Collective Energy Losses in Solids

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I.

IN this review I should like to discuss the progress which has been made during the past few years toward an understanding of the collective character of certain of the characteristic energy losses observed when fast electrons are scattered by thin solid films. Let me begin by defining what I mean by a collective, as compared to an individual particle, energy loss. We shall be interested in energy transfers of the order of 10 to 25 ev from the incident electron to the solid. For this energy region, the energy will, except in certain special cases, be absorbed by the valence electrons in the solid (electrons outside the closed atomic shells). On an individual particle picture, which certainly obtains if the influence of the Coulomb interaction between the valence electrons is slight, we would characterize the excitation spectrum of the valence electrons by a set of one particle energy differences, $\hbar\omega_{n0}$, corresponding to electronic transitions within the same band, or from one band to another. Where such transitions are excited by an incident fast charged particle, we are dealing with energy transfer to a single valence electron, in other words, an individual particle energy loss.

However, in many cases the Coulomb interaction between the valence electrons markedly influences the excitation spectrum of the system. The valence electrons in the solid, as a result of this interaction, are capable of carrying out collective oscillations at a high frequency which may differ substantially from the majority of the ω_{n0} and depends, approximately, only on the electron charge, mass, and density in the solid. When a fast charged particle excites such collective oscillations, we are dealing with energy transfer to a number of electrons moving cooperatively in consequence of their mutual interaction, and we call the associated energy loss collective. The valence electron collective oscillations resemble closely the electronic plasma oscillations observed in gaseous discharges. We introduce the term "plasmon" to describe the quantum of elementary excitation associated with this high-frequency collective motion. Under circumstances that we might expect plasmons to exist as well-defined entities, the energy of a plasmon is in the neighborhood of

$$\hbar\omega_p=\hbar\left(\frac{4\pi ne^2}{m}\right)^{\frac{1}{2}},$$

where n is the valence electron density and m is the free electron mass. Our study of collective energy losses becomes then a study of plasmon excitation in solids.

The introduction of a new elementary excitation requires, I believe, rather more justification in solid state physics than might be asked for in "curious particle" physics. In this review, I shall try to summarize the evidence, both experimental and theoretical, which points to the existence of the plasmon as a well-defined entity in nearly all solids. We shall see that experiments dealing with the characteristic energy losses provide us with the following information about plasmons in solids:

(1) Plasmon energy, derived from the magnitudes of the observed losses.

(2) Plasmon lifetime, derived from the width of the observed losses.

(3) Cross section for production of a plasmon by a fast charged particle, derived from the variation in observed losses with foil thickness and incident particle energy.

(4) Plasmon dispersion (the dependence of the plasmon energy on wavelength) derived from the dependence of energy loss on scattering angle.

(5) The minimum wavelength and maximum energy beyond which a plasmon cannot be regarded as a well-defined mode of excitation of the system, derived from the maximum scattering angle at which plasmon excitation is observed.

The following two sections are devoted to a development of the necessary theoretical background in terms of which we can evaluate the foregoing experimental information. In Sec. II we are principally concerned with the plasmon dispersion relation in solids, that is, with the energy we might expect a plasmon to possess in a given solid. This dispersion relation may be derived microscopically from a study of the equations of motion of the electrons or from a Hamiltonian formulation of the problem; it may also be obtained from a phenomenological macroscopic treatment of the solid in terms of an effective dielectric constant. We prefer to adopt the microscopic approach here because there are certain ambiguities in the use of the macroscopic dielectric constant which may only be resolved by actually carrying through the microscopic treatment. In Sec. III we consider the mechanism by which a plasmon is excited by a fast charged particle. We also discuss the way in which plasmon excitation may be distinguished from individual electronic excitation.

In Secs. IV and V we compare our theoretical predictions with the experimental observations concerning plasmons in solids. In Sec. VI we summarize the present situation and consider some of the desirable future lines of investigation in this field.

II.

Let us consider the interaction of an electron of momentum $\mathbf{P}_0$, position $\mathbf{R}_0$, with the valence electrons in a solid. We may take for our system Hamiltonian,

$$H=\sum_i \frac{p_i^2}{2m}+V(\mathbf{r}_i)+2\pi e^2 \sum_{i\neq jk} \frac{e^{i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x}_j)}}{k^2} + \frac{P_0^2}{2m}+\sum_{ik}\frac{4\pi e^2}{k^2}e^{i\mathbf{k}\cdot(\mathbf{R}_0-\mathbf{x}_i)}.^1 \quad (1)$$

The first term represents the electronic kinetic energy, the second the potential of the ion cores, the third the Coulomb interaction between the valence electrons. We are assuming that the influence of the core electrons on the valence electrons may be represented by a potential. (We return later to the cases in which this assumption does not apply.) The last two terms in (1) describe the kinetic energy of the external particle and its Coulomb interaction with the valence electrons. We see that the response of the valence electrons to the external particle depends only on the valence electron density fluctuation ρ_k. For we have

$$\rho_k=\int d\mathbf{x}\rho(\mathbf{x})e^{-i\mathbf{k}\cdot\mathbf{x}}=\int d\mathbf{x}\sum_i \delta(\mathbf{x}-\mathbf{x}_i)e^{-i\mathbf{k}\cdot\mathbf{x}_i} =\sum_i e^{-i\mathbf{k}\cdot\mathbf{x}_i} \quad (2)$$

so that the interaction between the external particle and the electron system may be written as

$$H_{\text{ext}}=\sum_k \frac{4\pi e^2}{k^2}\rho_k e^{i\mathbf{k}\cdot\mathbf{R}_0}. \quad (3)$$

The ρ_k describe the fluctuations in the electron density $\rho(\mathbf{x})$ about the average value $\rho_0=n$, and because of (3) furnish the "natural" variable for us to study in the energy loss problem.

The ρ_k also turn out to be the natural variable to use in studying the possible collective properties of a dense electron gas.[2] Such an investigation was first carried out for the free electron gas model of the solid, in which $V(\mathbf{r}_i)$ is assumed to be a constant. It is instructive to consider this model in some detail, as certain of the basic requirements for collective behavior, and hence plasmon excitation, already appear in this simplified problem. In BP III it is shown that the ρ_k satisfy the following operator equation of motion,

$$\frac{\partial^2\rho_k}{\partial t^2}+\omega_p^2\rho_k=\sum_i\left(\frac{\mathbf{k}\cdot\mathbf{p}_i}{m}-\frac{\hbar k^2}{2m}\right)^2 e^{-i\mathbf{k}\cdot\mathbf{x}_i} + \frac{4\pi e^2}{m}\sum_{k'\neq k}\frac{\mathbf{k}\cdot\mathbf{k}'}{(k')^2}\rho_{k'-k}\rho_k. \quad (4)$$

ω_p is the plasma frequency and is given by

$$\omega_p=\left(\frac{4\pi ne^2}{m}\right)^{\frac{1}{2}}. \quad (5)$$

Clearly to the extent that the terms on the right-hand side of (4) may be neglected, the density fluctuations display oscillatory behavior at a frequency ω_p, and we may expect the collective properties of the system to determine the energy loss spectrum of an incident charged particle. The oscillations are the analog of the classical longitudinal plasma oscillations found in a gaseous discharge.[3] In this case, because the oscillations take place at very high frequencies ($\hbar\omega_p\gg\kappa T$), we must consider the quantum character of the oscillation spectrum. We introduce the plasmon, of energy $\hbar\omega_p$, as our quantum of elementary excitation for the collective oscillations of the valence electrons. The valence electron density in solids ranges from $\sim 10^{22}$ to $\sim 10^{24}$, so that the corresponding plasmon energy $\hbar\omega_p$ varies from 4 ev to 30 ev. The energy required to excite a plasmon is of course far greater than that available thermally. For a given metal the plasmon energy also turns out to be greater than the kinetic energy of any individual conduction electron. As a result, we may only observe plasmon excitation by supplying energy from without to the valence electron system (in amounts greater than $\hbar\omega_p$), and this is what occurs when a fast charged particle passes through the solid.

The first term on the right-hand side of (4) represents the effect of the electron kinetic energy on the plasma oscillations. Following BP III, we may estimate its importance by averaging over electron momenta to obtain, approximately,

$$\sum_i\left(\frac{\mathbf{k}\cdot\mathbf{p}_i}{m}-\frac{\hbar k^2}{2m}\right)^2 e^{-i\mathbf{k}\cdot\mathbf{x}_i}\approx\left\{\frac{k^2\langle p^2\rangle_{\text{Av}}}{m^2}+\frac{\hbar^2k^4}{4m^2}\right\}\rho_k. \quad (6)$$

The term becomes comparable in importance with the term arising from the Coulomb interactions, $\omega_p^2\rho_k$, for a value of k such that

$$k^2\approx k_c^2\approx\frac{\omega_p^2}{\langle v^2\rangle_{\text{Av}}}\approx\frac{\omega_p^2}{v_0^2} \quad (7)$$

where $\mathbf{v}_0$ is the velocity of an electron at the top of the Fermi distribution of our electron gas. For our free electron solid, k_c^{-1} is of the order of the average electron spacing. For values of k which are small compared to k_c, the plasmons will be little affected by the electronic kinetic energy, and we may expect the system to behave collectively. On the other hand, for values of k which are large compared to k_c, the system will no longer behave collectively, the concept of the plasmon as an independent entity is no longer appropriate, and the density fluctuations and elementary excitations are those associated with a collection of individual electrons.[2]

The second term on the right-hand side of (4) repre-

[1] We carry out our Fourier expansions in a box of unit volume.

[2] D. Pines and D. Bohm, Phys. Rev. **85**, 338 (1952); Phys. Rev. **92**, 608 (1953), hereafter referred to as BP II and BP III.

