Coupling of Plasmons to Polar Phonons in Degenerate Semiconductors*

B. B. VARGA†
Argonne National Laboratory, Argonne, Illinois
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The coupling between longitudinal optical phonons and plasmons in degenerate polar semiconductors is investigated. At the appropriate carrier density (10^{17} to 10^{18} in III-V compounds) the free-carrier plasma frequency is comparable to the optical frequency, and the plasmons and phonons cease to be approximately independent excitations of the system. Then the two new normal modes are strong admixtures of phonons and plasmons. Several features of these modes are treated. In the long-wavelength limit the frequency and phonon strength are expressed as functions of the carrier density. The phonon strength is a measure of the amount of ionic motion present in a mode. The dispersion and the damping are discussed in a qualitative manner. The modes exhibit a repulsion and avoid intersection. Some experiments are considered in which these properties might be investigated. For example, the optical reflectivity gives the mode frequencies in the long-wavelength limit. The calculated shift of the frequencies by the interaction can be of the order of 5 meV at commonly used carrier concentrations.

INTRODUCTION

IN polar semiconductors the interaction between carrier electrons and lattice vibrations is strongest with the longitudinal optical modes. The transport properties at low temperatures are determined by impurity scattering and at higher temperatures by the polar scattering. When electrons are present in the conduction band, the screening effects modify both the optical mode frequency and the electron-phonon interaction. Treatments have been given previously of effects which occur when the carrier distribution is nondegenerate. Doniach[1] considered the case in which the lattice frequency is weakly modified. The dynamic electron space-charge polarization led to an enhanced phonon scattering at low temperature and density. Ehrenreich[2] found that the optical-phonon frequency was raised for wavelengths longer than the thermal wavelength of the electrons. The work of Woodruff[3] on the interaction of waves of current and lattice polarization showed that energy can be transferred from the space charge waves traveling on carriers drifting in an electric field to the optical vibrations.

If the carriers are degenerate, the frequencies of charge density fluctuations are comparable to optical phonon frequencies of about 5×10^{13} sec^{-1}. The coupling of the phonons to the plasmons then leads to important changes in the nature of the collective modes. In the III-V semiconductor compounds the electron density n in the degenerate case is of order 10^{18} cm^{-3}. In metals the density and the plasmon frequency are much higher, and the effect of this coupling is negligible. The degenerate carriers in the III-IV compounds still form a high-density electron gas, because of the small effective mass and large dielectric constant.[4] The effective r_s is less than 1, a bonus over the case of metals where r_s is in the range 2 to 5. The familiar self-consistent-field (SCF) theory should be quite reliable.[5]

In Sec. 1 we find the dielectric response function of the system consisting of polar optical phonons and degenerate conduction electrons. The polarizabilities of electrons and ions are additive in the self-consistent-field (SCF) theory. This result is derived from the equations of motion of Born and Huang and the Poisson equation. The two normal mode branches of the system are mixed phonons and plasmons. If only the frequencies were of interest, the consideration of the equations of motion would be superfluous. These equations are necessary to obtain the phonon strength of the modes, which is a measure of the amount of ion motion.

In Sec. 2 the properties of the two normal modes are given in the long-wavelength limit. The frequency and phonon strength are functions of the carrier density. Section 3 contains a qualitative discussion of the dispersion of the modes and the damping from decay into electron-hole pairs. The modes "repel" each other to avoid intersection.

Some observational consequences are treated in Sec. 4. The optical reflectivity gives the mode frequencies in the long-wavelength limit. Inelastic neutron diffraction may give information on the dispersion of the modes.

1. DESCRIPTION OF MODEL

The equations of Born and Huang[6] describe the optical motions of an ionic crystal with wavelengths long compared to a lattice constant. In this limit the ionic motions are described by a displacement field $\mathbf{w}=(M/v_a)^{1/2}(\mathbf{u}_+-\mathbf{u}_-)$ where $\mathbf{u}_+$ and $\mathbf{u}_-$ are the displacements of ions + and − from their equilibrium position, M is their reduced mass, and v_a the volume

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
† Present address: Palmer Physical Laboratory, Princeton University, Princeton, New Jersey.
[1] S. Doniach, Proc. Phys. Soc. (London) **73**, 849 (1959).
[2] H. Ehrenreich, J. Phys. Chem. Solids **8**, 130 (1959).
[3] T. Woodruff, Phys. Rev. **132**, 679 (1963).
[4] P. Wolff, Phys. Rev. **126**, 405 (1962).
[5] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, 8 (1954).
[6] M. Born and K. Huang, *The Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1956), 1st ed., p. 82.

of the unit cell. The equation of motion is

$$(\partial^2/\partial t^2)\mathbf{w}=b_{11}\mathbf{w}+b_{12}\mathbf{E}. \quad (1)$$

The first term on the right is the elastic restoring force; the second term is the force due to the local electric field on the ion, which is proportional to its effective charge $\pm se$. In Eq. (1) the fields are macroscopic, the average of the microscopic fields over several unit cells, so that the coefficient b_{12} contains the relation of $\mathbf{E}$ to the local field.

