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SOME OPTICAL EFFECTS OF PLASMA OSCILLATIONS IN A SOLID

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Three optical effects involving "plasmons" (collective oscillations of electrons in a solid) are considered: (a) excitation of a plasmon by absorption of an x-ray quantum and its effect on the structure of the x-ray absorption edge, (b) Raman scattering by a plasmon, (c) absorption of light of the plasmon frequency. The cross sections for all three processes are large.

A LTHOUGH data on characteristic energy losses by fast electrons in a solid may be explained semiquantitatively on the basis of the concept of collective electron oscillations,^{1,2} the question of the reality of these oscillations cannot be considered to have been completely cleared up. It therefore seems useful to consider other effects, and in particular optical ones. Two types of collective oscillations are possible in a "plasma" of free electrons in a solid – optically active ones capable of absorbing and emitting light, and optically inactive ones. However, indirect interaction with light is possible for oscillations of both types. In this article we

shall consider the following processes:

1. Excitation of a plasmon by the absorption of an x-ray quantum (this process is important for the structure of the absorption edge).

2. Excitation of a plasmon by inelastic scattering of a photon (Raman scattering).

3. Absorption of light of frequency of an optically-inactive plasma oscillation due to the virtual excitation of one of the inner electrons.

All these processes are due to the Coulomb interaction of a plasmon with the inner electrons. As will be shown below their probabilities are quite appreciable. The effects in which we are interested are not associated with plasma inhomogeneity; therefore, in order to make rough estimates, we can consider that the plasma oscillation has the form of a plane wave

$$\rho(\mathbf{r}, t) = \rho e^{i(\mathbf{k}\mathbf{r} - \boldsymbol{\omega}t)}; \ \rho = (\hbar k^2 \rho_0 / 2\omega m V)^{3/2};$$
$$\omega^2 = \omega_p^2 + \langle v^2 \rangle k^2; \ \omega_p^2 = 4\pi \rho_0 e^2 / m, \tag{1}$$

where V is the normalization volume; ρ_0 and $\langle v^2 \rangle$ are the density and the mean-squared velocity of plasma electrons. The wave number k is bounded from above by the condition $k \lesssim k_c$, and we shall assume that $\langle v^2 \rangle k_c^2 \ll \omega_p^2$, although in actual fact the inequality is satisfied with but a small margin. As a rule $\hbar \omega_p \lesssim me^4/\hbar^2$. The energy of the inner electrons which is of order of magntidue $Z_{eff}^2 me^4/\hbar^2$ already at $Z_{eff} \gtrsim 3$ is large compared to $\hbar \omega$. Thus, during the time $\hbar/Z_{eff}^2 me^4$ (period of motion of an inner electron) $\rho(\mathbf{r}, t)$ practically does not change. This allows us to treat the motion of the inner electrons keeping the configuration of the outer electrons fixed, and to treat the excitation of a plasmon by introducing the perturbing potential*

$$U(\mathbf{r}, t) = U(\mathbf{r}) e^{-i\omega t} = e \int \frac{\rho e^{i(\mathbf{kr}' - \omega t)}}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \frac{4\pi e\rho}{k^2} e^{i(\mathbf{kr} - \omega t)}.$$
(2)

For the sake of definiteness we shall assume that the inner electron is in the K-shell (it is, of course, not difficult to generalize this). In making rough estimates, it is sufficient simply to replace Z by Z_{eff} .

