}\mathbf{k}'}^{pp'}(\omega) = \bar{I}_{\mathbf{k}\mathbf{k}'}^{pp'}(\omega) - \{I_{\mathbf{k}\mathbf{k}'}^{p'p}(-\omega)\}^*,$$

$$(\bar{D}_{\mathbf{k}\mathbf{k}'}^{pp'})_{ee} = 2\pi i \sum_{\mathbf{p}_1, \mathbf{p}_2} \{ 2P_{\mathbf{p}\mathbf{p}_1, \mathbf{p}_2, \mathbf{k}}^{p'k'} (n_{\mathbf{p}'} \bar{n}_{\mathbf{p}_1} \bar{n}_{\mathbf{p}_2} \bar{n}_{\mathbf{k}'} - \bar{n}_{\mathbf{p}'} \bar{n}_{\mathbf{p}_1} n_{\mathbf{p}_2} n_{\mathbf{k}'} ) \delta(\xi_{\mathbf{p}'\mathbf{p}_1, \mathbf{p}_2, \mathbf{k}} - \hbar\omega)$$

$$- P_{\mathbf{p}\mathbf{k}', \mathbf{p}_1, \mathbf{p}_2}^{p'k'} (n_{\mathbf{p}'} n_{\mathbf{k}'} \bar{n}_{\mathbf{p}_1} \bar{n}_{\mathbf{p}_2} - \bar{n}_{\mathbf{p}'} \bar{n}_{\mathbf{k}'} n_{\mathbf{p}_1} n_{\mathbf{p}_2}) \delta(\xi_{\mathbf{p}'\mathbf{k}', \mathbf{p}_1, \mathbf{p}_2} - \hbar\omega) - \delta_{\mathbf{p}'\mathbf{k}'} \sum_{\mathbf{p}_1} P_{\mathbf{p}\mathbf{p}_1, \mathbf{p}_1, \mathbf{k}}^{p'k'} (n_{\mathbf{p}'} \bar{n}_{\mathbf{p}_1} \bar{n}_{\mathbf{p}_1} - \bar{n}_{\mathbf{p}'} \bar{n}_{\mathbf{p}_1} n_{\mathbf{p}_1} n_{\mathbf{p}_1}) \delta(\xi_{\mathbf{p}'\mathbf{p}_1, \mathbf{p}_2, \mathbf{k}} - \hbar\omega) \},$$

$$(\bar{I}_{\mathbf{k}\mathbf{k}'}^{pp'})_{ee} = \pi i \sum_{\mathbf{p}_1, \mathbf{p}_2} \{ 2P_{\mathbf{p}\mathbf{p}_1, \mathbf{p}_2, \mathbf{k}}^{p'k'} (n_{\mathbf{p}'} n_{\mathbf{p}_1} \bar{n}_{\mathbf{p}_2} + \bar{n}_{\mathbf{p}'} \bar{n}_{\mathbf{p}_1} n_{\mathbf{p}_2}) \delta(\xi_{\mathbf{p}'\mathbf{p}_1, \mathbf{p}_2, \mathbf{k}} - \hbar\omega)$$

$$- P_{\mathbf{p}\mathbf{k}', \mathbf{p}_1, \mathbf{p}_2}^{p'k'} (n_{\mathbf{p}'} \bar{n}_{\mathbf{p}_1} \bar{n}_{\mathbf{p}_2} + \bar{n}_{\mathbf{p}'} n_{\mathbf{p}_1} n_{\mathbf{p}_2}) \delta(\xi_{\mathbf{p}'\mathbf{k}', \mathbf{p}_1, \mathbf{p}_2} - \hbar\omega)$$

$$- \delta_{\mathbf{p}'\mathbf{k}'} \sum_{\mathbf{p}_1} P_{\mathbf{p}\mathbf{p}_1, \mathbf{p}_1, \mathbf{k}}^{p'k'} (n_{\mathbf{p}'} \bar{n}_{\mathbf{p}_1} \bar{n}_{\mathbf{p}_1} + \bar{n}_{\mathbf{p}'} n_{\mathbf{p}_1} n_{\mathbf{p}_1}) \delta(\xi_{\mathbf{p}'\mathbf{p}_1, \mathbf{p}_2, \mathbf{k}} - \hbar\omega) \},$$

$$(\bar{D}_{\mathbf{k}\mathbf{k}'}^{pp'})_{ep} = \pi i \sum_{\mathbf{q}} \{ \Phi_{\mathbf{p}\mathbf{q}}^{p'k'} [(n_{\mathbf{p}'} \bar{n}_{\mathbf{k}'} \bar{N}_{\mathbf{q}} - \bar{n}_{\mathbf{p}'} n_{\mathbf{k}'} N_{\mathbf{q}}) \delta(\xi_{\mathbf{p}'\mathbf{k}} - \hbar\omega_{\mathbf{q}} - \hbar\omega)$$

$$+ (n_{\mathbf{p}'} \bar{n}_{\mathbf{k}'} N_{\mathbf{q}} - \bar{n}_{\mathbf{p}'} n_{\mathbf{k}'} \bar{N}_{\mathbf{q}}) \delta(\xi_{\mathbf{p}'\mathbf{k}} + \hbar\omega_{\mathbf{q}} - \hbar\omega) \}$$

<sup>2)</sup>As a check, the kinetic equation (5) was derived by the author also by the technique of Konstantinov and Perel' [6]. Such a procedure is apparently more rigorous, since it does not involve uncoupling the correlation functions, but is more cumbersome than the one described above.

$$\begin{aligned}
& -\delta_{p'k'} \sum_{p_i} \Phi_{pp_iq}^k [(n_k \bar{n}_{p_i} \bar{N}_q - \bar{n}_k n_{p_i} N_q) \delta(\xi_{p'p_i} - \hbar\omega_q) \\
& - \hbar\omega) + (n_k \bar{n}_{p_i} N_q - \bar{n}_k n_{p_i} \bar{N}_q) \delta(\xi_{p'p_i} + \hbar\omega_q - \hbar\omega)], \\
& (\bar{I}_{kk'}^{pp'} - \frac{1}{2} \pi i \sum_q \{ \Phi_{pkq}^{p'k'} [(n_p \bar{N}_q + \bar{n}_p N_q) \delta(\xi_{p'k} - \hbar\omega_q) \\
& - \hbar\omega) + (n_p \bar{N}_q + \bar{n}_p N_q) \delta(\xi_{p'k} + \hbar\omega_q - \hbar\omega)] \\
& - \delta_{p'k'} \sum_p \Phi_{ppq}^k [(n_{p_i} \bar{N}_q + n_{p_i} N_q) \delta(\xi_{p'p_i} - \hbar\omega_q - \hbar\omega) \\
& + (\bar{n}_{p_i} N_q + n_{p_i} \bar{N}_q) \delta(\xi_{p'p_i} + \hbar\omega_q - \hbar\omega)] \}.
\end{aligned}$$