The lattice polarization

$$\mathbf{P}_L=b_{21}\mathbf{w}+b_{22}\mathbf{E} \quad (2)$$

consists of a part from the ionic displacements and a part from the polarizability of an ion charge distribution by the local field. The frequency-dependent dielectric function $\epsilon_L(\omega)$ of the lattice, which relates the lattice polarization to the field for a vibration with frequency ω, follows from Eqs. (1) and (2). We have

$$\mathbf{P}_L=(4\pi)^{-1}[\epsilon_L(\omega)-1]\mathbf{E}. \quad (3)$$

The spatial dispersion is neglected since only long-wavelength motions are of interest, as discussed later.

$$\epsilon_L(\omega)=1+4\pi b_{22}-4\pi b_{12}b_{21}/(b_{11}+\omega^2)$$
$$=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/[1-(\omega/\omega_0)^2]. \quad (4)$$

ϵ_0 is the static dielectric constant. ϵ_∞ is the high-frequency dielectric constant which is measured at frequencies high compared to ionic motions but low compared to electronic motions in an interband transition. ω_0 is measured as the absorption frequency of a thin film of the crystal. The longitudinal mode frequency is given by the root of ϵ_L at $\omega_l=(\epsilon_0/\epsilon_\infty)^{1/2}\omega_0$.

From studies of the reflectance in the infrared region, the optical mode parameters have been found for some III-V semiconductor compounds.[7]

When electrons are introduced into the conduction band by doping of the semiconductor, the longitudinal phonon will be a normal mode no longer, since the longitudinal electric field which accompanies such a phonon must couple strongly to the charge density fluctuations of the electron gas. This effect is most important when the plasma frequency is close to ω_l.[8]

The polarization of the coupled system $\mathbf{P}_T$ is the sum of the electronic part $\mathbf{P}_e$ and the ionic part $\mathbf{P}_L$. In Appendix A it is shown that it is accurate to take the response of the coupled system in a macroscopic electric field $\mathbf{E}$ to be the sum of the electron and the ion response taken separately. In other words, the relation of $\mathbf{P}_e(\mathbf{P}_L)$ to $\mathbf{E}$ is not affected by the presence of ions (electrons). Such additivity is easily shown using a SCF[9] treatment. The electrons are characterized by a screening length large compared to a lattice constant, and therefore respond only to the macroscopic field. The field of the displaced electrons is then macroscopic, so there is no local field correction for the ions which would change Eqs. (1) and (2). The corrections to the SCF approach should be small for these doped semiconductors for two reasons. First, the electrons form a degenerate Fermi gas at typical densities of about 10^{18} cm^{-3}, and the effective r_s is small so the Lindhard[5] dielectric function $\epsilon_e(q,\omega)$ is an accurate approximation. For example in GaSb at $n=1.25\times10^{8}$ cm^{-3} the value of $r_s^*=(3/4n)^{1/3}(m^*e^2/\epsilon_0\hbar^2)$ is 0.34 because of the large static dielectric constant $\epsilon_0\simeq17$ and the small effective mass $m^*=0.052m_e$. Second, the ions move slowly compared to the electrons, so they respond to the average potential.

The wave vector and frequency-dependent total dielectric function of the system is

$$\epsilon_T(q,\omega)=\epsilon_e(q,\omega)+\epsilon_\infty-1+(\epsilon_0-\epsilon_\infty)/[1-(\omega/\omega_0)^2]. \quad (5)$$

For long wavelengths the longitudinal and transverse dielectric function are equal for an isotropic solid.[10] The frequencies of the longitudinal modes are given by the roots of $\epsilon_T(q,\omega)$. The frequencies of transverse modes are given by

$$\omega^2=c^2q^2/\epsilon_T(q,\omega). \quad (6)$$

The longitudinal modes involve collective ion and electron motion. An external probe such as a neutron interacts only with the ions. The coupling strength of the neutron to a normal mode is proportional to the amount of ionic motion in the mode. For example, in inelastic neutron scattering with the emission of one quantum, the squared matrix element is proportional to the phonon strength[11]

$$S_m(k)=|\langle m|\varphi_{k,\lambda}|0\rangle|^2. \quad (7)$$

The symbols have the following significance: $|0\rangle$ is the exact ground state, $|m\rangle$ a one-quantum excited state of mode m of wave vector k, $\varphi_{k,\lambda}=b_{k,\lambda}+b_{-k,\lambda}^\dagger$ and $b_{k,\lambda}$ is the phonon destruction operator for wave vector k and polarization λ which is chosen as longitudinal.

