Interaction of Plasmons and Optical Phonons in Degenerate Semiconductors*

K. S. SINGWI† AND M. P. TOSI
Argonne National Laboratory, Argonne, Illinois

(Received 4 November 1965; revised manuscript received 5 January 1966)

The coupling between plasmons and polar phonons in a degenerate semiconductor is studied starting from an electron-phonon Hamiltonian which is valid in the long-wavelength limit. A truncated form of the Hamiltonian proves to be a good approximation near the crossover point of the uncoupled modes; and expressions for the phonon strengths and the sum rules are very simply derived from it. Plasmon damping is introduced phenomenologically and its effect on the behavior of the coupled modes is investigated. Model calculations of the effect of damping on the dispersion curves and reflectivity are made for the case of the degenerate semiconductor GaSb.

INTRODUCTION

THE interaction between the electric dipole moment associated with a longitudinal optical phonon and the electric field associated with a plasmon in a polar semiconductor implies a coupling between the two modes. Such a coupling has been studied by Gurevich *et al.*[1] and by Varga[2] for the case in which the carrier electrons form a degenerate gas. These treatments rest on the assumption that the polarizability of the electrons, in the random-phase approximation (RPA), and the polarizability of the ions contribute additively to the dielectric response function of the coupled system.

In the first section of this paper we give a Hamiltonian formulation of this problem in the long-wavelength limit. This formulation, in contrast to the earlier treatments, has the advantage of displaying explicitly the structure of the coupling term. The secular equation for the normal modes of the system, which are strong admixtures of phonons and plasmons, is, as expected, identical to that derived from the dielectric formulation based on the RPA.

An especially interesting case is the one in which the plasmon frequency is nearly equal to the phonon frequency, in which circumstance the effect of the coupling is most pronounced, leading to a marked change in the character of both modes. In Sec. II we show that a truncated form of the Hamiltonian is a good approximation in the vicinity of the resonance point. From this approximate Hamiltonian follow simply the mode splitting, the phonon strengths of the coupled modes, and the sum rules.

The treatment given in Secs. I and II, as well as the earlier treatments, have neglected the effects of short-range collisions, which should be taken into account when comparing the theoretical results with experimental observations. In the absence of a microscopic theory, we have resorted to a phenomenological treatment which allows numerical estimates of these effects to be made. This is done in Sec. III, where the effect of a damping of the plasmons on the coupled modes is evaluated as a function of carrier concentration and of (small) wave number, for values of the parameters corresponding to the case of GaSb. The mode splitting near the point of resonance is affected very little by a small amount of damping but decreases fairly rapidly as damping increases, until at a critical value of the plasmon lifetime it vanishes and the modes again cross; thus apparently violating the "no-crossing" theorem of von Neumann and Wigner.[3] The value of the critical damping is approximately four times the coupling constant. A similar effect in another context was also noticed by Lamb[4] in his study of the fine structure of the hydrogen atom.

We also calculate the reflectivity of GaSb for a given carrier concentration, for various values of the damping parameter. Even a small amount of damping produces a marked change in the reflectivity versus frequency curve.[5]

I. PLASMON-PHONON HAMILTONIAN

The classical interaction Hamiltonian in the electrostatic approximation between a longitudinal optical vibration in a polar crystal with two ions per unit cell and a system of electrons, as given by Born and Huang,[6] is

$$H_{\mathrm{int}}=-\omega_l\left[\frac{1}{4\pi}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]^{1/2}\int \mathbf{w}_l\cdot\mathbf{E}_{\mathrm{vac}}\,d\tau. \quad (1)$$

ω_l is the longitudinal optical frequency, ϵ_∞ and ϵ_0 are, respectively, the high-frequency and static dielectric

* Based on work performed under the auspices of the U. S. Atomic Energy Commission. A preliminary report of this work was presented at the A.P.S. meeting in Chicago [Bull. Am. Phys. Soc. **10**, 1085 (1965)].

† Also, Physics Department, Northwestern University, Evanston, Illinois.