In these formulas, summation over the spin indices has already been carried out. If we write the matrix elements of the interaction in the form

$$\begin{aligned}
W_{p_1 p_2 p_3 p_4} &= \delta_{\sigma_1 \sigma_2} \delta_{\sigma_3 \sigma_4} U_{p_1 p_2 p_3 p_4} - \delta_{\sigma_1 \sigma_3} \delta_{\sigma_2 \sigma_4} U_{p_1 p_3 p_2 p_4}, \\
B_{p_1 p_2 q} &= \delta_{\sigma_1 \sigma_2} B_{p_1 p_2 q},
\end{aligned}$$

where the quantities  $U$  and  $B$  no longer depend on the spin indices, then we get for  $P$  and  $\Phi$

$$\begin{aligned}
P_{p_1 p_2 p_3 p_4}^{p_1' p_2' p_3' p_4'} &= \sum_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} W_{p_1 p_2 p_3 p_4} \bar{V}_{p_1' p_2' p_3' p_4'} = 2 [(U_{p_1 p_2 p_3 p_4} \\
& - U_{p_1 p_3 p_2 p_4}) (U_{p_1' p_2' p_3' p_4'} - U_{p_1' p_3' p_2' p_4'}) + U_{p_1 p_2 p_4 p_3} U_{p_1' p_3' p_2' p_4'} + U_{p_1 p_2 p_4 p_3} U_{p_1' p_3' p_4' p_2'}], \\
\Phi_{p_1 p_2 q}^{p_1' p_2'} &= \sum_{\sigma_1 \sigma_2} B_{p_1 p_2 q} B_{p_1' p_2' (-q)} = 2 B_{p_1 p_2 q} B_{p_1' p_2' (-q)}.
\end{aligned}$$

The upper indices of the quantities  $P$  and  $\Phi$ , which coincide with the lower ones, are omitted. The right side of (5) is the collision integral of the electrons with the phonons and with one another in the case when the density matrix is not diagonal. We emphasize that the form of the collision integral does not depend on the cause of the nondiagonality. In this case, it is the possibility of the interband transitions ( $\rho_{pp'}^{(1)}$  =  $\delta_{p+g,p'} \rho_{p,p+g}^{(1)}$ ), but the cause might also be, for example, the spatial inhomogeneity of the electromagnetic field.

It is easy to verify that if  $\hbar\omega \ll \min \xi_{k+g,k}$ , then Eq. (5) for the diagonal elements of the density matrix goes over into the Gurzhi equation<sup>[7]</sup>, which was derived without allowance for the interband transitions (in<sup>[7]</sup> the equation was written out for the function  $f_p = \rho_{pp}^{(1)} - c^{-1} e A \partial n_p / \partial p$ ).

## 2. SOLUTION OF KINETIC EQUATION. "INTERBAND" PART OF THE ELECTRIC CONDUCTIVITY TENSOR

Although Eq. (5) has a cumbersome appearance, it can be readily solved in general form.

To each value of the quasimomentum  $p$  there correspond "resonant" frequencies  $\omega_{res} = \xi_{p+g,p} / \hbar$ , at which the interband transitions from the state  $p$  are the most intense. It is understandable that far from the resonant frequencies one can use the usual perturbation theory with respect to the constants of the  $ee$  and  $ep$  interactions. This means that it is possible to substitute in the collision integral the density matrix in the zeroth approximation in the interaction.

Let us consider now the vicinity of one of the resonant frequencies where the usual perturbation theory is not applicable. We shall show that the most significant among the terms of the Eq. (5) containing the  $ee$  and  $ep$  interactions are the non-integral terms of the collision integral, which are proportional to  $\rho_{pp'}^{(1)}$ , so that the relaxation-time approximation is applicable.

Exceptions are certain cases of a very special arrangement of the energy bands, which will be discussed later. In the relaxation-time approximation we have for

$\omega \approx \omega_{res}$

$$\begin{aligned}
\sum_{kk'} I_{kk'}^{pp'} \rho_{kk'}^{(1)} &\approx -i \gamma_{pp'} \rho_{pp'}^{(1)}, \quad \gamma_{pp'} = \gamma_p + \gamma_{p'}, \\
\gamma_p &= \gamma_p^{ee} + \gamma_p^{ep} = \pi \hbar^{-1} \sum_{p_1 p_2 p_3} P_{p p_1 p_2 p_3} (n_{p_1} \bar{n}_{p_2} \bar{n}_{p_3} \\
&+ \bar{n}_{p_1} n_{p_2} n_{p_3}) \delta(\xi_{p p_1 p_2 p_3}) + \frac{1}{2} \pi \hbar^{-1} \sum_{p_1 q} \Phi_{p p_1 q} [(n_{p_1} \bar{N}_q \\
&+ n_{p_1} N_q) \delta(\xi_{p p_1} - \hbar\omega_q) + (\bar{n}_{p_1} N_q + n_{p_1} \bar{N}_q) \delta(\xi_{p p_1} + \hbar\omega_q)], \\
\rho_{pp'}^{(1)} &= \frac{2e E v_{pp'} (n_{p'} - n_p)}{i \omega \eta_{pp'}}, \\
\eta_{pp'} &= \xi_{p'p} - \hbar\omega + i \hbar \gamma_{pp'}.
\end{aligned} \tag{6}$$

It is clear that the quantity  $\gamma_{pp'}^{-1}$  is of the same order of magnitude as the lifetime of the electron-hole type of excitation appearing as a result of absorption of a photon.

Substituting (6) in the right side of (5), we can easily ascertain under which conditions the relaxation-time approximation is applicable.

First, it is necessary to this end that the volume of the region in  $p$ -space, defined by the inequalities  $|\xi_p| \lesssim \hbar\omega_{res}$  and  $|\xi_{p+g,p} - \hbar\omega_{res}| \lesssim \hbar\gamma_{p,p+g}$  be much smaller than the volume of the region defined only by the first inequality. Second, the resonant frequencies corresponding to different direct interband transitions from the state  $p$  should not be too close:  $\xi_{p+g_1,p} - \xi_{p+g_2,p} \gg \hbar\gamma$ .

Thus, the relaxation time approximation is not suitable for the solution of the kinetic equation (5) near  $\omega_{res}$  only in those apparently rare cases when the energy bands are practically "parallel" near an appreciable section of the Fermi surface, and when band intersection takes place.