1. THE EDGE OF THE X-RAY ABSORPTION BAND

Let us consider an electron in the K shell which, as a result of absorbing a photon $\hbar\omega_0$, goes over into a state in the continuum (propagationvector \mathbf{k}_f), while a plasmon $\hbar\omega$ is excited (propagation-vector \mathbf{k}). The effective cross section of such a process is equal to

$$\sigma = \frac{2\pi V}{\hbar c} \int |M|^2 \,\delta\left(E - E_0\right) \frac{Vd \,\mathbf{k}_f}{(2\pi)^3} \frac{Vd \,\mathbf{k}}{(2\pi)^3} \;; \tag{3}$$

$$M = \sum_{n} \left\{ \frac{W_{fn}^{*} V_{n0}}{(\varepsilon_{0} + \hbar \omega_{0} - \varepsilon_{n})} + \frac{V_{fn} W_{n0}^{*}}{(\varepsilon_{0} - \hbar \omega - \varepsilon_{n})} \right\}.$$
 (4)

Here V is the operator for the interaction of the electron with radiation, W = eU is the operator for the interaction with the plasmon; ϵ_0 , ϵ_n are the energies of the electron in the initial and the intermediate states. The summation in (4) is carried out over the discrete states and the states of the continuum lying beyond the Fermi boundary. The principal contribution comes from the states in the continuum, and therefore only these states are taken into account below. Of particular importance are the states with $\epsilon_n \approx \epsilon_0 + \hbar \omega$ for which the denominator of the first term in (4) is small. One may neglect the second term in (4) since $|\epsilon_0| = (me^4/2\hbar^2)Z^2 \gg \hbar\omega$ and the denominator $(\epsilon_0 - \hbar \omega - \epsilon_n)$ is large for all ϵ_n . The matrix element V_{n0} differs from zero only if in the intermediate state l = 1, i.e.,

$$V_{n0} = V_{100}^{\times 1m} = ie\omega_{\times 1;10} \ \sqrt{\frac{2\pi\hbar}{\omega_0 V}} \frac{\sqrt{4\pi}}{3} Y_{1m}^* (\theta_e, \varphi_e) \int R_{\times 1} r^3 R_{10} dr,$$
(5)

where **e** is the polarization vector of the photon. The radial function of the initial state R_{10} differs from zero only near the nucleus for $r \leq \hbar^2/me^2 Z$ = a_0/Z . Therefore one can take for the radial function $R_{\kappa 1}$ for the state of wave number κ a function from the continuum of the motion of an electron in the Coulomb field due to a charge Ze. It is in this approximation that the same integral is evaluated in the theory of the photo-effect:³

$$\int R_{\varkappa 1} r^3 R_{10} dr = \frac{2^4 Z^3 \exp\left(-2\frac{Z}{\varkappa'} \arctan \frac{\varkappa'}{Z}\right)}{(Z^2 + \varkappa'^2)^{4/3} \left[1 - \exp\left(-2\pi Z/\varkappa'\right)\right]^{1/3}} \sqrt{\varkappa} a_0^2.$$
(6)

Here κ' is the dimensionless wave number (in atomic units). For small values of κ' which are of interest to us, $\kappa'/Z \ll 1$ and

$$V_{100}^{*1m} = i \left(\frac{4}{e}\right)^2 \frac{\sqrt{4\pi}}{3} Y_{1m}^{\bullet}(\theta_{\rm e}, \,\varphi_{\rm e}) \, e \left(\frac{2\pi\hbar\omega_0 \varkappa}{V}\right)^{l_{\rm e}} \frac{a_0^2}{Z^2} \,. \tag{7}$$

Here we have set

$$\omega_{\mathbf{x}\mathbf{1};\mathbf{10}} = \hbar^{-1} \left(\hbar^2 \mathbf{x}^2 / 2m - \varepsilon_0 \right) = \omega_0$$

For the evaluation of $W_{fn}^* = W_{k_f;\kappa_{1m}}^*$ we can take for the functions ψ_{k_f} and $\psi_{\kappa_{1m}}$ the free electron wave functions since the inner region in which it is necessary to take into account the field of the nucleus is not of great importance here. On setting $\psi_{k_f} = V^{-1/2} \exp(ik_f \cdot \mathbf{r})$, we obtain from (2)

^{*}In the original Hamiltonian one may neglect the terms $p^2/2m$ corresponding to the outer electrons. In this case the coordinates of the outer electrons will appear as parameters in the Schrödinger equation for the inner electrons. It is this fact which allows one to treat the excitation of a plasmon by introducing the potential (2) (see Bethe, $3 \S 15$). It is interesting to note that the effects under discussion are analogous to the interaction with light of molecular vibrations. Thus, process 1 corresponds to the vibrational structure of the absorption band, process 2 to Raman scattering, and process 3 to infra-red absorption.