[3] L. Tonks and I. Langmuir, Phys. Rev. **33**, 195 (1929).

sents the influence of nonlinear interactions between the density fluctuations on the equation of motion of the ρ_k. Because it is a nonlinear term, and the ρ_k for long wavelengths are reduced by Coulomb correlations,[4] we might expect it to be small, but a detailed study of its influence on the motion of the ρ_k is difficult to carry out within this framework. It is shown in BP III (where the entire problem is studied in the framework of a Hamiltonian formulation) that in fact the nonlinear term will always be considerably less important than the kinetic energy term for all $k<k_c$. Hence, the considerations of the preceding paragraph are sufficient to classify the collective *vs* individual particle behavior of the free electron gas.

The free electron model is a fairly good approximation for the behavior of a solid if we are dealing with a metal and we are concerned only with conduction electron transitions within a given band. If we wish to consider nonmetals, or the influence of transitions between different bands on the plasmon behavior, we must take into account the influence of $V(\mathbf{r}_i)$ in Eq. (1) on the electron motion. Such a treatment was first carried out by Mott,[5] who used a semiclassical approach to treat the plasma oscillation as a polarization wave in the solid. We here given an equivalent discussion,[6] which is somewhat more closely related to the above considerations.

As we have already remarked, we are interested in the matrix elements of ρ_k between different states of the valence electron system. Let us describe these states by the eigenstates of

$$H_0=\sum_i \frac{p_i^2}{2m}+V(\mathbf{r}_i).$$

Thus we have $H_0\Psi_n=E_n\Psi_n$ for the valence electron system. Because thermal energies are so small compared to the energy transfers in which we are interested, we can regard the valence electron system as being in its ground state before interaction with the fast charged particle takes place. We then wish to calculate the matrix element $(\rho_k)_{n0}$ between the ground state and all states n which differ from the ground state by momentum $\hbar\mathbf{k}$. By a study of the equation of motion of $(\rho_k)_{n0}$, we find, in analogy to (4),

$$\left[\frac{\partial^2\rho_k}{\partial t^2}+\omega_p^2\rho_k\right]_{n0}=-\omega_{n0}^2(\rho_k)_{n0}+\sum_{k'\neq k}\frac{4\pi e^2}{m(k')^2}\mathbf{k}\cdot\mathbf{k}'(\rho_{k'-k}\rho_k)_{n0}. \quad (8)$$

$\omega_{n0}=(E_n-E_0)/h$ is the frequency difference between states 0 and n for the valence electron system. Thus, for a metal, ω_{n0} corresponds to the energy difference for an electron making a transition within the same band, or from the conduction band to a higher band; for a semiconductor or insulator it will correspond to an electron going from the valence to the conduction or higher band. Once again we assume that the nonlinear term on the right-hand side of (8) may be neglected. The criterion that we get collective behavior is then that for the important matrix elements $(\rho_k)_{n0}$, $\omega_p^2\gg\omega_{n0}^2$. In these circumstances the Coulomb interaction between the electrons, as represented by ω_p^2, will dominate the individual particle behavior of the electrons, as represented by the ω_{n0}, and so it is perhaps not surprising that the ρ_k will continue to oscillate at a frequency near ω_p. (In other words, for such situations the most important force an electron feels is that due to the other electrons, rather than that due to the periodic field of the ions.) For the nearly free conduction electrons of a metal, the criterion $k\ll k_c$ is a special case of $\omega_{n0}\ll\omega_p$, since the free electron case we discussed describes well the influence of transitions within the conduction band on the collective behavior.

We can obtain a better idea of the influence of the individual particle motion on the collective behavior if we split up ρ_k into a collective part and an individual particle part, as was done in BP III. For the free electron gas this may be done by finding an operator which, within the linear approximation, has a pure oscillatory equation of motion. One then finds that the oscillatory part of ρ_k is given by

$$q_k=\sum_i \frac{\omega_p^2}{\omega^2-[(\mathbf{k}\cdot\mathbf{p}_i/m)-(\hbar k^2/2m)]^2}e^{-i\mathbf{k}\cdot\mathbf{x}_i}, \quad (9)$$

while the corresponding dispersion relation is

$$1=\frac{4\pi e^2}{m}\sum_i \frac{1}{[\omega-(\mathbf{k}\cdot\mathbf{p}_i/m)]^2-(\hbar^2k^4/4m^2)} \quad (10)$$

which for long wavelengths becomes

$$\omega^2\approx\omega_p^2+k^2\langle v^2\rangle_{\mathrm{Av}}+(\hbar^2k^4/4m^2). \quad (11)$$

The correction terms in (10) represent the change in the dispersion relation of the plasmons brought about by the coupling between the free electrons and the free plasmons, as represented by the first term on the right-hand side of (4). We see from (9) and (11) that for long wavelengths ($k\ll k_c$), $\rho_k\approx q_k$, so that the density fluctuations are almost completely collective in character. For $k\gg k_c$, on the other hand, $q_k\ll\rho_k$, and the ρ_k describe a collection of individual particles.

The analogous procedure for the case of valence electrons in a solid is given in NP. The collective component of the matrix element $(\rho_k)_{n0}$ is found to be

$$(q_k)_{n0}=\frac{\omega_p^2}{\omega^2-\omega_{n0}^2}(\rho_k)_{n0}, \quad (12)$$

[4] Thus, for long wavelengths the ρ_k behave like a collection of oscillators (in the absence of the nonlinear term). In this approximation, the mean square fluctuation of the ρ_k is determined by the zero-point energy of the plasmons and corresponds to $\langle\rho_k^2\rangle_{\mathrm{Av}}\sim(\hbar k^2/4m\omega_p)_{\mathrm{Av}}n$ as compared to the free electron value of n.

[5] N. F. Mott, Proceedings of the Tenth Solvay Congress, Bruxelles (1954).

[6] P. Nozieres and D. Pines, Phys. Rev. (to be published), hereafter referred to as NP.

while the dispersion relation becomes

$$1=\frac{4\pi e^2}{\hbar k^2}\sum_n \frac{2\omega_{n0}|(\rho_k)_{n0}|^2}{\omega^2-\omega_{n0}^2}. \quad (13)$$

We may write the dispersion relation (13) in the form

$$1=\frac{4\pi e^2}{m}\sum_n \frac{f_{n0}}{\omega^2-\omega_{n0}^2}, \quad (14)$$

where f_{n0} is a generalized oscillator strength for the transition of our electron system from the ground state to the excited state n, and is

$$f_{n0}=\frac{2m}{\hbar k^2}\omega_{n0}|(\rho_k)_{n0}|^2. \quad (15)$$

If we take the ground and excited states as being represented by Slater determinants of one-electron wave function $\varphi_\kappa(\mathbf{x}_i)$, the above relations become

$$1=\frac{4\pi e^2}{m}\sum_{\kappa K} \frac{f_{\kappa K}}{\omega^2-\omega_{\kappa K}^2}, \quad (16)$$

where $f_{\kappa K}$ is, in the long wavelength limit,

$$f_{\kappa K}=\frac{2m}{3\hbar}\omega_{\kappa K}\left|\int d\mathbf{x}\varphi_{\kappa+K}^*(\mathbf{x})\mathbf{x}\varphi_\kappa(\mathbf{x})\right|^2. \quad (17)$$

$f_{\kappa K}$ is the one-electron oscillator strength for a transition from state $\boldsymbol{\kappa}$ to state $\boldsymbol{\kappa}+K$, where K is a reciprocal lattice vector, and $\omega_{\kappa K}$ is the corresponding one-electron frequency difference. For $K=0$ (intra-band transitions), we have

$$f_{\kappa 0}=\frac{m}{\hbar^2}\frac{\partial^2 E(\kappa)}{\partial\kappa^2}=\frac{m}{m^*}, \quad (18)$$

where $E(\kappa)$ is the one-electron energy, and m^* is defined through (18). The dispersion relation in the form (16) is identical with that derived by Mott.[5]

The principal problem with the derivation of (14) or (16) is that it is difficult to estimate the validity of the linear approximation in this formulation. For instance, one might wonder whether a Lorentz polarization correction (which would only appear through the neglected terms), should in some cases be applied. We are also not able to treat simply the damping of the plasma oscillations by the individual electrons (it is assumed small). For these reasons it is desirable to carry out a treatment of the plasmon dispersion and absorption in the framework of a Hamiltonian formulation in which these problems may be studied.

The required treatment for the case of free electrons may be found in BP III. The generalization to valence electrons in a solid was first carried out by Kanazawa,[7] and has been independently studied by Adams.[8] We here describe briefly an analogous treatment given in NP. The basic Hamiltonian for the valence electron system in (1) may be rewritten as follows:

$$H=\sum_i \frac{p_i^2}{2m}+V(\mathbf{r}_i)+\sum_{i,j;k>k_c}\frac{2\pi e^2}{k^2}e^{i\mathbf{k}(\mathbf{x}_i-\mathbf{x}_j)}$$
$$+\sum_{k<k_c}\frac{P_kP^*{}_k}{2}+\frac{\omega_p{}^2Q_k{}^*Q_k}{2}$$
$$+\sum_{k<k_c}\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}}\left(\frac{\mathbf{k}\cdot\mathbf{p}_i}{m}-\frac{\hbar k^2}{2m}\right)Q_k e^{i\mathbf{k}\cdot\mathbf{x}_i}$$
$$+\sum_{\substack{ik,l<k_c\\ k\neq -l}}\frac{2\pi e^2}{m}\frac{\mathbf{k}\cdot\mathbf{l}}{|k||l|}Q_kQ_l\exp[i(\mathbf{k}+\mathbf{l})\cdot\mathbf{x}_i], \quad (19)$$

provided we impose a set of supplementary conditions on our extended system wave function,

$$\left(P_k-i\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}}\rho_k{}^*\right)\Psi=0 \quad (k<k_c). \quad (20)$$

In (19) and (20) we have introduced $n'=k_c{}^3/6\pi^2$ plasmon degrees of freedom in the coordinates Q_k and momenta P_k. The long-range part of the Coulomb interaction between the valence electrons has been redescribed in terms of the plasmons. The third term in (19) represents a short-range screened valence electron interaction, the fourth and fifth the field energy of the plasmons of frequency ω_p, and the sixth the linear plasmon-electron interaction. The remaining new term is the nonlinear plasmon electron interaction.

