Piezoelectric polaron and polaron pinning in *n*-CdS

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The cyclotron resonance of the piezoelectric polaron in *n*-CdS has been investigated using far-infrared spectroscopy at magnetic fields to 90 kOe. Both lamellar grating and Michelson Fourier-transform spectrometers were used with a 0.3-K Ge bolometer to study the photon energy region from 10 to 60 cm^{-1}. The theory of Miyake predicts that the frequency of the polaron's cyclotron resonance is shifted from the bare band electron resonance frequency according to the expression $\Delta\omega_c^p/\Omega_c \propto H^{-1}T^{2/3}$. The magnetic field dependence of the present cyclotron resonance confirms this expression; the cyclotron mass is decreased by piezoelectric polaron effects. The bare band mass in *n*-CdS has also been determined by taking into account the Fröhlich polaron interaction in addition to the piezoelectric polaron effects. For H parallel to the c axis this cyclotron mass is $(0.155 \pm 0.005)m$. Finally, the polaron pinning due to the 43-cm^{-1} optically inactive phonon has been observed.

I. INTRODUCTION

Microwave cyclotron-resonance experiments in *n*-Cds at 1.2–1.4 K yield an effective mass $m^* = 0.177m$ ($\vec{H} \parallel \vec{c}$) at 70 GHz,[1] while other experiments at 77 K give the effective mass $m^* = 0.20m$.[2,3] In order to resolve the difference between these effective masses Mahan and Hopfield[4] examined the temperature dependence of the piezoelectric polaron effects. Their preliminary theoretical paper stimulated several theoretical and experimental studies of the piezoelectric polaron which we now review. A zero-temperature quantum-mechanical calculation of the cyclotron resonance shift due to the piezoelectric polaron effects in a high magnetic field was undertaken by Larsen.[5] Miyake[6] calculated this shift at a finite temperature using both a higher-order approximation in the Green's-function formalism and second-order perturbation theory. He discussed the inadequacy of a second-order perturbation calculation for determining the cyclotron resonance shift in high magnetic fields and he predicted from the higher-order calculation that the piezoelectric polaron effects made the effective mass smaller than the bare band mass.

In far-infrared experiments Button *et al.*[7,8] observed a shift and a splitting of the electron cyclotron resonance line in *n*-CdS as a function of temperature by using a DCN laser (51.3 cm^{-1}) and a cw Bitter-type magnet to 180 kOe. They suggested that the splitting might be due to the piezoelectric polaron effects, but finally Cronburg and Lax[9] determined that the large shift as well as the splitting were due to interference effects in the presence of a magnetic plasma. Independently Narita *et al.*[10,11] determined the temperature dependence of the far-infrared cyclotron resonance by using an H_2O laser (84.2 cm^{-1}) and an intense pulsed magnet which gave magnetic field strengths up to 350 kOe.

Cyclotron phonon resonance in *n*-CdS at 85 kOe was observed by Nagasaka *et al.*[12] using the 84.2-cm^{-1} line of the H_2O laser. The results of the cyclotron phonon resonance experiments suggest that the separation between the $n=0$ and $n=1$ Landau levels at magnetic fields above 70 kOe is strongly modulated by the 43- and 306-cm^{-1} phonons; this modulation is in addition to that caused by the piezoelectric polaron effects associated with accoustic phonons.

In the present work, the author has used far-infrared spectroscopy to determine the cyclotron resonance frequency shift corresponding to piezoelectric polaron effects. The measurements have largely been conducted at frequencies below the 43-cm^{-1} phonon frequency to reduce the polaron effects associated with these optical phonons. The magnetic field dependence was investigated by using a lamellar grating interferometer and fields to 60 kOe. At fields greater than 60 kOe the 43-cm^{-1} phonon is nearly in resonance with the polaron's cyclotron frequency. In this regime polaron pinning occurs. This pinning was studied using a Michelson interferometer with a Mylar beamsplitter.