[1] V. L. Gurevich, A. I. Larkin, and Yu. A. Firsov, Fiz. Tverd. Tela 4, 185 (1962) [English transl.: Soviet Phys.—Solid State 4, 131 (1962)].

[2] B. B. Varga, Phys. Rev. **137**, A1896 (1965).

[3] J. von Neumann and E. P. Wigner, Physik Z. **30**, 467 (1929).

[4] W. E. Lamb, Jr., Phys. Rev. **85**, 259 (1952).

[5] After the completion of this work, A. S. Barker brought to our attention his recent measurements of the reflectivity of reduced $SrTiO_3$. The observed behavior of the reflectivity curve in the frequency region of the highest phonon mode is what one would expect from the calculations reported in Fig. 3. A quantitative analysis of the data by Barker indicates a sizable plasmon damping.

[6] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), 1st ed., Sec. 8.

constants, $\mathbf{w}_l$ is proportional to the longitudinal component of the relative displacement of the two ions in the cell, and $\mathbf{E}_{\text{vac}}$ is the electric field produced by the electrons in vacuum. The derivation of H_{int} involves two assumptions: (a) only the lattice polarization contributes to the Lorentz field correction for the effective field at the ions, and (b) the electrons feel only the macroscopic field. It can be shown that the use of the above two assumptions in the classical equations of motion for the ions and the electrons, together with the classical equations for the polarization, leads to the result that the polarizabilities of the ion system and the electron system are additive. The theory of Gurevich *et al.*[1] and of Varga[2] is based on this assumption.

We evaluate the field $\mathbf{E}_{\text{vac}}$ from the Poisson equation, where the charge density fluctuation associated with a long-wavelength plasmon is taken to be proportional to the local dilation in the electron gas. Expressing the dilation in terms of the displacement in the gas (see, e.g., Kittel[7]), we find

$$\mathbf{E}_{\text{vac}}(\mathbf{r})=4\pi e\left(\frac{n}{m^*V}\right)^{1/2}\sum_{\mathbf{k}}\mathbf{k}\frac{\boldsymbol{\varepsilon}_{\mathbf{k}}\cdot\mathbf{k}}{k^2}Q_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r}). \tag{2}$$

Here, m^* is the electron effective mass, n is the electron concentration, V is the volume of the system, $\boldsymbol{\varepsilon}_{\mathbf{k}}$ is the longitudinal polarization vector and $Q_{\mathbf{k}}$ is the usual plasmon normal coordinate. On the other hand, the relative displacement $\mathbf{w}_l$ can be written as

$$\mathbf{w}_l(\mathbf{r})=\frac{1}{\sqrt{V}}\sum_{\mathbf{k}}\boldsymbol{\varepsilon}_{\mathbf{k}}q_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{3}$$

where $q_{\mathbf{k}}$ is the phonon normal coordinate. The interaction Hamiltonian (1) then becomes

$$H_{\text{int}}=-\omega_l\omega_p\left[1-\frac{\epsilon_\infty}{\epsilon_0}\right]^{1/2}\sum_{\mathbf{k}}q_{\mathbf{k}}Q_{-\mathbf{k}}, \tag{4}$$

where ω_p is the plasmon frequency in the dielectric, defined by

$$\omega_p^2=4\pi ne^2/m^*\epsilon_\infty. \tag{5}$$

Expressing the normal coordinates in terms of creation and annihilation operators as

$$q_{\mathbf{k}}=(\hbar/2\omega_l)^{1/2}(a_{\mathbf{k}}+a_{-\mathbf{k}}^\dagger), \tag{6}$$

$$Q_{\mathbf{k}}=(\hbar/2\omega_p)^{1/2}(b_{\mathbf{k}}+b_{-\mathbf{k}}^\dagger), \tag{7}$$

we have the following expression for the total Hamiltonian (except for the zero-point energy terms):

$$H=\hbar\omega_l\sum_{\mathbf{k}}a_{\mathbf{k}}^\dagger a_{\mathbf{k}}+\hbar\omega_p\sum_{\mathbf{k}}b_{\mathbf{k}}^\dagger b_{\mathbf{k}} -\hbar C\sum_{\mathbf{k}}(a_{\mathbf{k}}b_{-\mathbf{k}}+a_{\mathbf{k}}b_{\mathbf{k}}^\dagger+a_{\mathbf{k}}^\dagger b_{\mathbf{k}}+a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger), \tag{8}$$