We present a solution of Eq. (5), valid in the vicinity of the resonant frequencies and far from them; this solution will be useful to us later<sup>3)</sup>:

$$\begin{aligned}
\rho_{pp'}^{(1)} &= \frac{eE}{i \omega \eta_{pp'}} \left\{ 2(n_{p'} - n_p) v_{pp'} \left( 1 - \frac{\hbar \gamma_{pp'}}{\eta_{pp'}} \right) + i \sum_{kk'} \frac{v_{kk'}}{\eta_{kk'}} L_{kk'}^{pp'} \right\}, \\
L_{kk'}^{pp'} &= -i [D_{kk'}^{pp'} + 2I_{kk'}^{pp'} (n_{k'} - n_k)].
\end{aligned} \tag{7}$$

We now obtain an expression for the electric conductivity tensor. In the approximation linear in the field, the electric current density is

$$j = \frac{e}{m\Omega} \text{Sp}(\rho^{(0)} + \rho^{(1)}) \left( p - \frac{e}{c} A \right) = \Omega^{-1} e \text{Sp} \rho^{(1)} v - \frac{ie^2 N}{m\omega} E,$$

where  $N$  is the density of the valence electrons.

We confine ourselves henceforth to crystals having an inversion center. In this case the matrix elements of the velocity and the matrix  $L$  can be chosen to be real. Using (7) and the definition of the electric conductivity tensor  $j^\alpha = \sigma^{\alpha\beta} E^\beta$ , we obtain, accurate to terms of higher order in  $\gamma$ ,

<sup>3)</sup>In the derivation of (7) we added in the energy denominator the quantity  $i \hbar \gamma_{kk'}$  in front of  $D_{kk'}^{pp'}$ . This can be done if  $\gamma_{kk'}$  is small, since  $D_{kk'}^{pp'} = 0$  when  $\xi_{kk'} = \hbar\omega$ .

$$\begin{aligned} \operatorname{Re} \sigma^{\alpha\beta} &= \frac{e^2}{\Omega\omega} \sum_{\substack{p' \rightarrow p = g_1 \\ k' \rightarrow k = g_2}} \{ [\xi_{p'p} - \hbar\omega]^2 + (\hbar\gamma_{pp'})^2 \} [(\xi_{k'k} - \hbar\omega)^2 \\ &+ (\hbar\gamma_{kk'})^2 (1 - \delta_{pk}\delta_{p'k'})]^{-1} (\xi_{p'p} - \hbar\omega)(\xi_{k'k} - \hbar\omega) v_{p'p}^\alpha v_{kk'}^\beta L_{kk'}^{\alpha\beta}, \quad (8) \\ \operatorname{Im} \sigma^{\alpha\beta} &= \frac{e^2}{\Omega\omega} \sum_{(p' \rightarrow p = g)} \frac{(\xi_{p'p} - \hbar\omega)(n_p - n_{p'}) v_{p'p}^\alpha v_{pp'}^\beta}{(\xi_{p'p} - \hbar\omega)^2 + (\hbar\gamma_{pp'})^2} - \frac{e^2 N}{m\omega} \delta_{\alpha\beta}. \end{aligned}$$

Let us discuss the physical meaning of the terms of the sum in (8) using ep collisions as an example. The transition of the electron from the state  $p_1$  to the state  $p_2$ , such that  $\xi_{p_2 p_1} = \hbar\omega$ , can follow different paths. Two different types of transition are illustrated by the Feynman diagrams in Figs. 1a and b. The electron is represented here by a solid line, the photon by a wavy line, and the phonon by a dashed line.

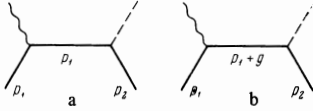


FIG. 1

In the case a, the electron absorbs a phonon and remains in the same band (the states  $p_1$  and  $p_2$  can belong to different bands). The contribution of such processes to the conductivity (these are the terms of the sum in (8) with  $g_1 = g_2 = 0$ ) will be called the "intraband" contribution. The intraband conductivity was calculated in [8-10].

In case b, the electron absorbs a photon and executes an interband transition by one of the reciprocal-lattice vectors  $g$  (in the reduced-band scheme this corresponds to a change in the band index with  $p$  unchanged). Thus, the transition from  $p_1$  to  $p_2$  proceeds via an intermediate state  $p_1 + g$ . If  $p_1$  and  $p_2$  pertain to different bands, then processes of this type are usually called indirect interband transitions. But  $p_1$  and  $p_2$  can belong to one band while the intermediate virtual state belongs to another. The latter type of process is possible if  $\hbar\omega < \Delta\epsilon$ , where  $\Delta\epsilon$  is the minimum width of the forbidden energy band. In this sense, the internal photoeffect in metals in the presence of collisions is a phenomenon having no threshold.

The sum in (8) contains also terms connected with interference of different manners of transition. The conductivity defined by all terms in (8) with the exception of the intraband terms will be called "interband." We note that owing to the presence of interference terms the diagonal components of the interband electric conductivity tensor may turn out to be negative, while the total electric conductivity ( $\operatorname{Re} \sigma_{\text{intra}}^{\alpha\alpha} + \operatorname{Re} \sigma_{\text{inter}}^{\alpha\alpha}$ ), naturally, is always positive.

### 3. INFLUENCE OF INTERBAND TRANSITIONS ON THE OPTICAL PROPERTIES OF METALS

#### A. Arbitrary Dispersion Law

The real part of the electric conductivity tensor determines the absorption of light by the metal. To calculate this part by formula (8) it is necessary to use a concrete model of the band spectrum. In the far-infrared region, however, and at frequencies close to the threshold of the internal photoeffect, the frequency and temperature dependences of the interband conductivity can be established in the general case.

