POLARON CYCLOTRON RESONANCE IN CdTe†

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Measurements have been made of the field dependence of the cyclotron mass of conduction-band electrons in the moderately polar semiconductor CdTe. These measurements, when compared with predictions deduced from the Fröhlich Hamiltonian by the novel variational calculation to be described, give the first quantitative experimental test of large-polaron theory.

We report here low-temperature cyclotron-resonance measurements in CdTe at various far-infared frequencies below the Reststrahl band. We find an increase of cyclotron mass with cyclotron frequency much too large to be explained by band nonparabolicity. Calculations which account for the polaron character of the resonating carrier give quantitative agreement with the data, although the electron–LO-phonon coupling constant required for best fit appears to be somewhat higher than calculated from dielectric data and Fröhlich's formula.

Landau level energies have been studied as a function of magnetic field in the very weakly polar semiconductor InSb in interband magnetoabsorption,[1] cyclotron resonance,[2,3] and impurity cyclotron resonance.[4,5] Because of the very weak coupling between electrons and LO phonons in InSb, appreciable linewidths, uncertainties in the rigid-lattice electron energies, and theoretical difficulties in accurately handling polaron effects for the exciton and impurity states, it has not so far been possible to test quantitatively the validity of large-polaron theory in this material.

The anomalously small Zeeman splitting reported by Brandt[6] and co-workers for an electron in a "hydrogenic" P state in the quite strongly polar insulator AgBr is in quantitative agreement with calculations based on the Fröhlich model; however, an additional assumption in the reported calculation is that the observed electrons were bound to a fixed, positive, point charge. This latter assumption is known to be only approximate for the center in question.

Cyclotron resonance has been reported previously in CdTe by Kanazawa and Brown.[7] Measurements were made at low fields ($\omega_0/\omega_{\mathrm{LO}} \ll 1$). In such fields ω_c gives a measure of the zero-field polaron mass. Since we do not independently know the band mass in CdTe, the low-field cyclotron-resonance mass determination does not enable us to test the validity of the Fröhlich Hamiltonian.

Mears, Stradling, and Inall have studied oscillations in the magnetoresistance of CdTe over a wide range of magnetic fields. Their data indicate significantly higher polaron masses than have been measured in weak-field cyclotron-resonance experiments. However, no adequate theory of magnetoresistance oscillations at moderate coupling strengths is yet available.

The theory of polaron cyclotron resonance, on the other hand, is much more tractable. If we denote the energy of the nth polaron Landau level by $E_p(n)$, then polaron theory predicts a characteristic decrease of $dE_p(n)/dH$ as $E_p(n)$ approaches $E_p(0)+\hbar\omega_{\mathrm{LO}}$ from below. Qualitatively speaking, the polaron effect introduces into the band energy an effective nonparabolicity which becomes extremely marked for states whose energy is nearly 1 LO-phonon energy above the ground state ($n=0$ polaron Landau level).

Previous theoretical calculations are not expected to be sufficiently accurate to describe quantitatively all the experimental data presented here. We introduce an improved theory of polaron Landau levels, which appears especially well suited for the electron–LO-phonon coupling strength of CdTe and for magnetic field strengths employed in the experiment.

Experiment.—To observe cyclotron resonance in CdTe we have studied the transmission of 2- to 5-mm-thick, undoped, n-type samples of low carrier concentration and high mobility ($n=10^{14}$-10^{15} cm^{-3} at 300°K, $\mu_{\mathrm{Hall}} > 5\times10^4$ cm^2/V sec). Far-infrared gas lasers were employed as sources of highly monochromatic, stable (<1% noise level), high-intensity (10-100 μW) incident

Table I. Comparison of observed cyclotron energies with energies calculated at the quoted resonance fields using $\alpha = 0.3$ and $\alpha = 0.4$. The experimental resonance energy at 114 kOe was measured at a sample temperature of 50°K using a Hg vapor lamp source and a Michelson interferometer. Nominal laser-line wavelengths are specified in parentheses.

