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Optical Properties and Donor States in Semiconducting CdF_2

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The infrared absorption spectra associated with Y, Gd, Tm, and In donors in semiconducting CdF_2 have been measured. Except for the In-doped sample, in which the infrared absorption has to be induced at low temperature, the absorption spectrum is practically independent of the particular dopant. The results are discussed in terms of both a tight-binding approximation and a hydrogenlike effective-mass approximation. The hydrogenic model, in conjunction with an assumption that the conduction band in CdF_2 is multivalleyed, is reasonably consistent with all the experimental results, and leads to a value for the polaron mass in CdF_2 of $0.23m_0$, where m_0 is the electron mass in vacuum.

I. INTRODUCTION

Cadmium fluoride is an interesting solid in at least two respects. First, it is a highly ionic wide-band-gap semiconductor,[1] and second, cyclotron resonance studies[2] suggest that it has an extremely large polaron mass. A number of studies of the optical[3-9] and electrical [10-12] properties of this material have been reported. The static and the high-frequency dielectric constants of CdF_2 are about 8 and 2.4, respectively.[7] From the transport studies, Khosla and Matz[10] deduced a polaron mass m_p of $0.9m_0$, and a bare conduction-band mass m^* of $0.45m_0$, where m_0 is the electron mass in vacuum. Eisenberger and co-workers[2] reported a polaron mass of $11m_0$, measured by cyclotron resonance and deduced from far-infrared absorption on the basis of a tight-binding model. Such a large discrepancy in the value of the effective mass determined by different methods clearly demands further experimentation and reinterpretation of the available results.

In the present work, we report the near-infrared absorption spectra of semiconducting CdF_2 doped with Y, Gd, Tm, and In. The experimental results are analyzed both in terms of the tight-binding approximation[2] and the hydrogenlike effective-mass approximation. The difficulties arising from the application of either method are discussed in some detail. A reasonably consistent picture of the experimental results is obtained on the basis of a hydrogenlike effective-mass theory if we assume that the conduction band in CdF_2 is multivalleyed.

II. EXPERIMENTAL PROCEDURES

The CdF_2 single crystals were grown in our laboratories. The technique for material preparation and crystal growth has been reported elsewhere.[3,4] Special precautions were taken for the purification of the material in order to minimize the compensating impurities, enabling us to use fairly low donor concentrations. Large dopant concentration causes line broadening, so that the structure in the absorption spectrum becomes unresolved. Typical dopant concentrations for our samples range from 5×10^{17} to 2.6×10^{18} cm^{-3}.

Polished samples, 0.01–1 mm thick, were used for absorption measurements. The samples were mounted in an Andonian variable-temperature cryostat. One atmosphere pressure of He or N_2 gas was kept in the sample chamber and the temperature probe was in contact with the metal mask where the sample was mounted. The absorption spectra were measured with a Perkin-Elmer model No. 210 grating monochromator in the wavelength range from 2–15 μ, and with a Cary 14R spectrometer in the range $\lambda = 0.2-3$ μ. The signal was detected by a thermocouple detector, a PbS detector, or a photomultiplier tube. The spectral resolution was better than 10 cm^{-1} throughout the infrared range. The absorption coefficient was calculated from the transmission data by assuming a constant surface-reflection loss. The reflectivity is small, and therefore corrections for multiple reflections were not necessary.

III. EXPERIMENTAL RESULTS

A typical infrared absorption spectrum of a Y-doped semiconducting CdF_2 sample at low temperature is shown in Fig. 1, along with the absorption spectrum of an undoped CdF_2 sample. At low phonon energies both samples show similar absorption. This absorption is attributed to the reststrahlen band and multiple-phonon-absorption processes. For photon energies higher than 0.1 eV, the undoped sample is practically transparent up to a photon energy of about 6 eV, where absorption due to band-to-band transitions begins. The semiconducting CdF_2 shows additional absorption in the infrared region. As shown in Fig. 1 for the Y-doped sample, there is a prominent absorption peak at 0.129 eV followed by a series of peaks and shoulders at higher photon energies spaced by approximately 0.040 eV. In addition, a weak absorption peak is observed at 0.105 eV and there are also two other peaks at 0.147 and 0.154 eV. The absorption peaks