The linear plasmon-electron interaction gives rise to two effects, a change in the plasmon frequency and an effective electron-electron interaction. It also gives rise to the absorption of a plasmon by the electron system. The shift in the plasmon spectrum due to this interaction is studied by carrying out a canonical transformation to eliminate the interaction to first order. The desired transformation is simply found and the results easily obtained if one works in a mixed representation, in which the plasmon operators are specified in a representation in which $H_0=\sum_i p_i^2/2m+V(\mathbf{r}_i)$ is diagonal. One consequence of the transformation is that the plasmon variables no longer appear in the transformed supplementary condition. Thus one finds a set of n' independent plasmons, of maximum momentum k_c, and a collection of $3n$ electrons which are somewhat constrained by the transformed subsidiary condition. The plasmon dispersion relation becomes

$$\omega^2=\omega_p{}^2+\frac{4\pi e^2}{\hbar k^2}\sum_n \frac{2\left|\left[\sum_i\left(\frac{\mathbf{k}\cdot\mathbf{p}_i}{m}-\frac{\hbar k^2}{2m}\right)e^{i\mathbf{k}\cdot\mathbf{x}_i}\right]_{n0}\right|^2}{\omega^2-\omega_{n0}^2}\omega_{n0}, \quad (21)$$

where ω_{n0} is as defined before.[8a]

[7] H. Kanazawa, Progr. Theoret. Phys. **13**, 227 (1955).
[8] E. N. Adams, Phys. Rev. **98**, 947 (1955).

[8a] In deriving (21) we have neglected the influence of plasmon damping on the dispersion relation. Such a damping correction should not be appreciable for cases in which plasmon excitation can be observed.

If we describe the ground and excited state of the valence electrons by means of Slater determinants, we obtain the results of Kanazawa.[7] The equivalence of (21) with (14) may be established by making use of the identity,

$$\omega_{n0}(\rho_k)_{n0}=\left[\sum_i\left(\frac{\mathbf{k}\cdot\mathbf{p}_i}{m}-\frac{\hbar k^2}{2m}\right)e^{i\mathbf{k}\cdot\mathbf{x}_i}\right]_{n0},$$

and the generalized f sum rule,

$$\sum_n f_{n0}=n,$$

so that thus far nothing new appears.

However, the Hamiltonian formulation permits the study of the terms which have been neglected in the derivation of (14) or (21). These are the nonlinear plasmon-electron interaction and the short-range electron-electron interaction. Close examination shows that the nonlinear plasmon-electron interaction gives rise to corrections to the plasmon dispersion relation which are analogous to the local field polarization corrections introduced by Lorentz. Furthermore, where the linear plasmon-electron interaction may be treated as a comparatively small perturbation ($\omega_{n0}<\omega_p$), it is straightforward to show that the nonlinear interaction and hence the local field corrections are negligible. This is perhaps not surprising since the use of a local field correction implies that a given electron may be regarded as localized in a given region in the crystal for the phenomenon under consideration and hence that its effective binding frequency ω_{n0} is large compared to all other frequencies of interest. When $\omega_p>\omega_{n0}$, this situation of course does not apply.

The short-range interaction between the electrons influences the plasmon spectrum because the electrons are coupled to the plasmons through the linear interaction term, and with each other through their screened Coulomb interaction. When we eliminate the linear plasmon-electron interaction, we thus automatically introduce a plasmon-electron-electron interaction term which can act to shift the plasmon frequency and absorb an excited plasmon. It is found that for $\omega_{n0}\ll\omega_p$, the shift in frequency is approximately the same as that for a gas of free electrons, and is

$$(\Delta\omega)^2\sim-k^2E_{\text{exch}}{}^{\text{s.r.}},\tag{22}$$

where $E_{\text{exch}}{}^{\text{s.r.}}$ is the exchange energy for the short-range interaction,

$$\sum_{k>k_c}\frac{2\pi e^2}{k^2}e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}.$$

This correction is usually rather smaller than the correction terms already indicated in (11).

There is a very close connection between the influence of the valence electrons on the plasmons and the optical properties of the solid. This comes about because the Hamiltonian which describes the interaction of a transverse electromagnetic wave with the valence electrons is essentially identical in form with those parts of (19) describing the plasmon field and its interaction with the electrons. The differences lie in that the photon is a transverse wave, and the free photon dispersion relation is

$$\omega_0^2=c^2k^2+\omega_p^2.$$

Thus, as is shown in NP, the modified frequency $\omega_{k\mu}$ for a photon of polarization $\boldsymbol{\varepsilon}_{k\mu}$ is

$$\omega_{k\mu}^2=c^2k^2+\omega_p^2+\frac{4\pi e^2}{m^2}\sum_n\frac{2\left|\left[\sum_i\boldsymbol{\varepsilon}_{k\mu}\cdot\mathbf{p}_ie^{i\mathbf{k}\cdot\mathbf{x}_i}\right]_{n0}\right|^2}{\omega^2-\omega_{n0}^2}\omega_{n0}.\tag{23}$$

In the long wavelength limit (23) becomes

$$\omega_{k\mu}^2=c^2k^2+\omega_p^2+\frac{4\pi e^2}{m}\sum_{\kappa K}\frac{f_{\kappa K}\omega_{\kappa K}^2}{\omega^2-\omega_{\kappa K}^2}.\tag{24}$$

We make the connection with the usual optical constants by writing

$$\omega_{k\mu}^2\epsilon(\omega)=c^2k^2,\tag{25}$$

where $\epsilon(\omega)$ is the dielectric constant for a frequency ω. One then finds the familiar expression for $\epsilon(\omega)$,

$$\epsilon(\omega)=1-\frac{4\pi e^2}{m}\sum_{\kappa K}\frac{f_{\kappa K}}{\omega^2-\omega_{\kappa K}^2}.\tag{26}$$

Thus a knowledge of the zero's of $\epsilon(\omega)$ would enable us to determine the plasmon dispersion relation from the optical data. This is, in fact, possible only for the alkali metals; the plasmon energies so obtained are discussed in the following section. The fact that the plasmon dispersion relation is equivalent to the condition $\epsilon(\omega)=0$ seems first to have been noticed by Mott.[5] The close relationship between the optical and plasma properties of a solid has been emphasized by Hubbard,[9] Frohlich and Pelzer,[10] and Fano.[11]

Thus far we have assumed that the influence of the core electrons on the plasmon behavior may be described by the potential $V(\mathbf{r}_i)$. This is not generally correct, since such a scheme does not allow for the polarization of the core by the plasmon fields. The influence of the core on the plasmon dispersion relation may be simply treated in the semiclassical approach of Mott, in which the core electrons are described by a set of oscillators of frequency ω_i and strength f_i. The result is

$$1=\frac{4\pi e^2}{m}\sum_{\kappa K}\frac{f_{\kappa K}}{\omega^2-\omega_{\kappa K}^2}+\frac{4\pi e^2}{m}\sum_i\frac{f_i}{\omega^2-\omega_i^2}.\tag{27}$$

In NP a Hamiltonian formulation of the problem is given. The core electrons are treated on an equal basis with the valence electrons. It is found necessary to

[9] J. Hubbard, Proc. Phys. Soc. (London) **A68**, 441 (1955).
[10] H. Frohlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955).
[11] U. Fano, Phys. Rev. (to be published). I should like to thank Dr. Fano for sending me a preprint of his paper.

modify somewhat the approach described above; however, the resultant plasmon dispersion relation is found to be identical with (27).

The damping of a plasma wave in a solid principally occurs via two mechanisms; the short-range interaction between the electrons and the linear plasmon-electron interaction. For the free electron gas only the first mechanism is available, since energy and momentum conserving transitions via the linear plasmon-electron intervaction are not possible. The plasmon lifetime due to the short-range electron-electron collisions is calculated by NP, and is found to be approximately

$$\frac{1}{\tau_1}\cong\frac{\hbar\omega}{(\hbar^2k^2/2m)}\omega_p. \tag{28}$$

This lifetime has the expected dependence on plasmon wavelength. Long wavelength plasmons have an extremely long lifetime, and the lifetime decreases as the square of the wavelength.

The linear plasmon-electron interaction in an actual solid provides a far more efficient absorption mechanism. The lifetime due to this mechanism (absorption of a plasmon by an electron which undergoes a band-band transition) was first calculated by Wolff.[12] It may be simply expressed in terms of the optical constants n and k, and is

$$1/\tau_2=nk\omega_p. \tag{29}$$

An equivalent result has been obtained by Kanezawa and by NP. Again optical experiments do not furnish us with values for n and k in the desired frequency range. We may generally expect, however, that since $1/\tau_2$ is proportional to the oscillator strengths and density of transitions of frequencies ω_{0n} in the immediate neighborhood of ω_p, wherever there is a large shift in the plasmon energy from the free electron value there should be a correspondingly large broadening of the observed energy loss.

III.