Resonance field (kOe)	Experimental energy (meV)	Calculated energy (meV)	
		$\alpha = 0.3$	$\alpha = 0.3$
31.17 ± 0.06	3.684 (337 μ)	3.684	3.684
54.76 ± 0.1	6.368 (195 μ)	6.391	6.372
$62.9^{+0.3}_{-0.9}$	7.221 (172 μ)	7.305	7.275
92.5 ± 0.5	10.454 (119 μ)	10.51	10.41
114.0 ± 0.6	12.52 ± 0.06	12.67	12.49

radiation. We used lines at 337, 195, 172, and 119 μ obtained from HCN, DCN, D_2O, and H_2O lasers, respectively. Sample transmission was recorded as a function of magnetic field in the Faraday configuration. No attempt was made to orient the CdTe specimens.

Measurements at low temperature ($T = 4.2$°K) were made using a superconducting solenoid and the 337- and 195-μ sources. Radiation transmitted by a light pipe impinged upon the sample, behind which was located a far-infrared GaAs detector.[9] Detector and sample were immersed in liquid He. Magnetic field strength and homogeneity were determined by means of an ^{27}Al NMR probe in close proximity to the sample.

The remaining measurements ($10° < T < 80$°K) were made in a Bitter magnet with a Golay detector.

The resonance field was determined at the point of minimum sample transmission. Results are given in Table I. Line shapes at various fields and temperatures are given in Fig. 1.

Theory.—Using the conventional Fröhlich Hamiltonian in "polaron units," we write, assuming a parabolic band,[10]

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1,$$
$$\mathcal{H}_0 = \pi^2 + \sum b_{\vec{k}}^{\dagger} b_{\vec{k}},$$
$$\mathcal{H}_1 = \sum \nu_k (e^{-i\vec{k}\cdot\vec{r}} b_{\vec{k}}^{\dagger} + e^{i\vec{k}\cdot\vec{r}} b_{\vec{k}}), \tag{1}$$

where π^2 is $[p + (e/c)\vec{A}]^2/2m$ written in appropriate units, with $\vec{A}$ representing the vector potential (in the Landau gauge) for the magnetic field H. In (1),

$$\nu_k = (4\pi\alpha/\Omega)^{1/2}(1/k)$$

and

$$\alpha = \frac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{e^2}{r_0 \hbar\omega_{\rm LO}}, \tag{2}$$

where $r_0 = (\hbar/2m\omega_{\rm LO})^{1/2}$ and m = electron band mass. The eigenvalues of π^2 are the usual Landau-level energies given in polaron units by $(n + \frac{1}{2})\omega_{\rm UC}/\omega_{\rm LO} + p_z^2$ where $\omega_{\rm UC}$ is the unperturbed

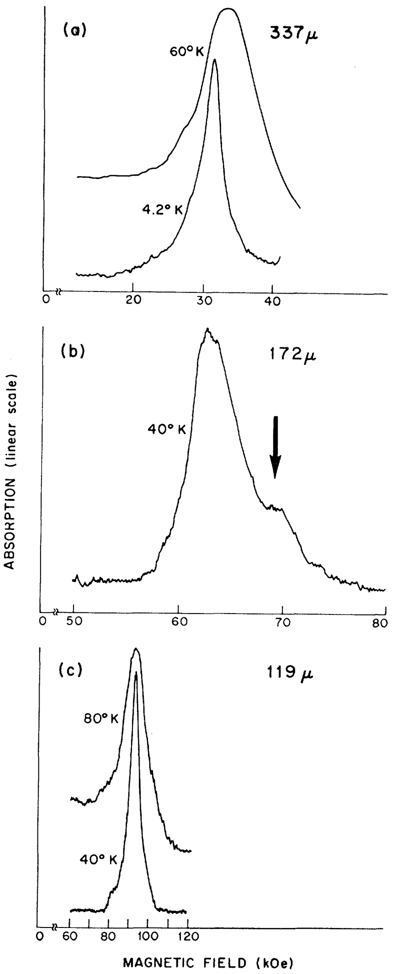

FIG. 1. Experimental cyclotron-resonance absorption line shapes. The zero point and scale units of the absorption are different for each curve.

cyclotron frequency, eH/mc. For small α we usually treat H_1 as a perturbation in second-order Rayleigh-Schrödinger (RS) perturbation theory. The perturbation expressions obtained have been evaluated numerically[11] for the ground state ($n=0$, $p_z=0$) and $n=1$ Landau level ($n=1$, $p_z=0$) as a function of field. Unfortunately, the RS perturbed $n=1$ energy diverges at high magnetic fields. This spurious divergence affects adversely the calculated $n=1$ perturbation energy even when $\omega_{\mathrm{UC}}/\omega_{\mathrm{LO}}$ is as small as 0.4 when $\alpha = 0.3$. Although the divergence difficulty can be avoided by using the Wigner-Brillouin perturbation theory, the accuracy of this method is known to be poor even at weak fields ($\omega_{\mathrm{UC}}/\omega_{\mathrm{LO}} \ll 1$) unless $\alpha \ll 1$.

