ABSORPTION OF X RAYS IN METALS

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The effect of interelectron interaction on the absorption of x rays is considered for a simple model of a metal. It is shown that no electron or hole bound states are possible. The spectrum near the absorption edge is determined.

THE absorption of short-wave light is usually described as a transition of an electron between energy bands in a crystal. The minimum frequency $\omega = E_f - E_i$ of a transition to the lowest of the unfilled states is called the absorption edge, and the absorption coefficient experiences a jump at this frequency. For x rays, E_i constitutes a narrow band corresponding to an internal atomic level. In metals the absorption edge corresponds to the transition from this level to the Fermi surface.

In a frequency region which is not too far from the absorption edge (when the photoelectron energy is comparable with the Fermi energy), the interaction between the electrons cannot be regarded as a small effect, and in principle the single-electron picture cannot be employed. However, in a qualitative treatment it is possible to attempt to take into account the interelectron interaction by perturbation theory. Such an account consists intuitively of first considering of the entire collision between the photoelectron and the Fermi electrons that cause its "damping." It is then necessary to take into account the contribution of the processes at which two or more photoelectrons or other excitations are produced, and also the influence of the interaction between the photoelectron and the "hole" in the shell of the ionized atom.

We shall first establish the connection between the absorption coefficient and the polarization operator in the crystal (this question arises because we cannot use the concept of macroscopic electromagnetic fields in the case of short waves, see[1], Secs. 28, 29). We shall then consider, for the simple model, the corrections to the expression for the interband transition.

1. ABSORPTION COEFFICIENT

Let us consider a system of electrons in a periodic field, through which passes a beam of x rays of frequency ω. The interaction in such a system can be written in the form

$$e \int j_i(\mathbf{r}, t) A_i(\mathbf{r}, t) d^3r,$$

where $A_i(\mathbf{r}, t)$—vector potential of the total electromagnetic field in the system ($\hbar = 1$, $c = 1$, a gauge with $\varphi = 0$ is used throughout). Then the field equations in the medium follow immediately from the Dyson equation for the photon Green's function. We write them for the time-dependent Fourier component $E_i(\mathbf{r}, \omega)$:

$$\left(\frac{\partial^2}{\partial x_i \, \partial x_k} - \delta_{ik} \frac{\partial^2}{\partial x_n^2} - \delta_{ik} \omega^2 \right) E_k(\mathbf{r}, \omega)$$

$$- \omega^2 \int P_{ik}(\mathbf{r}, \mathbf{r}', \omega) E_k(\mathbf{r}', \omega) d^3r' = 0. \qquad (1)$$

Here $P_{ik}(\mathbf{r}, \mathbf{r}', \omega)$—polarization operator of the crystal; in view of the translational symmetry, $P_{ik}(\mathbf{r}, \mathbf{r}', \omega) = P_{ik}(\mathbf{r} + \mathbf{a}, \mathbf{r}' + \mathbf{a}, \omega)$, where $\mathbf{a}$—lattice vector.

Let the crystal have the form of a plane-parallel plate of thickness L (Fig. 1); let us find the attenuation of a plane wave $E_y^{(0)} e^{i\omega x}$, passing through the plate. We choose L such that this attenuation is small. Introducing the induction

$$D_i(\mathbf{r}, \omega) = E_i(\mathbf{r}, \omega) + \int P_{ik}(\mathbf{r}, \mathbf{r}', \omega) E_k(\mathbf{r}', \omega) d^3r',$$

we rewrite (1) in the form

$$(\Delta + \omega^2) D_i(\mathbf{r}, \omega)$$

$$= \omega^2 \int \left(\frac{\partial^2}{\partial x_i \, \partial x_k} - \delta_{ik} \frac{\partial^2}{\partial x_n^2} \right) P_{kl}(\mathbf{r}, \mathbf{r}', \omega) E_l(\mathbf{r}', \omega) d^3r'. \quad (2)$$
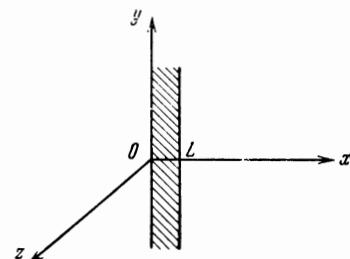