To obtain the phonon strength it is useful to consider the phonon Green's function, defined as

$$D(k,t)=-i\langle 0|\tau\{\varphi_k(t)\varphi_k^\dagger(0)\}|0\rangle, \quad (8)$$

where τ is the time-ordering symbol. In the frequency representation,

$$D(k,\omega)=\sum_m S_m(k)\left(\frac{1}{\omega-\omega_m+i0^+}-\frac{1}{\omega+\omega_m-i0^+}\right). \quad (9)$$

The residue at the pole of D at $\omega=\omega_m$ is S_m.

From Eqs. (1), (2), and the vanishing of the total displacement field $\mathbf{E}+4\pi(\mathbf{P}_e+\mathbf{P}_L)$, the equation of

[7] G. Picus, E. Burstein, B. Hemvis, and M. Hass, J. Phys. Chem. Solids 8, 282 (1959).
[8] S. Engelsberg and B. Varga, Phys. Rev. 136, A1582 (1964).
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motion of $\mathbf{w}$ is

$$(\partial^2/\partial t^2)\mathbf{w}=b_{11}\mathbf{w}-[4\pi b_{12}b_{21}/(\epsilon_e+4\pi b_{22})]\mathbf{w}, \quad (10)$$

where ϵ_e is a matrix in space time. Since φ_k is proportional to w_k, the equation of motion of $D(k,t)$ is[12]

$$(\partial^2/\partial t^2)D(k,t)=-2\omega_l\delta(t) +[b_{11}-4\pi b_{12}b_{21}/(\epsilon_e+4\pi b_{22})]D(k,t). \quad (11)$$

The b's may be found from (4), and on taking the Fourier time transform of Eq. (11)

$$D^{-1}(k,\omega)=(2\omega_l)^{-1}[(\omega^2-\omega_0{}^2-\omega_0{}^2 \times(\epsilon_0-\epsilon_\infty)/(\epsilon_e(k,\omega)+\epsilon_\infty-1)]. \quad (12)$$

Expand D^{-1} near $\omega=\omega_m$ and compare with Eq. (9) to get

$$S_m{}^{-1}=\frac{\omega_m}{\omega_l}+\frac{[1-(\omega_m/\omega_0)^2]^2}{2(\epsilon_0-\epsilon_\infty)}\frac{\omega_0{}^2}{\omega_l}\frac{\partial\epsilon_e}{\partial\omega}(k,\omega_m). \quad (13)$$

A sum rule on the phonon strength can be derived by using the retarded commutator Green's function

$$D_R(k,t)=-i\langle 0|[\varphi_k(t),\varphi_k{}^\dagger(0)]|0\rangle\theta(t), \quad (14)$$

$$\left(\frac{\partial}{\partial t}\right)D_R(k,t=0^+)=-i\langle 0|\left[\left(\frac{\partial}{\partial t}\right)\varphi_k,\varphi_k{}^\dagger\right]|0\rangle=-2\omega_l$$

$$=-i\int\omega D_R(k,\omega)d\omega/2\pi. \quad (15)$$

The contour of ω is to be closed downwards.[13] The spectral representation[13] of D_R is obtained by putting $+i0^+$ in both places in Eq. (9), so that the cut lies entirely below the real axis. On performing the integration in (15) we obtain

$$\sum_m \omega_m S_m(k)=\omega_l \quad (16)$$

for each k. In the absence of free carriers, for each k there is only one longitudinal mode $|m\rangle$ of frequency ω_l and unit phonon strength.

2. THE LONG-WAVELENGTH LIMIT

The systems in which we are interested are the III-V compounds. The band structure for example in GaSb[14] consists of a central minimum with isotropic effective mass 0.052 (in units of the free electron mass), and subsidiary minima lie in the [111] directions with density of states effective mass 17.3. We take the density and the temperature low enough so that all electrons are in the central valley, and forego a description of the interesting effects which arise when the carriers are thermally excited into the [111] valleys.[15]

At zero wave vector,

$$\epsilon_e(0,\omega)=1-4\pi ne^2/m^*\omega^2. \quad (17)$$

m^* is the mass in the central minimum. Note that no screening effect of the ions on the valence electrons, as represented by a background dielectric constant, has been included in (17). The above expression is valid when the central valley energy is parabolic and the periodic part of the Bloch function is independent of the electron wave vector in the valley. In InSb the nonparabolic energy[16] requires a modification of the formulas.