Let us now consider the production of a plasmon by a fast charged particle. This was first calculated in BP II, where a semiclassical approach based on the density fluctuation method was used to calculate the mean free path λ for single plasmon production. The energy loss to the plasmons was treated by methods analogous to those used for the Čerenkov effect; the phenomena are quite similar in that energy and momentum conserving processes induced by the linear field-particle interaction can take place. A quantum treatment along these lines may be found in P IV.[13] A macroscopic treatment using an effective dielectric constant has been given by Hubbard[9] and Frohlich and Pelzer.[10] We here wish to sketch a somewhat different derivation of the plasmon production process which is similar to that used by Ferrell[14]; it enables us to consider the angular distribution of the electrons which have excited plasmons, and it yields results identical with those found in BP II and P IV.

The interaction between the fast charged particle and the valence electrons is specified by (3). Consider now the long wavelength part of this interaction,

$$\sum_{k<k_c}\frac{4\pi e^2}{k^2}\rho_k e^{i\mathbf{k}\cdot\mathbf{R}_0}. \tag{30}$$

When we carry out the canonical transformations which eliminate the electron-plasmon interaction [and lead to the plasmon dispersion relation (23)] we find that (30) is transformed to[15]

$$\sum_{k<k_c} i\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}}P_k e^{i\mathbf{k}\cdot\mathbf{R}_0}, \tag{31}$$

where P_k is the momentum of a plasmon of energy $\hbar\omega$ and wave vector $\mathbf{k}$. If we now treat the effect of this interaction on the fast charged particle by first-order perturbation theory, we obtain, as the probability per unit time that the particle produces a plasmon of wave vector $\mathbf{k}$ and energy $\hbar\omega$ and is scattered into an element of solid angle $d\Omega$,

$$w=\frac{d\Omega}{2\pi a_0}\frac{\omega P_0}{\hbar k^2} \tag{32}$$

where a_0 is the Bohr radius. In Fig. 1 we show the conditions imposed by the conservation of momentum. It may readily be verified that

$$\hbar^2k^2=(\Delta p)^2+P_0^2\theta^2=P_0^2(\vartheta^2+\vartheta_E^2) \tag{33}$$

where

$$\vartheta_E=\frac{\Delta p}{P_0}=\frac{1}{2}\frac{\hbar\omega}{E_0}\ll 1 \tag{34}$$

and E_0 is the incident fast particle energy ($E_0\gg\hbar\omega$).

Using (32) and (33) it may easily be shown that the differential cross section per valence electron for scattering through an angle ϑ is

$$\sigma(\vartheta)d\Omega=\frac{d\Omega}{2\pi n a_0}\frac{\vartheta_E}{\vartheta^2+\vartheta_E^2}. \tag{35}$$

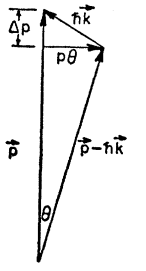


FIG. 1. Energy and momentum conservation for a fast electron which excites a plasmon.

[12] P. Wolff, Phys. Rev. **92**, 18 (1953).
[13] D. Pines, Phys. Rev. **92**, 626 (1953), hereafter referred to as P IV.
[14] R. A. Ferrell, Phys. Rev. **101**, 554 (1956).
[15] There is also a screened electron-electron interaction term which we neglect. See Eq. (42) of P IV.

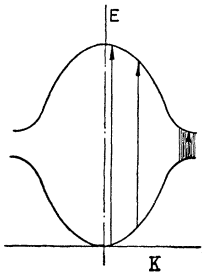


FIG. 2. Schematic diagram showing allowed low momentum transfer band-band transitions. In order that a sharp loss line appear a group of transitions, such as those indicated by the shading, must be markedly favored.

The maximum scattering angle ϑ_c is given by

$$\vartheta_c \sim (\hbar k_c/P_0) \tag{36}$$

and we have $\vartheta_E \ll \vartheta_c \ll 1$ for typical experimental situations in the scattering of kilovolt electrons. We then find, on integrating (35) over solid angle, a cross section for plasmon production which is

$$\sigma \cong \frac{\vartheta_E}{na_0} \ln\frac{\vartheta_c}{\vartheta_E} = \frac{\hbar\omega}{2na_0E_0} \ln\frac{k_cP_0}{m\omega}. \tag{37}$$

This corresponds to a mean free path for the production of a plasmon λ given by

$$\lambda = 2a_0\left(\frac{E_0}{\hbar\omega}\right)\frac{1}{\ln(k_cP_0/m\omega)}. \tag{38}$$

For the excitation of a 15-ev plasmon by a 10-kv electron we find a mean free path of $\sim$250 A for typical values of k_c encountered in metals. The maximum scattering angles ϑ_c expected are of the other of a few hundredths of a radian.

We further remark that the probability of two plasmon excitation by an incident fast charged particle is so small that this possibility may be neglected in considering the scattering of fast electrons by thin films. What one expects, instead, is repetition of the single plasmon production act. Thus the probability for an electron to excite N plasmons in passing through a foil of thickness t is given by the Poisson distribution

$$P_N(t) = \frac{1}{N!}\left(\frac{t}{\lambda}\right)^N e^{-t/\lambda}.$$

Before going on to a consideration of the experimental results on plasmon production it is useful to consider briefly the alternative possibility that a given energy loss might be of an individual particle character (that is, correspond to a band-band transition for an individual valence electron). Suppose we consider a metal and assume that the observed energy loss corresponds to excitation of an electron from the conduction band to a higher band. If we are concerned with a relatively low-energy transition ($<$15 ev, say,) then we will be concerned with excitation to the nearest band, which will in general have a rather different shape. The situation in the nearly free electron approximation is shown in Fig. 2. We see that the only way we could expect to observe a fairly sharp energy loss (width Γ small compared to loss value ΔE) is if the transition probability varies rather sharply within the band, and is large for only a comparatively small number of the possible band-band transitions. If we neglect the Coulomb interaction between the electrons, we may calculate quite simply the probability per unit time that the fast incident particle give up energy $\Delta E = \hbar\omega_{n0}$ to a single valence electron. We obtain

$$w = \frac{d\Omega}{2\pi a_0}\frac{4\pi e^2}{m}\frac{f_{n0}\hbar}{\Delta E}\frac{P_0}{\hbar k^2}. \tag{39}$$

If we are interested in an energy loss of width Γ about a given ΔE, we should include in our expression (32) all band-band transitions which could contribute in this energy region. We then find

$$w = \frac{d\Omega}{2\pi a_0}\left(\frac{\hbar\omega_p}{\Delta E}\right)\left(\frac{n_{Av}}{n}f_{Av}\right)\frac{P_0\omega_p}{\hbar k^2}, \tag{40}$$

where f_{Av} is the average oscillator strength for the transition ΔE and n_{Av}/n is the relative number of electons in the band which contribute appreciably to the transition.

On comparing (40) with (32) we see that for $\hbar\omega_p \approx \Delta E \approx \hbar\omega$ the probability for energy transfer to a single valence electron is reduced over that for plasmon production by a factor

$$\frac{n_{Av}}{n}f_{Av}.$$

Now f_{Av} is generally somewhat less than unity, and as we have seen, n_{Av}/n must be small compared to unity if we are to observe a relatively sharp energy loss. Hence we expect plasmon production to dominate band-band transitions for momentum transfer less than k_c. In NP it is shown that this conclusion is strengthened if one takes into account Coulomb correlations between the valence electrons. For the correlations act to reduce the individual electron part of the matrix element $(\rho_k)_{n0}$ by a factor of $(\omega_{n0}/\omega_p)^2$ for $\omega_{n0} < \omega_p$. The expression (40) then becomes

$$w_{\text{corr}} \sim \frac{d\Omega}{2\pi a_0}\left(\frac{\Delta E}{\hbar\omega_p}\right)^3\left(\frac{n_{Av}}{n}f_{Av}\right)\frac{P_0\omega_p}{\hbar k^2} \tag{41}$$

so that we expect the cross section for energy transfer $\Delta E < \hbar\omega_p$ to an individual electron to be reduced over that for plasmon excitation by a factor

$$\left(\frac{\Delta E}{\hbar\omega_p}\right)^3\frac{n_{Av}}{n}f_{Av}. \tag{42}$$

This conclusion is not surprising when we recall that the stopping power of the valence electrons depends only on a sum rule and is independent of the mechanism

of the energy transfer.[15a] The effect of the Coulomb correlations is to enhance considerably the probability for an energy transfer $\hbar\omega$ to the valence electron assembly. The correlations must then at the same time act to reduce the probability for individual particle transitions, in order to preserve the sum rule for the stopping power. In (42) we see the combined effect of the enhancement at the plasmon energy and the corresponding inhibition of the low energy band-band transition.

IV.

We now turn to a consideration of the experimental evidence for plasmon excitation in solids.[16] It was clear from the pioneer experiments of Ruthemann[17] and Lang[18] that two kinds of situations prevail in the characteristic loss spectrum of a thin solid film. For Be and Al, they observed several comparatively narrow loss lines, in multiples of a basic loss quantum, ~19 ev for Be, ~15 ev for Al. On the other hand, for Cu and Ag they found only a single loss line, which was considerably broader than the lines for Be and Al, and occurred at ~20 ev for Cu and ~23 ev for Ag.

Let us compare these values with the free electron plasmon quantum (calculated assuming the valence electrons are free). We find good agreement for Be and Al, with plasmon energies of 19 ev and 16 ev, respectively. On the other hand, for Cu and Ag the free electron plasmon energies are 11 ev and 9 ev. Thus, if we seek to explain both types of lines as plasmon excitation, we must understand why for Be and Al the valence electrons behave as if free (as far as plasmon behavior is concerned) and several loss lines are observed, whereas for Cu and Ag the plasmon energy is considerably higher than the free electron value, and only a single loss line is observed. The answer to the first puzzle was provided by Mott,[5] who showed that if the valence electrons are weakly bound, and the core electrons are strongly bound (with respect to the free electron plasmon energy $\hbar\omega_p$), the solid state environment would not greatly affect the plasmon energy. The answer to the second question was provided by Herring[19] and Wolff,[12] who showed that the coupling of the plasmons to the core electrons in Cu and Ag would be expected to broaden the plasma resonance and increase the plasmon energy substantially.