$$W_{\mathbf{k}_{f};\mathbf{x}_{1m}} = \frac{4\pi\rho}{k^{2}} \frac{e^{2}}{V\overline{V}} \int \exp\left(-i\,\mathbf{k}_{f}\mathbf{r} - i\,\mathbf{k}\mathbf{r}\right) R_{\mathbf{x}_{1}}\left(r\right) Y_{1m}(\theta,\,\varphi)\,d\,\mathbf{r}.$$
(8)

In the expansion of the factor $\exp(-i\mathbf{p}\cdot\mathbf{r})$ with $\mathbf{p} = \mathbf{k} + \mathbf{k}_{f}$ into spherical waves, the term with $\boldsymbol{\ell} = 1$ is important, and is given by

$$-i\frac{4\pi}{p}\sqrt{\frac{\pi}{2}}R_{p1}\sum_{m'}Y_{1m'}^{\bullet}(\theta,\varphi)Y_{1m'}(\theta_{\mathfrak{p}},\varphi_{\rho});$$

$$R_{p1}=-\sqrt{\frac{2}{\pi}}\frac{d}{dr}\frac{\sin pr}{pr}.$$
(9)

Substituting (9) into (8) we obtain

$$W^{*}_{\mathbf{k}_{f};\mathbf{x}1m} = -i \frac{4\pi\rho e^{2}}{k^{2}} \left(\frac{8\pi^{3}}{V}\right)^{1/2} \frac{\delta(\rho-x)}{\rho} Y_{1m}(\theta_{\rho}, \varphi_{\rho}).$$
(10)

Thus, according to (1), (4), and (10)

$$M \sim \sum_{m} Y_{1m}^{\bullet}(\theta_{e}, \varphi_{e}) Y_{1m}(\theta_{p}, \varphi_{p}) \int \frac{\delta(x-p) V \overline{x} dx}{p(\varepsilon_{0}+\hbar\omega_{0}-\hbar^{2}x^{2}/2m)}$$
$$= \frac{3}{4\pi} \frac{ep}{p} \frac{1}{V \overline{p}(\varepsilon_{0}+\hbar\omega_{0}-\hbar^{2}p^{2}/2m)}; \qquad (11)$$

$$\sigma = \left(\frac{4}{e}\right)^4 e^2 \hbar \omega \omega_0 \frac{e^2}{\hbar c} \frac{a_0^4}{4\pi Z^4}$$

$$\times \int \frac{\cos^2 \theta_{\mathbf{k}+\mathbf{k}_f,\mathbf{e}} \delta \left(E-E_0\right) d \mathbf{k}_f d \mathbf{k}}{k^2 |\mathbf{k}+\mathbf{k}_f| \left\{\varepsilon_0 + \hbar \omega_0 - \hbar^2 \left(\mathbf{k}+\mathbf{k}_f\right)^2 / 2m\right\}^2} .$$
(12)

From the law of conservation of energy it follows that

$$\varepsilon_0 + \hbar \omega_0 = \hbar \omega + \hbar^2 k_f^{0/2} m, \ \delta \left(E - E_0 \right) = \left(m / \hbar^2 k_f \right) \delta \left(k_f - k_f^0 \right)$$

Moreover, the approximation employed by us requires that $\hbar^2 k_f^{02}/2m \gg \hbar\omega$ should hold, so that $k_f^0 \gg k_c$. Therefore we can put in (12)

$$\cos^2\theta_{\mathbf{k}+\mathbf{k}_f,\mathbf{e}} \approx \cos^2 \theta_{\mathbf{k}_f,\mathbf{e}}, |\mathbf{k}_f + \mathbf{k}| \approx k_f,$$
$$\varepsilon_0 + \hbar\omega_0 - \hbar^2 (\mathbf{k} + \mathbf{k}_f)^2 / 2m \approx \hbar\omega.$$