[7] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 35.

where the coupling constant C is given by

$$C=\tfrac{1}{2}[\omega_l\omega_p(1-\epsilon_\infty/\epsilon_0)]^{1/2}. \tag{9}$$

The diagonalization of the Hamiltonian (8) yields the following equation for the coupled mode frequencies ω_i $(i=1, 2)$:

$$\omega_i^2=\tfrac{1}{2}(\omega_l^2+\omega_p^2)\pm\tfrac{1}{2}[(\omega_l^2-\omega_p^2)^2+16C^2\omega_l\omega_p]^{1/2}. \tag{10}$$

Equation (10) is equivalent to Eq. (19) of Varga,[2] which was derived by equating the total dielectric function to zero. At resonance, where $\omega_p=\omega_l$, we have

$$\omega_i=\omega_l[1\pm 2C/\omega_l]^{1/2}. \tag{11}$$

As a side remark, we may point out that the coupling constant of our problem, given by Eq. (9), goes over to the standard polaron coupling constant[8] if we replace $\hbar\omega_p/2$ by $4\pi e^2/k^2\epsilon_\infty$.

II. TRUNCATED HAMILTONIAN

We shall now study the following truncated form of the Hamiltonian (8):

$$H_{\text{tr}}=\hbar\omega_l\sum_{\mathbf{k}}a_{\mathbf{k}}^\dagger a_{\mathbf{k}}+\hbar\omega_p\sum_{\mathbf{k}}b_{\mathbf{k}}^\dagger b_{\mathbf{k}} -\hbar C\sum_{\mathbf{k}}(a_{\mathbf{k}}b_{\mathbf{k}}^\dagger+a_{\mathbf{k}}^\dagger b_{\mathbf{k}}). \tag{12}$$

Let us introduce two new operators $A_{\mathbf{k}}$ and $B_{\mathbf{k}}$ defined by[9]

$$a_{\mathbf{k}}=A_{\mathbf{k}}\cos\theta+B_{\mathbf{k}}\sin\theta, \tag{13a}$$

$$b_{\mathbf{k}}=B_{\mathbf{k}}\cos\theta-A_{\mathbf{k}}\sin\theta. \tag{13b}$$

The choice of the transformation coefficients ensures that the new operators $A_{\mathbf{k}}$ and $B_{\mathbf{k}}$ satisfy the same commutation relations as the old ones. The transformed Hamiltonian is diagonal if

$$\tan(2\theta)=2C/(\omega_l-\omega_p) \tag{14}$$

and the normal-mode frequencies are given by

$$\omega_1=(\omega_l-\omega_p\tan^2\theta)/(1-\tan^2\theta), \tag{15}$$

$$\omega_2=(\omega_p-\omega_l\tan^2\theta)/(1-\tan^2\theta). \tag{16}$$

At the resonance point $\omega_p=\omega_l$, and therefore $\theta=\pi/4$. In this case the normal-mode frequencies become

$$\omega_1=\omega_l+C, \tag{17}$$

$$\omega_2=\omega_l-C, \tag{18}$$

and their separation is $2C$. By comparison with Eq. (11), it can be seen that Eqs. (17) and (18) are correct to order C/ω_l, and the mode splitting is correct to order $(C/\omega_l)^2$.

It is easy to see that the coupled-mode frequencies

[8] T. D. Lee, F. Low, and D. Pines, Phys. Rev. 90, 297 (1953).

[9] In the more general case, where the frequencies and the coupling parameter depend on wave number, the transformation (13) would still be valid except that the angle θ would be k-dependent.

