

Verification of polaron cyclotron-resonance theory and determination of the coupling constant in *n*-CdTe

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Cyclotron-resonance measurements of the electron effective mass (polaron mass) in *n*-CdTe have been performed in the far infrared at several different laser frequencies, ranging from 29.65 to 127.5 cm^{-1} , in the region for which $\omega_c < \omega_{\text{LO}}$, but approaching very closely to the reststrahlen absorption ($\omega_{\text{TO}} = 145 \text{ cm}^{-1}$; $\omega_{\text{LO}} = 171 \text{ cm}^{-1}$). Excellent agreement is found between the measured values of electron mass and those calculated from polaron cyclotron-resonance theory for a polaron coupling constant $\alpha = 0.40 \pm 0.03$.

I. INTRODUCTION

It has been recognized for several years that CdTe is, in practical terms, one of the best possible materials for testing experimentally the predictions of polaron cyclotron-resonance theory¹ and hence the effects of large polaron formation on the Landau-level structure of polar semiconductors. Three reasons are: it is one of the few polar semiconductors which has a relatively large electron-phonon interaction (polaron coupling constant, $\alpha = 0.4$), a small electron effective mass ($m^*/m_0 \approx 0.1$), and finally a mobility high enough to permit the measurement of sharp, narrow, intraband cyclotron resonance (CR) transitions at frequencies closely approaching the strong reststrahlen band. The small mass permits resonant fields to be used within the range of steady magnetic fields practically available in the laboratory ($\sim 200 \text{ kG}$). Polaron theory¹ predicts an increase with frequency of the cyclotron resonance (CR) effective mass as the longitudinal-optical (LO) phonon is approached from below. This is caused largely by electron-phonon coupling with a slight contribution from conduction-band nonparabolicity in the case of CdTe, as indicated in the solid curve of Fig. 1.

CdTe is a direct-band-gap semiconductor which crystallizes in the zinc-blende structure. Its lowest conduction-band minimum is nearly parabolic and is characterized by simple Landau levels in a magnetic field. At low temperature, its reststrahlen absorption band is characterized by

longitudinal (LO) and transverse-optical (TO) mode frequencies, centered at $\omega_{\text{LO}} = 171 \text{ cm}^{-1}$ and $\omega_{\text{TO}} = 145 \text{ cm}^{-1}$, respectively. With the presently available power from cw submillimeter lasers ($\sim 1 \text{ mW}$), one finds that transmission spectroscopy can not be performed on CdTe specimens (even as thin as 1 mm) at frequencies above about 130 cm^{-1} , owing to the broad TO mode absorption which extends to frequencies above 160 cm^{-1} . Despite this constraint, it is still possible to measure cyclotron-resonance masses to frequencies within 75% of the LO phonon frequency, and to determine the increase in electron mass to a high degree of precision, through the use of precisely fixed laser frequencies of narrow bandwidth.

Previous measurements,^{2,3} made at frequencies up to 101 cm^{-1} , from which the polaron coupling constant was tentatively put at $\alpha = 0.28$, have now been extended to frequencies of 118.6 and 127.5 cm^{-1} , where polaron effects are larger. It is the purpose of this paper to show that the present and previous measurements are consistent with a coupling constant $\alpha = 0.4$, as supported by polaron CR theory,¹ and to show that this value of α is not consistent with those obtained from the definition in the simple Fröhlich continuum model, given by

$$\alpha = (e^2/\hbar)(m_B^*/2\hbar\omega_{\text{LO}})^{1/2}(1/\epsilon_\infty - 1/\epsilon_0), \quad (1)$$

where ω_{LO} is the LO phonon frequency, ϵ_∞ and ϵ_0 are the high-frequency and static dielectric constants, respectively, and m_B^* is the bare band-