FIG. 1

We are interested in the solution of this equation in vacuum (where $D = E$), to the right of the plate, where by assumption it should differ from the incident wave. To calculate the correction we can put in the right side of (2) $E = (0, E_y^{(0)} e^{i\omega x}, 0)$, after which we get

$$D_y^{(1)}(\mathbf{r}, \omega) = E_y^{(1)}(\mathbf{r}, \omega)$$
$$= \frac{E_y^{(0)}}{4\pi} \int \frac{e^{i\omega|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} f_{yy}(\mathbf{r}_1, \mathbf{r}', \omega) e^{i\omega x'} d^3 r_1 d^3 r', \qquad (3)$$

$$f_{yy}(\mathbf{r}, \mathbf{r}', \omega) = \omega^2 \sum_{k=1}^{3} \left(\frac{\partial^2}{\partial x_k \partial y} - \delta_{ky} \Delta \right) P_{ky}(\mathbf{r}, \mathbf{r}', \omega). \qquad (4)$$

In addition to the main beam, there will be emitted from the crystal scattered beams which satisfy the Laue condition (and also incoherently scattered light). To exclude these, let us average (3) in a plane perpendicular to the transmitted beam, i.e., with respect to the variables y and z. Using the relation

$$\iint \frac{e^{i\omega|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} dy\, dz = \frac{2\pi i}{\omega} e^{i\omega(x-x_1)}, \qquad \omega \neq 0,$$

we get

$$\overline{E_y^{(1)}(\mathbf{r}, \omega)} = E_y^{(1)}(x, \omega)$$
$$= \frac{iE_y^{(0)}}{2\omega} e^{i\omega x} \int f_{yy}(\mathbf{r}_1, \mathbf{r}', \omega) e^{i\omega(x'-x_1)} d^3 r_1 d^3 r'. \qquad (5)$$

The quantity $P_{ik}(\mathbf{r}, \mathbf{r}', \omega)$ can be represented in the form

$$P_{ik}(\mathbf{r}, \mathbf{r}', \omega) = \sum_b \int \frac{d^3 k}{(2\pi)^3} P_{ik}^b(\mathbf{k}, \omega) e^{i\mathbf{k}\mathbf{r}} e^{-i(\mathbf{k}+2\pi\mathbf{b})\mathbf{r}'},$$

$$P_{ik}^b(\mathbf{k}, \omega) = \int P_{ik}(\mathbf{r}, \mathbf{r}', \omega) e^{-i\mathbf{k}\mathbf{r}} e^{i(\mathbf{k}+2\pi\mathbf{b})\mathbf{r}'} d^3 r\, d^3 r'. \qquad (6)$$

Substituting (4) and (6) in (5), we obtain

$$E_y^{(1)}(x, \omega) = \frac{1}{2} i\omega^3 P_{yy}^0(\mathbf{q}, \omega) E_y^{(0)} e^{i\omega x} L, \qquad \mathbf{q} = (\omega, 0, 0)$$

and the ratio of the intensities of the incident and transmitted beams is

$$I / I_0 \approx 1 - \omega^3 \mathrm{Im}\, P_{yy}^0(\mathbf{q}, \omega) L. \qquad (7)$$

From this we get the "absorption coefficient"

$$\sigma = \omega^3 \mathrm{Im}\, P_{yy}^0(\mathbf{q}, \omega), \qquad (8)$$

where, in accordance with (6)

$$P_{yy}^0(\mathbf{q}, \omega) = \int P_{yy}(\mathbf{r}, \mathbf{r}', \omega) e^{i\omega(x-x')} d^3 r\, d^3 r'. \qquad (9)$$