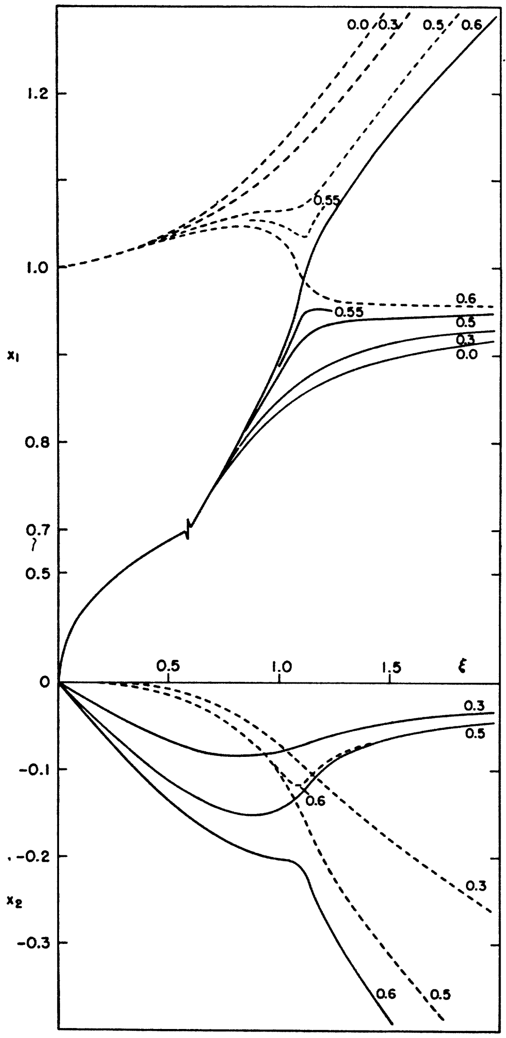

FIG. 1. The real (x_1) and imaginary (x_2) parts of the normal-mode frequencies ω/ω_l in the long-wavelength limit, as functions of $\xi=\omega_p^2/\omega_l^2$ for various values of the damping parameter $\beta=(\tau\omega_l\xi)^{-1}$. $\epsilon_0/\epsilon_\infty=1.1$. Note the change in the ordinate scale at $x_1=0.7$.

given by Eqs. (15) and (16) satisfy the following sum rules:

$$\omega_1\cos^2\theta+\omega_2\sin^2\theta=\omega_l, \tag{19}$$

$$\omega_1\sin^2\theta+\omega_2\cos^2\theta=\omega_p. \tag{20}$$

Clearly, the quantities $\cos^2\theta$ and $\sin^2\theta$ play the role of phonon strengths for the first and the second mode, respectively. The expression for $\cos^2\theta$ in terms of the coupling constant is

$$\cos^2\theta=\tfrac{1}{2}+\tfrac{1}{2}[1-4C^2/(4C^2+(\omega_l-\omega_p)^2)]^{1/2}. \tag{21}$$

At the point of resonance the phonon strength is equally divided between the two modes.

It remains to discuss under which conditions the truncated Hamiltonian (12) provides a good description of the problem. The terms neglected in arriving at (12) can be expressed through the new operators $A_{\mathbf{k}}$ and $B_{\mathbf{k}}$ as follows:

$$\begin{aligned}H-H_{\mathrm{tr}}=&-\hbar C(\cos^2\theta-\sin^2\theta)\sum_{\mathbf{k}}(A_{\mathbf{k}}B_{-\mathbf{k}}+A_{\mathbf{k}}^\dagger B_{-\mathbf{k}}^\dagger)\\&-\hbar C\cos\theta\sin\theta\sum_{\mathbf{k}}(B_{\mathbf{k}}B_{-\mathbf{k}}+B_{\mathbf{k}}^\dagger B_{-\mathbf{k}}^\dagger\\&-A_{\mathbf{k}}A_{-\mathbf{k}}-A_{\mathbf{k}}^\dagger A_{-\mathbf{k}}^\dagger).\end{aligned} \tag{22}$$