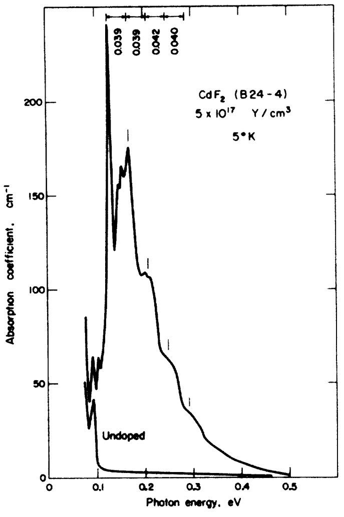

FIG. 1. Infrared absorption of a yttrium-doped semiconducting CdF_2 sample and of an undoped sample at 5 °K. The nominal dopant concentration is 5×10^{17} cm^{-3}.

and shoulders show a very regular repetition, with a spacing corresponding to approximately the zone-edge LO-phonon energy.[5] Figure 2 shows the infrared absorption of semiconducting CdF_2 at 80 °K with three different dopants: Y, Gd, and Tm. It is seen that the three absorption spectra are nearly identical in shape, the only difference being in their absolute magnitudes, which are dependent not only on the dopant concentrations but also on the degree of compensation.

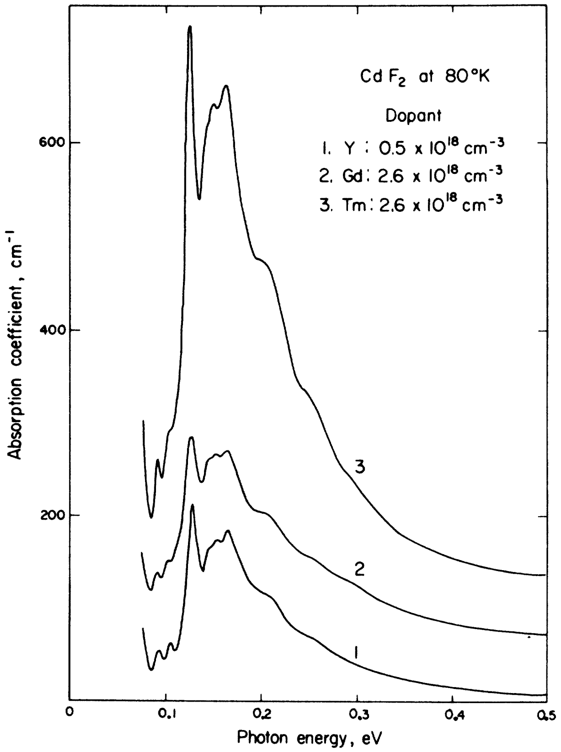

FIG. 2. Comparison of infrared absorption of semiconducting CdF_2 with different dopants: Y, Gd, and Tm. The curves are displaced in the vertical direction for clarity.

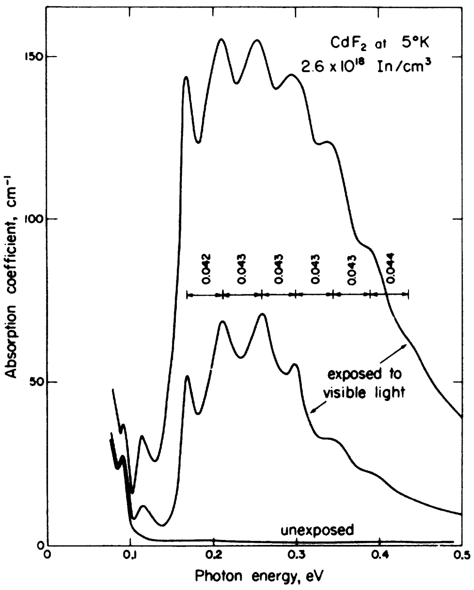

FIG. 3. Induced infrared absorption of a semiconducting CdF_2 : In sample. The two upper curves correspond to absorption induced by different amount of visible light. The lower curve shows that unexposed CdF_2 : In sample, like an undoped sample, has little near-infrared absorption.