1. Let us consider first the region of relatively low frequencies, where  $\omega \ll \omega_{\text{thr}}$ ,  $\hbar\omega \ll \epsilon_F$ , and  $\omega\tau \gg 1$ . At such frequencies, the damping  $\gamma$  in the energy denominators of (8) can be neglected, and this expression takes the form

$$\operatorname{Re} \sigma^{\alpha\beta} = \frac{e^2}{\Omega\omega} \sum_{\substack{p' \rightarrow p = g_1 \\ k' \rightarrow k = g_2}} \frac{v_{p'p}^\alpha v_{kk'}^\beta}{(\xi_{p'p} - \hbar\omega)(\xi_{k'k} - \hbar\omega)} L_{kk'}^{\alpha\beta}. \quad (9)$$

We note that if  $\omega\tau \gg 1$ , the inequality  $\omega \gg \omega_D$  is usually satisfied, where  $\omega_D$  is the maximum phonon frequency. For simplicity, therefore, we can neglect in the equation for  $L$  the energy of the phonon in the  $\delta$ -functions expressing the energy conservation. We then obtain

$$\begin{aligned} (L_{kk'}^{\alpha\beta})_{ep} &= \pi \sum_q (2N_q + 1) \left\{ \Phi_{p'k'}^{\alpha\beta} [(n_{p'} - n_k) \delta(\xi_{p'k} - \hbar\omega) \right. \\ &+ (n_{k'} - n_p) \delta(\xi_{k'p} - \hbar\omega)] - \sum [\delta_{k,p'} \Phi_{p'q}^{\alpha\beta} (n_{p'} - n_{p_1}) \delta(\xi_{p'p_1} - \hbar\omega) \\ &\left. + \delta_{k,p} \Phi_{p,p'}^{\alpha\beta} (n_{p_1} - n_p) \delta(\xi_{p,p} - \hbar\omega)] \right\}. \end{aligned}$$

Let us determine first the frequency and temperature dependences of the terms in the sum of (9) with  $g_1$  and  $g_2 \neq 0$ . By virtue of the condition  $\omega \ll \omega_{\text{thr}}$  we can discard  $\omega$  in the energy denominators of these terms. Further, from physical considerations and from the structure of the expression for  $L$  it is clear that the initial and final states of the interband transitions with collision should lie in a narrow layer near the Fermi surface. The width of this layer is determined by the inequality  $\xi \lesssim \hbar\omega$ ,  $T$ . Therefore the initial and final states everywhere in (9), with the exception of the energy  $\delta$ -functions and the Fermi distribution functions, can be regarded as lying on the Fermi surface.

Thus, the terms of the sum in (9) with  $g_1$  and  $g_2 \neq 0$  depend on  $\omega$  and  $T$  in the following manner:

$$(\operatorname{Re} \sigma^{\alpha\beta})_{\text{inter}}^{\text{ep}} \sim \omega^{-1} \int (n_1 n_2 \bar{n}_3 \bar{n}_4 - \bar{n}_1 \bar{n}_2 n_3 n_4) \delta(\xi_{1234} + \hbar\omega) d\xi_1 d\xi_2 d\xi_3 d\xi_4, \quad (10)$$

$$(\operatorname{Re} \sigma^{\alpha\beta})_{\text{inter}}^{\text{ep}} \sim \omega^{-1} f(T/\Theta) \int (n_1 - n_2) \delta(\xi_{12} + \hbar\omega) d\xi_1 d\xi_2. \quad (11)$$

At arbitrary electron and phonon dispersion laws, we can establish only the asymptotic forms of the function  $f(T/\Theta)$  in two limiting cases:

$$f(T/\Theta) = \begin{cases} A + B(T/\Theta)^3 & \text{if } T \ll \Theta \\ CT/\Theta & \text{if } T \gg \Theta \end{cases}, \quad (12)$$

where  $\Theta$  is the Debye temperature, and  $A$ ,  $B$ , and  $C$  are constants on the order of unity.

Let us consider now the terms of the sum in (9), in which, for example,  $g_1 = 0$ . Although the dependence of each such term on  $\Theta$  and  $T$  contains, compared with (10) and (11), an additional factor  $\omega^{-1}$ , the structure of the expression for  $L$  is such that the lowest order in the frequency drops out from the sum. The annihilation of the lowest order occurs in terms containing  $L_{k,k+g_2}^{\text{pp}}$  and  $L_{k+g_2,k}^{\text{pp}}$ .

Thus, expressions (10) and (11) give the dependence of the entire interband part of the electric conductivity on  $\omega$  and  $T$ .

We introduce the effective electron collision frequency  $\nu$ , defined by the equation  $\operatorname{Re} \sigma = e^2 N \nu / m \omega^2$ . We then obtain from (10) and (11)

$$\nu_{\text{inter}}^{ee} = \nu_0^{ee} \frac{(\hbar\omega)^2 + (2\pi kT)^2}{\varepsilon_F^2} \left( \frac{\omega}{\omega_{\text{thr}}} \right)^2, \quad (13)$$

$$\nu_{\text{inter}}^{ep} = \nu_0^{ep} f\left(\frac{T}{\Theta}\right) \left( \frac{\omega}{\omega_{\text{thr}}} \right)^2, \quad (14)$$

where  $f(T/\Theta)$  is given by formula (12).

Let us compare these results with the expressions for the "interband" contribution to the effective collision frequency, obtained in [9,10]:

$$\nu_{\text{intra}}^{ee} = \nu_0^{ee} \frac{(\hbar\omega)^2 + (2\pi kT)^2}{\varepsilon_F^2}, \quad \nu_{\text{intra}}^{ep} = \nu_0^{ep} f(T/\Theta). \quad (15)$$

A plot of the function  $\varphi(T/\Theta)$  is presented below in Fig. 3. The values of  $\nu_0^{ee}$  and  $\nu_0^{ep}$  in these formulas have the same order of magnitude as in (13) and (14).

Thus, the collision frequencies  $\nu_{\text{intra}}^{ee}$  and  $\nu_{\text{inter}}^{ep}$  have the same dependence on  $\omega$  when  $\hbar\omega \gg kT$ , and can be of the same order of magnitude at a reasonable ratio of the quantities  $\nu_0^{ee}$  and  $\nu_0^{ep}$ . A distinguishing feature of the quantity  $\nu_{\text{inter}}^{ep}$  compared with  $\nu_{\text{intra}}^{ee}$  is the dependence of the coefficient preceding  $\omega^2$ , on the temperature. Such a temperature dependence was observed in [11].

The main contribution to the effective collision frequency in the far infrared region ( $\omega \ll \omega_{\text{thr}}$ ) is made by the intraband ep processes, while near the threshold frequency of the internal photoeffect the main contribution is made by the interband processes.

2. Let us consider now the frequency region close to the threshold of the direct interband transitions. The interband conductivity in the vicinity of the threshold frequency  $\omega_{\text{thr}}$  was obtained without allowance for the electron collisions in [3]. At an arbitrary dispersion law, a typical situation is one of the two illustrated in Figs. 2a and b. In these figures, the shaded regions correspond to p-space regions from which direct interband transitions are possible: in these regions the initial states of the transition are occupied and the final ones are free. The temperature is assumed to be so low that the diffuseness of the Fermi step can be neglected.

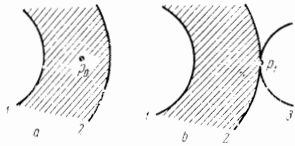


FIG. 2. 1—The surface  $\xi_p = 0$ , 2— $\xi_{p+g} = 0$ , 3— $\xi_p + g - \xi_p = \hbar\omega$ .

