

Theory of Plasma Waves in Metals

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The Hartree approximation is used to investigate the effect of the crystal lattice on plasma oscillations in metals. The plasma frequency is given by $\omega^2 = 4\pi e^2 n_0 \langle 1/m_i^* \rangle$, where the average is over filled electron states. For free electrons this equation reduces to that given by Bohm and Gross: for insulators $\langle 1/m_i^* \rangle = 0$ and there are no oscillations.

In metals with occupied d bands, such as Cu, Ni, and Ag, there is a strong coupling between the plasma wave and the d electrons which gives rise to frequency broadening. This explains why the plasma lines observed by Ruthemann and Lang are so much wider in these elements than in Be or Al. Further confirmation of this mechanism could be obtained by repeating their experiments on the transition metals Sc–Ni.

I

THE subject of plasma oscillations in solids has recently received considerable attention from both the experimental and theoretical point of view. Investigations by Ruthemann¹ and Lang² have demonstrated the existence of such oscillations in several elements and, in addition, have disclosed a number of interesting features concerning them. Moreover, calculations by Pines and Bohm³ have shown that the frequencies and rates of energy loss observed by these workers are in accord with those to be expected from the theory of plasma oscillations. These calculations, however, are based on a theory which takes no account of couplings of the plasma to either the lattice or core electrons and which cannot, therefore, be expected to explain the marked differences in behavior between various elements that were observed by Ruthemann and Lang. The purpose of this paper is twofold: to point out that the Hartree approximation⁴ is a useful tool for investigating such couplings, and to apply it to study their effect on experiments such as those of Ruthemann and Lang. It should be emphasized that this work is not a quantum theory of plasma oscillations since it treats them throughout on a semiclassical basis similar to that sometimes used in studying the interaction of radiation with matter.

II

As has been pointed out by Pines and Bohm, a plasma oscillation is essentially a long-range ordering; typical plasma behavior depending mainly upon the individually weak, but cumulatively large, Coulomb interactions of many particles at relatively large distances from one another. Furthermore, intimate collisions between these particles do not contribute to the organized nature of the motion (as they would, for example, in a sound wave) but, on the contrary, tend to disrupt it. Thus, except for these damping effects which, in the case of metals, are pretty well suppressed by the

operation of the exclusion principle, one would expect an approximation which neglects interparticle correlation, such as that of Hartree, to provide a good description of the plasma oscillations. To illustrate and test this hypothesis let us at first consider briefly the problem of oscillations in a gas of free electrons. The solutions of this problem are well known from the work of Bohm and Gross⁵ and will provide a convenient check of the Hartree approximation in this case. Then, having established the validity of our method, we may generalize the results obtained from this simple example to take into account the effects of the metallic lattice.

Working in a moving coordinate system in which the plasma wave is at rest, the Hartree equations are

$$-\frac{\hbar^2}{2m}\nabla^2\varphi_i + e\left[\sum_j \int \frac{|\varphi_j(r')|^2 dr'}{|r-r'|} - U\right]\varphi_i = E_i\varphi_i. \quad (1)$$

Here U is the potential of a uniform positive charge distribution which exactly cancels the average potential due to electrons, and φ_i and E_i are, respectively, the wave function and energy of the i th electron. The difference,

$$\sum_j \int \frac{|\varphi_j(r')|^2}{|r-r'|} dr' - U, \quad (2)$$

represents the potential caused by any fluctuation of electron density—it is just the potential generated by the plasma oscillation and will be denoted by V . If the coordinates are chosen so that the plasma wave is moving in the z direction, V becomes a function of z only and the equations separate. The solutions are

$$\varphi_j = \exp[i(k_x x + k_y y)]U_j(z), \quad (3)$$

where $U_j(z)$ is a solution of the ordinary differential equation

$$-(\hbar^2/2m)\partial^2 U_j/\partial z^2 + eV U_j = \epsilon_j U_j \quad (4)$$

and

$$\epsilon_j = E_j - \hbar^2 k_x^2/2m - \hbar^2 k_y^2/2m.$$

We may now take advantage of the fact that $V(z)$ is in

¹ G. Ruthemann, *Ann. Phys.* **2**, 113 (1948).