The formula for the interband transition is obtained from (8) by using the expression for the polarization operator in the zeroth approximation:

$$P_{ik}^{(0)}(\mathbf{r}, \mathbf{r}', \omega) = -ie^2 \int \frac{d\omega_1}{2\pi} \left(\frac{\partial}{\partial x_i} G^0(\mathbf{r}, \mathbf{r}', \omega_1) \right)$$
$$\times \left(\frac{\partial}{\partial x_k'} G^0(\mathbf{r}', \mathbf{r}, \omega_1 - \omega) \right), \qquad (10)$$

where G^0—Green's function of the electron in a periodic field.

$$G^0(\mathbf{r}, \mathbf{r}', \omega) = \sum_s \int \frac{d^3 k}{(2\pi)^3} \frac{\psi_{sk}(\mathbf{r}) \psi_{sk}^*(\mathbf{r}')}{\omega - \varepsilon_s(\mathbf{k}) \pm i0}. \qquad (11)$$

Here $\psi_{sk}(\mathbf{r})$—Bloch functions; the plus sign in the denominator is taken for the free states and the minus sign for the occupied states.

After integration with respect to ω_1, there are left in (10) only those terms containing products of the functions of the occupied and free states. In the study of a small range of frequencies near the edge, the essential transition is from a single internal level, which we shall now take into account. Let the term of the sum in (11) with $s = 0$ correspond to this level. From (8)—(11) it follows that

$$\sigma^{(0)} = \pi e^2 \omega^3 \sum_s \int \frac{d^3 k}{(2\pi)^3} |M_{sk,0}|^2 \delta(\varepsilon_s - \varepsilon_0 - \omega), \qquad (12)$$

$$M_{sk,0} = \int \psi_{sk}^* (\boldsymbol{\alpha}\nabla) \psi_0 e^{i\mathbf{q}\mathbf{r}} d^3 r. \qquad (13)$$

The summation in (12) is carried out only over the free state.

If we assume approximately that the matrix element of the transition depends only on the energy, then $\sigma^{(0)} \sim N(E) P(E)$, where N—density of states, $P = |M|^2$—transition probability, and $E = \omega - \omega_{\lim}$. When account is taken of the finite lifetime of the "hole" on the internal level, the δ-function in (12) is replaced by the dispersion factor

$$\frac{1}{\pi} \frac{\Gamma}{(\varepsilon_s - \varepsilon_0 - \omega)^2 + \Gamma^2}$$

where 2Γ—width of the internal level.

2. CORRECTION TERMS

According to (12), absorption in the metal begins jumpwise at a frequency equal to the sum of the Fermi energy and the energy of the internal level. To investigate the corrections to this expression, let us consider a simple model, in which there are only two bands—the internal level and the "conduction band," in which the energy assumes positive values. The electrons in the conduction band are regarded as free (i.e., the periodic field of the ions is taken into consideration only as the average positive charge that ensures neutrality of the system). A weak Coulomb interaction is assumed between the electrons ($e^2/v \ll 1$, where v—velocity on the Fermi surface). The effects of the anisotropy and of the interaction with the lattice vibrations on the x-ray absorption were investigated previously (see, for example,[2]).

The first-order perturbation-theory diagrams
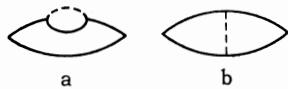
FIG. 2

are shown in Fig. 2. Before we proceed to estimate these diagrams, we make the following remarks: inasmuch as we are considering an inhomogeneous system, we must write down in the coordinate representation expressions corresponding to different diagrams, and then obtain with the aid of (8) and (9) the corrections to the absorption coefficient. However, in the model which we have assumed, it is necessary to retain in those electron Green's functions, whose arguments contain the photon frequency ω, only the "hole" term in the expansion (11), corresponding to the internal level; in the denominators of these terms, the large value of ω is offset by the energy ϵ_0 of the internal level. To the contrary, if the argument of the Green's function does not contain ω, we are left only with the "electronic" term corresponding to the conduction band, and their denominators do not contain the large quantity ϵ_0. Therefore the corrections to σ are similar to the expressions for the diagrams in the momentum representation.