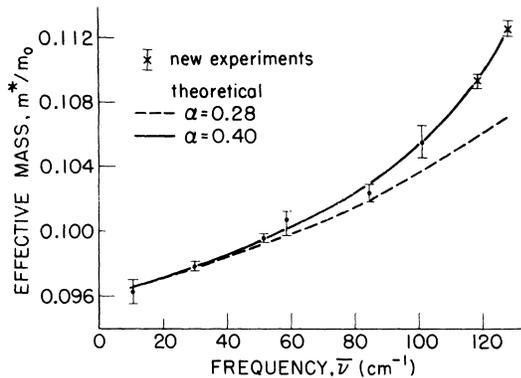


FIG. 1. Plot of the measured and calculated polaron masses for the electron as a function of CR frequency in n -type CdTe. The solid curve, which contains a small theoretically computed correction for conduction band nonparabolicity, was calculated from Larsen's polaron CR theory (Ref. 5), assuming $\alpha=0.40$; the experimental points, which fall along the solid curve, were measured from the CR absorption minima.

edge effective mass. The observed discrepancy between the values of α calculated from Eq. (1) and the value determined from CR results is undoubtedly one of the more significant findings of the present work, since it clearly shows that caution must be exercised in determining α from the Fröhlich formula using experimentally measured optical dielectric constants. In this regard, we believe that α is much more precisely defined by the CR results, since the polaron CR theory depends only upon the energy band and lattice parameters (E_G , $\hbar\omega_{LO}$, and m_B^*/m_e) which can be measured to a high precision, rather than upon a particular choice of the dielectric constants, which are not only difficult to define for the dynamical model under investigation, but even more difficult to measure precisely.

II. EXPERIMENTAL METHOD

A 2-mm-thick melt-grown CdTe specimen was used in these measurements; it was also used to remeasure the low-frequency resonances reported originally by Waldman *et al.*² The low-temperature peak in its measured Hall mobility was approximately 1×10^5 cm²/V sec and its electron concentration was on the order of a few times 10^{12} at temperatures near that of liquid helium. CR was also performed on a similar specimen of only slightly lower peak mobility with essentially identical results.

The CR absorption measurements were performed in the M.I.T. National Magnet Laboratory, using a submillimeter laser spectrometer of standard design and construction, the details of which have been described elsewhere.⁴ Principal-

ly, the spectrometer comprised a 175-kG Bitter solenoid, cw gas lasers employing D₂O, H₂O, HCN, and DCN gas, an evacuated light pipe transmission system, a flow-through helium cryostat, and a liquid-helium-cooled Ge bolometer detector. All measurements were made in the Faraday configuration. Specimen temperatures were measured by means of a calibrated carbon-resistance thermometer, thermally anchored to the small heat sink on which the specimen was mounted. The specimen temperature did not vary more than 2 or 3 K from the measured value, once thermal equilibrium was established. The magnetic field was calibrated periodically by means of a secondary standard (NMR primary standard), and the error in the measured values of the resonant fields did not exceed +0.1% at the highest fields.

III. COMPARISON OF THEORY AND EXPERIMENT

Through use of the variational principle, Larsen⁵ has obtained the energy spectrum of polaron Landau levels in moderately polar semiconductors by calculating the unperturbed energy levels interacting with one-phonon states according to the Fröhlich Hamiltonian. The details of Larsen's calculation, which treats both general and simple limiting cases of polarons in ellipsoidal energy bands, have been described and are an extension of his original theoretical treatment of the polaron energy-level spectrum in a magnetic field.¹

The present CR measurements were performed at temperatures between 6 and 50 K and at frequencies as high as 118.6 and 127.5 cm⁻¹, radiated by D₂O and H₂O gas lasers, respectively. In the spectrum of Fig. 2, absorption resonances typical of the low- and high-frequency results are shown. The high-frequency absorption at

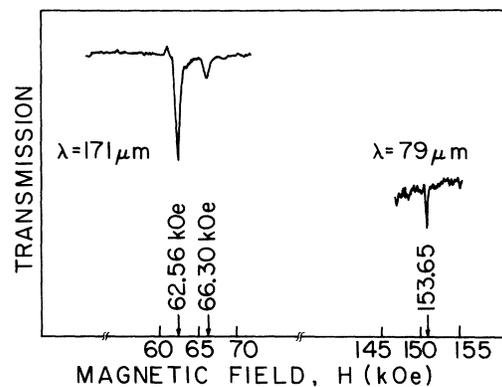


FIG. 2. Low-temperature cyclotron resonance absorption spectra of n -CdTe at frequencies of 58.25 and 127.5 cm⁻¹. The small absorption line at 66.3 kG and frequency of 58.25 cm⁻¹ has not been identified.