² W. Lang, *Optik* **3**, 233 (1948).

³ D. Pines and D. Bohm, *Phys. Rev.* **83**, 221 (1951); **85**, 338 (1952).

⁴ D. R. Hartree, *Cambridge Phil. Soc.* **24**, 89 (1928).

⁵ D. Bohm and E. P. Gross, *Phys. Rev.* **75**, 1851 and 1864 (1949).

general a slowly varying function⁶ and solve for U_j by the WKB method. The complete wave function is found to be

$$\varphi_j = (1 - eV/\epsilon_j)^{-\frac{1}{2}} \exp[i(k_x x + k_y y)] \times \exp\left\{\pm i \int [2m(\epsilon_j - eV)]^{\frac{1}{2}} dz / \hbar\right\}. \quad (5)$$

The final step in this example is to apply the self-consistency condition, i.e., to require that the electron density ρ and the potential V generated by it satisfy Poisson's equation

$$\nabla^2 V = -4\pi\rho = -4\pi e \left[n_0 - \sum_{j=1}^N |\varphi_j|^2 \right]. \quad (6)$$

Substitution of Eq. (5) into this relation leads immediately to the nonlinear differential equation for V ,

$$\nabla^2 V = 4\pi e \sum_{j=1}^N \left[\frac{1}{(1 - eV/\epsilon_j)^{\frac{1}{2}}} \right] - 4\pi e n_0. \quad (7)$$

(The term $-4\pi e n_0$ represents the smeared out positive charge density which cancels the term independent of V in the sum. This cancellation is necessary since $V \equiv 0$ must be a solution.) Equation (7) is identical with that obtained by Bohm and Gross and, when linearized, leads immediately to the dispersion relation,

$$\omega^2 = 4\pi e^2 n_0 / m + \bar{v}^2 k^2, \quad (8)$$

derived by them.

Thus we see that in the free-electron case the Hartree approximation leads in a simple and direct way to the fundamental equations of the plasma theory. We may feel confident, therefore, in applying this method to more complicated problems than that of a free-electron gas. In particular, the work of the next section will show that it makes possible a description of plasma waves when the electrons are moving through a crystal lattice.

III

To generalize the preceding results to the case of an electron plasma moving in a lattice field we use a method developed by Wannier,⁷ and discussed in considerable detail in a paper of Slater's.⁸ In the work of these authors it is shown that wave functions of electrons in a lattice which is perturbed by a slowly varying potential have the form

$$\varphi_\alpha = \sum_\lambda [\Psi_j(Q_\lambda) a(\mathbf{r} - \mathbf{Q}_\lambda)], \quad (9)$$

where the a 's are the localized wave functions first introduced by Wannier, and the sum is over all lattice

⁶ Throughout this work the assumption will be made that V is slowly varying. If this is not true the wavelengths become comparable with the interparticle separation and the whole concept of a plasma oscillation loses its validity.

⁷ G. H. Wannier, Phys. Rev. **52**, 191 (1937).

⁸ J. C. Slater, Phys. Rev. **76**, 1952 (1949).

sites. Furthermore, Slater shows that the Ψ_j satisfy the differential equation

$$[E_0(-i\hbar\nabla) + eV]\psi_j = i\hbar\dot{\psi}_j; \quad (10)$$

$E_0(-i\hbar\nabla)$ being the operator obtained by replacing the momentum by $-i\hbar\nabla$ in the energy-momentum relation. In the case we are considering V is the plasma potential which we now take to be harmonic, corresponding to a linearized version of Eq. (7). The differential equation for ψ then reads

$$[E_0(-i\hbar\nabla) + eV_0 \cos\{k(z - v_\omega t)\}]\psi = i\hbar\dot{\psi}. \quad (11)$$