On setting also $\hbar\omega_0 \approx Z^2 m e^4/2\hbar^2$ we obtain

$$\sigma = \frac{2\pi}{3} \left(\frac{4}{e}\right)^4 \frac{e^2}{\hbar c} \left(\frac{me^4}{\hbar^3 \omega}\right) \frac{a_0^2}{Z^2} (a_0 k_c). \tag{13}$$

Let us compare (13) with the cross section for the ordinary photo-effect evaluated in the same approximation (cf. Bethe³):

$$\sigma_0 = \frac{2\pi^2}{3} \left(\frac{4}{e}\right)^4 \frac{e^2}{\hbar c} \frac{a_0^2}{Z^2}.$$
 (14)

Since $a_0k_c \sim 1$ we have $\sigma \sim \sigma_0$.

It is easy to generalize formulas (13) and (14) to the case when the level density of final states dk_f/dE is an arbitrary function (it is customary to explain the structure of the absorption edge just by such a non-uniformity of the level density⁴):

$$\sigma = \frac{2\pi}{3} \left(\frac{4}{e}\right)^4 \left(\frac{e^2}{\hbar c}\right)^2 \left(\frac{me^4}{\hbar^3 \omega}\right) \frac{a_0^2}{Z^2} a_0 k_c \hbar c \alpha(E') \left(\frac{2E' \hbar^2}{me^4}\right)^{1_*};$$
$$E' = \hbar \omega_0 - \hbar \omega - \frac{Z^2 me^4}{2\hbar^2}; \qquad (15)$$

$$\sigma_0 = \frac{2\pi^2}{3} \left(\frac{4}{e}\right)^4 \left(\frac{e^2}{\hbar c}\right)^2 \frac{a_0^2}{Z^2} \quad \hbar c \alpha \left(E\right) \left(\frac{2E\hbar^2}{me^4}\right)^{1/2};$$

$$E = \hbar \omega_0 - \frac{Z^2 me^4}{2\hbar^2}. \tag{16}$$

2. RAMAN SCATTERING

Let ω_0 and \mathbf{e}_0 be the frequency and the polarization vector of the incident photon, and ω' , \mathbf{e}' those of the scattered photon. The matrix element which determines the probability of excitation of a plasma oscillation by the scattering of the photon is equal to (we have here omitted the terms whose denominators are large)

$$M = \sum_{n,k} \frac{V_{0h}^* W_{kn}^* V_{n0}}{(\varepsilon_0 + \hbar \omega_0 - \varepsilon_n) (\varepsilon_0 + \hbar \omega_0 - \varepsilon_k - \hbar \omega)}.$$
 (17)

We assume that $\hbar\omega_0$ is close to $|\epsilon_0|$. In this case, as before, the main role is played by the states of the continuum with energies $\hbar^2 \kappa_1^2/2m$, $\hbar\kappa_2^2/2m \ll Z^2me^4/\hbar^2$. Therefore $V_{n\theta}$ and V_{0n}^* are evaluated in exactly the same way as in the preceding section. For W_{kn}^* we shall obtain instead of (8)

$$W_{kn}^{\bullet} = W_{\mathbf{x}_{1}1m'}^{\bullet \mathbf{x}_{1}1m'} = \frac{4\pi\rho e^{2}}{k^{2}} \int R_{\mathbf{x}_{1}1}(r) R_{\mathbf{x}_{1}1}(r)$$

$$\times Y_{1m'}^{\bullet}(\theta, \varphi) Y_{1m'}(\theta, \varphi) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}.$$
(18)

We expand the function $R_{\kappa 1}Y_{1m} = \psi_{\kappa 1m}$ into plane waves:

$$\psi_{\mathbf{x}\mathbf{1}m} = \int a_{\mathbf{p}} e^{i\mathbf{r}\mathbf{p}} d\mathbf{p};$$

$$a_{\mathbf{p}} = -\frac{4\pi i}{(2\pi)^{s}p} \sqrt{\frac{\pi}{2}} \delta(\mathbf{x}-p) V_{\mathbf{1}m}(\theta_{\mathbf{p}}, \varphi_{\mathbf{p}}). \tag{19}$$