For the In-doped sample, the absorption spectrum is quite different. When CdF_2 : In is cooled in the dark, the infrared absorption normally observed at room temperature becomes weaker and is not detectable below about 100 °K. The absorption spectrum is the same as that of an undoped sample, as shown by the curve marked "unexposed" in Fig. 3. Unlike the other dopants, In in CdF_2 shows an absorption band in the visible region whose magnitude increases with decreasing temperature and is proportional to the decrease of the infrared absorption band.[4] At temperatures lower than 30 °K, a stable infrared absorption band can be induced by exposing the sample to light absorbed in the visible band. The induced absorption starts to decay when the sample is raised to a higher temperature, and at $T \gtrsim 120$ °K one cannot induce any infrared absorption even when the sample is continuously exposed to a strong tungsten lamp. The induced absorption spectrum of CdF_2 : In at 5 °K is shown in Fig. 3. The mechanism for the changes of absorptions and for the light-induced absorption has been discussed elsewhere.[4] Figure 3 shows that the induced absorption in the In-doped sample is similar to the infrared absorption of the samples with other dopants. The most prominent peak is now at 0.165 eV, instead of 0.129 eV, as in the other cases. There is also the series of peaks and shoulders spaced at 0.042–0.044 eV. At the lower photon energy, the weak peak at 0.12 eV is probably related to the weak absorption peak at 0.105 eV in samples with other dopants. The peaks that would correspond to those at 0.147 and 0.154 eV are missing. They may be merged with the peak at 0.207 eV.

The temperature dependence of this infrared absorption in semiconducting CdF_2 has been studied. The data for a Y-doped sample at a few selected temperatures are shown in Fig. 4. With increasing temperature, the fine structure in the absorption spectrum becomes unresolved and a broad absorption band is observed at higher temperatures. The peak height of the sharp absorption line at 0.129 eV decreases rapidly with increasing sample temperature and at 200 °K it is barely resolved. However, its width does not broaden significantly with increasing temperature. On the other hand, the multiple-phonon line at 0.094 eV is still clearly resolved. Thus one cannot explain the temperature dependence on the basis of thermal broadening alone. It seems likely that there is an energy state located just above the ground state from which the 0.129-eV transition is initiated. Since the 0.129-eV line is not completely resolved, it is difficult to determine precisely the strength of this transition at different temperatures. Such a determination would allow one to calculate the energy of the upper ground state. A rough estimate places this upper state at a few hundredths of an eV above the ground state. This is in agreement with the energy 0.022 eV for ground-level splitting for semiconducting CdF_2, as determined by far-infrared absorption[2] and by Raman scattering.[5] These measurements will be discussed further in the following sections.

IV. DISCUSSION

A. Source of Infrared Absorption

The origin of the near-infrared bands in semiconducting CdF_2 was established in an earlier paper[3]; they are clearly due to transitions originating from the un-ionized donor states. Here we will further discuss the relation between the near- and the far-infrared absorption and the Raman scattering which are observed in CdF_2 only after the sample is converted to the semiconducting state. Eisenberger *et al.*[2] have reported the observation of a sharp absorption line at 178 cm^{-1} in CdF_2 doped with Gd, Yb, Nd, Tb, Y, and Lu. Eisenberger and Adlerstein[5] observed a Raman line at 180 cm^{-1} in samples doped with Lu, Gd, Yb, and Nd. The intensities of both the infrared and the Raman line were proportional to the number of donors. The shape of the spectrum was fairly independent of the particular dopant. At temperatures below 35 °K, both lines showed little temperature dependence. The far-infrared line could not be observed for $T > 35$ °K owing to the strong background absorption of phonons. The Raman line was measured for temperatures up to 77 °K. The linewidth showed little broadening, whereas its magnitude decreased significantly when the sample temperature was increased. Based on the similarity in energy and temperature dependence, the 178-cm^{-1} absorption line and the 180-cm^{-1} Raman line were interpreted as coming from the same transition. Two possible explanations were offered for the far-infrared line,[2] first, that it arises from transitions between the ground state of donor electrons and a slightly higher energy state, and second, that the phonons become infrared active through electron-phonon interaction, because the calculation[5] showed a sharp peak in the phonon density of states for CdF_2 at approximately 178 cm^{-1}. This high density of states, however, corresponds to phonons at the edge of Brillouin zone. Momentum cannot be conserved in a one-phonon Raman process involving zone-edge phonons. Therefore, it does not seem possible for the infrared line and the Raman line to arise from the same transition. On the other hand, the near-infrared