The total dielectric function is

$$\epsilon_T(0,\omega)=\epsilon_\infty+\frac{\epsilon_0-\epsilon_\infty}{1-(\omega/\omega_0)^2}-\frac{4\pi ne^2}{m^*\omega^2}. \quad (18)$$

The roots are at $\omega=\omega_z$. We define $\alpha=\epsilon_0/\epsilon_\infty$, $\eta=w_z{}^2/\omega_l{}^2$, and $\xi=\omega_p{}^2/\omega_l{}^2$, where $\omega_p=(4\pi ne^2/m^*\epsilon_\infty)^{1/2}$ is the plasma frequency when the electron interactions are screened by the high-frequency dielectric constant of the lattice. Note that ξ is proportional to n. Then

$$\eta=\tfrac{1}{2}(1+\xi)\pm\tfrac{1}{2}(1+2\xi[1-2\alpha^{-1}]+\xi^2)^{1/2}. \quad (19)$$

The phonon strength S is given by

$$S^{-1}=\eta^{1/2}+\frac{(1-\eta\alpha)^2}{\alpha(\alpha-1)}\frac{\xi}{\eta^{3/2}}. \quad (20)$$

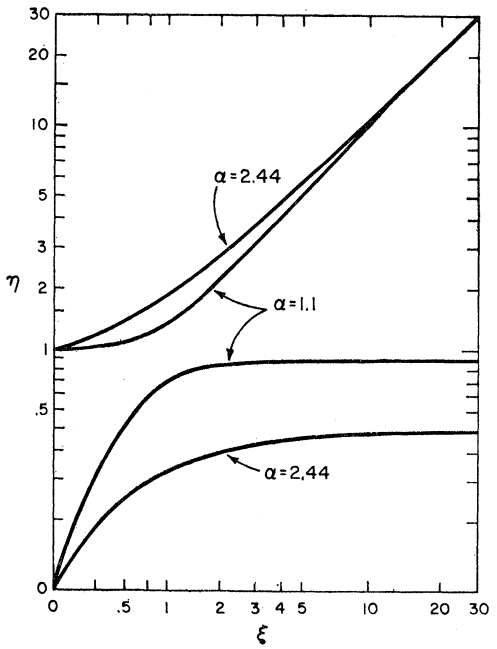

FIG. 1. The longitudinal normal modes $\eta=\omega^2/\omega_l{}^2$ of the system in the long-wavelength limit, as a function of $\xi=\omega_p{}^2/\omega_l{}^2$. The strong and weak coupling cases are $\alpha=1.1$ and 2.44, respectively.

[12] The details of Eq. (11) are discussed in Appendix B.

[13] V. L. Bonch-Bruevich and S. V. Tyablikov, *The Green Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), pp. 18, 21.

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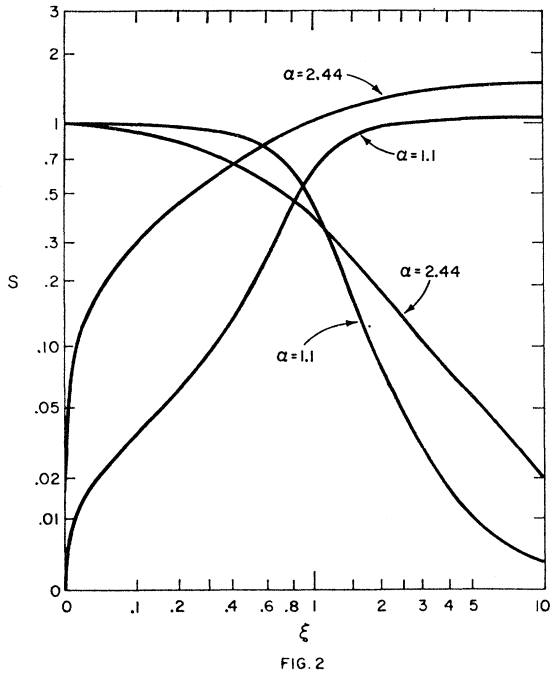

FIG. 2. The phonon strength S of the two normal modes as a function of ξ.

In the limit of small ξ we have to order ξ

$$\eta=1+\xi(1-\alpha^{-1}) \\ =\xi\alpha^{-1}, \tag{21}$$

and

$$S=1-\tfrac{3}{2}\xi(1-\alpha^{-1}) \\ =\xi^{1/2}\alpha^{-1/2}(\alpha-1). \tag{22}$$

The upper mode is mainly a phonon which is shifted up by a small amount from the frequency ω_l. The lower mode is mainly a plasma motion screened by the static lattice dielectric constant. The sum rule (16) checks to order ξ.

In the limit of large ξ we neglect terms of order ξ^{-1} obtaining

$$\eta=1+\xi-\alpha^{-1} \\ =\alpha^{-1}[1-\xi^{-1}(1-\alpha^{-1})], \tag{23}$$

and

$$S=(1-\alpha^{-1})\xi^{-3/2} \\ =\alpha^{1/2}. \tag{24}$$

The upper mode is mainly a plasmon, screened by the high-frequency dielectric constant ϵ_∞. The lower mode is a screened phonon at ω_0, the restoring force in Eq. (1) being entirely elastic. Note that the phonon strength is greater than one. This perhaps unusual circumstance arises from the fact that the ground state is the normal mode vacuum, which is not a phonon vacuum.