Then

$$W_{kn}^{*} = \frac{\rho e^{2}}{8\pi^{2}k^{2}} \int \frac{\delta(x_{1} - p_{1}) \delta(x_{2} - p_{2})}{p_{1}p_{2}} Y_{1m}(\theta_{p_{1}}, \varphi_{p_{1}})$$
$$\times Y_{1m'}(\theta_{p_{1}}, \varphi_{p_{2}}) e^{l(p_{1} - p_{1} - \mathbf{k})\mathbf{r}} d\mathbf{p}_{1} d\mathbf{p}_{2} d\mathbf{r}; \qquad (20)$$

$$\mathcal{M} \sim \sum_{mm'} \int Y_{1m} \left(\theta_{\mathbf{p}_{1}}, \varphi_{\mathbf{p}_{1}}\right) Y_{1m'} \left(\theta_{\mathbf{p}_{2}}, \varphi_{\mathbf{p}_{2}}\right) Y_{1m}^{\star} \left(\theta_{\mathbf{e}_{*}}, \varphi_{\mathbf{e}_{*}}\right) Y_{1m'}^{\star} \left(\theta_{\mathbf{e}}, \varphi_{\mathbf{e}}\right) \times \frac{\delta \left(\mathbf{x}_{1} - p_{1}\right) \delta \left(\mathbf{x}_{2} - p_{2}\right) \delta \left(\mathbf{p}_{1} - \mathbf{p}_{2} - \mathbf{k}\right) \sqrt{\mathbf{x}_{1}\mathbf{x}_{2}} d\mathbf{p}_{1} d\mathbf{p}_{2} d\mathbf{x}_{1} d\mathbf{x}_{2}}{p_{1}p_{2} \left\{\varepsilon_{0} + \hbar\omega_{0} - \hbar^{2}\mathbf{x}_{1}^{2} / 2m\right\} \left\{\varepsilon_{0} + \hbar\omega_{0} - \hbar\omega - \hbar^{2}\mathbf{x}_{2}^{2} / 2m\right\}} \cdot$$

$$(21)$$

Summing over m, m' and integrating over $d\kappa_1$ we shall obtain

$$M = -\left(\frac{4}{e}\right)^{4} \frac{\pi}{2} \frac{\rho e^{4\hbar}}{k^{2}} \frac{V\omega'\omega_{0}}{V}$$

$$\times \int \frac{\cos\theta_{\mathbf{p}_{s}+\mathbf{k},\,\mathbf{e}_{s}}\cos\theta_{\mathbf{p}_{s}+\mathbf{k},\,\mathbf{e}_{s}}\cos\theta_{\mathbf{p}_{s},\mathbf{e}'}\,d\,\mathbf{p}_{2}}{\sqrt{p_{2}|\mathbf{p}_{2}+\mathbf{k}|} \{\varepsilon_{0}+\hbar\omega_{0}-\hbar^{2}(\mathbf{p}_{2}+\mathbf{k})^{2}/2m\}} \{\varepsilon_{0}+\hbar\omega_{0}-\hbar\omega-\hbar^{2}p_{2}^{2}/2m\}}$$
(22)

Leaving out of consideration, as usual, the special resonance case $\hbar\omega_0 + \epsilon_0 = \hbar^2 k^2/2m$ and $\hbar\omega_0 + \epsilon_0 - \hbar\omega = \hbar^2 k^2/2m$ we can neglect in (22) the small region $p \approx k$ and consider that $p \gg k$. Finally, integration yields

$$M = -\left(\frac{4}{e}\right)^4 \frac{4\pi^2}{6} \frac{\rho e^4}{k^2} \frac{\sqrt{\omega_0 \omega'}}{\omega V} \frac{a_0^4}{Z^4} \frac{m}{\hbar^2} \ln \frac{\varepsilon_0 + \hbar\omega_0 - \hbar\omega}{\varepsilon_0 + \hbar\omega_0} \cos \theta_{e_0 e'}. \tag{23}$$