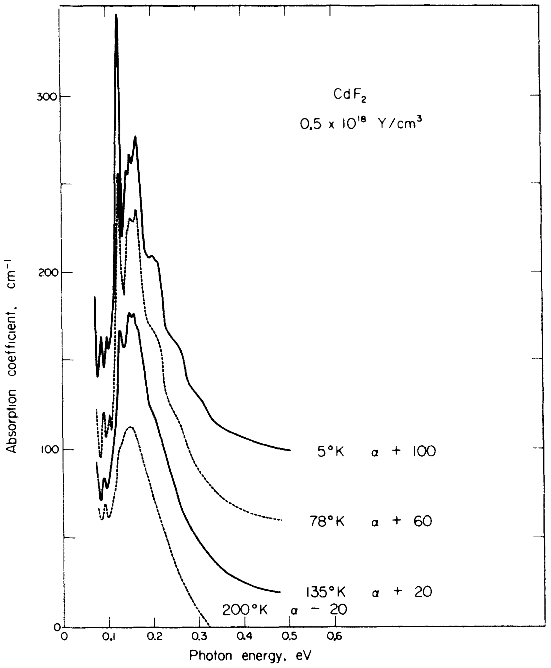

FIG. 4. Temperature dependence of a Y-doped semiconducting CdF_2 sample. The curves are displaced vertically.

absorption at 0.129 eV has the same characteristics as the far-infrared line and the Raman line. In particular, the temperature dependence of linewidth and intensity and the dependence on donor concentration are similar for all three transitions. The near-infrared spectrum is also independent of the particular dopant except for the case of In, which we will discuss separately in Sec. IV C. If we assume that there is a level located at approximately 0.02 eV above the ground state, the temperature dependence of all those sharp lines can be explained as discussed in the last section. Thus we conclude that the near- and far-infrared absorption and the 180-cm^{-1} Raman line are probably due to transitions from the same ground state, and donor electrons may be responsible for such transitions.

B. Tight-Binding Model

Eisenberger and co-workers[2,5] used a zero-order tight-binding model to interpret the 178-cm^{-1} absorption line. They proposed that because of the relatively large electron affinity of Cd^{2+}, both the conduction electrons and the electrons bound to the donors were localized on Cd^{2+} sites. In such a model, the electrons may hop between different Cd^{2+} sites. Such hopping may be characterized by a single tunneling integral parameter β, if one considers only hopping between nearest neighbors. If one takes account of polaron effects, the value β is somewhat lowered in comparison with the rigid-lattice approximation. The result shows that the width of the polaron conduction band is 16β and the polaron mass is $\hbar/2\beta a^2$, where $a = 5.45$ Å is the lattice constant for CdF_2. For the bound polarons, the energy is determined by the Coulomb energy between the electrons and the donor ions $E = -e^2/\epsilon r$, where ϵ is an effective dielectric constant and r is the distance between the donor and the Cd^{2+} site where the electron is localized. The energy level is further split because the electrons can hop between different Cd^{2+} sites corresponding to the same value of r. Thus the ground state of the bound polarons is split into four levels, equally spaced by an energy 2β. The symmetry of these levels in order of increasing energy are A_{1g}, T_{1u}, T_{2g}, and $E_g + T_{2u}$. The 178-cm^{-1} absorption line can be identified as A_{1g}-to-T_{1u} transition, which is the only type of infrared transition allowed by symmetry. With this identification, the polaron mass of CdF_2 will be $11.2m_0$, and the width of the polaron conduction band will be approximately 0.18 eV. The cyclotron resonance of CdF_2 measured by Eisenberger and co-workers[2] also gives a polaron mass of $11m_0$. Thus the high value of the effective mass has some experimental support. However, the experimental results of the Raman effect, near-infrared absorption, carrier concentration, mobility, and thermoelectric power cannot be interpreted on the basis of such a large polaron mass. A discussion of these difficulties is given in a later section.