Analogous difficulties with perturbation theories arise in the zero-field case and have been overcome by the variational calculation described by Larsen.[12] We generalize the *Ansatz* used there by introducing the unnormalized trial function

$$U[\varphi_n(\vec{\mathrm{r}}) + \sum_{n'=0}^{N} \sum_{\vec{\mathrm{k}}} c_{nn'}(\vec{\mathrm{k}})\varphi_{n'}(\vec{\mathrm{r}}) b_{\vec{\mathrm{k}}}^{\dagger}]|0\rangle \qquad (3)$$

as the approximate nth polaron Landau-level wave function. In Eq. (3) the $c_{nn'}(\vec{\mathrm{k}})$ are variational parameters, φ_n is the nth harmonic-oscillator electronic wave function, $|0\rangle$ is the phonon-vacuum state, and U is the unitary transformation given by[10]

$$U = \exp(-i\vec{\mathrm{r}}\cdot\sum \vec{\mathrm{k}} b_{\vec{\mathrm{k}}}^{\dagger} b_{\vec{\mathrm{k}}}) \exp[2ip_x p_y(\omega_{\mathrm{LO}}/\omega_{\mathrm{UC}})] \times \exp[\sum f_k (b_{\vec{\mathrm{k}}}^{\dagger} - b_{\vec{\mathrm{k}}})], \qquad (4)$$

where $f_k = -\nu_k/(1+k^2)$. The value of N at which the sum is truncated in (3) is chosen by requiring that the calculated energy change negligibly upon increasing N. For $n=0$, 1 and 2 states, we find $N=20$ is ample for $\omega_{\mathrm{UC}}/\omega_{\mathrm{LO}} < 1$.

Spectral densities at energies above $E_p(0) + \hbar\omega_{\mathrm{LO}}$ can be calculated in the same approximation as (3) by applying the method of Rodriguez and Schultz[13] to this problem. Details of the calculations for excitation energies above and below $\hbar\omega_{\mathrm{LO}}$ will be submitted for publication elsewhere.

In order to compare theory with experiment we must calculate α for CdTe from (1). Although $\hbar\omega_{\mathrm{LO}}$ is well known (21.1 meV), and the band mass m can be well estimated from the low-frequency cyclotron mass ($m = 0.09$), considerable uncertainty remains in α because of uncertainties in ϵ_0 and ϵ_∞. From the infrared reflectivity found by Mitsuishi[14] and co-workers, $\epsilon_\infty = 7.13$, and from the direct measurement by Berlincourt, Jaffe, and Shiozawa,[15] $\epsilon_0 = 9.6 \pm 0.2$. Assuming that these values, measured near 90°K, are essentially unchanged at temperatures ranging from 4 to 80°K, we obtain the value $\alpha = 0.28$ for CdTe at our experimental temperatures. Considering all the uncertainties, we believe this value should be accurate to within 20%.

The conduction band of CdTe should show a small but measurable nonparabolicity even in the absence of polaron effects, due to interaction of the conduction band with the nearest valence bands. Neglecting spin, the Landau-level energies for $\alpha = 0$ are given to a good approximation by

$$-\frac{E_G}{2} + \frac{E_G}{2}\left[1 + \frac{4}{E_G}(n+\tfrac{1}{2})\hbar\frac{eH}{mc}\right]^{1/2}, \qquad (5)$$

where E_G = band gap = 1.6 eV in CdTe. One can show that for sufficiently large band gap the corrected *polaron* Landau-level energies are