Polaron pinning due to optical phonons has previously been investigated in far-infrared cyclotron and interband magneto-optical absorption experiments in *n*-InSb,[13-16] and *n*-CdTe.[17] In these experiments, the reststrahlen band obscured the cyclotron resonance pinning. In the wurtzite structure of CdS, however, the 43-cm^{-1} phonon is not infrared active and the polaron pinning is remarkably clear.

II. EXPERIMENTAL

The measurements of the cyclotron resonance absorption were made on a cadmium sulfide sample with donor concentration of 7.1×10^{15} cm^{-3}.

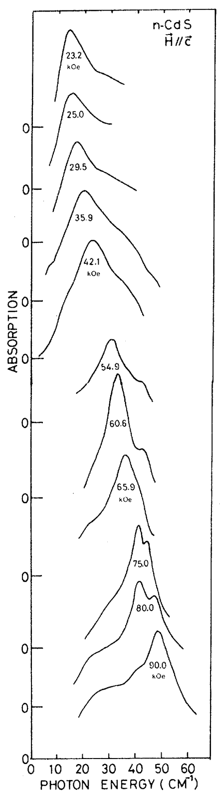

FIG. 1. Absorption spectra of the far-infrared cyclotron resonance in n-CdS ($N_D - N_A = 7.1 \times 10^{15}$ cm^{-3}) at 19 K for magnetic fields from 23.2 to 90 kOe. The magnetic field direction is parallel to the c axis.

The size of the specimen was $1.7 \times 6 \times 6$ mm. The c axis was perpendicular to the surface of the plate.

The magnetic field was generated by a superconducting magnet, cooled to 1.2 K, which produced magnetic fields up to 90 kOe. The magnetic field was applied parallel to the c axis of the CdS crystal in the Faraday configuration. The specimen temperatures of 19 and 38 K were obtained by using a heater. The temperatures were measured at the specimen chamber 350 mm above the pumped ^{3}He bolometer[19] by using 1-kΩ carbon resistors placed in the middle of the light pipe.

The transmission spectra were measured between 5 and 40 cm^{-1} using a lamellar grating interferometer, and between 15 and 65 cm^{-1} using a Michelson interferometer with 0.001-in. Mylar beam splitter. A 1.5-mm-thickness LiF crystal and a sheet of black polyethylene were used as low-temperature filters.

III. PIEZOELECTRIC POLARON MASS

The results of the cyclotron resonance experiments at 19 K on n-CdS with an impurity concentration of 7.1×10^{15} cm^{-3} are shown in Fig. 1. In the present work, we are mainly concerned with the shift of the main absorption peak in the spectra which corresponds to the piezoelectric polaron effects. However after discussing the piezoelectric polaron effect we shall briefly consider pinning of the polaron cyclotron resonance due to the 43-cm^{-1} phonon.

The experiments were performed at 38 and 19K. The peak positions of the spectra versus the magnetic field are shown in Fig. 2. The figure shows the dependence of the cyclotron resonance frequency over a wide range of the magnetic fields. The triangles represent data obtained at 38 K, while the open circle points were obtained at 19 K. The straight lines (a, b, and c) correspond to the cyclotron resonance frequency of electrons having effective bare band masses $m_b' = 0.174m$, $0.182m$, and $0.188m$, respectively. The three lines pass through the origin as expected for bare electrons. The experimental data points are located above the straight lines with the most marked deviation occurring for the low-field region. This behavior is expected for the piezoelectric polaron. According to Miyake's theory[6] of the piezoelectric polaron, the cyclotron resonance frequency shift is given by

$$\Delta\omega_C^P/\Omega_C = 0.18(\lambda^{2/3}) , \qquad (1)$$

where $\lambda = \sqrt{2}\,\alpha_P (l/a_B)(kT/\hbar\Omega_C)$, α_P is the dimensionless piezoelectric coupling constant, $l = (m_b\Omega_C/\hbar)^{1/2}$ is the radius of the lowest Landau state, $a_B = (m_b e^2/\hbar^2\epsilon_S)^{-1} = 4.82 \times 10^{-8}(m_b/m)^{-1}$ is the effective Bohr radius for the static dielectric constant ϵ_S