TABLE I. Measured and calculated electron mass in CdTe.

Laser energy or frequency (meV) (cm ⁻¹)	Measured mass $m_{cy}^*(B)/m_e$	Calculated mass $\alpha=0.35$	Calculated mass $\alpha=0.40$
0	...	0.0965	0.0963
3.684 29.65 (337 μ m) HCN	0.097 94	0.097 99	0.097 93
6.368 51.27 (195 μ m) DCN	0.099 54	0.099 38	0.099 46
7.221 58.25 (172 μ m) D ₂ O	0.100 84 (0.100 31)	0.099 90	0.100 06
10.454 84.32 (119 μ m) H ₂ O	0.102 43 (0.102 83)	0.102 35	0.102 76
12.52 101.0 (99.0 μ m) FT ^a	0.1054	0.104 73	0.105 37
14.704 118.6 (84.3 μ m) D ₂ O	0.1093 \pm 0.005	0.108 48	0.109 44
15.808 127.5 (78.4 μ m) H ₂ O	0.1124 \pm 0.0005	0.111 37	0.112 51

^a The resonance at 101.0 cm⁻¹ (99.0 μ m) was measured in a Fourier-transform (FT) spectrometer.

$\hbar\omega = 127.5$ cm⁻¹ appears to be very weak, owing to the high background absorption from the reststrahlen band. At the two highest frequencies we observe narrow CR absorption lines (<1.5 kG half-width), centered at 138.8 and 153.7 kG, and determine CR masses of $m_{cy}^*(B)/m_e = 0.1093 \pm 0.0005$ and $m_{cy}^*(B)/m_e = 0.1124 \pm 0.0005$, respectively. We take the measured band edge effective mass in CdTe to be the value determined by microwave⁶ CR which is $m_{cy}^*(B=0)/m_e = 0.0963 \pm 0.0008$. Thus, at 127.5 cm⁻¹ we find an increase in effective mass of nearly 17% which can be attributed almost entirely to the strong electron-LO-phonon interaction in this polar semiconductor.

Table I summarizes the experimental and theoretical results. For completeness, we have included the low-temperature CR measurements,² made at lower frequencies on a CdTe specimen of lower peak mobility (approximately half that of the present samples). CR was performed on the present samples at several of these lower frequencies and the measured masses were identical, to within experimental error. However, the remeasured mass values at $\lambda = 172$ and 119 μ m were found to be somewhat closer to the theoretical (calculated) values for $\alpha = 0.40$. These remeasured values are shown in parentheses in the second column of Table I. The remeasured values were obtained at $T < 20$ K, and we did not observe the previously reported shoulder on the $n = 1 \rightarrow n = 2$ Landau-level transitions.² The measurements summarized in Table I are believed to be characteristic of high-purity, high-mobility, n -type CdTe. At each experimental frequency

the polaron masses, $m_{cy}^*(B)/m_e$, have been calculated from theory,^{1,5} for values of $\alpha = 0.35$ and 0.40, and are entered in the two right-hand columns of Table I. These calculations include corrections for band nonparabolicity.⁵

