Dynamical electrical conductivity of n-type PbTe

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The frequency-dependent conductivity of the n-type semiconductor PbTe is explored theoretically in the far-infrared frequency regime, where plasma edges associated with the coupled plasmon–longitudinal-optical-phonon modes have been studied recently by Burkhard and co-workers. A theory which assumes, as we proposed earlier, that scattering of electrons off the coupled plasmon–LO-phonon modes provides the dominant contribution to the free-carrier relaxation rate provides a good account of the data; we find in this material that the contribution from (dynamically) screened impurity scattering is smaller than this principal contribution by two orders of magnitude. The calculation also shows a strong temperature variation of the real part of the frequency-dependent conductivity with origin in the softening of the coupled plasmon–LO-phonon modes of this incipient ferroelectric material.

From an analysis of the reflectivity of doped semiconductors in the infrared, one may deduce information about the relaxation rate $1/\tau(\Omega)$ of the free carriers. With sufficient data in hand, one may study the variation of this important parameter with frequency Ω, the temperature, or the magnetic field. Doped, polar semiconductors are of considerable interest in this regard since the free carriers may scatter off the coupled LO-phonon–plasmon modes observed, for example, in light scattering experiments.[1] Recently, Burkhard, Bauer, and Lopez-Otero[2] have reported reflectivity studies of a PbTe film deposited on a BaF_2 substrate; here we report calculations which show that scattering of electrons from the longitudinal coupled modes provides a contribution to $1/\tau(\Omega)$ that accounts for all features in their data very nicely. Before we discuss our results, we comment on its relation to earlier work.

Not long ago, Mycielski, Aziza, Mycielski, and Balkanski reported data on the magnetic field variation of the free-carrier relaxation rate in n-type PbSe.[3] The data were interpreted by invoking the inelastic scattering of electrons off impurities, with the surrounding screening cloud excited in the scattering event. A subsequent paper by Mycielski and Mycielski[4] explored this mechanism, within a certain approximation scheme. At the same time, we also examined[5] this scattering mechanism, in a framework that is clearly more complete, as discussed below. Burkhard and coworkers interpret one of the two reflectivity dips prominent in their recent data (near 150 cm^{-1}) by invoking the description of inelastic scattering of free carriers from impurities, as described in Ref. 4.

We have also formulated a theory of the scattering of free carriers from the coupled LO-phonon–plasmon modes, in zero magnetic field.[6] A subsequent work extends the calculation to include the influence of a strong magnetic field.[7] Here explicit contact was established with the data on n-PbSe reported by Mycielski *et al.*[3] The theory provides an excellent account of the variation of the free-carrier relaxation rate with both frequency and magnetic field,[8] with no adjustable parameters. At the same time, we recalculated the contribution from inelastic scattering off impurities for this material and find it smaller than that from the LO-phonon–plasmon modes by more than one order of magnitude. The physical reason is that in this material [and also in PbTe (see below)] the impurity potential is screened very strongly by the large static dielectric constant; on the other hand, the collective modes always generate strong fluctuating electric fields which couple to the free carriers efficiently through the Fröhlich mechanism.

We conclude our summary of earlier work with a technical comment. In their study of inelastic scattering from ionized impurities, Mycielski and Mycielski[4] assume the inverse of the wave vector and frequency-dependent dielectric constant $1/\epsilon(q,\Omega)$ is dominated by the plasmon pole, and, in fact, they keep only this portion and overlook the contribution from particle-hole excitations. In fact, our complete calculations[5,7] show the latter dominates the former; see, for example, Fig. 4 of Ref. 5 where the plasmon contribution is found, for heavily doped CdTe, to be a minor feature in $1/\tau(\Omega)$ imposed on the strong background from particle-hole pairs. One may compare this figure with Fig. 3 of Ref. 2, which displays the result given by the analytic formula of Ref. 4. For the Pb salts, as pointed out earlier,[7] the ratio of the plasmon contribution to that from the particle-hole background is very much smaller still, to the point where it is completely negligible. The analytic formula derived by Mycielski and Mycielski,[4] and an equivalent formula also given for pedogogical reasons by us,[5] provides a poor approximation to the contribution to $1/\tau(\Omega)$ from inelastic scattering-off impurities in any of the materials or parameter regimes we have examined.