$$E_p(n) - \langle\pi^4\rangle_n / E_G,$$

where $\langle\,\rangle_n$ denotes expectation value in the nth polaron Landau-level wave function. To a sufficient approximation in our work we can replace $\langle\pi^4\rangle_1 - \langle\pi^4\rangle_0$ by $2(\hbar\omega_0)^2$, giving for the calculated energy (including band nonparabolicity) of the $n=0$ to $n=1$ transition

$$\hbar\omega_c = E_p(1) - E_p(0) - 2(\hbar\omega_c)^2/E_G. \qquad (6)$$

We expect that corrections to (6) from a more rigorous treatment of the polaron effects in a nonparabolic band would be typically of order $\alpha\hbar\omega_{\mathrm{LO}}E_p(1)/E_G$ and therefore are very likely to be negligible. A more complete band calculation which includes the spin-orbit split-off valence bands changes (6) only slightly if we use the value $\Delta = 0.9$ eV.[16] We find that the spin splitting at the bottom of the conduction band is of the order of $0.05\hbar\omega_c$ so that our neglect of spin energy in (6) is well justified.

Results.—In Table I we compare observed and calculated energies of the $n=0$ to $n=1$ Landau-level transitions. The zero-field polaron masses used in the calculations were obtained by forcing agreement between (6) and the resonant field observed at 337-μ excitation. We obtain in this way polaron masses of 0.0966 and 0.0963 for $\alpha = 0.3$ and 0.4, respectively, both in excellent agreement with 0.0963 ± 0.0008.[17]

Results for $\alpha = 0.3$ and 0.4 are in agreement with measured resonance energies to within estimated experimental uncertainty, although energies calculated for $\alpha = 0.3$ are systematically higher than observed.

The field dependence of the transition energy of the resonances reported in this paper completely rules out the possibility that any of them arise from a shallow (~14-meV binding energy) donor impurity transition. One of us (D.C.) has in fact studied the magneto-optical spectrum of the shallow donor in CdTe. This work will be the subject of a future publication.

Nonparabolic band effects at $\alpha = 0$ cannot alone account for the data. At 119 μ, for example, the band nonparabolic effect accounts for less than $\frac{1}{3}$ of the observed shift of the cyclotron mass. Low carrier concentrations ($\omega_p/2\pi$ estimated to be less than 30 GHz at 4.2°K) and high mobility ($\omega\tau > 20$) preclude the possibility of line shifts due to magnetoplasma or lifetime effects in our experiments.

Some resonances were observed to shift, and all to broaden, with increasing temperature. For example, the 337-μ resonance field increases with increasing temperature, shifting 5% from its 4.2° value at 60°K [see Fig. 1(a)]. This behavior appears to be due mainly to thermal population of higher Landau levels ($n = 1$, 2, 3) giving rise to additional cyclotron transitions. Thus at 60°K the 337-μ resonance has a significant contribution from the $n = 2$ to $n = 3$ transition, which, largely because of polaron nonparabolicity, occurs at higher field than the low-temperature transition ($n = 0$ to $n = 1$).

On the other hand, calculations show that the energy of the 119-μ photon is never equal to the $n = 1$ to $n = 2$ transition energy for any value of the magnetic field, as suggested by Fig. 2. Thus no temperature shift is expected and none is observed [Fig. 1(c)].

An arrow in Fig. 1(b) indicates the shoulder, shifted about 10% from the main absorption peak, observed on the 172-μ resonance at 40°K. Taking this shoulder to be the $n = 1$ to $n = 2$ transition, we obtain calculated transition energies of 7.38 and 7.21 meV for $\alpha = 0.3$ and $\alpha = 0.4$, respectively, as compared with the observed value of 7.22 meV. Interestingly, the 172-μ main resonance appeared to shift downward in field by about 0.5 to 1% at 20°K, but the weakness of the absorption at this temperature precluded accurate measurement of peak position or of the relative strength of the shoulder.