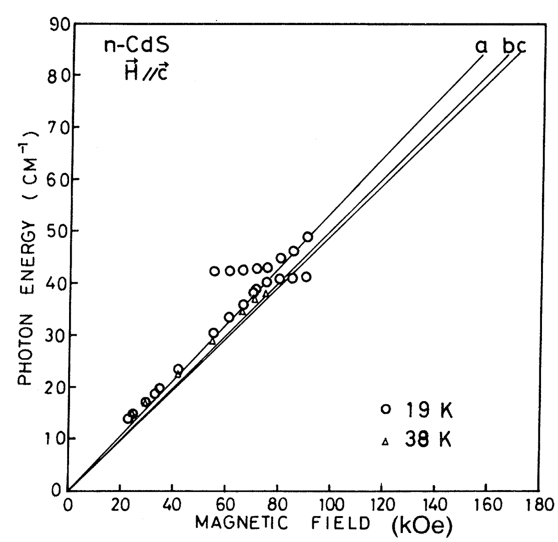

FIG. 2. Magnetic field dependence of the photon energies corresponding to the observed absorption peaks at 19 and 38 K. The straight lines correspond to the free-electron cyclotron resonance for the three effective masses (a, $0.174m$; b, $0.182m$; c, $0.188m$).

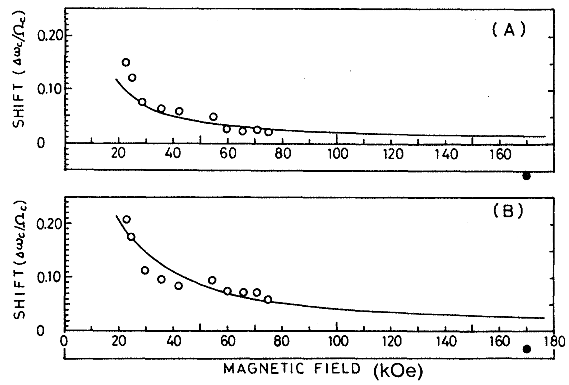

FIG. 3. Magnetic field dependence of the shift of the cyclotron resonance frequency at 19 K. Open circles (○) represent the shifts which were calculated from experimental data, and solid lines represent the theoretical shifts. In (A) the parameters $m_b = 0.174_M$ and $\alpha_p = 0.035$[20] were used; in (B) the parameters are $m_b = 0.182\,m$ and $\alpha_p = 2.8 \times 0.035$. Solid circles are experimental points using the cyclotron mass $m_C^* = 0.188\ m$ determined at 35 K using the 84.2-cm^{-1} line of an H_2O laser (Ref. 12).

$= 9.10$, T is the temperature, and $\Omega_C = 1.76 \times 10^{-7} \times [H(m_b/m)^{-1}]$ is the angular cyclotron frequency. In Miyake's theory, m_b was defined as the bare band mass, but the conduction electrons should interact with the LO phonons as well as the acoustic phonons. We therefore define a pseudo bare band mass to include the LO phonon effects; this definition is legitimate inasmuch as the shift due to the LO phonon, $\Delta\omega_C^{LO}/\Omega_C$, is almost independent of the magnetic field for $\hbar\Omega_C \ll \hbar\omega_{LO}$. In Fig. 3(A) the experimental shift at 19 K from the resonance frequency expected for a pseudo bare mass of $0.174m$ is plotted along with the theoretical curve using a piezoelectric coupling constant of $\alpha_P = 0.035$.[20] In Fig. 3(B) the same approach is taken using a pseudo bare mass of $0.182\ m_e$ and a coupling constant of 2.8×0.035. While the data are not sufficiently precise to accurately determine both parameters in Miyake's theory, the theory clearly explains both the absolute value and the functional form of the polaron's cyclotron resonance shift using reasonable values for these parameters.