We shall see that solids generally fall into the one category or the other, insofar as their characteristic energy loss spectra are concerned. Where the loss line is comparatively narrow, it is found at nearly the free electron plasmon energy, and usually several loss lines are observed. On the other hand, where the loss line is broad usually only a single line is observed, at an energy considerably displaced from the free valence electron plasmon energy.

Consider the case of weak valence and strong core binding, that is $\omega_{\kappa K}^2 \ll \omega^2 \ll \omega_i^2$ for those transitions $\omega_{\kappa K}$, ω_i for which the oscillator strength is appreciable. In this case we may approximate (16) by

$$1 \cong \frac{4\pi e^2}{m} \sum_{\kappa K} \frac{f_{\kappa K}}{\omega^2} - \frac{4\pi e^2}{m} \sum_i \frac{f_i}{\omega_i^2}. \tag{43}$$

We use the sum rule $\sum_K f_{\kappa K} = 1$, and introduce the static core dielectric constant,

$$\epsilon_c = 1 + \frac{4\pi e^2}{m} \sum_i \frac{f_i}{\omega_i^2}. \tag{44}$$

We then obtain

$$\omega^2 \approx \omega_p^2/\epsilon_c \tag{45}$$

for our expected plasmon dispersion relation. In these circumstances ϵ_c will be of order unity, since we have assumed that the core electrons are tightly bound. Since both Al and Be are metals for which we have weak valence and strong core binding, it is thus not surprising that there is agreement between the free electron plasmon value and the experimentally observed loss line. Such agreement encourages one to attempt a similar comparison for other solids.

In comparing our theoretical value (45) for the plasmon loss line with experiment, we must take into account the fact that for many solids rather different energy loss spectra have been observed by different experimenters. The experimental situation with regard to the characteristic energy loss spectra has been reviewed by Marton *et al.*[20] and has been discussed by Dr. Marton at this conference,[21] so we shall not go into details on the possible reasons for such discrepancies here. Among these are the difficulties with sample purity in dealing with films a few hundred A thick, and possible damage to the films by impurity deposit in the course of electron bombardment.[22] Further, differences in film thickness, bombarding energy, and angular aperture of the spectral analyzer would, according to (35) and (38), cause a difference in the number of plasmon lines observed.

In Fig. 3 and Fig. 4 we present a partial summary of the characteristic energy losses thus far observed. We

[15a] Precisely because the stopping power is mechanism insensitive, we will not enter upon a detailed discussion of its calculation here. Historically, the first utilization of the plasma aspects of the electron gas in metal was made by Kronig and Korringa [Physica **10**, 406, 800 (1943)] in a consideration of the influence of electron interaction on the stopping power of a metal. The relative contribution of the individual electrons and the plasmons to the stopping power is discussed in P IV.

[16] The material in this section is largely drawn from NP and an article by D. Pines in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1.

[17] G. Ruthemann, Naturwissenschaften **29**, 648 (1941); **30**, 145 (1942); Am. Physik (6) **2**, 113 (1938).

[18] W. Lang, Optik **3**, 233 (1948).

[19] C. Herring (private communication).

[20] Marton, Leder, and Mendlowitz, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. 7.

[21] L. Marton, Proceedings of Maryland Conference on Electron Physics.

[22] D. Gabor and G. W. Jull, Nature **175**, 718 (1955).

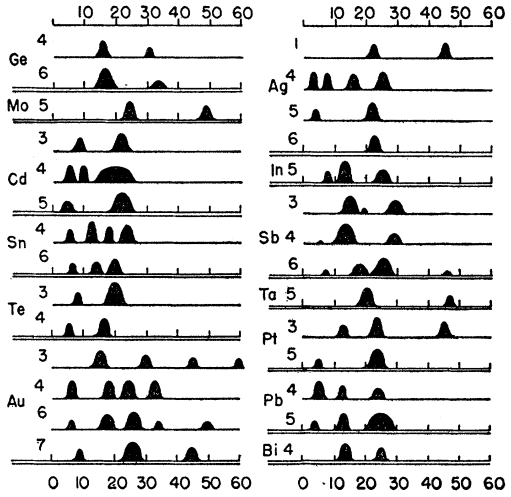


FIG. 3.

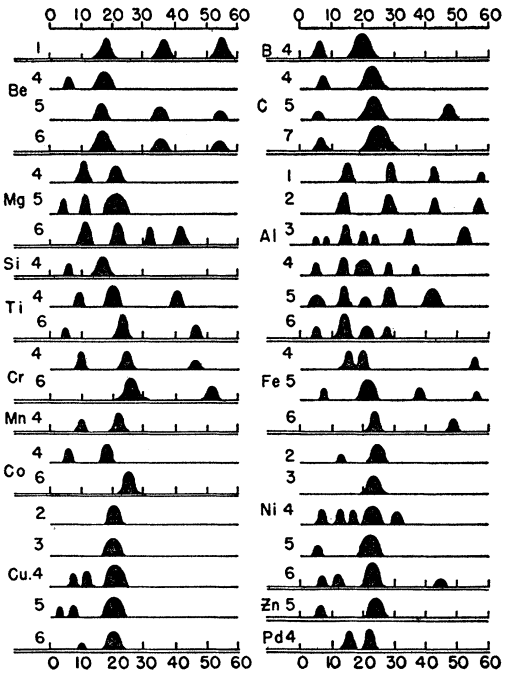


FIG. 4.

FIGS. 3 and 4. Experimental results on characteristic energy losses [taken from *Solid State Physics* (Academic Press, Inc., New York, 1955)], Vol. 1, p. 432. The energy losses are in ev. The code numbers refer to the work of the following investigators: (1) Ruthemann[17]; (2) Lang[18]; (3) G. Möllenstedt, Optik **5**, 499 (1949); (4) Marton and Leder[23]; (5) W. Kleinn, Optik **11**, 226 (1954); (6) W. Watanabe, J. Phys. Soc. Japan **9**, 1035 (1954); (7) Gabor and Jull.[22]

have attempted to identify the experimental plasmon loss on the basis of the following criteria:

(1) Where a solid has been investigated in several different experiments, we consider only those loss lines which have been found by all observers.

(2) Either the loss appears through a series of equally spaced lines or only one rather broad line is found under the circumstances which would have precluded observing the multiple losses.

(3) In cases where the relative intensity of the different loss lines is given, the plasmon losses are identified with the most prominent lines in the spectrum.

(4) Where several different values for a given loss line have been reported, we take an uncritical average of the various values in arriving at an experimental loss value.

We have been led, in part, to these criteria by the considerations of the preceding section which indicate that the plasmon lines should be the most prominent lines in the loss spectrum.

In Table I we compare theory and experiment for those solids for which we expect the criteria of weak valence and strong core binding to be well satisfied. $\hbar\omega$ is the calculated plasmon energy according to (45) and ΔE_{obs} is our identification of the experimental loss which we should expect to correspond to plasmon excitation according to the discussion given in the preceding paragraph. We have kept only two significant figures in ΔE_{obs} and $\hbar\omega$ because neither quantity can be regarded as known to any greater accuracy. We see that the agreement is really quite good. Furthermore, where the discrepancy is greatest, for B and C, it is in a direction which we can understand. For these substances, the valence electrons are comparatively tightly bound, so that we might expect that band-band transitions of quite high energy could be important in determining plasmon behavior. If the energy of such transitions $\hbar\omega_{\kappa K}$ is larger than $\hbar\omega_p$, then we would, according to (16), expect the plasmon energy to be lowered, which it appears to be. A somewhat less precise way of putting this is to say that to a certain extent not all the valence electrons are free to take part in plasmon excitation, and so we observed a reduced plasmon energy.

We might also expect that the alkali metals fall into the category of weak valence and strong core binding. Here it is rather difficult to be confident of the information provided by the experiments on characteristic energy losses[23] because the oxidation problem is so severe. However, for the alkali metals the optical work of Wood[24] on the change from the reflecting to the transmitting region provide us with direct evidence on

[23] L. Marton and L. B. Leder, Phys. Rev. **94**, 203 (1954).
[24] R. W. Wood, Phys. Rev. **44**, 353 (1933); R. W. Wood and C. Lukens, Phys. Rev. **54**, 332 (1938).

the plasmon energy, since according to (26) this change should occur for a photon energy equal to the plasmon energy. In Table II we compare the optically determined plasmon energy with the theoretical value calculated using[25] (45). We have given for comparison the free electron value and that experimental value of Marton and Leder which lies closest to the optical value. We see that the agreement between our calculated value and the optical value is quite good. The remaining small discrepancies can easily be explained by low energy band-band transitions which will act to increase somewhat the calculated values.

For most of the solids in Table I we should expect to find a rather narrow line whose width could in principle be calculated from (29) if the pertinent optical data were available. Since it is not, we must rely upon qualitative considerations. With strong core and weak valence binding there will be relatively few transitions at frequencies comparable to ω, and for such transitions the oscillator strengths tre probably small. In consequence for a metal like Al we might expect a plasmon lifetime of the order of $(10/\omega_p)\sim 10^{-15}$ sec and perhaps even longer. Other substances for which comparatively long lifetimes might be anticipated would be Be, Mg, and Ge. For most of these solids the true widths have probably not been measured, since the experimetal widths appear no greater than the width observed for electrons which have suffered no energy loss in the thin film. On the other hand, the fact that B and C have rather broader lines (and shorter plasmon lifetimes $\sim 10^{-16}$ sec) follows if we assume that the binding of the valence electrons is not completely negligible for these solids, a consideration which appears likely on the basis of the observed frequency shift. It is surprising that there is such good agreement between $\hbar\omega$ and ΔE_{obs} for Si, since it too is found to have a broad loss line.