For example, for the diagram of Fig. 2b we have

$$-e^2 \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} \int \frac{d^3p_1}{(2\pi)^3} \int \frac{d^3p_2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} M^*_{p_1,0} [\omega_1 - \varepsilon(p_1)$$

$$+ i0 \, \text{sign} \, (p_1 - p_F)]^{-1} (\omega_1 - \nu - i0)^{-1} D(k, \omega_2)$$

$$\times [\omega_1 - \omega_2 - \varepsilon(p_2) + i0 \, \text{sign} \, (p_2 - p_F)]^{-1}$$

$$\times (\omega_1 - \omega_2 - \nu - i0)^{-1} M_{0,p_2} \int \psi_{p_1}^*(r_1) e^{ikr_1} \psi_{p_2}(r_1) \, d^3r_1$$

$$\times \int \varphi_0^*(r_2) e^{-ikr_2} \varphi_0(r_2) \, d^3r_2. \tag{14}$$

Here ψ_p—electron functions, φ_0—hole functions; $\nu = \omega + \epsilon_0$. If we choose a plane wave as the conduction-band function ψ_p, then the integral with respect to d^3r_1 yields $(2\pi)^3 \delta(p_2 - p_1 + k)$. The integral with respect to d^3r_2 can be regarded as independent of k. The matrix elements $M_{p,0}$ are determined from (13), where, in accordance with the radiation condition, the asymptotic value of $\psi_{ks} = \psi_p$ must be chosen in the form of a sum of a plane and converging wave.

The function $D(k, \omega)$ is used in place of the Coulomb expression $4\pi e^2/k^2$ to describe the effective interaction between the electrons, which, as is well known, is of the form

$$D(k, \omega) = 4\pi e^2 / [k^2 + \varkappa^2 \Pi(k, \omega)],$$

$$\Pi(k, \omega) = 1 - \frac{\omega}{2vk} \ln \left| \frac{\omega + vk}{\omega - vk} \right| + i\pi \frac{|\omega|}{2vk} \theta(vk - |\omega|),$$

$$k \ll p_F. \tag{15}$$

We now proceed to estimate the corrections and consider first the diagram 2b. The interaction between the extracted electron and the "hole" can lead in principle to the appearance of absorption lines corresponding to transitions to the discrete levels of this system. The formation of such "bound states" in the metal is hindered by the screening of the interaction by the conduction electrons. The screening is established within a time on the order of $1/\omega_0 = \sqrt{3\pi}(e^2/v)^{-1/2}/4\epsilon_F$. On the other hand, the interaction itself lasts a finite time, which at any rate does not exceed (in order of magnitude) the lifetime $1/\Gamma$ of the internal level. We shall show presently that in those cases when the screening does not have time to be established, the contribution of the diagram is small, and no discrete levels arise.

The correction to σ from the diagram of Fig. 2b is the imaginary part of (14). In the case of a Coulomb interaction (i.e., $D = 4\pi e^2/k^2$), the diagram would have a singularity $\ln^2[(\nu - \epsilon_F)/\epsilon_F]$ at the edge frequency. We shall therefore obtain estimates only for this frequency, $\nu = \epsilon_F$. Actually the integral (14) is always finite even in the case of Coulomb interactions, owing to the finite width of the internal level. Let $\gamma = \Gamma/\epsilon_F$. Then when $\gamma \ll 1$ the integral will have an order of magnitude $e^2 (\ln \gamma)^2/v$, and when $\gamma \gg 1$ the order of magnitude is $e^2/v\gamma^{1/2} = e^2 \sqrt{m/\Gamma}$.