At resonance the first term vanishes, and the second term can be expected to be small since it involves terms approximately equal in magnitude and opposite in sign. For the case of GaSb, to be discussed in the next section, Eq. (11) gives frequency changes of $+14$ and -16%, whereas Eqs. (17) and (18) give changes of $\pm15\%$. Thus we may safely conclude that the truncated Hamiltonian is a rather good approximation in the vicinity of the resonance point. On the other hand, it is a poor approximation far away from the resonance point. For instance, in the limit $\omega_p\gg\omega_l$, the frequency of the lower mode should tend to the frequency ω_0 of the transverse optical phonons, whereas Eq. (15) gives $\omega_1=[1-\frac{1}{4}(1-\epsilon_\infty/\epsilon_0)]\omega_l$. For the case of PbTe considered by Cowley and Dolling,[10] where $\omega_p\approx7\omega_l$, the frequencies of the lower mode as computed from Eq. (10) and from Eq. (15) are $0.99\omega_0$ and $2.5\omega_0$, respectively. Similar considerations apply to the phonon strengths.

III. EFFECTS OF DAMPING

We shall first consider the effect of a finite plasmon lifetime on the character of the coupled modes in the limit of infinite wavelength. We determine the coupled-mode frequencies, which are now complex, from the zeros of the dielectric response function; that is,

$$\epsilon(\omega)=\epsilon_\infty+\frac{\epsilon_0-\epsilon_\infty}{1-(\omega/\omega_0)^2}-\frac{\omega_p^2\epsilon_\infty}{\omega(\omega+i/\tau)}=0. \tag{23}$$

Here, τ is the plasmon lifetime, which has been introduced phenomenologically in the electron dielectric function.[11] In the following model calculations, we take τ as inversely proportional to the electron concentration. Such an assumption is justifiable if the damping of the plasmons is governed by the amount of doping. We wish to point out, however, that this assumption will not materially affect the behavior of the coupled-mode frequencies given in Fig. 1 near the crossover point. Phonon damping is neglected in this calculation.

Equation (23) may be rewritten in reduced units as

$$1+\frac{\alpha-1}{1-\alpha x^2}-\frac{\xi}{x(x+i\beta\xi)}=0, \tag{24}$$

where $\alpha=\epsilon_0/\epsilon_\infty$, $\xi=\omega_p^2/\omega_l^2$, $\beta=(\tau\omega_l\xi)^{-1}$, and $x=\omega/\omega_l=x_1+ix_2$. In Fig. 1 we plot the values of x_1 and x_2 as

[10] R. A. Cowley and G. Dolling, Phys. Rev. Letters 14, 549 (1965).

[11] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 208.

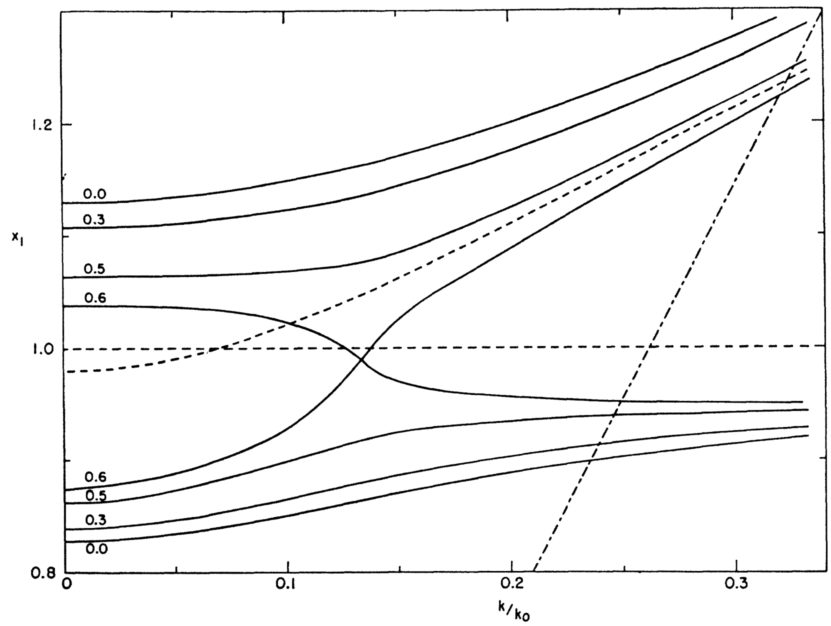

FIG. 2. The dispersion of the normal modes of the coupled system, for various values of the damping parameter β. $\epsilon_0/\epsilon_\infty=1.1$, $\omega_p^2/\omega_l^2=0.96$, and $E_F=2\hbar\omega_0$. The broken lines represent the modes of the uncoupled system. The hyphenated line gives the boundary of the particle-hole excitation continuum for $\beta=0$.