In Fig. 1 we exhibit the two branches η of Eq. (19) for values of α chosen to represent the systems GaSb ($\alpha=1.1$) and an alkali halide ($\alpha=2.44$). For GaSb the quantity ξ is $1.6\times10^{-18}\,n$, and the effective charge[7] s on an ion is 0.30, which corresponds to a weak coupling system. The strong coupling case $\alpha=2.44$ shows a strong repulsion of the modes and large phonon mixing. The phonon strengths are shown in Fig. 2. For $\alpha=2.44$ (1.1) the phonon strength of each mode is greater than 0.2 for $0.05<\xi<2$ ($0.5<\xi<1.4$).

3. THE DISPERSION OF THE MODES

We investigate the behavior of the modes as a function of wave vector q, as given in the present approximation. We must recall some difficulties in this approach. For q which are not small compared to the Fermi wave vector k_F, the Lindhard dielectric function is larger than the true dielectric function.[17] Thus the change found in the longitudinal phonon frequency will be too large. We expect, however, the qualitative features to be correct. These are illustrated by a numerical calculation since the analytic expressions are complicated.

The longitudinal modes are shown in Fig. 3 for the given parameters. Since k_F is only a few percent of a Brillouin zone boundary vector, the dispersion of the optical modes of the ionic lattice can be neglected. In the uncoupled system the electron motions are computed as if the ions were held fixed. Accordingly the electron interactions are screened by ϵ_∞. The plasmon line a begins at ω_p and passes into the con-

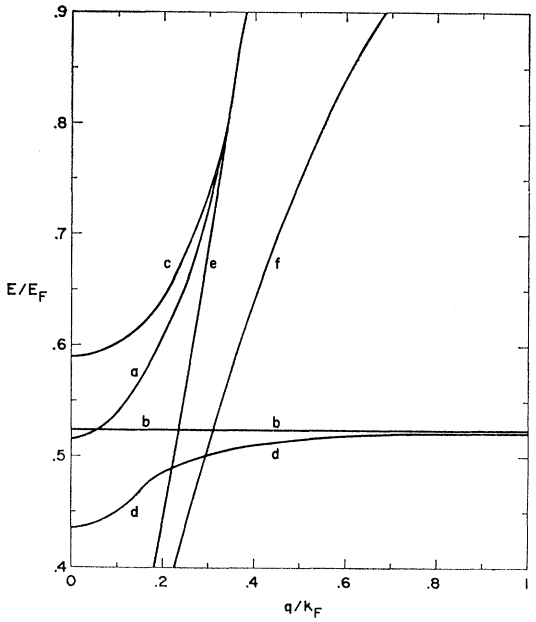

FIG. 3. The dispersion of the longitudinal modes of the coupled system, in lines c and d. $\alpha=1.1$, $\epsilon_\infty=18$, $\xi=0.96$, and $E_F/\omega_0=2$. The abscissa is $(q/k_F)=x$, wave vector in units of the Fermi vector. The ordinate is energy in units of the Fermi energy E_F. Lines a and b are modes of the uncoupled system, the plasmon and the optical phonon, respectively. Line e is $x(x+2)$, the boundary of the continuum of particle-hole excitations. Line f is the boundary of the region within which $\mathrm{Im}\epsilon_e(q,\omega)$ is proportional to ω.

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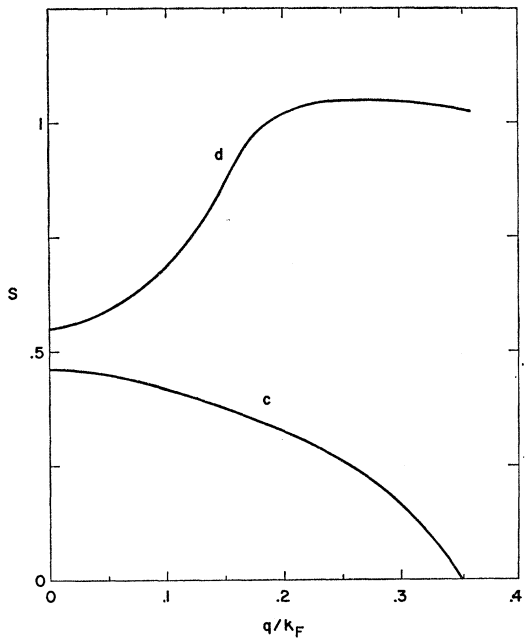

FIG. 4. The phonon strength S of the modes c and d as a function of q/k_F.