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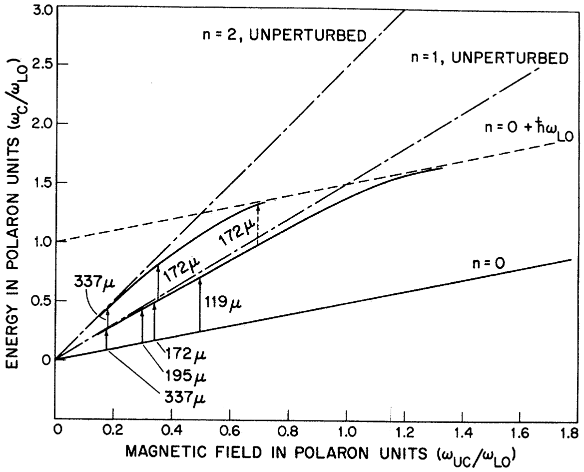

FIG. 2. Semischematic plot of polaron $n = 0$, 1, and 2 Landau-level energy versus magnetic field for excitation energies less than $\hbar\omega_{LO}$. A cursory search for the 172-μ transition indicated by the dashed arrow was unsuccessful.

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OPTICAL PROPERTIES AND ENERGY-BAND STRUCTURES OF SOLID MERCURY*

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Optical properties exhibit the different behavior of valence electrons in the liquid and the solid phases of mercury. Interband transitions occurring only in the solid were identified with the help of energy-band calculations.

Optical properties of liquid Hg indicate that the valence electrons of this metal can be regarded as free-electron-like. For photon energies reaching from the infrared to the near uv, the optical behavior of liquid Hg can be satisfactorily described by the Drude theory.[1] This means that in this energy range the two quantities, plasma frequency and relaxation time, are sufficient for a complete description of the interaction of the valence electrons with an external electromagnetic field. This also means that the valence electrons are not involved in any interband transitions to higher conducting states. Transition from core states to the conduction band have been observed in the reflection spectrum of liquid Hg by Wilson and Rice.[2] It therefore seems that only core electrons participate in interband excitations in liquid Hg.

The question remains whether this situation is similar or changed in the crystalline phase of Hg. Therefore, optical experiments were carried out on crystalline Hg to illuminate this problem and to examine whether the crystallization shows an immediate effect in the behavior of the valence electrons.

Reflectivity measurements on solid Hg were obtained by following a method described elsewhere.[3] The sample cell was made out of copper and the sample substrates consisted of a flat sapphire window which closed one end of the cell, and a 90° sapphire prism with a window base which closed the other. Opaque polycrystalline films of Hg were formed by evaporating Hg under high-vacuum conditions in the cell from a heated crucible and condensing it on the substrates which were kept at liquid-nitrogen temperatures. Data were taken immediately after condensation, at 100 K. Two independent measurements, the near-normal reflectivity and the reflectivity at an incidence angle of 45°, were taken and this allowed a complete determination of the optical properties of solid Hg.[3] A total of four runs were made. The experimental error was 0.5%.

The reflectivities of solid and liquid Hg are shown in Fig. 1. Whereas the experimental reflectivity of liquid Hg follows closely the predicted Drude behavior between 0.5 and 3.5 eV, a dramatic change in the reflectivity of solid Hg is recognized immediately.

Even at photon energies in the infrared the reflectivity of the solid falls off rapidly and shows strong and explicit structure. It is quite obvious that the observed structure originates from energy absorptions of the valence electrons in interband transitions. Keeton and Loucks[4] have calculated electron energy bands of Hg using the relativistic augmented-plane-wave method. Their results are shown in Fig. 2. As they point out, the bands are free-electron-like with splittings due to the combined effect of the crys-

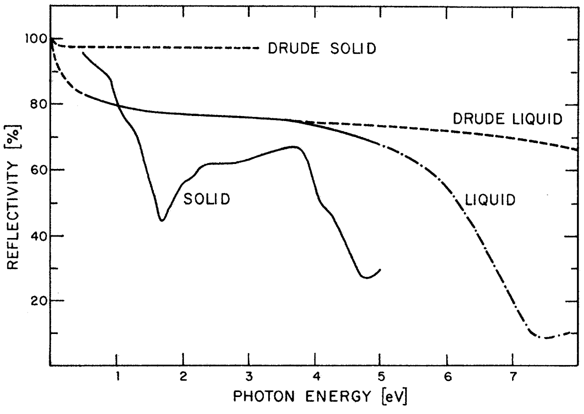

FIG. 1. Normal reflectivity of liquid and solid mercury. The Drude curves are indicated for comparison. (Dash-dot, after Wilson and Rice, Ref. 2.)