We now turn to the calculation which forms the basis of the present paper. Our procedure for defining $1/\tau(\Omega)$ follows that employed by Mahan,[9] which proceeds by comparing the high-frequency limit of the conductivity provided by the Kubo formalism with the phenomenological Drude form. When $\Omega\tau(\Omega)>1$, one obtains

$$\frac{1}{\tau(\Omega)}=-\frac{m^*}{ne^2\Omega^2}\,\mathrm{Im}[G(\hbar\Omega+i\eta)]\ , \tag{1}$$

with m^* the effective mass of the carriers assumed to reside in a band of spherical symmetry, n is their concentration, $G(\hbar\Omega+i\eta)$ is a Green's function defined below, and η is a positive infinitesimal. With $\hbar\omega_n=(2n+1)\pi/\beta$, the Matsu-

bara frequency, and u a complex time, one has

$$G(i\omega_n)=\int_0^\beta du\, e^{i\omega_n u}G(u)\ , \tag{2}$$

with

$$G(u)=+\frac{1}{V}\left\langle T\left[\left(\frac{\partial j_x}{\partial u}\right)_u\left(\frac{\partial j_x}{\partial u}\right)_0\right]\right\rangle\ . \tag{3}$$

Here j_x is the current operator, $\beta=1/k_BT$, and V is the sample volume. The above thermal Green's function was calculated within the framework of the imaginary time many-body formalism in which the diagrammatic approach is developed by taking into account each of the two carrier scattering mechanisms discussed above. In an earlier treatment, we have calculated G in the presence of magnetic field,[7] and then taking the zero-field limit in the formula obtained provides results equivalent to those used here and earlier.[5] Here we do not repeat the details of the calculations but sketch the physics and quote the final expression.

Our model Hamiltonian to evaluate G is as follows:

$$H=H_e+H_{e\text{-ph}}+H_{e\text{-imp}}\ , \tag{4}$$

where H_e is the electronic part with the Coulomb interactions between electrons included, while $H_{e\text{-ph}}$ and $H_{e\text{-imp}}$ give the couplings between electrons with the LO-phonon modes and electrons with ionized impurities, respectively. Explicit forms are given in Eq. (2.13), Eq. (2.16), and Eq. (2.26) of Ref. 7. By calculating the derivative of the current operators $(\partial j_x/\partial u)$, we compute the Green's function under the condition $\Omega\tau(\Omega)>1$. Our final result for $1/\tau(\Omega)$, or equivalently $\mathrm{Re}\sigma(\Omega)$ in zero magnetic field due to the polar phonon scattering, is written as follows:

$$\mathrm{Re}\sigma(\Omega)=-\frac{2e^4(\omega_l^2-\omega_t^2)}{\epsilon_\infty m^{*2}\Omega^3 V}\sum_{\vec{q}}\left(\frac{q_x}{q}\right)^2\int_{-\infty}^{\infty}d\omega[n(\omega)-n(\omega+\Omega)]A(q,\omega)\,\mathrm{Im}\left[\frac{\chi_0(q,\omega+\Omega+i\eta)\epsilon_L(\omega+\Omega+i\eta)}{\epsilon_T(q,\omega+\Omega+i\eta)}\right]\ , \tag{5}$$

where ω_l, ω_t, and ϵ_∞ are the LO- and TO- (transverse optical) phonon frequency and optical dielectric constant, respectively. The functions A, ϵ_L, and χ_0 are defined by Eqs. (2.21), (2.25), and (3.9) in Ref. 7, respectively. The total dielectric function ϵ_T divided by ϵ_L is $\epsilon_T/\epsilon_L=1-4\pi e^2\chi_0/q^2V\epsilon_L$. If the free-carrier density is vanishingly small and ϵ_L is neglected, Eq. (5) yields the well-known expression due to the bare LO-phonon scattering.[10,11] When ϵ_L becomes anomalously large, ϵ_T/ϵ_L goes to one so that the electronic screening effect on the single-particle excitations is suppressed much as is seen from Eq. (5).

Figure 1 shows the dispersion relations of the coupled plasmon–LO-phonon modes (L_+ and L_-) for n-type PbTe with $n=8\times10^{16}$ cm^{-3} at the temperature $T=5$ K, as found by evaluating the solutions of $\epsilon_T(q,\omega)=0$. The hatched region indicates the single-particle (SP) excitations. Taking into account this behavior of the elementary excitations in the (q,ω) plane, we have computed $\mathrm{Re}\sigma(\Omega)$ for n-type PbTe in the far-infrared frequency regime through use of Eq. (5). Figure 2(a) gives the computed results for $\mathrm{Re}\sigma(\Omega)$ at $T=0$ K, as a function of frequency. The broken-dotted curve shows the contribution from emission of *bare* LO phonons in this material, in the absence of the Coulomb interactions. The full curve indicates the contribution from the combined emission process of the true L_+ and L_- normal modes of the material, along with that from the SP excitations. The structure near 240 cm^{-1} is of particular interest. Our treatment of scattering from the coupled LO-phonon–plasmon modes necessitates including electron-electron interactions in the Hamiltonian and the calculation of the optical response. Then, as argued many years ago by Ron and Tzoar,[12] general conservation laws require the introduction of certain diagrams which couple the photon to *pairs* of longitudinal normal modes.[13] These are included in our past and present treatments, and allow absorption of the photon by two short wavelength L_- modes. These interfere with the single-particle continuum, as one may see from Fig. 1. The low-lying peak around 40 cm^{-1} comes from the scattering produced by the soft L_- modes. It should be noted that its magnitude is comparable with that found for the bare LO-phonon emission contribution, denoted by the broken-dotted curve. This is because of the large value of ϵ_L at low temperatures in this frequency regime. The shoulderlike structure around 120 cm^{-1} comes from the combined scattering produced by the L_+ and L_- modes.