As before, V is a slowly varying function of its argument and this suggests a solution of the form

$$\psi = \exp[i(p_x x + p_y y)/\hbar] \times \exp[iS(z - v_\omega t)] \exp[-iEt/\hbar], \quad (12)$$

with a subsequent expansion of S into a power series in \hbar ,

$$S = (S_0/\hbar) + S_1 + \dots \quad (13)$$

This procedure leads to equations for S_0 , S_1 , etc., completely analogous to those obtained in the more usual version of the WKB approximation. However, the calculation is somewhat lengthy and we defer it to the appendix, giving here only the differential equations which determine S_0 and S_1 ;

$$E_0(p_x, p_y, S_0') + eV_0 \cos\{k(z - v_\omega t)\} = v_\omega S_0' + E, \quad (14)$$

$$\partial E / \partial p_x(p_x, p_y, S_0') \hbar S_1'$$

$$+ \frac{1}{2} \frac{\partial^2 E_0}{\partial p_x^2}(p_x, p_y, S_0') \frac{\hbar}{i} S_0'' = \hbar v_\omega S_1'. \quad (15)$$

[Notice that p_x and p_y only enter these equations parametrically. For brevity, therefore, we will suppress the dependence of the energy and its derivatives on them and in the future write $E_0(p_x, p_y, S_0')$ merely as $E_0(S_0')$, etc.] To solve for S_0' , we find the root of the equation

$$E_0(p) - v_\omega p = E, \quad (16)$$

as a function of the energy E . In terms of this root, which we denote by $p(E)$, the solution of Eq. (14) is

$$S_0 = \int^{z - v_\omega t} p[E - eV_0 \cos(kq)] dq. \quad (17)$$

The second equation integrates immediately, just as in the conventional WKB method, and we find

$$S_1 = -\frac{1}{2} \ln \left[\frac{\partial E_0}{\partial p_x}(S_0') - v_\omega \right]. \quad (18)$$

The wave functions are, therefore

$$\psi_j = \exp \left\{ \pm (1/\hbar) \int^{x-v_\omega t} p[E_j - eV_0 \cos(kq)] dq \right\} / \left[\frac{\partial E_0}{\partial p_z} (S_0') - v_\omega \right]^{\frac{1}{2}}. \quad (19)$$

To complete the calculation we apply the consistency condition in the form

$$\nabla^2 V = 4\pi e [\sum_j |\psi_j|^2 - 1]. \quad (20)$$

Notice that here, instead of the charge density, we use its average over a lattice cell. This approximation, without which the equations become exceedingly complicated, will be made throughout the rest of this work. Its validity is difficult to estimate, but this type of approach is the usual one and has been used with success on a number of problems (see Slater's paper⁸ for references).

After linearizing Eq. (20), a straightforward algebraic manipulation (see Appendix) such as that performed by Bohm and Gross leads to the dispersion relation

$$\omega^2 = 4\pi e^2 n_0 \left\langle \frac{1}{m_z^*} \right\rangle + \left\langle \frac{(\partial E / \partial p_z)^2}{m_z^*} \right\rangle \frac{k^2}{\langle 1/m_z^* \rangle}, \quad (21)$$

where $1/m_z^* = \partial^2 E / \partial p_z^2$, and the indicated averages are taken over filled electron states. The form of this equation is hardly a surprise (especially the appearance of m_z^* in the first term on the right-hand side) since the most natural generalization of Eq. (8) would be to replace m by the effective mass. However, it is worth noting that, besides giving the correct answer for free electrons, Eq. (21) also gives a reasonable result in a radically different limit, namely, when all occupied bands are completely full and the substance under consideration is an insulator. In this case the average, $\langle 1/m_z^* \rangle$, is taken over full bands only and, since E_0 is a periodic function, this quantity is then zero. Thus, we conclude that plasma oscillations do not exist in insulators and, further, that in conductors the electrons in filled bands do not contribute to the oscillations. Physically this is only what one would expect since it is hard to conceive of a charge density fluctuation within a full band.