Fig. 2a pertains to the case when  $p_0$  is the point of the minimum of the interband energy  $\xi_{p+g} - \xi_p$  and is situated inside the shaded region, and consequently, at frequencies  $\omega > \omega_{\text{thr}} = \xi_{p_0+g} - \xi_{p_0}$  ( $\omega \approx \omega_{\text{thr}}$ ) the interband transitions come from a small vicinity of the point  $p_0$ . In this case [3]

$$\text{Re } \sigma_{\text{inter}} \sim \begin{cases} 0 & \text{if } \omega < \omega_{\text{thr}} \\ \sqrt{\omega - \omega_{\text{thr}}} & \text{if } \omega > \omega_{\text{thr}} \end{cases}, \quad \omega \approx \omega_{\text{thr}}$$

In case b, the point of the minimum of the interband energy lies outside the shaded region. The threshold frequency is determined in this case from the condition that the surface  $\xi_{p+g} - \xi_p = \hbar\omega$  be tangent to one of the surfaces bounding the shaded region. In this case

$$\text{Re } \sigma_{\text{inter}} \sim \begin{cases} 0 & \text{if } \omega < \omega_{\text{thr}} \\ \omega - \omega_{\text{thr}} & \text{if } \omega > \omega_{\text{thr}} \end{cases}, \quad \omega \approx \omega_{\text{thr}}$$

Thus, if we disregard the influence of the collisions, the derivatives of the interband electric conductivity with respect to the frequency have singularities at the threshold. It is clear that allowance for the collisions eliminates these singularities.

To calculate the interband electric conductivity near the threshold it is sufficient to retain in (8) only the term

$$\text{Re } \sigma_{\text{inter}}^{\alpha\beta} = \frac{2e^2 \hbar}{\Omega \omega} \sum_p \frac{v_{p+g,p}^\alpha v_{p,p+g}^\beta (n_p - n_{p+g}) \gamma_{p,p+g}}{(\xi_{p+g,p} - \hbar\omega)^2 + (\hbar\gamma_{p,p+g})^2}.$$

The calculations lead to the following result for the case corresponding to Fig. 2a.

$$\text{Re } \sigma_{\text{inter}}^{\alpha\beta} = \frac{e^2 v_{p_0+g,p_0}^\alpha v_{p_0,p_0+g}^\beta (M_1 M_2 M_3)^{1/2}}{\pi \hbar^2 \omega} (\omega - \omega_{\text{thr}} + \sqrt{(\omega - \omega_{\text{thr}})^2 + \gamma_{p_0,p_0+g}^2})^{1/2}, \quad \omega \approx \omega_{\text{thr}}$$

where  $M_1^{-1}$ ,  $M_2^{-1}$ , and  $M_3^{-1}$  are the principal values of the tensor  $(\partial^2 / \partial p^\alpha \partial p^\beta) \xi_{p_0+g, p_0}$ . The main contribution to the conductivity is made by a thin layer near the surface  $\xi_{p+g} - \xi_p = \hbar\omega$ ; its width is determined by the condition  $|\xi_{p+g} - \xi_p - \hbar\omega| \lesssim \hbar\gamma$ .

The situation is different in the case shown in Fig. 2b. It turns out that the regions of p-space that are far from the surface  $\xi_{p+g} - \xi_p = \hbar\omega$  can give in this case an appreciable contribution to the conductivity if  $|\omega - \omega_{\text{thr}}| \lesssim \gamma$ . Therefore in this case we cannot calculate the conductivity without a specific electron dispersion law. However, the derivative of the conductivity with respect to the frequency is determined by states close to  $p_1$ . The calculations yield

$$\text{Re } \sigma_{\text{inter}}^{\alpha\beta} = \frac{e^2 v_{p_1+g,p_1}^\alpha v_{p_1,p_1+g}^\beta R_a R_b}{2\pi \hbar^2 \omega (R_a + R_b) (\mathbf{v}_{p_1+g} - \mathbf{v}_{p_1})^2} J(\omega),$$

$$\frac{\partial}{\partial \omega} J(\omega) = \pi^{-1} \arctg \frac{\omega_{\text{thr}} - \omega}{\gamma_{p_1,p_1+g}},$$

where  $R_a$  and  $R_b$  are the curvature radii of the surfaces in contact at the point  $p_1$ .

When  $\omega - \omega_{\text{thr}} \gg \gamma$ , of course, the expressions for the conductivity from [3] are valid and  $J(\omega) = \omega - \omega_{\text{thr}}$ .

## B. Model of Weak Pseudopotential

The model of the weak local pseudopotential was successfully used for the determination of different optical characteristics of polyvalent nontransition and alkali metals [12,13]. In this section we calculate, on the basis of the model of the weak pseudopotential, the contribution of the interband transitions to the optical characteristics of metals.

A characteristic feature of interband transitions in polyvalent alkali metals is their connection with the Bragg reflection of electrons [12]. The correctness of this statement can be easily verified by an analysis of the following expressions for the interband energy and the nondiagonal matrix elements of the velocity operator as functions of the quasi-momentum:

$$\varepsilon_{p+g,p} = \varepsilon_{p+g} - \varepsilon_p = 2V_g \sqrt{1 + x^2}, \quad x = \frac{(g/2 - p_1)g}{2V_g m}, \quad (16)$$

$$\mathbf{v}_{p+g,p} = -V_g \mathbf{g} / m \varepsilon_{p+g,p}, \quad (17)$$



where  $V_g$  is the Fourier component of the pseudopotential and  $p_\perp$  is the projection of the quasimomentum on the reciprocal-lattice vector. These formulas can be readily obtained by using perturbation theory with respect to the parameter  $V_g/\epsilon_F$  and neglecting the dispersion law near the intersections of the Bragg planes<sup>4)</sup>.

The probability of a direct interband transition by the reciprocal lattice vector  $g$  is proportional to the square of the matrix element of the velocity and to the interband density of states  $(2\pi\hbar)^{-3} |\nabla p_{p+g, p}|^{-1}$ . It is seen from (16) and (17) that the quantity  $v_{p+g, p}$  is not small only near the corresponding Bragg plane, and the interband density of states tends to infinity when this plane is approached ( $x \rightarrow 0$ ). Thus, in the model of the weak pseudopotential, the most significant contribution to the internal photoeffect is made by the immediate vicinities of the Bragg planes.

The special role of the Bragg planes explains the sharp difference between the structure and intensity of the bands of quantum absorption in polyvalent and in alkali metals. In polyvalent metals, the Fermi surface crosses a number of Bragg planes. Therefore the interband conductivity, calculated without allowance for collisions of the electrons and for other factors, has in this case an infinite maximum at the threshold of the internal photoeffect. It is understandable, that allowance for the collisions of the electrons leads to a finite height of the photoeffect maxima.