The finite temperature behavior of $\mathrm{Re}\sigma(\Omega)$ is shown in Fig. 2(b). Here we have taken account of the temperature variation of ϵ_∞, ϵ_s, and ω_t in the full expression of Eq. (5). There remain characteristic structures associated with the

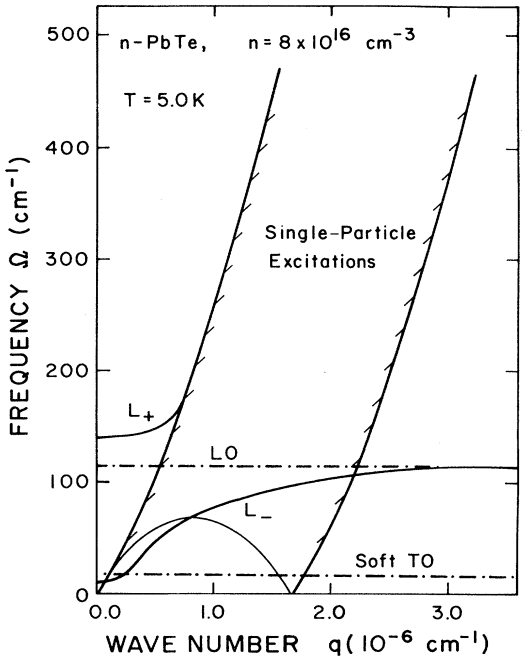

FIG. 1. Dispersion relation of the L_+ and L_- modes at 5 K in n-type PbTe with $n=8\times10^{16}$ cm^{-3}. The hatched region is that occupied by the single-particle excitations.

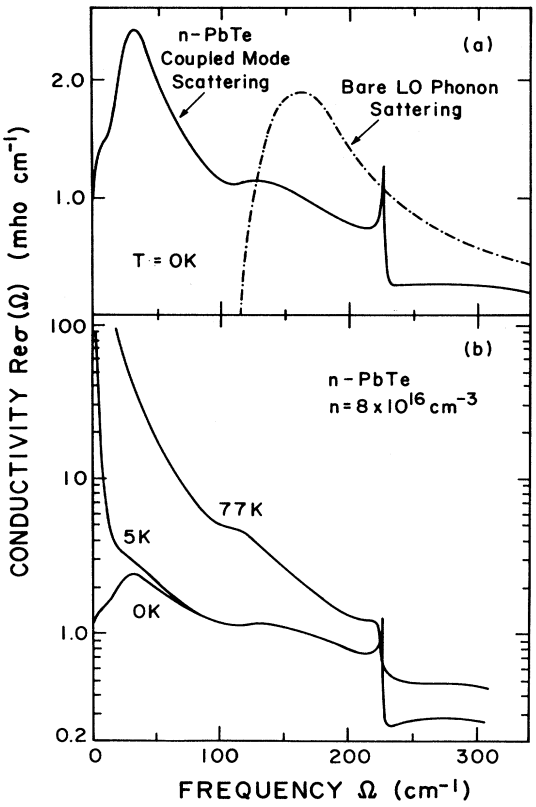

FIG. 2. (a) Real part of conductivity as a function of frequency $\mathrm{Re}\sigma(\Omega)$ at 0 K by free-carrier scattering off the L_+ and L_- modes. (b) Finite temperature behavior of $\mathrm{Re}\sigma(\Omega)$ as a function of Ω at 0, 5, and 77 K.