As far as experimental verification of Eq. (21) is concerned, the best metal with which to work is probably Li, since for this element there is a good theory which predicts an m^* value differing appreciably from unity. The calculations of Silverman and Kohn⁹ indicate that $1/m_z^*$ is about 0.73 for Li, which means that the value of ω observed in an experiment should differ from that calculated with Eq. (8) by about 15 percent.

⁹ R. A. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950).

IV

Before going on with the discussion of the effect of interband transitions on the plasma oscillations, it is well to clear up one possible objection to the work of the previous section. This objection concerns the use of the Hartree equations with their neglect of electron exchange. Intuitively one might suspect that exchange, at least in the long-wavelength limit, would have a negligible effect since its contribution to the plasma energy will be proportional to the square of the electron density fluctuation $(\delta\rho)^2$, while the Coulomb energy is

$$\frac{1}{2} \int \frac{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (22)$$

and to keep this expression finite for small k we must choose $\delta\rho \sim k$ which means that in the limit $k \rightarrow 0$ the exchange energy goes to zero compared to the Coulomb energy.

That this argument is correct for a free-electron gas, can be shown explicitly by use of the Fock¹⁰ equations. The details of this work will be left to the appendix since they are rather lengthy, and here we will be content to quote the result that exchange affects only the term proportional to k^2 in Eq. (8). Thus, for almost all cases of interest, the Hartree equations are adequate for description of plasma oscillations.

V

One of the most interesting features of the work of Ruthemann and Lang is the fact that in certain metals (Al, Be) they observed sharp resonances in the curves of intensity *versus* energy loss whereas in others (Cu, Ag, Ni) the peaks are very broad, their width being comparable to the energy of the plasma quanta absorbed. Herring¹¹ has suggested that this broadening is due to strong coupling between electrons in overlapping s and d bands which makes possible a rapid transfer of energy from a plasma oscillation in the s band to a single d electron, thus leading to a short life and large energy width for the oscillations. In this section we will compute, in so far as possible, the energy broadening of plasma oscillations due to this interaction. The section will also contain a short discussion of the shift in plasma frequency due to s - d coupling.

To calculate the width of a plasma oscillation due to interband transitions, we first determine the rate at which plasma oscillations excite electrons and then use the uncertainty principle to obtain the energy broadening. For this purpose we must extend Eq. (10) to include terms that cause these transitions. Such an extension has recently been carried out in detail by Adams,¹² and to find the potential causing interband transitions we need only Eq. (49b) of his paper. Using this for-

¹⁰ V. Fock, Z. Physik **61**, 126 (1930).

¹¹ C. Herring (private communication).

¹² E. N. Adams, II, Phys. Rev. **85**, 41 (1952).

mula, it is readily seen that the matrix element for excitation of an electron by a plasma oscillation is identical with that for absorption of a photon of the same energy. Furthermore, this is also the matrix element of the plasma potential V between the two states in different bands. This is as one might expect since, as we mentioned earlier, Eq. (10) only includes intraband effects and takes no account of the operation of the potential in causing transitions between them.

Taking advantage of the fact that these matrix elements are the same we may express the energy width in terms of the parameter $n\hbar k$ for optical absorption which has been measured by Minor¹³ and Meier¹⁴ for Cu and Ag. After normalizing V_0 so that the plasma energy,

$$-\frac{1}{8\pi} \int V \nabla^2 V d\tau, \quad (23)$$

is that of one plasma quantum, we find the following exceedingly simple relation connecting the energy width ΔE and $n\hbar k$:

$$\Delta E/\hbar\omega_p = n\hbar k. \quad (24)$$

If experimental values of $n\hbar k$ existed in the proper frequency range, Eq. (24) would give immediately the desired width. Unfortunately, the work of Minor and Meier only extends down to wavelengths of about 2000Å (~ 5 eV) which is rather far from the 20 eV at which we wish to evaluate $n\hbar k$. However, the values they quote for 2000Å lie between one and two and this indicates that, barring an exceedingly rapid change of $n\hbar k$ with frequency, the values of $\Delta E/\hbar\omega_p$ will be close to those observed by Ruthemann and Lang. For the alkali metals, on the other hand, the observed $n\hbar k$ values are generally smaller by about a factor of 10, and this tends to confirm Herring's surmise. In this picture, energy broadening is caused by excitation of both s and d electrons but since the latter are both more numerous and more tightly bound, they will be excited most often and contribute the major portion of the frequency width whenever their excitation is energetically possible. These conclusions are in complete agreement with the results of Ruthemann and Lang.