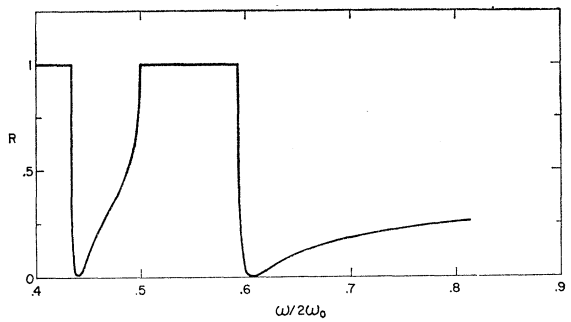

FIG. 5. The reflectivity R as a function of $y=(\omega/2\omega_0)$. The parameters are $\alpha=1.1$, $\epsilon_\infty=18$ and $\xi=0.96$.

tinuum of particle-hole excitations with the boundary e at the cutoff $q_c=0.35k_F$. For $q>q_c$ the plasmon is rapidly damped and ceases to be a well-defined excitation. In the coupled system, as the upper mode c approaches the plasmon line near the cutoff, its phonon strength shown in Fig. 4 drops to zero rapidly. The phonon strength of the lower mode d is about 1 near line e, and goes to a maximum of $\alpha^{1/2}=1.05$ at frequency ω_0.

The damping of the modes c and d in our treatment is due only to the process of decay into a single particle-hole pair. In this approximation the modes are undamped to the left of e in Fig. 4.

The behavior of the modes can be discussed on the basis of the differential equation they satisfy.

$$\frac{d\omega}{dq}=-\frac{\partial\epsilon_e}{\partial q}\Big/\left(\frac{\partial\epsilon_e}{\partial\omega}+\frac{\partial\epsilon_L}{\partial\omega}\right). \tag{25}$$

For the upper mode c near cutoff the second term in the denominator is negligible compared to the first, which has a logarithmic singularity on line e. The numerator has the same kind of singularity, and the intersection of c with e is tangential, as is that of a with e. Equation (25) then becomes identical to the equation of the plasmon line a, and c is a highly damped plasmon to the right of e. For the lower mode d near line e, $\partial\epsilon_L/\partial\omega$ diverges near ω_0 and therefore $d\omega/dq$ is a small quantity. The mode is flat for $q>0.2k_F$, and only a small imaginary part can build up from the imaginary part of ϵ_e in the numerator of (25). At $q=0.5k_F$ the ratio of imaginary part to real part is -7×10^{-3}, and at $q=k_F$ it is -1.3×10^{-3}. As remarked above, the effect of logarithmic singularities requires d to cross e tangentially, which indicates a sudden large change of slope in d. The region of q over which the slope changes is extremely small, of the order of $10^{-200}k_F$, and hence unobservable. The phonon strength in this region also drops to zero. The same phenomenon occurs on crossing line f. To the right of f the single normal mode d almost exhausts the phonon strength sum rule (16); therefore, the effect on the optical phonon of the coupling to the electron-hole pair excitations is very slight. The large effect comes from the coupling with the coherent electron plasma motion which leads to the splitting of the modes a and b into c and d.

4. POSSIBLE OBSERVABLE CONSEQUENCES

We now take up the question of the experimental observation of the mode splitting and discuss a few examples.

Information on the long-wavelength limit can be obtained from reflectivity measurements. The optical reflectivity R at normal incidence is given by $R=|\epsilon^{1/2}-1|^2/|\epsilon^{1/2}+1|^2$, where $\epsilon=\epsilon_T(0,\omega)$. In Fig. 5, R is plotted against the frequency. There are two regions where R falls rapidly from 1 to 0, while in the uniform electron gas there is only one reflection edge at the plasma frequency. The higher reflection edge is at the frequency of the upper normal mode of Fig. 1. The lower region is bounded by two reflection edges, the one below at the lower normal mode of Fig. 1, and the one above at ω_0. The parameters of Fig. 5 correspond to the following values in GaSb: $n=6\times10^{17}$, $r_s^*=0.43$, Fermi energy $E_F=49$ meV, $\omega_l=29$ meV, and $\omega_p=28$ meV.

The widths of the reflecting and transmitting regions of Fig. 5 can be varied by doping, or for suitable carrier concentrations by changing the temperature, as mentioned in Sec. 2. For example in GaSb with $n=1.25\times10^{-18}$ cm^{-3}, ω_p^2 and the parameter ξ of Fig. 1 decrease by 4% on going from 1 to 20°K, because of the excitation of carriers into the [111] minima.[15] Over the larger temperature range from 90 to 300°K with $n=1.6\times10^{18}$, ω_p^2 was found experimentally to

decrease by about 25%.[18] If ξ is of the appropriate size in Fig. 1, such a variation would lead to an observable change in both the upper and lower reflection edges.