Expression (23) must be multiplied by the number ξ of electrons in the shell (for the K-shell $\xi = 2$). The effective cross section for the process is equal to (**q** is the propagation vector of the scattered photon; moreover, we have set $\sqrt{\omega_0 \omega'} = \omega_0 = Z^2 m \times e^4/2\hbar^3$)

$$\sigma = \frac{2\pi V}{\hbar c} \int |M|^2 \delta \left(E - E_0\right) \frac{Vd \,\mathbf{k}}{(2\pi)^3} \frac{Vd \,\mathbf{q}}{(2\pi)^3} \\ = \left(\frac{2}{\epsilon}\right)^8 \left(\frac{2}{3}\right)^3 \left(\frac{me^4}{\hbar^3\omega}\right) \left(\frac{e^2\xi}{mc^2}\right)^2 a_0 k_c \left\{\ln\frac{\varepsilon_0 + \hbar\omega_0 - \hbar\omega}{\varepsilon_0 + \hbar\omega_0}\right\}^2.$$
(24)

Let us compare (24) with the effective cross section for coherent scattering. In order to estimate the order of magnitude of the latter we can take the classical expression

$$\sigma_0 = (8\pi/3) \left(\frac{Ze^2}{mc^2} \right)^2.$$
 (24a)

The ratio of the cross sections for incoherent and coherent scattering is thus equal in order of magnitude to

$$\frac{\sigma}{\sigma_0} = \frac{1}{9\pi} \left(\frac{2}{e}\right)^8 \left(\frac{me^4/\hbar^2}{\varepsilon_0 + \hbar\omega_0}\right) \left(\frac{\hbar\omega}{\varepsilon_0 + \hbar\omega_0}\right) a_0 k_c \frac{\xi^2}{Z^2} \,. \tag{24b}$$

Here we have set

$$\ln \frac{\varepsilon_0 + \hbar \omega_0 - \hbar \omega}{\varepsilon_0 + \hbar \omega_0} \approx \frac{\hbar \omega}{\varepsilon_0 + \hbar \omega_0}.$$

3. ABSORPTION AT THE PLASMA OSCILLA-TION FREQUENCY

The probability of excitation of an "opticallyinactive" plasma oscillation by the absorption of a photon of frequency $\omega_0 = \omega$ and propagation vector **q** is determined by the matrix element

$$M = \sum_{n} \left\{ \frac{W_{0n}^* V_{n0}}{\varepsilon_0 + \hbar \omega_0 - \varepsilon_n} + \frac{V_{0n} W_{n0}^*}{\varepsilon_0 + \hbar \omega - \varepsilon_n} \right\}.$$
 (25)

The small terms $\hbar\omega_0$ and $\hbar\omega$ in the denominators may be neglected so that therefore both terms in (25) are of the same order of magnitude. In this case there is no longer any justification for assuming that ϵ_n is small, and therefore V_{n0} and V_{0n} will be determined by relations (5) and (6). In $W_{n0}^* = W_{100}^{*K1m}$, just as in V_{n0} , the principal contribution comes from the small region r $\lesssim a_0/Z$. It is therefore convenient to expand W into spherical waves:

$$W(\mathbf{r}) = \rho e^2 \int \frac{e^{i\mathbf{k}\mathbf{r}'}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

$$\approx \rho e^2 \sum_{l,m} \frac{4\pi}{2l+1} \int \frac{r^l}{r'^{l+1}} e^{i\mathbf{k}\mathbf{r}'} Y^{\bullet}_{lm}(\theta, \varphi) Y_{lm}(\theta', \varphi') d\mathbf{r}'.$$
(26)