An attempt to compute the value of the matrix element for excitation by numerical integration using plane waves for the excited electron and a Hartree¹⁵ function of the Cu^+ ion for the electron in the $3d$ band was rather unsuccessful. For 5-eV quanta it gave values smaller by more than factor of three than those obtained from Eq. (24); hence the result calculated for 20-volt quanta ($\Delta E/\hbar\omega_p \sim 1/80$) can hardly be considered reliable. The discrepancy probably has its origin in the fact that the wave functions of a $3d$ electron in Cu^+ and in the metal are quite different in the region far

from the nucleus where a large part of the contribution to the matrix element arises.

In conclusion, therefore, it is reasonable, that s - d coupling in metals such as Cu, Ni, and Ag is responsible for the large widths of the plasma energies observed by Ruthemann and Lang. This tentative conclusion could be checked by repeating their experiments on the transition elements, Sc through Ni. If our interpretation is correct, the widths of the absorption peaks should be observed to increase from element to element as the $3d$ shell is filled.

In addition to inducing interband transitions, the terms neglected in Eq. (10) will also cause a shift in frequency of the plasma oscillation. This effect is very marked in Cu, Ni, and Ag where the frequencies obtained from Eq. (21) (choosing $m^*=m$) are roughly half of those observed experimentally. A very crude estimate, using second-order perturbation theory and the optical absorption data to give the magnitude of the matrix elements, indicates that the energy shift is of the order 10 eV for these elements. Of course, since the shift is so large, perturbation theory can, at best, give a semiquantitative result but it is encouraging that the order of magnitude and direction of the effect are in agreement with experiment.

VI

In the preceding sections the Hartree approximation has been used to describe the behavior of plasma oscillations in metals. The results, in general, are in accord with observation but it is abundantly clear that more experiments are needed to test the somewhat tentative conclusions set forth here as well as to provide a springboard for further theoretical work in this field.

In conclusion, the author would like to express his thanks to Conyers Herring, Gregory Wannier, and P. W. Anderson with whom he has had a number of interesting conversations on the topics discussed here.

APPENDIX A

The principal problem in deriving Eqs. (14) and (15) of the text is to find the effect of operating on $\psi = e^{is}$ with $E_0(Px, Py, -i\hbar\partial/\partial z)$. For this purpose we expand E_0 into a power series

$$E_0\left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right) = \sum_n \left[a_n \left(\frac{\hbar}{i}\right)^n \frac{\partial^n}{\partial z^n} \right] \quad (1a)$$

and consider separately the effect of each term on ψ . Our problem, therefore, is reduced to the evaluation of $\partial^n(e^{is})/\partial z^n$. Furthermore, because we plan later to keep only terms up to the first power in \hbar , we drop all derivatives of S of higher order than the second since, to this approximation, they do not contribute. With these restrictions it is readily verified (by induction,

¹³ R. S. Minor, Ann. Physik **10**, 581 (1903).

¹⁴ W. Meier, Ann. Physik **31**, 101 (1910).

¹⁵ D. R. Hartree, Proc. Roy. Soc. (London) **157**, 490 (1936).

for example) that

$$\frac{\partial^n}{\partial z^n}(e^{iS}) = \left[(iS')^n + i \frac{n(n-1)}{2} S'' (iS')^{n-2} \right] e^{iS}, \quad (2a)$$

whence

$$\begin{aligned} E_0 \left(\frac{\hbar}{i} \frac{\partial}{\partial z} \right) &= \sum_n \left\{ a_n \left(\frac{\hbar}{i} \right)^n \left[(iS')^n \right. \right. \\ &\quad \left. \left. + i \frac{n(n-1)}{2} S'' (iS')^{n-2} \right] \right\} e^{iS} \\ &= E_1 (\hbar S') + \frac{1}{2} \frac{\partial^2 E_0}{\partial p_z^2} (\hbar S')^2 (iS''). \end{aligned} \quad (3a)$$

Expanding S into a power series in \hbar ,

$$S = (S_0/\hbar) + S_1 + \dots, \quad (4a)$$

and collecting terms of zero and first degree in \hbar in Eq. (11), we arrive immediately at the differential equations for S_0 and S_1 given in the text.