We now turn to the complete expression with the function $D(k, \omega)$ determined from (15). When $\Gamma \ll \omega_0$, the screening has time to become established, and the order of magnitude of the diagram (Fig. 2b) is $(e^2/v)^{3/2}$. In the opposite case, $\Gamma \gtrsim \omega_0$, the diagram has the order of the Coulomb integral, i.e., $e^2 \sqrt{m/\Gamma} < e^2/v$ for large γ and $e^2 (\ln \gamma)^2/v$ for small γ. This latter quantity is also small, since γ cannot be smaller than $\omega_0/\epsilon_F \approx \sqrt{e^2/v}$. The attraction by the hole is therefore always insignificant in our model.

It is known that the Coulomb interaction in a metal should be sufficiently well screened. Otherwise the metal will be generally unstable and turn into a dielectric[3]. Actually the Bohr radius for quasiparticles should be larger than the Debye radius. This condition is a result of the inequality $e^2/v \ll 1$ which we have used.

Since vertex-type inserts corresponding to interaction with an internal level can be neglected, the corrections to the absorption coefficient are determined by the corrections to the electron Green's function. We write the latter in the form

$$[\omega - \varepsilon(p) - \Sigma_1(\omega, p) \pm i\Sigma_2(\omega, p)]^{-1}.$$

In the model in question the value of Σ is small

and is determined by the insert in the electron line, shown in Fig. 2a. Σ_1 can be included in ϵ, and the absorption coefficient takes the form

$$\sigma = \text{const} \cdot \text{Im} \int_{\varepsilon_F}^{\infty} \frac{P(\varepsilon)N(\varepsilon)\,d\varepsilon}{\nu - \varepsilon + i\Sigma_2(\nu,\sqrt{2m\varepsilon})}. \qquad (16)$$

Using the spectral representation of the function $D(k,\omega)$, we obtain

$$\Sigma_2(\nu,p) = \text{Im}\, i \int \frac{D(k,\omega)}{\nu - \omega - \varepsilon_1} \frac{d\omega\, d^3k}{(2\pi)^4}$$

$$= \int_{\varepsilon_F < \varepsilon_1 < \nu} \frac{d^3k}{(2\pi)^3} \text{Im}\, D(k, \nu - \varepsilon_1). \qquad (17)$$

Here $\varepsilon_1 \approx \epsilon(p) + \nu k$.

Near the absorption edge, i.e., for ν close to ϵ_F, the region of importance in (17) is $k \gtrsim \kappa$, and then $\nu - \epsilon_F \ll \nu\kappa$. According to (16) we have

$$\sigma \sim \frac{1}{\pi}\left(\frac{\pi}{2} + \tan^{-1}\frac{c}{\nu - \varepsilon_F}\right), \quad \nu > \varepsilon_F, \quad c^{-1} \approx (e^2/\nu)\,\omega_0.$$

The absorption is reduced because of the attenuation of the photoelectrons with energy larger than ϵ_F.

For ν close to $\epsilon_F + \omega_0$, it is necessary to take into account in (17) the residue in the plasma pole. We have

$$\Sigma_2 = -\frac{e^2}{\nu} \frac{\omega_0}{2\pi} \ln \left| \frac{\sqrt{\varepsilon} + \sqrt{\nu - \omega_0}}{\sqrt{\varepsilon} - \sqrt{\nu - \omega_0}} \right| \theta(\nu - \varepsilon_F - \omega_0).$$

This expression is valid when $|\epsilon - \nu| \lesssim \omega_0$. At the

frequency $\nu = \nu_0 = \epsilon_F + \omega_0$, the absorption experiences a jump (of order $\sqrt{e^2/\nu}$ relative to the total width), and near the jump $\sigma \sim -x \ln x$, where $x = (\nu - \nu_0)/\nu_0$, $\nu > \nu_0$. The absorption is increased by the transitions in which plasma oscillation is excited in addition to the photoelectron. The probability of transitions were calculated by Sobel'man and Feĭnberg[4].

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