functions of ξ for various values of the damping parameter β, for a value of $\alpha=1.1$, corresponding to the case of GaSb.[12] It is apparent that for small values of β the effect on the real part of the mode frequencies is small, but as β increases the splitting of the modes decreases fairly rapidly and the two curves cross again for $\beta=0.58$ at a value of ξ of about 1.1. The critical value of β is about $4C/\omega_l$. Before the critical value of β is reached, at small (large) values of ξ, the lower (upper) branch of x_1 corresponds to essentially pure plasmon motion and the pertinent value of x_2 is correspondingly large, whereas the upper (lower) branch of x_1 corresponds to essentially pure phonon motion with a small x_2. Above the critical value of β, the two normal modes maintain their respective character for all values of ξ; in other words they are essentially independent, except right in the vicinity of the crossover point where some remnant of the coupling is still present, as indicated by the curvature of x_2 for the two branches.

A semiclassical treatment of the dielectric response function of an electron gas for finite wave number, based on the Boltzmann equation, has been given by Warren and Ferrell.[13] Their expression, when expanded in powers of the wave number, is

$$\epsilon_l(\mathbf{k},\omega)=1-\frac{\omega_p{}^2\epsilon_\infty}{\omega(\omega+i/\tau)}\left[1+\left(\frac{3}{5}+\frac{i}{3\omega\tau}\right)\frac{v_0{}^2k^2}{(\omega+i/\tau)^2}+\left(\frac{3}{7}+\frac{2i}{5\omega\tau}-\frac{1}{9\omega^2\tau^2}\right)\frac{v_0{}^4k^4}{(\omega+i/\tau)^4}+\cdots\right],\quad(25)$$

where v_0 is the Fermi velocity and τ is the relaxation time for the distribution function. For the case $\tau=\infty$, the above semiclassical expression agrees with the Lindhard formula[14] only to order k^2, the coefficient of the k^4 term for the latter expression being $(3/7)+(\omega/2v_0k_0)^2$, where $\hbar k_0$ is the Fermi momentum.

To investigate the effect of damping on the dispersion curves for the coupled modes, we have adopted the expression (25), retaining only terms of order k^2. The equation which determines the modes is then the following:

$$1+\frac{\alpha-1}{1-\alpha x^2}-\frac{\xi}{x(x+i\beta\xi)}\left[1+\left(\frac{3}{5}+\frac{i\beta\xi}{3x}\right)\frac{v_0{}^2k^2/\omega_l{}^2}{(x+i\beta\xi)^2}\right]=0.\quad(26)$$

In Fig. 2 we plot x_1 as a function of k/k_0 for a range of values of β, having chosen $\alpha=1.1$, $\xi=0.96$, and $E_F=2\hbar\omega_0$. It is apparent that the effect of damping on the dispersion curves is analogous to the effect discussed previously for the case $k=0$. The value of the critical damping is again about $4C/\omega_l$. We may remark that the truncated semiclassical expression for the electron response function becomes unreliable with increasing k/k_0, as is evident from the fact that the dispersion curve of the plasmon-like mode for $\beta=0$ crosses the boundary of the continuum of particle-hole excitations instead of being tangential to it. On the other hand, for $k/k_0\lesssim0.2$, the dispersion curves at zero damping computed from Eq. (26) agree well with those reported by Varga.

---

[12] The numerical values of the relevant physical quantities for this system, as given by Varga (Ref. 2), are $\epsilon_\infty\cong18$, $\hbar\omega_l=29$ meV, and $m^*=0.052m_e$.

[13] J. L. Warren and R. A. Ferrell, Phys. Rev. **117**, 1252 (1960).