To derive the dispersion relation from Eq. (20) consider

$$|\psi_j|^2 = 1 \left/ \left[\frac{\partial E_0}{\partial p_z} (S_{0j}') - v_\omega \right] \right. \quad (5a)$$

Treating the plasma potential as small, we write $S_{0j} = p_j + \delta S_{0j}$. δS_{0j} is proportional to V_0 (to first order) and is obtained by expanding Eq. (16) into powers of the plasma potential and equating coefficients of the linear terms in V_0 . The result is

$$\delta S_{0j}' = -eV_0 \cos[k(z - v_\omega t)] \left/ \left[\frac{\partial E_0}{\partial p_z} (p_j) - v_\omega \right] \right. \quad (6a)$$

Substituting this back into the expression for $|\psi_j|^2$ and again keeping only linear terms in V_0 , we arrive at the dispersion law

$$\left[\sum_j \left\{ \frac{\partial^2 E}{\partial p_z^2} (p_j) \left/ \left[\frac{\partial E}{\partial p_z} (p_j) - v_\omega \right]^2 \right\} + k^2 \right\} \cos k(z - v_\omega t) = 0. \quad (7a)$$

This expression may now be expanded, making use of the fact that for long waves $v_\omega \gg \partial E / \partial p_z$, in the same way as was done by Bohm and Gross to give the dispersion law, Eq. (21).

APPENDIX B

To solve the Fock equations in the presence of a plasma oscillation, we make use of the fact that for free electrons plane waves are an exact solution. Working from these as a base, we treat the effects of the plasma potential as a small perturbation and thus are able to make the differential equations linear. More explicitly,

the Hartree-Fock equations are

$$\begin{aligned} \frac{\hbar^2}{2m} \nabla^2 \psi_i + e^2 \sum_j \int \frac{|\psi_j(r')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \psi_i(r) \\ - e^2 \sum_j \int \psi_j^* \frac{(r') \psi_i(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \psi_j(r) = E_i \psi_i(r), \end{aligned} \quad (1b)$$

to which we attempt a solution of the form

$$\psi_i = e^{i\mathbf{k}_i \cdot \mathbf{r}} [1 + \alpha(\mathbf{k}_i) e^{i\mathbf{k}_i \cdot \mathbf{r}} + \beta^*(\mathbf{k}_i) e^{-i\mathbf{k}_i \cdot \mathbf{r}}], \quad (2b)$$

knowing that for $\alpha = \beta = 0$ we have an exact solution. Substituting these tentative wave functions into (1b) and keeping only linear terms in α and β , we find that they do, indeed, satisfy the equations provided the coefficients obey the following set of linear, homogeneous, algebraic equations:

$$\begin{aligned} (\hbar^2/2m) \alpha(\mathbf{k}_i) (\mathbf{k}_i + \mathbf{k})^2 + e^2 \sum_j \alpha(\mathbf{k}_j) C_{\mathbf{k}} \\ + e^2 \sum_j \alpha(\mathbf{k}_j) C_{\mathbf{k}} - e^2 \sum_j \beta(\mathbf{k}_j) C_{\mathbf{k} + \mathbf{k}_i - \mathbf{k}_j} \\ - e^2 \sum_j \alpha(\mathbf{k}_i) C_{\mathbf{k} + \mathbf{k}_i - \mathbf{k}_j} - e^2 \sum_j \alpha(\mathbf{k}_j) C_{\mathbf{k}_i - \mathbf{k}_j} \\ = E_i \alpha(\mathbf{k}_i), \end{aligned} \quad (3b)$$