Now let us turn to our second category of solids, those for which we do not expect to have weak valence and strong core binding. In the transition metals, for instance, suppose we treat both the s and d electrons as valence electrons. We should then not expect to be able to neglect band-band transitions as we increase the total number of valence electrons, since when we begin to have a large core charge, some of the valence electrons will be quite tightly bound, and hence have important high energy band-band transitions. We then have a case of strong valence binding. We could discuss this effect in the following qualitative way. Consider the dispersion relation (16). If we take all s and d electrons as valence electrons, then we can certainly neglect the core transitions. Further we see that band-band transitions which are lower in energy than the free electron plasmon energy will act to push it up, whereas those which lie higher act to depress it. Thus as we go through the transition elements in order of increasing valency, we should expect that at first our calculated plasmon energy will be on the low side of the experimentally observed value. For there will be low frequency band-band transitions which act to increase the plasmon energy over the value given by (45). As we increase the valency, some of the valence electrons will become quite tightly bound, so that high frequency ($\omega_{\kappa K}\gg\omega_p$) band-band transitions begin to have an appreciable oscillator strength. Such transitions depress ω from the value (45). Thus, we might expect that there is a valency region in which the effect of low-lying levels is essentially canceled by the high-lying levels, and we find very nearly the value (45). For a valency greater than this we definitely expect to be on the high side of the experimental value, if we use (45).

This qualitative picture appears to be consistent with the experimental results, as may be seen from Table III. Once again $\hbar\omega$ is the value calculated taking into account core polarization, and ΔE_{obs} is the experimental plasmon loss selected on the basis of the criteria discussed earlier. We see that for Ti, which has four valence electrons, we obtain too low a plasmon energy using (39). For Cr, which has six valence electrons, we appear to be in the region for which the effects of band-band transitions cancel out. Beyond Cr, the band-band transitions definitely act to depress the plasmon energy below (39). A further indication that for six electrons outside a closed shell the low-frequency band-band transitions tend to neutralize the high-frequency transitions comes from the plasmon energies in Mo, Te, W, and Se, which may be seen from Table III to be at very nearly the free electron value.

We are not really justified in trying to reach any conclusions regarding the plasmon lifetimes on the basis of such very qualitative considerations. However, a hypothesis which appears not inconsistent with experiment is the following. We might expect the loss lines to be broader in the region of six valence electrons,

TABLE I. A comparison of $\hbar\omega$ with ΔE_{obs} for solids in which the valence electrons are weakly bound and the core electrons are tightly bound ($\omega_{\kappa K}^2<\omega^2<\omega_i^2$). Z denotes the number of valence electrons per atom we have assumed take part in plasma oscillation.

Element	Be	B	C	Mg	Al	Si	Ge
Z	2	3	4	2	3	4	4
$\hbar\omega$(ev)	19	24	25	11	16	17	16
ΔE_{obs}(ev)	19	19	22	10	15	17	17

[25] A similar table was first given by R. A. Ferrell.[14]

TABLE II. A comparison of $\hbar\omega$ with the optical data and the observed energy losses for the alkali metals. All energies are given in ev.

Element	$\hbar\omega_p$	$\hbar\omega$	$\hbar\omega_{\text{opt}}$	ΔE_{obs}
Li	8.1	8.0	8.02	9.5
Na	6.0	5.7	5.91	5.4
K	4.4	3.9	3.94	3.8
Rb	4.0	3.4	3.65	
Cs	3.6	2.9	3.27	

TABLE III. A comparison of $\hbar\omega$ with ΔE_{obs} for solids for which either the valence electrons are not weakly bound or the core electrons are not tightly bound. Z denotes the number of valence electrons per atom we have assumed to take part in plasma oscillation.

Element	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	4	6	7	8	9	10	11	12
$\hbar\omega$	17	24	28	31	34	35	36	32
ΔE_{obs}	22	24	22	21	21	23	20	23
Element	Se	Mo	Pd	Ag	Cd	In	Sn	Sb
Z	6	6	10	11	12	3	4	5
$\hbar\omega$	18	23	31	30	28	11	12	14
ΔE_{obs}	20	25	22	23	20	12	12	15
Element	Te	Ta	W	Pt	Au	Tl	Pb	Bi
Z	6	5	6	10	11	3	4	5
$\hbar\omega$	15	20	23	30	30	12	13	14
ΔE_{obs}	18	21	22	23	24	17	13	13

since here both high- and low-frequency band-band transitions act to damp the plasma oscillation, whereas for a valence of four or eight, only low- or high-frequency transitions, respectively, give rise to important damping effects. This conclusion is in agreement with the experimental findings of Marton and Leder, who find the Cr and Mn lines to be roughly twice as wide as those observed for Ti and Co[26]; it is not in agreement with the results of Watanabe.[27]

Consider now the noble metals. Here we encounter a case of weak core binding. For such metals two approaches are possible. One is that suggested by Wolff. If we consider, for instance, the plasmon formed from the "s" electron interaction in Cu, we find an energy of $\sim$11 ev. Such an energy is, however, large compared to the energy required to excite one of the "d" core electrons to the "s" band ($\sim$4 ev). We must therefore take into account the influence of the core-valence transitions on the plasmon behavior. This is a rather strong interaction, which consequently acts to broaden the plasmon line considerably and shift its position appreciably. It cannot be treated accurately by perturbation theory, but Wolff has made a rough estimate which leads to the correct order of magnitude for the broadening and shift. We might similarly assign the large broadening and shift in Ag and Au to this mechanism.

Because of the energy required to excite a core electron is so very small in these metals, we might alternately argue that the core electrons should rather be regarded as valence electrons insofar as their plasmon behavior is concerned. For Cu we then have eleven valence electrons, and a plasmon energy of 36 ev. This energy we would then expect to be reduced considerably by high-frequency band-band transitions, so that it is not surprising that the observed value is markedly lower at 20 ev. Thus we can regard the noble metals as a case of weak core or strong valence binding; the former picture is probably more suited to quantitative calculations.

When we consider the divalent metals Zn and Cd, we find that here, too, the core electrons cannot properly be regarded as tightly bound. The "s" electron plasmon energy is 13 ev for Zn whereas the energy required to excite a core electron is probably somewhat less than 10 ev. A similar situation obtains for Cd, where the "s" electron plasmon energy is $\sim$11 ev, and the energy for core excitation is about 10 ev. These metals should clearly be treated on the same basis as the noble metals, and we can understand the origin of the large breadth and shift of the loss lines on the basis of the valence electron-core coupling.

On the other hand, when we consider the metals beyond Cd, (In, Sn, Sb, and Te), we appear to be in much better shape. Although the core electrons for In and Sn are not truly tightly bound (with excitation energies of $\sim$17 and 22 ev), so that the cores are rather polarizable ($\epsilon_c \sim 1.35$ and 1.23, respectively), we find plasmon energies at very nearly the values predicted by the dispersion relation (39). Tl, on the other hand, is clearly a metal for which the core electrons continue to play an important role in determining the plasmon energy. The good agreement for Sb and Te, Ta and W, and Pb and Bi may be the result of cancellation between the effect of low-frequency and high-frequency band-band transitions on the plasmon energy, as discussed above. It should be noted that even though there is good numerical agreement between $\hbar\omega$ and ΔE_{obs}, the line widths for these elements are definitely greater than those observed for Be, Mg, Al, and Ge.

We now consider a comparison between theory and experiment for the energy losses in compounds. We here calculate the plasmon energy neglecting the correction for core polarizabilities, which should be an excellent approximation for the tightly bound cores of the compounds we consider. We take the total number of valence electrons appropriate to the compound in question (e.g., Al_2O_3 yields six from Al and eighteen from O) in order to calculate $\hbar\omega$. In choosing ΔE_{obs} we are guided by the same considerations we followed for the case of monatomic solids, and in Table IV we compare ΔE_{obs} with $\hbar\omega$ calculated assuming the binding of the valence electrons is weak compared to the plasmon energy $\hbar\omega$.

We see first of all that this proves to be a surprisingly successful assumption. There is generally close agreement between $\hbar\omega$ and ΔE_{obs}. For the sulfides, PbTe, PbSe, Mica, BeO, MgO, Li_2CO_3, $C_2(OH)_2$, MoO_3, and SiO_2 the two values are essentially the same. This would appear to indicate that for these substances the important valence band-conduction band transitions have energies which are rather smaller than the plasmon

[26] It should be noted that our approach to the transition metals is rather different from that of Wolff.[12] Wolff discusses plasmon behavior by considering the "s" electron plasmons in interaction with individual d electrons. He is then led to the conclusion that loss lines continue to broaden as one goes through the transition elements in order of increasing valency. This conclusion appears to be in contradiction with experiment.

[27] H. Watanabe, quoted in Marton *et al.*[20]

TABLE IV. A comparison of $\hbar\omega$ with ΔE_{obs} for compounds. Z denotes the average number of valence electrons per atom we assume take part in plasma oscillation. The investigators are Marton and Leder (ML), Watanabe (W), and Mollenstedt (M).