The points plotted in Fig. 1 represent results obtained at the various laser frequencies, except for the point at 101 cm⁻¹, which was obtained from Fourier-transform spectroscopy,² and the lowest frequency point, which was obtained from microwave CR at 310 GHz.⁶ The two points in the upper right-hand corner of the plot represent the present measurements made at 118.6 and 127.5 cm⁻¹, while the lower frequency mass points at 84.32, 58.25, 51.27, and 29.65 cm⁻¹ were taken from the previously reported laser frequency measurements.² The solid curve is a plot of the theoretically calculated masses for $\alpha = 0.40$, as given in Table I, while the dashed curve was generated from an earlier theoretical calculation,² assuming $\alpha = 0.28$. As noted in Ref. 2, the $\alpha = 0.28$ value employed in this calculation was obtained from the Fröhlich formula, Eq. (1), using $\hbar\omega_{LO} = 21.1$ meV (170 cm⁻¹), $m_B^*/m_e = 0.090$, and the best available values of the dielectric constants: $\epsilon_\infty = 7.13$ (Ref. 11); $\epsilon_0 = 9.6 \pm 0.2$ (Ref. 9). A plot of the theoretical mass points for $\alpha = 0.35$ (Table I) would lie between the solid and dashed curves of Fig. 1. A comparison of the experimental and theoretical results in Fig. 1, particularly at the two new high frequencies described in the present work, clearly indicates that the theoretical curve for $\alpha = 0.40$ provides the best fit to all of the experimental data. In fact, assuming the validity of the variational calculation for polaron

Landau levels, the present measurements limit the allowed variation in the chosen value of the coupling constant to $\alpha = 0.40 \pm 0.03$.

We turn now to a consideration of the values of α calculated from the Fröhlich formula [Eq. (1)]. In calculating α from Eq. (1), we will require a value of the bare band-edge effective mass m_B^* . For $\alpha < 1$, m_B^* can be obtained to a very good approximation from either

$$m_B^* = m_p^* (1 - \frac{1}{8}\alpha)$$

or

$$m_B^* = m_p^* (1 - \frac{1}{12}\alpha) / (1 + \frac{1}{12}\alpha), \quad (2)$$

where m_p^* is the zero-field polaron mass, and we may assume, to a very good approximation, that m_{cy}^* (at microwave frequencies) = $m_p^*(B=0)$, since the band nonparabolicity is very small in CdTe. The value of m_{cy}^* at microwave frequencies, denoted above as $m_{cy}^*(B=0)$, Ref. 6, has been measured to a high precision. Similarly, ω_{LO} is precisely determined from Raman scattering measurements,⁷ which puts its value at $\omega_{LO} = 171 \text{ cm}^{-1}$. And both of these parameters were measured at helium temperature or below. Unfortunately, the published dielectric data for CdTe are not of high precision and vary widely, even under identical experimental conditions.⁸⁻¹³ Since α is a sensitive function of the dielectric constants, there remains a large uncertainty in its value, as noted by Simmonds.¹⁴ This is particularly true for values of α determined from the Fröhlich formula. Johnson *et al.*¹⁰ have determined ϵ_∞ and ϵ_0 from optical interference measurements, performed on the same sample, above and below the reststrahlen frequency, at a temperature of 8 K, which closely approximates the experimental temperature of the present measurements (mostly between 6 and 20 K). They obtain the values: $\epsilon_\infty = 6.7 \pm 0.3$ and $\epsilon_0 = 9.0 \pm 0.4$. Using these values in Eq. (1) together with $\omega_{LO} = 171 \text{ cm}^{-1}$ and $m_B^*/m_e = 0.090 \pm 0.001$, from Eq. (2), we obtain $\alpha = 0.30 \pm 0.09$. The large uncertainty in this value of α clearly reflects the large uncertainties in the measured values of the dielectric constants chosen for the calculation; it is typical of the α 's calculated from the Fröhlich formula, using the various published values of the dielectric constants for CdTe.

Measurements of polaron effects on the Zeeman splitting of the shallow donor impurity states in CdTe, made by Cohn *et al.*,³ seemed to indicate that α was about 0.4, in agreement with the present CR measurements on the conduction-band electron. They found that the theoretically computed $1s \rightarrow 2p^+$ transition frequencies for $\alpha = 0.4$ provided a much better fit to their experimental