[14] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, 8 (1954).

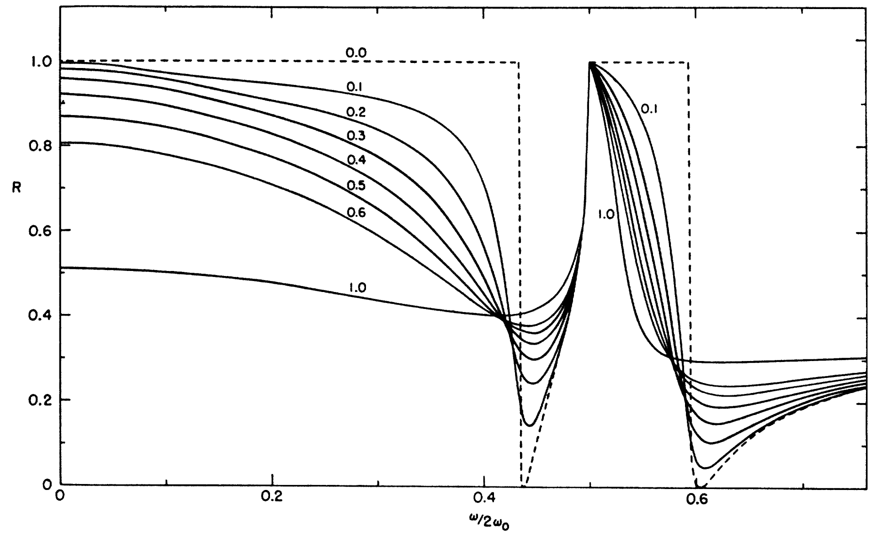

FIG. 3. Reflectivity R as a function of $\omega/2\omega_0$, for various values of the damping parameter β. The parameters are $\epsilon_0/\epsilon_\infty=1.1$, $\epsilon_\infty=18$, and $\omega_p^2/\omega_t^2=0.96$.

Direct information on mode splitting can be obtained from optical-reflectivity measurements. It is, therefore, of some interest to investigate the effect of damping on the reflection coefficient. The optical reflectivity R at normal incidence is given by the familiar expression

$$R=|\epsilon^{1/2}-1|^2/|\epsilon^{1/2}+1|^2, \tag{27}$$

where ϵ is the dielectric function of the system at zero wave number, which we have used previously in Eq. (23). We plot in Fig. 3 the coefficient R as a function of $\omega/2\omega_0$ for various values of the damping parameter β, for the values of the constants used for the calculations illustrated in Fig. 2. It is at once clear that even a small amount of damping produces marked changes in the reflectivity curve. Specifically, we note that the two transmission windows fill up rather rapidly, the low-frequency one filling up at a much faster rate, and that the high-frequency peak narrows rapidly. Above the critical damping the only outstanding feature of the reflectivity curve is the narrow peak at $\omega=\omega_0$.

IV. GENERAL REMARKS

In principle it is possible to observe the coupled plasmon and phonon modes through inelastic-neutron-scattering experiments, but in actual practice it is difficult since the wave numbers of interest are very small. Nevertheless, there are strong indications from the experiments of Cowley and Dolling[10] in PbTe that there is a shift in the phonon frequency in the range of small wave numbers, which is consistent with the theory of plasmon-phonon coupling. In the special case when the plasmon and the phonon frequencies are nearly the same, it is a straightforward matter to evaluate the differential scattering cross section using the simple expressions for the coupled-mode frequencies and the phonon strengths derived in Sec. II. It must, however, be borne in mind that these formulas are strictly valid only in the limit of zero wave number. Inelastic scattering of light could, in principle, also give information on the coupled plasmon-phonon modes. The formula for the differential scattering cross section can be derived analogous to that for inelastic neutron scattering.

It would be highly desirable to have optical reflectivity measurements available for polar degenerate semiconductors in the frequency range of interest, since both the effects of coupling and damping are very marked in this physical property.

ACKNOWLEDGMENTS

We wish to thank John E. Robinson for interesting discussions and E. Davis, student aide for the summer 1965, for programming the calculations.