The Fermi surface of alkali metals does not reach the limits of the first Brillouin zone. Therefore the maxima of the photoeffect, which are connected with direct interband transitions, are much less pronounced here than in polyvalent metals, and lie in the shorter-wavelength region of the spectrum. Electron collisions have a very slight effect on their form, but it will be shown below that they lead to the appearance of additional quantum-absorption bands.

Substituting expressions (16) and (17) in (8), we can easily verify that in the lowest order in  $V_g$  there remain only those interband conductivity terms in which either  $g_1 = g_2$  or one of these vectors is equal to zero. Terms of the former type correspond to the interband transitions proper, accompanied by collisions, while those of the second type correspond to interference between the interband and intraband transitions.

We confine ourselves henceforth, for simplicity, to metals with cubic lattice symmetry, for which the electric conductivity is isotropic. The generalization to include the anisotropy case entails no difficulty.

We use the isotropic Debye model for the phonons.

1. Polyvalent nontransition metals. The interband conductivity of polyvalent non-transition metals was calculated in<sup>[12]</sup>, where an attempt was made to take into account qualitatively the influence of the collisions on the width and height of the maxima of the photoeffect. In particular, it is shown in this paper that the interband conductivity can be represented in the following form:

$$\sigma_{\text{inter}} = \sum_g n_g \sigma_g,$$

where  $n_g$  is the number of physically-equivalent Bragg planes corresponding to the given  $|g|$ , and  $\sigma_g$  is the contribution of one Bragg plane to the interband conductivity. To each  $g$  there corresponds an absorption band with a threshold frequency  $\omega_{\text{thr}} = 2V_g/\hbar$  (this is seen directly from (16)).

The main task of this section is a rigorous account of the influence of electron collisions on the interband conductivity of polyvalent metals.

We present first the result of a calculation of the damping of the single-particle excitation,  $\gamma_p$ , which enters in (8). In the zeroth approximation in  $V_g/\epsilon_F$  we have<sup>5)</sup>

$$\gamma_p^{ee} = \gamma_0^{ee} \frac{\xi_p^2 + (\pi k T)^2}{\epsilon_F^2}, \quad \gamma_0^{ee} = \frac{m^2 u^2 \epsilon_F^2}{(2\pi)^3 \hbar^7}, \quad (18)$$

$$u^2 = \frac{\int (u_{p_1-p_1}^2 + u_{p_2-p_1}^2 - |u_{p_1-p_1} u_{p_2-p_1}|) \delta(p + p_1 - p_2 - p_3) d\Omega_1 d\Omega_2 d\Omega_3}{\int \delta(p + p_1 - p_2 - p_3) d\Omega_1 d\Omega_2 d\Omega_3}$$

$$\gamma_p^{ep} = \gamma_0^{ep} \psi\left(\frac{T}{\Theta}\right), \quad \gamma_0^{ep} = \frac{\Delta^2 m q_D^3}{4\pi \hbar^4 p_F},$$

$$\psi\left(\frac{T}{\Theta}\right) = \int_0^1 \left(1 + \frac{2}{\exp(x\Theta/T) - 1}\right) x^2 dx. \quad (19)$$

Here  $p, p_1, p_2$ , and  $p_3$  are the momenta of the electrons located on the Fermi surface (in the zeroth approximation in  $V_g/\epsilon_F$  it can be regarded as a sphere),  $d\Omega$  is the solid-angle element, and  $q_D$  is the end-point momentum of the phonons. A plot of the function  $\psi(T/\Theta)$  is shown in Fig. 3.

We note that the presented dependences of  $\gamma^{ee}$  and  $\gamma^{ep}$  on  $\xi$  are valid for any dispersion law if  $\xi \ll \epsilon_F$ .

Allowance for the dependence of the damping  $\gamma$  on  $\xi$  would greatly complicate further calculations. It is known from experiment<sup>[14]</sup> that in the spectral region under consideration, the most effective for polyvalent metals are electron-phonon collisions. We shall therefore assume for simplicity that  $\gamma = \gamma^{ep}$ .

Substituting (16), (17), (19) in (8) and performing the calculations, we get

$$\text{Re } \sigma_g = \text{Re } \sigma_g^{ee} + \text{Re } \sigma_g^{ep},$$

$$\text{Re } \sigma_g^{ee} = \frac{\gamma_0^{ee} g V_g \epsilon_F^{-2}}{48\pi \hbar^3 \omega^2} [(\hbar\omega)^2 + (2\pi k T)^2] J_1\left(\frac{\omega}{\omega_{\text{thr}}}\right),$$

$$\text{Re } \sigma_g^{ep} = \frac{\gamma_0^{ep} g V_g \epsilon_F^{-2}}{6\pi \hbar^3 \omega^2} \left[ J_1\left(\frac{\omega}{\omega_{\text{thr}}}\right) \psi\left(\frac{T}{\Theta}\right) - \left(\frac{q_D}{p_F}\right)^2 J_2\left(\frac{\omega}{\omega_{\text{thr}}}\right) \varphi\left(\frac{T}{\Theta}\right) \right],$$

$$J_1\left(\frac{\omega}{\omega_{\text{thr}}}\right) = \frac{(\omega^2 + \omega_{\text{thr}}^2 + t^2) \omega_{\text{thr}}}{\sqrt{2} t^2 \sqrt{t^2 + \omega_{\text{thr}}^2 - \omega^2 + \gamma^2}} - 1, \quad (20)$$

$$J_2\left(\frac{\omega}{\omega_{\text{thr}}}\right) = \frac{\sqrt{2} \omega \omega_{\text{thr}} \gamma}{t^2 \sqrt{t^2 - \omega_{\text{thr}}^2 + \omega^2 - \gamma^2}} - 1,$$

$$t^2 = [(\omega_{\text{thr}} \mp \omega)^2 + \gamma^2]^{1/2} [(\omega_{\text{thr}} - \omega)^2 + \gamma^2]^{1/2},$$

$$\gamma = 2\gamma_0^{ep} \psi(T/\Theta),$$

$$\varphi\left(\frac{T}{\Theta}\right) = \int_0^1 \left(1 + \frac{2}{\exp(x\Theta/T) - 1}\right) x^4 dx.$$

A plot of the function  $\varphi(T/\Theta)$  is shown in Fig. 3.

<sup>4)</sup>The characteristic dimension of the p-space region where the influence of the intersection of two Bragg planes is important is proportional to  $(V_g/\epsilon_F)^2$ .