and

$$\begin{aligned} (\hbar^2/2m) \beta(\mathbf{k}_i) (\mathbf{k}_i - \mathbf{k})^2 + e^2 \sum_j \alpha(\mathbf{k}_j) C_{\mathbf{k}} \\ + e^2 \sum_j \beta(\mathbf{k}_j) C_{\mathbf{k}} - e^2 \sum_j \alpha(\mathbf{k}_j) C_{-\mathbf{k} + \mathbf{k}_i - \mathbf{k}_j} \\ - e^2 \sum_j \beta(\mathbf{k}_i) C_{-\mathbf{k} + \mathbf{k}_i - \mathbf{k}_j} - e^2 \sum_j \beta(\mathbf{k}_j) C_{\mathbf{k}_i - \mathbf{k}_j} \\ = E_i \beta(\mathbf{k}_i). \end{aligned} \quad (4b)$$

Here $C_{\mathbf{k}} = \int (\exp(i\mathbf{k} \cdot \boldsymbol{\sigma} / \sigma)) d\boldsymbol{\sigma}$, and use has been made of the fact that this integral is real in taking the complex conjugate of the second equation.

These are very complicated equations but in the absence of the exchange terms they simplify enormously and are readily soluble, leading to the formula given in Sec. II. Therefore, we adopt a perturbation theory approach, solving first without the exchange terms and then using these solutions to obtain a first-order correction due to exchange. If we set $\sum_j \alpha(\mathbf{k}_j) = A$ and $\sum_j \beta(\mathbf{k}_j) = B$, the simplified equations have solutions

$$\alpha(\mathbf{k}_i) = \frac{e^2 C_{\mathbf{k}} (A + B)}{[E_i - (\hbar^2/2m) (\mathbf{k}_i + \mathbf{k})^2]}, \quad (5b)$$

$$\beta(\mathbf{k}_i) = \frac{e^2 C_{\mathbf{k}} (A + B)}{[E_i - (\hbar^2/2m) (\mathbf{k}_i - \mathbf{k})^2]}.$$

Neglecting exchange completely the consistency conditions,

$$\sum_i \alpha(\mathbf{k}_i) = A = \sum_i \frac{e^2 C_{\mathbf{k}} (A + B)}{[E_i - (\hbar^2/2m) (\mathbf{k} + \mathbf{k}_i)^2]}, \quad (6b)$$

$$\sum_i \beta(\mathbf{k}_i) = B = \sum_i \frac{e^2 C_{\mathbf{k}} (A + B)}{[E_i - (\hbar^2/2m) (\mathbf{k} - \mathbf{k}_i)^2]},$$

would lead directly to the formulas of Sec. II which

were derived from the Hartree equations. Since, however, we are interested in including exchange to first order, we substitute (5b) into (3b) and find the solutions

$$\alpha(\mathbf{k}_i) = e^2 \left\{ (A+B)C_k \left(1 - \frac{2me^2}{\hbar^2} \sum_j \left[\frac{C_{\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j} - C_{\mathbf{k}_i-\mathbf{k}_j}}{2(\mathbf{k} \cdot \mathbf{k}_j)} \right] \right) \right\} / \left\{ (\hbar^2/2m)(\mathbf{k}_i+\mathbf{k})^2 - E_i - e^2 \sum_j C_{\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j} \right\}, \quad (7b)$$

$$\beta(\mathbf{k}_i) = e^2 (A+B)C_k \left\{ 1 + \frac{2me^2}{\hbar} \sum_j \left[\frac{C_{-\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j} - C_{\mathbf{k}_i-\mathbf{k}_j}}{2\mathbf{k} \cdot \mathbf{k}_j} \right] \right\} / \left\{ (\hbar^2/2m)(\mathbf{k}_i-\mathbf{k})^2 - E_i - e^2 \sum_j C_{-\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j} \right\}. \quad (8b)$$

In obtaining these formulas we have dropped exchange corrections to E in (5b) when substituting these into (3b). Also, we have neglected k^2 compared to $\mathbf{k} \cdot \mathbf{k}_j$ in several places.