We shall then obtain

$$W(\mathbf{r}) = \sum_{l,m} r^{l} Y^{\bullet}_{lm}(\theta, \varphi) \eta_{lm},$$

$$\eta_{lm} = \frac{4\pi\rho e^{2}}{2l+1} \int \frac{e^{i\mathbf{k}\mathbf{r}}}{r^{l+1}} Y_{lm}(\theta, \varphi) d\mathbf{r}.$$
(27)

Only the term with l = 1 is important for W_{100}^{*K10} in (27). Expansion of exp($i\mathbf{k} \cdot \mathbf{r}$) into spherical waves (9) yields:

$$\begin{aligned} \eta_{1m} &= i \, \frac{16\pi^2}{3} \frac{\rho e^2}{k} \, Y_{1m} \left(\theta_{\mathbf{k}}, \, \varphi_{\mathbf{k}} \right), \\ W \left(\mathbf{r} \right) &= i \, \frac{16\pi^2}{3} \frac{\rho e^2}{k} \, \mathbf{r} Y_{1m}^* \left(\theta, \, \varphi \right) \, Y_{1m} \left(\theta_{\mathbf{k}}, \, \varphi_{\mathbf{k}} \right); \end{aligned} \tag{28}$$

$$W_{100}^{*\times 1m} = -i \frac{(4\pi)^{3/2}}{3} \frac{\varphi e^2}{k} Y_{1m}^*(\theta_k, \varphi_k) \int R_{\times 1} r^3 R_{10} dr.$$
 (29)

For the radial integral in (29) we have Eq. (6). Taking into account the fact that $\omega_{\kappa_1; 10} = \hbar^{-1} \times (\hbar^2 k^2/2m - \epsilon_0)$ we shall obtain

$$M \sim \sum_{m} \{Y_{1m}^{\bullet}(\theta_{e}, \varphi_{e}) Y_{1m}(\theta_{k}, \varphi_{k}) + Y_{1m}(\theta_{e}, \varphi_{e}) Y_{1m}^{\bullet}(\theta_{k}, \varphi_{k})\}$$
$$\times \int_{\overline{(Z^{2} + x'^{2})^{5}} \{1 - \exp\left(-\frac{2\pi Z}{x'}x'\right)\}}^{Z^{6}} \approx \frac{3\cos\theta_{ek}}{16\pi e^{4}Z^{2}}, \qquad (30)$$

and finally

$$M = -\left(\frac{2}{e}\right)^4 \frac{16}{9} (2\pi)^{*_{J_a}} \frac{\rho e^3}{k\hbar} \sqrt{\frac{\hbar}{\omega_0 V}} \frac{a_0^2}{Z^2} \cos \theta_{ek}.$$
 (31)

Therefore the transition probability is equal to

$$dW = \frac{2\pi}{\hbar} \int |M|^2 \,\delta\left(E - E_0\right) \frac{Vd\,\mathbf{q}}{(2\pi)^3}$$
$$= 4\left(\frac{2}{e}\right)^8 \left(\frac{2}{3}\right)^4 \left(\frac{e^2}{\hbar c}\right)^2 \frac{\omega^2}{c} \frac{a_0^4}{Z^4 V} \cos^2\theta_{\mathbf{ek}} \,do. \tag{32}$$

In order to obtain the energy S absorbed per second it is necessary to multiply (32) by $\hbar\omega$, and also, since the plasma oscillation is normalized over the volume V, by the total number of electrons in a given shell equal to $\xi V/V_0$ where V_0 is the atomic volume. If the incident beam has an intensity $I_0(\omega) d\omega do erg/cm^2$ -sec then on averaging S over the directions of the polarization vector **e** we shall obtain [cf. the derivation of formula (17.19) of Heitler⁵]

$$S = \frac{1}{9} \left(\frac{2}{e}\right)^8 \left(\frac{8\pi}{3}\right)^3 \left(\frac{e^2}{\hbar c}\right)^2 \frac{a_0^2 \xi}{V_0} \frac{c a_0 I_0}{Z^4} \, do. \tag{33}$$

The energy absorbed by an ordinary single electron excitation is equal to⁵

$$S = \frac{4\pi^2}{3} \frac{e^2}{\hbar c} \omega |\mathbf{x}_{ab}|^2 I_0(\omega) \, do; \ |\mathbf{x}_{ab}|^2 = \frac{1}{2} f\left(\frac{me^4}{\hbar^3 \omega}\right) a_0^2, \quad (34)$$

where $\,f\,$ is the strength of the transition oscillator.