Miyake[6] determined the cyclotron resonance frequency shift for the quantum limit ($kT \ll \hbar\Omega_C$), whereas the present experiment is in the regime $kT \sim \hbar\Omega_C$. The Landau state energy is expressed by $E_n' = E^{(0)}(n, p_z, X) + \Delta(n, p_z, X; E_n')$, where $E^{(0)}(n, p_z, X)$ is the energy of the unperturbed Landau state, n is the quantum number, p_z is the z component of the polaron momentum, X is the center coordinate of the cyclotron orbit and Δ is the shift of the Landau state due only to the electron–acoustic-phonon interaction through the piezoelectric field. In the quantum limit all of electrons are in the $n = 0$ (ground) Landau state. Far infrared radiation excites electrons from the ground state to the first excited state. In this case, the observed shift can be considered to be the difference between $\Delta(n = 1, p_z, X)$, the shift of the excited state, and $\Delta(n = 0, p_z, X)$, that of the ground state. The experimental conditions are shown in Table I. The distribution function for the electrons is given by $f = [\exp(\hbar\Omega_C/kT) + 1]^{-1}$. When the cyclotron resonance frequency is observed by using far-infrared radiation of 14 and 23.2 cm^{-1} at 19 K, the distribution factors for the $n = 1$ Landau state are 0.26 for 14 cm^{-1} and 0.15 for 23.2 cm^{-1}. Thus for cyclotron resonance observations at these frequencies more than three quarters of the electrons in the conduction band are in the $n = 0$ Landau state. We therefore anticipate that we can apply the quantum limit theory to the experimental results at a temperature of 19 K without substantial error.

The contribution of the optical phonons to the polaron cyclotron mass has been included in the pseudo bare band mass introduced earlier. This contribution may be determined from knowledge of the optical phonon frequencies and their Fröhlich polaron coupling constants. Arguello, Rousseau, and Porto[18] investigated the Raman scattering in n-CdS and determined the phonon frequencies of the Raman active phonons. All of these Raman active phonons are associated with longitudinal polarization waves in the crystal and they therefore contribute to the electron phonon interaction. However, the amplitude of the polarization field due to the ~306-cm^{-1} LO phonons must be larger than the amplitudes of the other Raman active optical phonons since the scattering cross section of the ~306-cm^{-1} LO phonons is much bigger than the cross section due to the others. We therefore assume that the contribution to the polaron mass from the optical phonon interactions is determined solely by the 306-cm^{-1} phonon with the exception of the regions in which polaron pinning is observed. This assumption implies that the value of the coupling constant[20] $\alpha_{LO} = 0.64$ may be attributed to the ~306-cm^{-1} LO phonons alone.

Under these conditions Larsen[21] determined the

TABLE I. Typical far-infrared cyclotron resonance conditions.

T(K)	$\hbar\Omega_C = 14\ cm^{-1}$ $kT/\hbar\Omega_C$	f	$\hbar\Omega_C = 23.2\ cm^{-1}$ $kT/\hbar\Omega_C$	f
19	0.94	0.26	0.57	0.15
38	1.89	0.37	1.14	0.29

difference between the shift of the first excited state and that of the ground state to be

$$\Delta\omega_C^{\mathrm{LO}}/\Omega_C = -\tfrac{1}{6}\alpha_{\mathrm{LO}} - \tfrac{3}{20}(\Omega_C/\omega_{\mathrm{LO}})\alpha_{\mathrm{LO}}\,, \qquad (2)$$

where $\alpha_{\mathrm{LO}} = 0.64$,[20] $\omega_{\mathrm{LO}} \simeq 306\ \mathrm{cm^{-1}} = 5.77\times10^{13}\ \mathrm{sec^{-1}}$. Thus the shift of the cyclotron resonance frequency in n-CdS is given by

$$\Delta\omega_C^{\mathrm{LO}}/\Omega_C = -0.11 - (1.66\times10^{-15})\Omega_C\,. \qquad (2')$$