The photoconductivity of p-type GaSb and InSb has recently been found to exhibit a periodic variation with the photon energy.[19] The period corresponds to the energy of the polar mode which couples strongly to the excited carriers. With the proper p-type doping one may be able to observe two sets of oscillations, with periods given by the two normal modes. A complicating factor is the existence of light and heavy hole bands which may also give rise to two periods.[20]

The dispersion of the normal modes and the phonon strength could, in principle, be determined by inelastic neutron scattering. The actual physical parameters however tend to make such experiments impractical.

When neutrons pass through the crystal, they can absorb a quantum of a thermally excited normal mode, and thus pick up the energy and momentum of the mode. The technique has been used to measure the optical frequency in Ge.[21] There are several difficulties with the technique in the present system. The mode splitting occurs over a very small part of the total phonon phase space, which makes the associated inelastic scattering cross section very small. Since the energy transfer to the neutron is large, but the momentum transfer is small, the incident neutron must be very fast (energy large compared to $\hbar\omega_0$), and the outgoing neutron will be too fast for its energy to be measured accurately by the standard time-of-flight method. Also the scattering angle will be quite small. The investigation of the normal modes over such a small range of wave vectors (from $q=0$ to k_F) appears to be an order of magnitude beyond present experimental sensitivity.

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APPENDIX A

If we treat the conduction electrons as external changes of density $\rho(x,t)$ then the Poisson equation for $\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}_L$ is

$$\nabla\cdot\mathbf{D}=4\pi\rho(x,t). \tag{A1}$$

The validity of Eqs. (1) and (2) depends on the relation (contained in the constants b) of the local field $\mathbf{E}_{LF}$ at an ion to the macroscopic field. We argue that the correct relation is

$$\mathbf{E}_{LF}=\mathbf{E}_e+\mathbf{E}_L+(4\pi/3)\mathbf{P}_L=\mathbf{E}+(4\pi/3)\mathbf{P}_L, \tag{A2}$$

where $\mathbf{E}_e$ and $\mathbf{E}_L$ are the macroscopic fields due to the electrons and the ions, respectively. The last two terms of the second expression are evidently the contribution to $\mathbf{E}_{LF}$ due to ionic displacements.[22] The equation then contains the assumption that the macroscopic field due to electrons is equal to their microscopic field.

Suppose there is given an ionic displacement field of long wavelength varying as $\exp(i\mathbf{q}\cdot\mathbf{r})$. Take a simple model of point ions in a cubic lattice with equilibrium locations $(j_1,j_2,j_3)p=\mathbf{x}_{J,0}$ where the j's are integers and p is a lattice constant, the charge being $(-1)^M$ where $M=j_1+j_2+j_3$. The change in potential V due to the displacement field

$$\mathbf{x}_J=\mathbf{x}_{J,0}+(-1)^M\hat{q}w_q\exp(i(\mathbf{q}\cdot\mathbf{r}-\omega t))+\text{c.c.} \tag{A3}$$

has the Fourier component

$$V(\mathbf{k})=\Omega^{-1}\int V(\mathbf{x})\exp(-i\mathbf{k}\cdot\mathbf{x})d^3x$$

equal to

$$V(\mathbf{k})=-iN\Omega^{-1}4\pi|\mathbf{k}|^{-1}\hat{k}\cdot\hat{q}w_q\delta_{\mathbf{q}+\boldsymbol{\kappa},\mathbf{k}}, \tag{A4}$$

where N is the number of ions, Ω the volume, and $\boldsymbol{\kappa}$ a reciprocal lattice vector. This is valid if $w_q|\mathbf{k}|<1$, otherwise $V(\mathbf{k})$ is smaller because of interference effects. Thus, the ionic field has Fourier components $\mathbf{E}(\mathbf{k})$ with $\mathbf{k}=\mathbf{q}+\boldsymbol{\kappa}$ which are approximately equal to the one another up to a cutoff wave vector beyond which they decrease to zero. The electrons in this vibrating field will respond to the various field components by setting up a field with components $[\epsilon_e^{-1}(k,\omega)-1]\mathbf{E}(\mathbf{k})$. Only the long-wavelength induced field, with $\mathbf{k}=\mathbf{q}$, is large. For example, if the Fermi-Thomas approximation is used, $\epsilon_e=1+(k_{FT}^2/k^2)$ and the induced field is $[-k_{FT}^2/(k^2+k_{FT}^2)]E(\mathbf{k})$ where $k_{FT}^2=0.66r_s^*k_F^2$ is the Fermi-Thomas screening vector. Since k_{FT} is less than a percent of a zone edge vector, all components except $\mathbf{k}=\mathbf{q}$ are negligible. The physical reason for this is that the high Fourier components of the ionic field vary rapidly over a unit cell, but the Fermi-Thomas screening distance, which is the smallest distance for a reasonable electron response, is of the order of 100 lattice constants. Accordingly, the electrons contribute only to the macroscopic field and do not require a local field correction. Therefore, Eqs. (1) and (2), which were originally derived on the basis of Eq. (A2) for the perfect ionic crystal,[22] are valid here also.