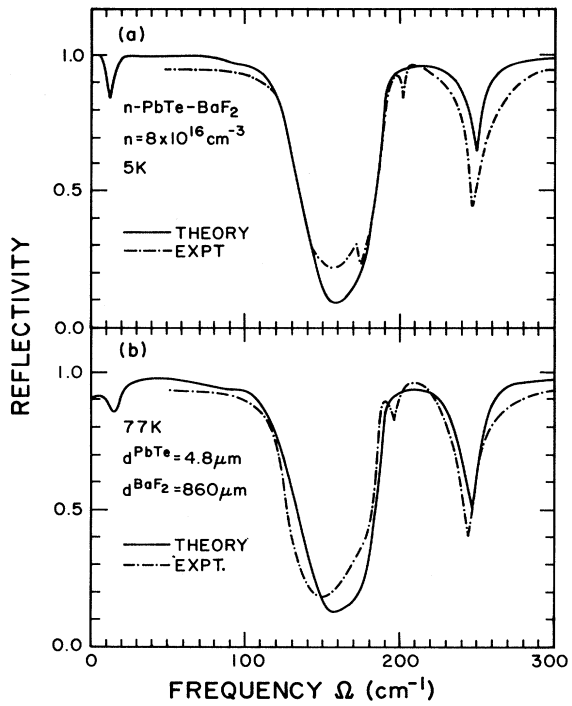

FIG. 3. (a) Calculated reflectivity at 5 K of n-type PbTe on BaF_2 substrate in the far-infrared with $\mathrm{Re}\sigma(\Omega)$ in Fig. 2(b). The broken-dotted line denotes the experimental results from Ref. 2. (b) Calculation of reflectivity at 77 K in comparison with the experiments.

dynamical interactions of electron and phonons in $\mathrm{Re}\sigma(\Omega)$, even at finite temperatures. The low-lying nature of the coupled modes provides a strong increase of $\mathrm{Re}\sigma(\Omega)$ at low frequencies through their increasing population at finite temperatures. Since $\mathrm{Re}\sigma(\Omega)=ne^2/m^*\Omega^2\tau$ for $\Omega\tau>1$ in the Drude's approximation, there are substantial deviations from the Ω^{-2} behavior expected in a simple picture which ignores the frequency variation of the relaxation time. Figures 3(a) and 3(b) show the computed reflectivity from n-type PbTe film on BaF_2, with the above results of $\mathrm{Re}\sigma(\Omega)$ at 5 and 77 K, respectively. We use the reflectivity formula for a two-layer system, which is written in terms of the complex refractive index and thickness (d) of both the PbTe film and the BaF_2 substrate. We put $d^{\mathrm{PbTe}}=4.8$ μm, $d^{\mathrm{BaF_2}}=860$ μm, $\epsilon_\infty^{\mathrm{PbTe}}=33.0$, $\epsilon_\infty^{\mathrm{BaF_2}}=2.16$, $(\epsilon_s-\epsilon_\infty)^{\mathrm{PbTe}}=1300$, $(\epsilon_s-\epsilon_\infty)^{\mathrm{BaF_2}}=5.04$, $\omega_t^{\mathrm{PbTe}}=17.5$ cm^{-1}, and $\omega_t^{\mathrm{BaF_2}}=185.0$ cm^{-1} at 5 K, from Ref. 2. The phonon widths Γ^{PbTe} and $\Gamma^{\mathrm{BaF_2}}$ in ϵ_L are assumed to be 0.2 and 6 cm^{-1} at 5 K, respectively. In Fig. 3(b) we used $\omega_t^{\mathrm{PbTe}}=22.5$ cm^{-1}, $\Gamma^{\mathrm{PbTe}}=6$ cm^{-1} with the same values for other quantities with Fig. 3(a). The broken curve shows the experimental results by Burkhard *et al.*[2] As is evident, the present computations reproduce all the features induced by the PbTe, including their temperature variation. However, we underestimate the depth of the reflectivity dip at 250 cm^{-1}, at $T=5$ K, while the dip at 150 cm^{-1} associated with the L_+ mode is overestimated somewhat. This suggests we underestimate the scattering rate near 150 cm^{-1} at low temperature, from the intrinsic mechanism considered here. The feature at 250 cm^{-1} is an interference minimum of the PbTe/BaF_2 structure. In such a film there are undoubtedly sources of temperature-independent disorder scattering. Note the plasma edge near 15 cm^{-1}, which we find is very sensitive to $\mathrm{Re}\sigma(\Omega)$. It is not affected by Γ^{PbTe} in ϵ_L so that detailed observation of this edge will give an important experimental check of the present analysis of $\mathrm{Re}\sigma(\Omega)$.

In conclusion, we have calculated $\mathrm{Re}\sigma(\Omega)$ for n-type PbTe with $n=8\times10^{16}$ cm^{-3} in the far-infrared frequency regime on the basis of free-carrier–polar-phonon scattering, where the complex nature of the longitudinal normal modes of the material (including single-particle excitations) has been fully recognized. We obtain a very good account of the data reported in Ref. 2 with this mechanism, with no adjustable parameters. Also, the inelastic scattering of electrons from impurities invoked in Ref. 2 is found to be a small contribution to the total free-carrier relaxation rate in PbTe, as we concluded earlier in PbSe.[7] The data do provide evidence for an additional scattering mechanism in the film, since we fail to properly reproduce the full depth of the reflectivity dip near 150 cm^{-1}, at $T=5$ K. In our view, this additional scattering likely comes from either impurities located near the interface, or possibly scattering from elementary excitations localized on the interface. It would be of very great interest to explore experimentally the dip which appears in our calculations near 15 cm^{-1}, which owes its origin to the very low-frequency L_- mode.

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