<sup>5)</sup>It is assumed in the calculation that  $\hbar\omega_D \ll \xi_p \ll \epsilon_F$ , since in the optical region the energy of the optical quantum  $\hbar\omega \approx |\xi_p - \xi_{p'}|$  satisfies these inequalities.

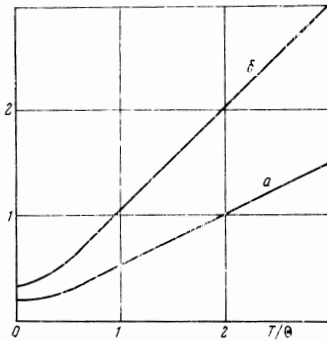


FIG. 3. The functions  $\varphi(T/\Theta)$  (a) and  $\Psi(T/\Theta)$  (b).

To the left of the maximum of the photoeffect at  $\omega_{\text{thr}} - \omega \gg \gamma$ , the functions  $J_1(\omega/\omega_{\text{thr}})$  and  $J_2(\omega/\omega_{\text{thr}})$  greatly simplify

$$J_1\left(\frac{\omega}{\omega_{\text{thr}}}\right) = \left[1 - \left(\frac{\omega}{\omega_{\text{thr}}}\right)^2\right]^{-1/2} - 1, \quad J_2\left(\frac{\omega}{\omega_{\text{thr}}}\right) = \left[1 - \left(\frac{\omega}{\omega_{\text{thr}}}\right)^2\right]^{-1/2} - 1.$$

In particular, when  $\omega \ll \omega_{\text{thr}}$  the "interband" effective collision frequencies are equal to

$$\begin{aligned} \nu_{\text{inter}}^{ee} &= \sum_g n_g \frac{\gamma_0^e g V_g m}{2\pi \hbar^3 N} \frac{(\hbar\omega)^2 + (2\pi kT)^2}{\epsilon_F^2} \left(\frac{\omega}{\omega_{\text{thr}}}\right)^2, \\ \nu_{\text{inter}}^{ep} &= \sum_g n_g \frac{\gamma_0^p g V_g m}{2\pi \hbar^3 N} \left[3\psi\left(\frac{T}{\Theta}\right) - \left(\frac{q_D}{p_F}\right)^2 \psi\left(\frac{T}{\Theta}\right)\right] \left(\frac{\omega}{\omega_{\text{thr}}}\right)^2. \end{aligned} \quad (21)$$

The presented dependences of the interband collision frequencies on  $\omega$  and  $T$  at  $\omega \ll \omega_{\text{thr}}$  correspond to relations (13) and (14) for arbitrary electron and phonon dispersion laws.

The form of the maximum of the photoeffect ( $|\omega - \omega_{\text{thr}}| \lesssim \gamma$ ) is determined by the following expression:

$$\begin{aligned} \text{Re } \sigma_g &\sim 1 / \sqrt{x + \Delta\omega}, \\ x &= \gamma / (\Delta\omega)^2 + \gamma^2, \quad \Delta\omega = \omega_{\text{thr}} - \omega. \end{aligned} \quad (22)$$

Finally, to the right of the maximum, when  $\omega - \omega_{\text{thr}} \gg \gamma$ , the interband conductivity is not connected with collisions and is given by (see<sup>[12]</sup>)

$$\text{Re } \sigma_g = e^2 g V_g / 6\pi \hbar^4 \omega \sqrt{\omega^2 - \omega_{\text{thr}}^2}. \quad (23)$$

Let us compare now the results obtained in this section with the available experimental data.

Golovashkin, Motulevich, and Shubin<sup>[15,16]</sup> observed in their experiments on aluminum and lead, in the far infrared region ( $\omega \ll \omega_{\text{thr}}$ ), a quadratic dependence of the effective collision frequency on  $\omega$ , with a coefficient that was essentially temperature-dependent. Identification of this part of the effective frequency with  $\nu_{\text{inter}}^{ep}$  leads to reasonable agreement with experiment.

The form of the maximum of the photoeffect, determined by expression (22), is close to the experimental one. The characteristic width of the maximum  $\gamma$  can be calculated by determining the coefficient  $\gamma_0^{ep}$  in formula (20) from a comparison of expressions (15) and (21) with the experimental data in the far infrared region of the spectrum.

The value of  $\gamma$  obtained in this manner at room temperature corresponds to the experimentally known<sup>[14]</sup> width of the maximum. But at helium temperature the width of the maximum for different polyvalent metals turns out to be larger by 3–10 times than given by calculation.

The reasons for this discrepancy are possibly as

follows. First, we have used an approximation in which we did not take into account the distortion of the dispersion law near the intersection of several Bragg planes. Although the contribution of such regions of  $p$ -space to the interband transitions is a quantity of higher order of smallness with respect to the parameter  $V_g/\epsilon_F$ , the number of intersections is large (for example, in fcc crystals the Bragg plane corresponding to the reciprocal-lattice vector (111) is intersected near the Fermi surface by six other Bragg planes).

If we taken into account the intersections, then it turns out that the equation  $\nabla_p \epsilon_{p+g, p} = 0$  is satisfied not on the entire Bragg plane, but only at individual points (high-symmetry points of the Brillouin zone), and therefore the maxima of the photoeffect will not be infinitely sharp even in the absence of collisions. An estimate shows that the intersections can lead to the following value of the relative width of the maximum:  $\Delta\omega/\omega_{\text{thr}} \approx 1/3$ .

Second, the reason for the large width of the maxima may be the nonlocality of the pseudopotential<sup>[17]</sup>. The matrix element of the nonlocal pseudopotential in the plane-wave representation depends not only on the difference of the momenta (i.e., of the reciprocal-lattice vectors  $g$ ), as we have assumed so far, but also on the momentum itself. From symmetry considerations it follows that  $V_g$  on the Bragg plane can depend only on the momentum projection  $p_{\parallel}$  on this plane. Near the intersection of the Fermi surface with the Bragg plane, this dependence can be represented in the form

$$V_g = V_g^0 + \alpha v_F p_{\parallel},$$

where  $\alpha$  is a dimensionless constant. The value of the energy gap  $\epsilon_{p+g, p}$  between two bands will not be a constant on the Bragg plane, and this leads to an additional width of the maximum  $\Delta\omega/\omega_{\text{thr}} \approx \alpha$ . In order to explain in this manner the experimental width of the maximum, we must assume  $\alpha = 0.3$ – $0.5$ .