Compound	ZnS	PbS	Sb_2S_3	MoS_2	PbTe	PbSe	Mica	BeO	MgO
Z	4	5	5.6	6	5	5	4.7	4	4
$\hbar\omega$(ev)	17	16	18	23	14	15	24	29	25
ΔE_{obs}(ev)	17	15	19	21	15	15	25	29	25
Investigator	ML	ML	ML	W	ML	ML	M	W	W

Compound	Li_2CO_3	$Ca(OH)_2$	MoO_3	SiO_2	Al_2O_3	TeO_2	SnO_2	KBr	KCl	NaCl
Z	4	3.2	6	5.3	4.8	6	5.3	4	4	4
$\hbar\omega$(ev)	24	21	24	25	27	23	26	13	14	16
ΔE_{obs}(ev)	24	22	25	25	23	18	20	13	13	16
Investigator	W	W	W	W	W	ML	W	ML	ML	ML

energies $\hbar\omega$. In Al_2O_3, TeO_2, and SnO_2 there is perhaps more in the way of covalent binding than for the preceding compounds, and this appears to have the expected effect on the plasmon energies. For, just as was the case with C, tight valence binding will give rise to important high-frequency band-band transitions, and so act to decrease the plasmon energy from $\hbar\omega_p$. The effect in these compounds is of the order of magnitude to be expected from the observed shift in C.

The possible plasmon loss lines in KBr, KCl, and NaCl are rather difficult to identify because in both KBr and KCl there are a large number of loss lines of nearly equal intensity, whereas for NaCl the collodion film used as a backing contributes to the loss spectrum. However, the experimental loss lines we quote seem to be the most intense, and are in fact repeated with decreasing intensity. It is interesting to note that they are in agreement with our calculated plasmon energies.

V.

In the preceding section we considered the experimental information about the energy and lifetime of plasmons in solids. In this section we discuss the information which may be derived from an experimental study of the mechanism of interaction of the incident fast charged particle with the plasmon assembly. Thus we shall consider the mean free path for plasmon production, and the angular distribution of electrons which have given up energy to the plasmons.

Unfortunately there is little accurate information available concerning the mean free path for plasmon excitation. From the values quoted by Lang[18] for the variation in plasmon excitation in Al with foil thickness we may infer a quite approximate mean free path of somewhat less than 180 A. This is in agreement with the theoretical value of 190 A calculated from (38) for the 7-kev electrons used by Lang. Recently Blackstock, Ritchie, and Birkhoff[28] have carried out a careful investigation of plasmon excitation in Al, Mg, and Cu by electrons which range in energy from 20 kev to 100 kev. We reproduce in Fig. 5 their results for plasmon excitation in Al at 45 kev and 100 kev. It may be seen from the relative shift of the various loss lines that the mean free path for plasmon excitation decreases with increasing incident electron energy, as we should expect from (38). Blackstock *et al.* have carried out a detailed comparison of (38) with experiment for Al, varying both foil thickness and bombardment energy, and find satisfactory agreement between theory and experiment. The situation they find for Mg is somewhat ambiguous. They observe a number of loss lines in multiples of $\sim$10 ev and a variation in the appearance of these lines with bombardment energy. However, different methods of determining the thickness of the Mg foils lead to quite different results, one of which is in fair agreement with (38). For Cu, on the other hand, they find only a single loss at $\sim$23 ev regardless of foil thickness and incident electron energy. The line is quite broad so that a careful estimate of λ is difficult. They find a mean free path which, within experimental error, is in agreement with expected theoretical values.

Marton, Simpson, and McGraw[29] have investigated the angular distribution of 20-kev electrons scattered by a thin gold film. Their experimental results on the variation of beam intensity with angle of those electrons which have lost 24 ev have been analyzed in detail with the aid of (35) by Ferrell.[14] He shows that the experimental results are consistent with the hypothesis thtt the 24-ev loss corresponds to plasmon excitation.

Watanabe[30] has studied the variation of energy loss with angle for the scattering of 25-kev electrons by Be, Mg, Al, Ge, and graphite. His experimental results provide valuable information on the plasmon dispersion relation and the critical wave vector k_c beyond which the plasmon cannot be regarded as an independent entity.

If the free electron picture is valid for a given solid, the plasmon energy as a function of wave vector may, according to (11) be written as

$$\Delta E(k)=\hbar\omega_p\left(1+\frac{\hbar\omega^2}{m\omega_p}\alpha\right), \tag{46}$$

where

$$\alpha=\frac{3}{5}\frac{E_0}{\hbar\omega_p}, \tag{47}$$

[28] Blackstock, Ritchie, and Birkhoff, Phys. Rev. **100**, 1078 (1955).

[29] Marton, Simpson, and McCraw, Phys. Rev. **99**, 495 (1955).

[30] H. Watanabe, J. Phys. Soc. Japan **11**, 112 (1956).

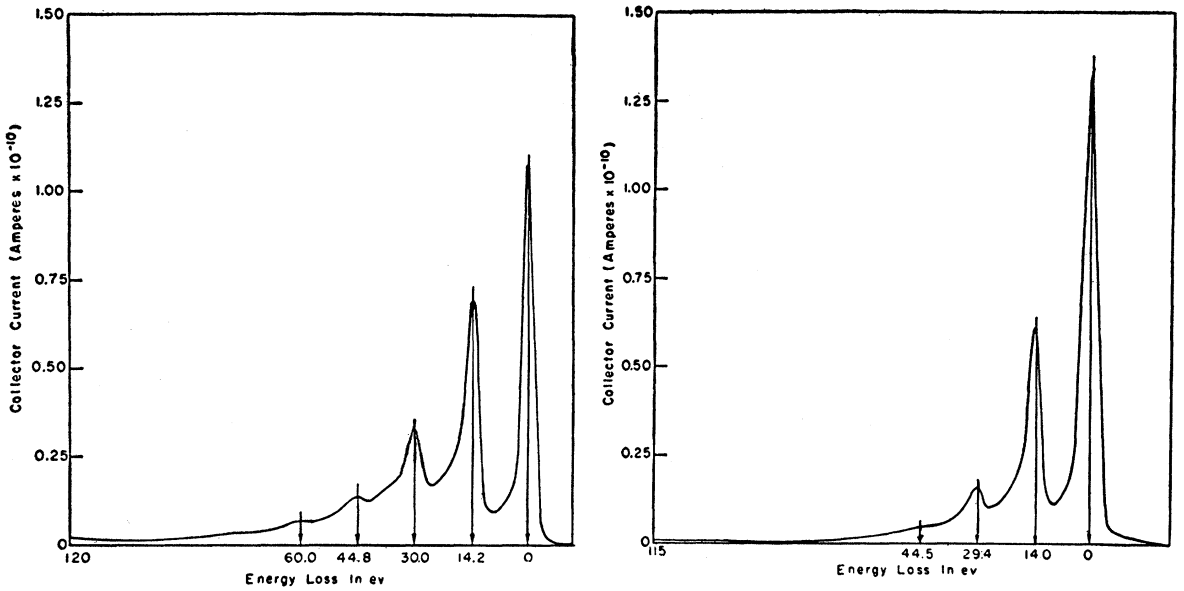


FIG. 5. Energy spectrum of electrons initially at 45 kev and 100 kev, respectively, after passing through a 15 $\mu g/cm^2$ Al foil (taken from Blackstock, Birkhoff, and Ritchie[28]). Peak to right represents electrons which have lost no energy. Other peaks at $\sim$15 ev interval correspond to plasmon excitation.

and we have taken $(\hbar k^2\alpha/m\omega_p)$ as rather smaller than unity. E_0 is the energy of an electron at the top of the Fermi distribution. In NP it is shown that the expression (46) should be quite generally valid for $k \lesssim k_c$; α will usually be altered from the free electron value, (47) by short-range electron-electron interactions and by band-band transitions. According to (33), which expresses the conservation of energy and momentum, we have $\vartheta \sim k/P_0$ for the angle ϑ by which an electron of momentum P_0 is scattered upon excitation of a plasmon of momentum k. We thus find from (46)

$$\Delta E = \hbar\omega_p + \frac{P_0^2}{m}\alpha\theta^2 \tag{48}$$

for the relation between the angle by which the electron is scattered and the energy of the plasmon responsible for the energy loss and scattering.

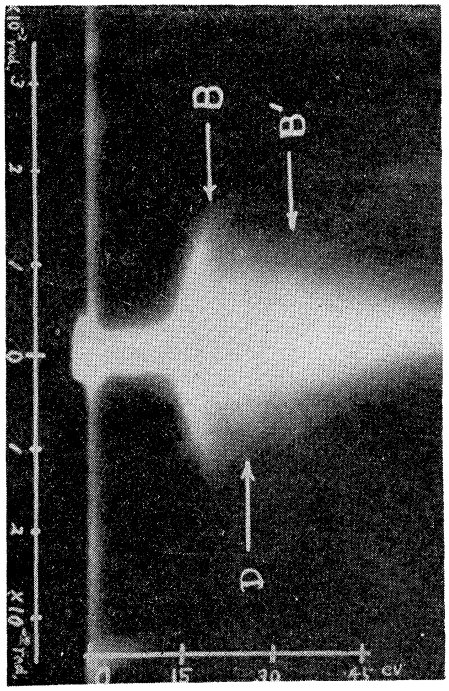


FIG. 6. Energy loss spectrum for Al (from Watanabe[30]). The ordinate represents the angle by which the electron is scattered, the abscissa the energy of the scattered electrons (measured from zero, for electrons which have not been scattered in the foil).

In Figs. 6 and 7 we reproduce Watanabe's results for aluminum. The lines B and B^1 correspond to the 15-ev and 30-ev losses, and represent electrons which have excited one and two plasmons, respectively. The variation of energy loss with angle for these electrons is that expected from (48). On the other hand, the straight diffuse line represented by D corresponds to the 23-ev loss line. Lines similar to B are also found by Watanabe in Be (19 ev), Mg (10.5 ev), Ge (16.5 ev), and graphite (7.5 ev). Lines similar to D were found in MgO (11.4 ev), Ag (25 ev), and Au (25 ev).