Thus (33) corresponds to absorption with an effective value of the square of the matrix element equal to

$$|\mathbf{x}_{ab}|_{eff}^{2} = \left(\frac{2}{e}\right)^{8} \left(\frac{4}{3}\right)^{4} \frac{a_{0}^{3}\xi}{V_{0}} \left(\frac{me^{4}}{\hbar^{3}\omega}\right) \frac{a_{0}^{2}}{Z^{4}},$$
 (35)

and differing from (34) essentially only by the factor Z_{eff}^{-4} .

4. DISCUSSION OF THE RESULTS

It follows from (13) and (14) that the mechanism discussed above for the excitation of plasmons by the absorption of x-ray quanta is a very effective one. Let us investigate in what way can this process have an effect on the structure of the absorption edge. The formulas obtained above are valid at distances from the absorption boundary which exceed ω by several fold, so that consequently it is not possible to draw unambiguous conclusions with respect to the shape of the curve in the region $\hbar\omega_0 + \epsilon_0 \approx \hbar\omega$. According to (13), σ does not depend on k_f^0 ; it therefore seems probable that there is no additional maximum at a distance $\hbar\omega$ from the boundary. From (15) and (16) it follows that if the function α (E), and consequently σ_0 , have a maximum, then σ also has a similar maximum but shifted by an amount $\hbar\omega$. This fact may turn out to be important for the intepretation of the structure of the absorption edge. It was noted earlier² that in a number of cases the values of the discrete losses coincide with the distances between the maxima of the structures of the K and L x-ray absorption edges, and the opinion was expressed that this coincidence should be related to the concept of plasmons.

This process is also sufficiently effective with respect to Raman scattering. Therefore in the reflected (scattered) light one can expect the appearance of long wave satellites $\omega_0 - \omega$.

Generally speaking, all electrons - both the inner ones, and also those close to the periphery -take part in the absorption of light of frequency of an "optically-inactive" plasma oscillation. According to (35), the principal role is played by the latter ($Z_{eff} \approx 1$). The approximation used above is not suitable in this case. Nevertheless it is obvious that the effectiveness of the mechanism considered above increases as $Z_{eff} \rightarrow 1$. One is here dealing essentially with the same mechanism which is used to explain the large width of plasmon levels - the exchange of energy between the plasmon and the individual electron which undergoes transitions between conduction bands.⁶⁻⁸ Since this mechanism leads to a considerable broadening of the plasmon levels, it is not surprising that the probability of excitation of the plasmon due to the virtual excitation of the electron is large (for $Z_{eff} \rightarrow 1$).

Because of this effect, the division of plasma oscillations into "optically-inactive" and "inactive" ones becomes quite arbitrary, and signifies only the separation of the mechanism of the process.

In addition to the optical effects investigated above, which are associated with excitation of plasmons, a number of other effects can also take place, for example, the emission of an x-ray quantum in the transition $n's \rightarrow n''s$ (without the excitation of a plasmon such a transition is evidently impossible). It may be shown that the probability of such a transition is proportional to $(Z'_{eff}Z''_{eff})^{-2}$.

In conclusion it must be noted that, in principle, all the processes considered above are possible also in the case that a second electron participates in them in place of a plasmon. However, for a plasmon, in the case that it involves several peripheral electrons, the corresponding transition probabilities should be greater [cf., for example, (24b) where σ/σ_0 is proportional to ω , i.e., to $\sqrt{\rho_0}$]. Apparently the most promising method of identifying plasma effects is to make use of the dependence of ω on the effective number of electrons taking part in a plasma oscillation.

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