The total dielectric function of the system, $\epsilon_T(q,\omega)$ gives the polarization $\mathbf{P}_T=\mathbf{P}_e+\mathbf{P}_L$ induced by the electric field $\mathbf{E}\sim\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]$ via

$$\mathbf{P}_T=(4\pi)^{-1}[\epsilon_T(q,\omega)-1]\mathbf{E}. \tag{A5}$$

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The ionic part $\mathbf{P}_L$ is given in Eq. (3). The electronic part $\mathbf{P}_e$ in the SCF treatment[9] is

$$\mathbf{P}_e=(4\pi)^{-1}[\epsilon_e(q,\omega)-1]\mathbf{E}, \quad \text{(A6)}$$

where ϵ_e is the Lindhard function[5] under the conditions discussed at the beginning of Sec. 2.

This completes the discussion of Eq. (5).

APPENDIX B

The Hamiltonian $\mathcal{H}$ of the system is written on p. 100 of Ref. 6. The part describing the free motion of the longitudinal modes is

$$\mathcal{H}_0=\tfrac{1}{2}\sum_k(\mu_k^\dagger\mu_k+\omega_l^2\nu_k^\dagger\nu_k), \quad \text{(B1)}$$

where $\nu_k=\nu_{-k}^\dagger=(2\omega_l)^{-1/2}\varphi_k$ is the plane-wave normal mode coordinate (polarization index omitted) and $\mu_k^\dagger$ is the canonically conjugate momentum. The ν's (μ's) commute among themselves.

The phonon Green's function (7) gives

$$(\partial^2/\partial t^2)D(k,t)=-i\langle 0|\{\delta'(t)[\varphi_k,\varphi_k^\dagger]+\delta(t)[\partial\varphi_k/\partial t,\varphi_k^\dagger]+\tau(\partial^2\varphi_k(t)/\partial t^2)\varphi_k^\dagger\}|0\rangle, \quad \text{(B2)}$$

where the phonon operators without time argument are taken at time zero. The first commutator vanishes. In the second commutator, we need the equation of motion of φ_k.

$$i(\partial\varphi_k/\partial t)=[\varphi_k,\mathcal{H}]=[\varphi_k,\mathcal{H}_0]=i(2\omega_l)^{1/2}\mu_k. \quad \text{(B3)}$$

The second equality holds since only ν (not μ) appears in the electron-phonon interaction in $\mathcal{H}$. Thus the second commutator of Eq. (B2) is $2\omega_l$. The last term in Eq. (B2) is evaluated by substituting φ_k for $\mathbf{w}$ in Eq. (10). The net result is Eq. (11).

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Perturbation Approach to the Polaron Self-Energy in the Intermediate Coupling Range

W. VAN HAERINGEN
Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands
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By using a diagram technique, it is shown that the polaron energy can be expanded in electron-recoil terms. Together with the common expansion in powers of the coupling constant, a double series is obtained in which many cancellations occur. A subseries is isolated which gives the Lee-Low-Pines (L.L.P.) result in the intermediate coupling range. This subseries can be seen to consist of partial contributions of a certain class of perturbation diagrams. This answers the question put by Pines as to which perturbation diagrams contribute to the L.L.P. result.

1. INTRODUCTION

THE well-known intermediate coupling result of the polaron has been derived by Lee, Low, and Pines[1] (L.L.P.) and independently by Gurari[2] and Tiablikov.[3] All three methods are essentially variational methods. Pines[4] has asked which perturbation diagrams have to be summed in order to obtain the intermediate coupling result. In this article we shall present an answer to his question. The answer may give us more insight into the L.L.P. result.

First, we briefly review those aspects of the polaron problem which are relevant for our purpose. In polar crystals, one of the basic problems is to study the interaction between electrons and the vibrations of the lattice ions. The electrons are supposed to be free, with effective masses in which the effect of the fixed periodic lattice is taken into account. One diagonalizes the Hamiltonian for the ionic motions in the harmonic approximation and obtains the collective excitations, called phonons. Now the electron is said to interact with the phonons. The strength of the interaction is measured in terms of a dimensionless coupling constant α. Considering only interactions with what is termed the optical branch, the problem is called the polaron problem. The electron will be surrounded by a "polarization cloud," resulting in a heavier mass. One aim is to determine this new mass. If $\alpha\ll 1$, this can certainly be done by means of lowest order perturbation theory. However, in real crystals one has $\alpha\approx 2$–6, in which range simple perturbation theory fails for the polaron mass. Lee, Low, Pines,[1] Gurari,[2] and Tiablikov[3] developed a method to find the self-mass in this α range. All three use variational techniques. L.L.P. take as an ansatz for the polaron wave function a function in which the electron is "dressed" with phonons, distributed according to a Poisson distribution. A similar

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