data than did the theoretically computed frequencies for $\alpha = 0.3$. In recent measurements of the shallow hydrogenic donor resonance in CdTe, Simmonds¹⁴ has reached similar conclusions and suggests that the coupling constant lies in the range: $0.35 < \alpha < 0.40$. However, the accuracy of the polaron theory used to fit the impurity resonance data has not been sufficient to allow for a definitive determination of α . As in the present work, Simmonds also concluded that the values of α computed from Eq. (1), using published values of CdTe optical and dielectric constants, are systematically less than 0.35, and generally near 0.30. In fitting his impurity resonance data to the hydrogenic rydberg formula, Simmonds has derived a value for the static dielectric constant, $\epsilon_0 = 9.9 \pm 0.1$, somewhat higher than the 9.6 ± 0.2 value employed by Cohn *et al.* Using this higher value of ϵ_0 , in Eq. (1), together with $\epsilon_\infty = 6.7 \pm 0.3$, Ref. 10, and the appropriate values of ω_{LO} and m_B^* , Simmonds finds that $\alpha = 0.37 \pm 0.05$. Though not strictly valid, it is perhaps interesting that this combination of dielectric constants in the Fröhlich formula yields a value of α close to that which best fits the present cyclotron resonance results for the conduction-band electron ($\alpha = 0.40 \pm 0.03$). The calculation of polaron effects from the Zeeman transitions of shallow donor impurities is complicated by several problems of a fundamental nature. One such problem arises from the fact that it is difficult to separate the effects of central cell perturbation on the ground state of the impurity from those due to the electron-phonon interaction. Fortunately, this complication is peculiar only to bound state transitions, and not to those of intraband cyclotron resonance, on which the present CdTe results rests.

IV. CONCLUSIONS

Excellent quantitative agreement has been obtained between theoretical predictions and experimental measurements of polaron cyclotron resonance over the entire frequency range from 29.65 to 127.5 cm^{-1} for a value of polaron coupling constant $\alpha = 0.40$. This is regarded as a verification of polaron cyclotron resonance theory. We are, on the other hand, distressed to find that computation of the polaron coupling constant from the Fröhlich formula gives a great disparity of values ranging from $\alpha = 0.2$ to 0.4, when various combinations of the published values of the dielectric constants are employed in the computation. Indeed, we have been unable to find published values of the low-temperature dielectric constants which, when substituted in Eq. (1), yield a value of $\alpha = 0.4$. We must, therefore, suggest that either all of the measurements of the dielectric con-

stants for CdTe are grossly inaccurate, or the simple definition of coupling constant given in the Fröhlich continuum model is inadequate, or both. At present, it is our opinion that the best low-temperature values of the CdTe optical and dielectric constants are the following: $\omega_{LO} = 171 \text{ cm}^{-1}$; $\omega_{TO} = 145 \text{ cm}^{-1}$; $\epsilon_0 = 9.0 \pm 0.4$; and $\epsilon_\infty = 6.7 \pm 0.3$. The ω_{LO} value was taken from Ref. 7; the others are from Ref. 10 and all were measured at temperatures of 8 K or below. We conclude by noting that, given the validity of polaron CR theory in CdTe, the best fit between theory and experiment is obtained for a polaron coupling constant $\alpha = 0.40 \pm 0.03$, which contrasts with $\alpha = 0.30 \pm 0.09$, obtained from the Fröhlich formula Eq. (1) and the low-temperature values of the optical and dielectric constants cited above. We have failed to resolve the discrepancy between these two values of α despite the large uncertainty in the values obtained from the simple Fröhlich definition. There is a need for more precise measurements of the dielectric constants on high quality specimens at low temperature not only to reduce this uncertainty, but also to provide an unambigu-

ous test of the validity of the simple definition of coupling constant given in Eq. (1).

It has recently come to our attention that similar CR measurements have been performed on AgBr ($\alpha \approx 1.6$) in order to measure polaron effects. These measurements¹⁵ were made at two frequencies (microwave and at $\lambda = 337 \mu\text{m}$), the highest of which fell some 110 cm^{-1} below the LO phonon frequency. At $337 \mu\text{m}$, a 5% increase in the electron effective mass was observed. In spite of the higher coupling constant of AgBr, we conclude that our CdTe results provide a more sensitive and definitive test of polaron cyclotron resonance theory, over a wide range of frequencies, closely approaching ω_{LO} .

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