In Table V we compare the experimental values of α with the free electron value (47) for those elements for which a B-type loss line was observed. We see that the agreement is quite good for Be and Al, and a bit less so for Mg and Ge. In a sense we find the agreement more surprising than the disagreement, since many factors in addition to the free electron kinetic energy contribute to α. The loss lines for Be, Mg, Al, and Ge we have previously identified as corresponding to plasmon excita-

tion. The 7-ev loss line in graphite certainly does not correspond to the plasmon formed from all the valence electrons ($\hbar\omega\sim25$ ev). It might correspond to a plasma oscillation of the π electrons in graphite (one per C atom) which appear to have a good chance of oscillating independently at a considerably lower frequency. If we assume these are weakly bound, we find $\hbar\omega\sim12$ ev, in fair agreement with the 7 ev observed. (The agreement might be improved by taking into account the "static" polarization of the remaining valence electrons.) It is scarcely surprising that in this case the free electron value of α is not in agreement with that observed experimentally.

The D lines are all quite broad, so that one would not expect a well-defined variation of energy loss with angle. The 23 ev observed for Al might correspond to plasmon excitation in Al_2O_3; the 25-ev losses for Ag and Au are consistent with the hypothesis of plasmon excitation. On the other hand, the 11.4-ev line for MgO is likely to be a band-band transition.

From the maximum energy loss observed in a pattern like B, one can infer a maximum wave vector k_c beyond which the plasmon does not exist as a well-defined mode of excitation of the system. We have estimated this quantity elsewhere[16] by carrying out a variational calculation to minimize the ground-state energy of a gas of free electrons. The value so obtained was

$$k_c\sim0.353r_s^{\frac{1}{2}}k_0, \tag{49}$$

where k_0 is the wave vector of an electron at the top of the Fermi distribution and r_s is the average inter-electron spacing measured in units of the Bohr radius.

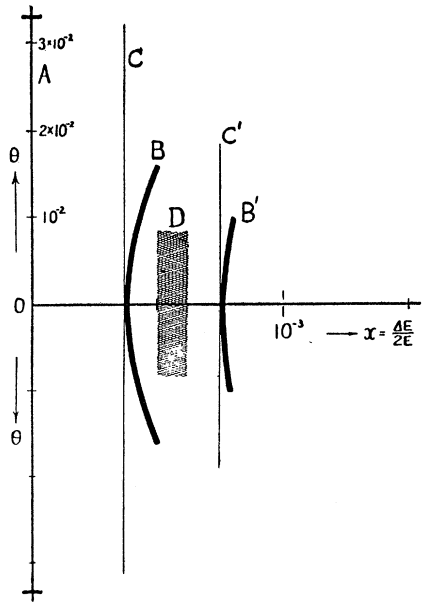


FIG. 7. The energy loss *vs* angle diagram constructed from Fig. 6 (from Watanabe[30]). The ordinate is the scattering angle in radians, the abscissa is the energy loss divided by twice the incident electron energy.

TABLE V. Comparison of experimental and theoretical plasmon dispersion relation.

Element	α_{exp}	α_{free}
Be	0.42±0.04	0.45
Mg	0.62±0.04	0.44
Al	0.50±0.05	0.45
Ge	0.83±0.15	0.45
C	1.0 ±0.3	0.40

For Al we should expect a maximum scattering angle, $\vartheta_c\sim k_c/P_0$ of $\sim1.1\times10^{-2}$ rad for the 25-kev electrons used by Watanabe. Watanabe finds instead that ϑ_c is experimentally somewhat higher, being $\sim1.5-1.8\times10^{-2}$ rad. This somewhat higher k_c may receive an explanation in the recent work of Ferrell and Quinn.[31] They find that even a comparatively short-range interaction between electrons may lead to a collective energy loss, so that the cutoff in collective excitations is not really sharp. Instead, beyond the value k_c for which the plasmon picture is not suitable according to (49), there still exist collective modes with energies in the region of the plasmon energy. Ferrell and Quinn estimate that the increase in the effective cutoff for collective excitation is of the order of magnitude of that observed in Al.

VI.

In conclusion it is perhaps useful to turn once more to the question of whether all the energy loss acts we have discussed should properly be regarded as corresponding to plasmon excitation. In the case of the sharp loss lines observed for Be, Mg, Al, and Ge there can certainly be little question. The energy losses appear where we expect them to on theoretical grounds, and the dispersion of the energy loss with scattering angle is also in good agreement with theoretical expectation. Again, the agreement between theory and experiment for the optical properties of the alkali metals argues strongly for the existence of plasmons in these metals. I believe that the evidence derived from Table III is equally good. The general variation of plasmon energy through the elements listed there is completely consistent with experiment. In a sense, what puzzles exist have to do with why the agreement is so good, rather than with explaining existing disagreements. And this statement applies perhaps even more strongly to the compounds considered in Table IV.

When we are dealing with a very broad loss line, as is the case for a number of the materials considered above, the question naturally arises as to whether one need invoke a new elementary excitation to explain it. For if we do so, the width of the line is a clear indication that the excitation has an extremely short lifetime because there are a large number of possible electronic band-band transitions in its immediate vicinity. One might then argue that the line could be more satis-

[31] R. Ferrell and J. J. Quinn, Bull. Am. Phys. Soc. Ser. II, **1**, 44 (1956).

factorily explained on the basis of a superposition of sharp individual electronic loss lines, and that better experiments will establish a fine structure to the loss line. (Of course such a fine structure is not ruled out for the solution of the rather complicated plasmon dispersion relation.) In a sense such an argument is always correct, in that we are dealing with a collection of individual electrons and any excitation can, in principle, be described in terms of their motion. The essential point is that where the correlations between the electrons are so important that they determine the character of a given excited state, a description in terms of the individual electrons is quite complicated, and perhaps not even useful. It is under just such circumstances that it is convenient and simple to introduce a collective mode to describe the excited state, and this is what we have done with the plasmons. As we have mentioned such a description is obviously called for with the narrow lines. I believe it is equally useful with the broad lines we have considered, for the position and intensity of the lines indicates that Coulomb correlations have contributed to an important enhancement and shift of the energy loss, making a plasmon description the more appropriate one.

Certainly individual electron band-band transitions will take place, and I am inclined to assign many of the low-lying loss lines we have not considered to this mechanism. Clearly a great deal of work is needed to render such an interpretation plausible in the light of the known band structure and anticipated transition probabilities for a given solid.[32] I do not believe the correlations between the x-ray fine structure and the characteristic loss lines discussed by Leder, Mendlowitz, and Marton[33] establishes the individual particle character of the loss lines. For one thing, the processes are quite different. In one case we have a core electron which makes a transition to a state at the top of the valence band, or to one of the higher bands. In the other we deal with an average over all transitions from the valence to the higher bands. It would be quite surprising if the variation in the density of initial states in the latter case did not frequently lead to significant differences in the two processes. A tentative explanation of the similarity of the energy differences might be given along the following lines. The correlation between the valence electrons which gives rise to plasmon excitation is just such as to enhance the density of states of the system at a distance $\hbar\omega$ above the ground state of the valence electron assembly, so that a transition of the core electron to such a state would be definitely favored. Such an enhancement would then give rise to fine structure in the x-ray absorption spectrum.

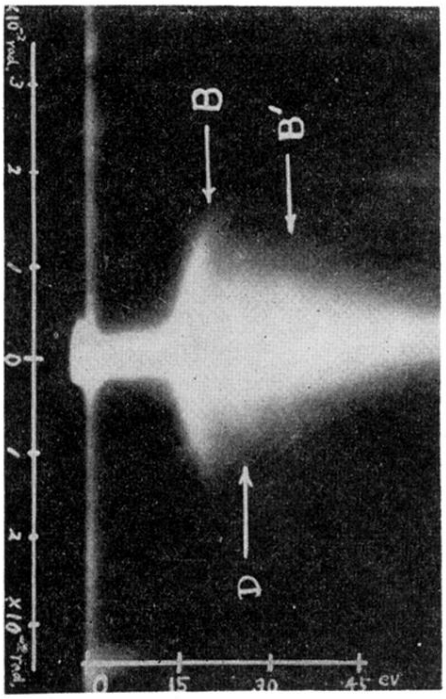
It is obvious that a great deal of work, both experimental and theoretical, lies ahead before we may feel that our understanding of the energy loss spectra is truly satisfactory. The existing discrepancies between the work of different investigators on the same material must certainly be resolved. It would be desirable to extend the sort of surveys of energy loss spectra which has been carried out to include as many as possible of the thus far uninvestigated elements and compounds. It will be interesting to see whether the most prominent energy losses thus found continue to fit in so well with the predicted plasmon behavior. Furthermore, it should now prove fruitful for an investigator to concentrate upon a given material, both theoretically and experimentally, in order to obtain as complete an understanding as possible of the origin of the different energy losses (whether single or repetitions of elementary events, whether plasmon or a band-band transition), their variation with angle, relative cross sections, and the like. Another interesting question worthy of investigation is the dependence of the plasmon production cross section on foil thickness for very thin foils which has been discussed by Gabor.[34]

Let me conclude with a word of cheer to the experimentalist in this field. In working with the plasmon, the solid state physicist is able to outdo his elementary particle brethen in at least one important respect. The most short-lived elementary particle which has thus far been observed is the π^0 meson which has a lifetime of $\sim 10^{-14}$ sec. On the other hand in the plasmon we are able to observe an elementary excitation with a lifetime as short as 10^{-16} sec.

[32] The work of Rudberg and Slater [Phys. Rev. **50**, 150 (1936)] should be mentioned in this connection.

[33] Leder, Mendlowitz, and Marton, Phys. Rev. **101**, 1460 (1956).

[34] D. Gabor, Phil. Mag. Ser. 8, **1**, 1 (1956).



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