**2. Alkali metals.** The theory of quantum absorption of light by alkali metals, using the model of "almost free electrons" (see, for example,<sup>[13]</sup>), has made it possible to explain more or less satisfactorily the optical properties of these metals in the infrared and visible regions of the spectrum. In particular, this theory makes it possible to determine the value of the long-wave absorption threshold  $\omega_{\text{thr}}$ , which is connected with direct interband transitions by the reciprocal-lattice vector  $g$ :

$$\omega_{\text{thr}} = g(g - 2p_F) / 2m\hbar.$$

However, numerous experiments reveal the presence in most alkali metals of an "extra" sharp absorption peak pertaining to frequencies smaller than  $\omega_{\text{thr}}$ <sup>[1]</sup>. Insofar as we know, the additional peak appears most clearly in potassium<sup>[18]</sup>. The threshold frequency of this peak  $\omega'_{\text{thr}}$  is approximately half as large as  $\omega_{\text{thr}}$ . Different attempts to explain the origin of the additional peak cannot be regarded as satisfactory<sup>[1]</sup>.

We think that it is possible to relate the additional peak with the electron transitions resulting from collisions from occupied states under the Fermi surface into a region near the Bragg plane. The following

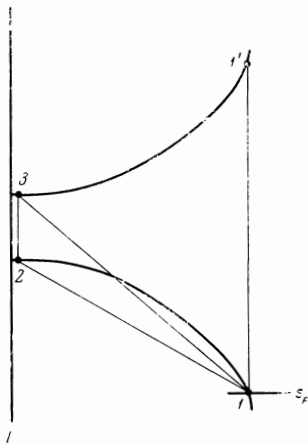


FIG. 4. Two energy bands in the plane passing through the center of the Brillouin zone perpendicular to the Bragg plane (reduceband scheme). I—Bragg plane.

process can contribute to the additional peak (see Fig. 4);

a) An electron colliding, say, with a phonon goes over from state 1 to state 2, and then executes a direct interband transition to state 3 under the influence of the electromagnetic field. The matrix element  $v_{23}$  of the latter interband transition is not small (states 2 and 3 lie near the Bragg plane), and therefore such processes lead, at the appropriate frequencies, to a noticeable increase of light absorption.

b) The electron falls in the upper band (state 3) as a result of a collision, and then returns to the initial band (state 2).

c) The foregoing two processes can interfere with a direct transition from the initial state to the final state under the influence of the collision. The threshold frequencies of the considered interband transitions with collision, equal respectively to  $(\epsilon_3 - \epsilon_1)/\hbar$  and  $(\epsilon_2 - \epsilon_1)/\hbar$ , can be regarded as equal, since the quantity  $\epsilon_3 - \epsilon_2 = 2V_g$  is exceedingly small for alkali metals<sup>6)</sup>. On the other hand, the threshold of the direct interband transitions is equal to  $\omega_{thr} = (\epsilon_1' - \epsilon_1)/\hbar$ . It is easy to verify that (16) leads to  $\omega'_{thr} = \omega_{thr}/2$  at  $\hbar\omega_{thr} \ll \epsilon_F$  and  $\hbar\omega'_{thr} \gg V_g$ .

d) At frequencies  $\omega > \omega'_{thr}$ , the frequency dependence of the "intraband" contribution to the electric conductivity also changes sharply, since the approach of the final state of the "intraband" transition to the Bragg plane changes strongly the velocity of the electron in this state as well as the matrix element of the transition.

The conductivity  $\text{Re } \sigma'_g$  corresponding to the additional peak can be calculated by using expression (8). It is probable that, just as in polyvalent metals, the most effective in the spectral region under consideration are electron-phonon collisions, and we therefore confine ourselves to these collisions only. Retaining only the lowest order terms in  $\gamma$  and  $V_g$ , we obtain

$$\text{Re } \sigma'_g = \frac{\gamma_0^2 g V_g e^2 q D^2}{6\pi \hbar^3 p_F^2} \varphi\left(\frac{T}{\Theta}\right) \frac{\omega - \omega'_{thr}}{\omega^3}, \quad \omega > \omega'_{thr} \quad (24)$$

$\omega'_{thr} = 1/2 \omega_{thr}$ ,

where  $\varphi(T/\Theta)$  is given by formula (21).

<sup>6)</sup>For example, Ham's band calculation [20] give the following value for the Fourier component of the pseudopotential of Na, namely  $V_{110} = 0.1$  eV.

We note that the form of the function, which determines the temperature dependence of the conductivity in the additional peak, and even its sign depends strongly on the choice of the model of the electron-phonon interaction. Insofar as we know, it is impossible at present to give preference to any of the existing models<sup>[19]</sup>. In the derivation of (24) we used the following expression for the matrix element of the electron-phonon interaction in the plane-wave representation<sup>7)</sup>:

$$B_{p_1 p_2 q} = \Delta \Omega^{-1/2} q^{1/2} \delta_{p_2 - p_1 + q}.$$

The noticeable dependence of the height of the additional peak on the temperature agrees with experiment<sup>[18]</sup>.

The interband conductivity  $\text{Re } \sigma_g$  connected with the direct band-band transitions, at frequencies much lower than the upper threshold frequency for these transitions, is equal to<sup>[13]</sup>

$$\text{Re } \sigma_g = \frac{g V_g^2 e^2}{12\pi \hbar^4} \frac{\omega - \omega_{thr}}{\omega^3}, \quad \omega > \omega_{thr}. \quad (25)$$

From a comparison of expressions (24) and (25) we see that the ratio of the maximum values of the conductivity for both bands is of the order of

$$\frac{\text{Re } \sigma'_{max}}{\text{Re } \sigma_{max}} \approx \frac{\hbar \gamma_0^2}{V_g} \varphi\left(\frac{T}{\Theta}\right).$$

In alkali metals, the values of  $V_g$  are exceedingly small, and therefore the ratio of the heights of the two bands is close to unity (in potassium, the additional peak at room temperature is higher than the principal peak connected with the direct interband transitions).

The frequency dependence of the conductivity in the additional peak and its threshold frequency, determined by expressions (24), are in good agreement with experiment<sup>[18]</sup>.

In conclusion, the author is deeply grateful to R. N. Gurzhi for directing this work, and also to G. P. Motulevich and A. I. Golovashkin for a discussion of the results of the work and for valuable remarks.

Note added in proof (13 January 1970). In a recent paper, H. Bitter and E. Gerlach (J. Phys. Chem. Sol. 30, 659, 1969) explain the additional peaks of absorption in alkali metals, just as in our case, as being due to indirect interband transitions of electrons in the  $\mathbf{p}$ -space region close to Bragg planes. The electric conductivity at the peak was calculated, however, without allowance for the contribution of the intraband transitions and the interference terms. The frequency dependence of the electric conductivity differs from that obtained by us. The reason for the discrepancy lies apparently in the fact that the authors of the cited paper used an incorrect expression for the energy near the Bragg plane.

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