By using Eqs. (1) and (2′) we can obtain the cyclotron frequency $\Omega_C' = \Omega_C + \Delta\omega_C^P + \Delta\omega_C^{\mathrm{LO}}$ under the piezoelectric interaction and the Fröhlich interaction, where $\Delta\omega_C^P$ is positive and $\Delta\omega_C^{\mathrm{LO}}$ is negative. The cyclotron mass is increased by the electron–LO-phonon interaction, while it is reduced by the piezoelectric polaron effects. Comparing the calculated cyclotron resonance frequency Ω_C' to the experimental data at 19 K shown in Fig. 2 the bare band mass has been determined to be $m_b = (0.155 \pm 0.005)m$.[22]

The experimental results lead us to the following conclusions:

(i) The experimental results exhibit fairly good correspondence with the prediction of Miyake's theory for the piezoelectric polaron: $\Delta\omega_C^P/\Omega_C \propto H^{-1}T^{2/3}$.

(ii) However, in the theory of the piezoelectric polaron the width of the Landau states has a very important role. The piezoelectric polaron shift strongly depends upon the scattering term of the Landau states in the denominators of the perturbation calculation. The scattering by the acoustic phonon through the piezoelectric field has been taken into account in the polaron theory at finite temperatures, but the scattering by the LO phonons has not. The phonon number of the LO phonons can be large even in the quantum limit. Thus, in the higher-temperature region of the quantum limit, $kT/\hbar\Omega_C < 1$, the piezoelectric polaron shift of the cyclotron resonance frequency decreases more rapidly with temperature due to the broadening of the polaron states by the LO phonons than would be expected from the piezoelectric polaron theories such as Miyake's.

(iii) In order to investigate the temperature dependence of the piezoelectric polaron mass we must work under the constraint that the LO phonon occupation number N_q be much smaller than unity. In CdS this constraint implies that we observe the cyclotron resonance by using radiation of energy $\hbar\Omega_C < 43\ \mathrm{cm^{-1}}$ (the lowest frequency of the optical phonons in n-CdS) and at temperatures below 20 K ($Nq \sim 0.04$ for the 43-cm^{-1} phonon).

IV. POLARON PINNING

As the magnetic field was increased to bring the cyclotron resonance and the 43-cm^{-1} LO phonon energy into proximity, the absorption spectra became increasingly more complex, as shown in Fig. 1. The absorption spectra of the cyclotron resonance have one peak in the magnetic field region from 23.2 to 42.1 kOe, whereas satellite lines at high $h\nu$ appear above 54.9 kOe. The relative amplitudes and positions of these two absorption lines depend strongly on the magnetic field. The strength of the satellite increases with the magnetic fields from 54.9 to 80 kOe. At sufficiently high fields ($\gtrsim 90$ kOe) the absorption peak at high $h\nu$ is no longer a satellite, but has become the main line of the cyclotron resonance with a weak satellite at 43 cm^{-1}.

Further data were taken at a temperature of 38 K as shown in Fig. 2. Over most of the region covered the triangle points of 38 K lie below the 19-K open circle points. As the magnetic field is increased to 75 kOe, the separation of the two kinds of data points increases as shown in Fig. 2. Such behavior is expected from the temperature dependence of the phonon number density which appears in the matrix element calculated in second-order perturbation theory for the electron-phonon interaction Hamiltonian. The phonon population number of the 43-cm^{-1} phonon is given by $N_q = [\exp(\hbar\omega_{\mathrm{LO}}/kT) - 1]^{-1}$. The value of N_q changes from 0.04 to 0.24 as the temperature changes from 19 to 38 K. Qualitatively, the theoretical results of the Fröhlich interaction agree with the measured temperature dependence for the shift of the cyclotron resonance frequency. The temperature dependence of the shift of the cyclotron-resonance frequency will be discussed in a future publication.

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