To complete the calculation we apply the consistency conditions,

$$\sum_i \alpha(\mathbf{k}_i) = A \quad \text{and} \quad \sum_i \beta(\mathbf{k}_i) = B,$$

and proceed exactly as we did with Eqs. (6b). After doing a certain amount of algebra, we arrive at the dispersion relation,

$$\omega^2 = \frac{4\pi e^2 n_0}{m} \left\{ 1 - \frac{4\pi e^4 m^2}{\hbar^4} \times \sum_{i,j} \left[\frac{6\mathbf{k} \cdot (\mathbf{k}_i - \mathbf{k}_j)}{(\mathbf{k} \cdot \mathbf{k}_i)^2 (\mathbf{k} \cdot \mathbf{k}_j) (\mathbf{k}_i - \mathbf{k}_j)^4} \right] \right\} + \bar{v}^2 k^2. \quad (9b)$$

In this expression, the $\mathbf{k}_i, \mathbf{k}_j$ in the sum are wave numbers in the coordinate system in which the plasma wave is at rest. Transforming to the laboratory system ($\mathbf{k}_i \rightarrow (\mathbf{k}\omega/k^2)(m/\hbar) + \boldsymbol{\lambda}_i$), we immediately verify that the exchange correction in (9b) is proportional to k^2 , which confirms the statement in Sec. IV.

Some Electrical and Optical Properties of Synthetic Single Crystals of Zinc Sulfide

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The fundamental optical absorption edge and the temperature dependence of electrical conductivity of synthetic single crystals of hexagonal zinc sulfide have been measured, as well as the photoconductivity near the absorption edge. The fundamental absorption coefficient is 1 mm^{-1} at a photon energy of $(3.58 \pm 0.02) \text{ eV}$ and increases exponentially by a factor of ten every 0.07 eV up to 10^3 mm^{-1} . The logarithm of the electric resistivity varies linearly as a function of the inverse absolute temperature with a slope of $(3.77 \pm 0.1) \text{ eV}/2k$. A peak in the spectral variation of photoconductivity has been observed at the optical absorption edge.

I. INTRODUCTION

INFORMATION pertinent to the energy gap between the valence band and the conduction band of an insulator or a semiconductor can be deduced from experimental data by two general techniques. First, the energy gap can be calculated from the temperature variation of intrinsic conductivity (or conduction electron density). Alternatively, one can study the long-wavelength edge of the fundamental optical absorption band by making measurements of the spectral variation of the absorption coefficient or the photoconductivity.

Gudden and Pohl^{1,2} report a sharp rise of photoconductivity at approximately 3350A in natural crystals of zinc blende and in zinc sulfide phosphors. Gisolf³ reports the ultraviolet limit of transmission

of powdered samples of pure zinc sulfide (wurtzite) to be 3350A. This measurement was confirmed by Reynolds and Czyzak⁴ on single crystals of synthetic wurtzite.

It is the purpose of this paper to report experiments relating to the band gap of the hexagonal form (wurtzite) of zinc sulfide. Measurements of photoconductivity and optical absorption have been made more exactly than in previously published work. In addition, temperature dependence of electrical conductivity has been measured.

This work was done with synthetic single crystals of zinc sulfide. These crystals were grown in an evacuated quartz container as described by the author elsewhere⁵ and in a long quartz tube in an atmosphere of hydrogen by a technique similar to that reported by Reynolds

¹ B. Gudden and R. Pohl, *Z. Physik*, **5**, 176 (1921).

² B. Gudden and R. Pohl, *Physik Z.*, **23**, 417 (1922).

³ J. H. Gisolf, *Physica*, **6**, 84 (1939).

⁴ D. C. Reynolds and S. J. Czyzak, *Phys. Rev.*, **79**, 543 (1950).

⁵ W. W. Piper, *J. Chem. Phys.*, **20**, 1343 (1952).