We have already noted that Eisenberger and Adlerstein[5] interpreted the 180-cm^{-1} absorption line. This transition, in the tight-binding approximation, is an A_{1g}-to-T_{1u} transition, which is symmetry forbidden for the Raman transition. It was argued that through intertrap coupling, the symmetry of the states was partially destroyed by a perturbation without a significant shift in energies. If this suggestion is correct, one also expects to observe two stronger Raman lines at frequencies double and triple the 178-cm^{-1} infrared line, corresponding to the allowed Raman transitions from A_{1g} ground states to split-off T_{2g} and E_g levels, respectively, as predicted by the tight-binding calculation. Those two lines have not been reported. The tight-binding calculation also predicts some line spectrum in the near-infrared region corresponding to transitions to higher T_{1u} states. Using $2\beta = 178$ cm^{-1} and the absorption data given in Sec. III, we calculated that the second-lowest-energy-allowed infrared transition would correspond to the observed absorption line at 0.105 eV if $\epsilon = 18$, or 0.129 eV if $\epsilon = 14$. The static dielectric constant ranges from 7.78 at 80 °K to 8.49 at 300 °K and $\epsilon_\infty = 2.4$. If we assume, for the moment, that the large polaron mass is correct, then the electron-phonon coupling constant is very large ($\alpha \sim 6$). We expect the effective dielectric constant to be between ϵ_0 and ϵ_∞ and, in the limiting case, equal to ϵ_0. However, one needs a value twice the static dielectric constant to get approximate agreement between theory and experiment. With such a large effective dielectric constant, a bound polaron state will not exist in this approximation at distances greater than two lattice constants away from the donor ion. Furthermore, this approximation will not give different spectra for different impurities, and thus cannot explain the different spectral peaks observed in the case of the In-doped sample.

The cyclotron resonance was measured at $\omega/2\pi = 12.730$ GHz and the data were fit with an $\omega\tau = 0.9$–2.1. A mass of $11m_0$ implies a carrier mobility of 2000–4000 cm^2/V sec. At low temperature, the mobility may be limited by neutral impurity scattering, which can be expressed[13] by $m^* e^3/20N\epsilon\hbar^3$, where N is the number of neutral impurities. This gives an upper limit for mobility, in CdF_2 with 0.03 mole% Gd, of about 2500 cm^2/V sec, using $m^* = 11m_0$ and $\epsilon = \epsilon_0$. While this value of mobility fits the cyclotron resonance data, the same data also show that $\omega\tau$ changed from 2.1 to 0.9 in the temperature range 1 – 4.5 °K, whereas the concentration of neutral impurities remained constant. Therefore, some other mechanism is competing with neutral impurity scattering. In order to be consistent with the cyclotron resonance data, this mechanism should also make the relaxation time increase with increasing temperature in this temperature range. Such a temperature dependence has been observed in piezoelectric semiconductors.[14,15] However, CdF_2 cannot be piezoelectric, since it has inversion symmetry. A possible mechanism which would give such a temperature dependence of τ is that some very shallow traps exist, located at an energy about 1 meV or less below the conduction band. This explanation is consistent with the temperature dependence of the resistivity[16] and the photoconductivity[17] in CdF_2 at low temperature. However, if such traps exist so close to the conduction band, the measured cyclotron mass is likely to be strongly influenced by them.

At room temperature, the polaron bandwidth, as derived from the tight-binding approximation, is about $6kT$; the normal formulas for semiconductors are still applicable for either large or small polarons[18] and μ_d and μ_H are equal. In this temperature range, polar optical-phonon scattering becomes important. The calculated mobility for CdF_2 using a polaron mass $11m_0$ would be of the order of unity even if all scattering mechanisms other than the polar optical scattering were neglected, yet the measured Hall mobility[11] is as large as 16 cm^2/Vsec.

The density of states at the polaron band minimum is proportional to $m_p^{3/2}$. For a compensated semiconductor, the conventional relations are[19]

$$N(n+N_A)/(N_D-N_A-n)=\beta N_c e^{-E_a/kT} \ , \qquad (1)$$

where

$$N_c = 2(2\pi m_p kT/\hbar^2)^{3/2} \ , \quad n = r/R_H e \ .$$

We shall assume $r=1$, i.e., $\mu_H=\mu_d$, and we shall let β^{-1}, the degeneracy factor of the ground-state impurity level, be equal to 2. The activation energy E_a was determined to be around 0.1 eV.[11] If the value $m_p = 11m_0$ is used, then the extrinsic exhaustion range should start at about 100 °K. Neither the Hall measurement[11] nor the free-carrier absorption[3] shows any indication of exhaustion of extrinsic carriers for temperatures up to 470 °K. In addition, an analysis of the thermoelectric power data,[11] which depends essentially on the carrier concentration and the effective mass, contradicts the assumption of a large polaron mass.

In view of all these difficulties, we conclude that the tight-binding approximation does not give a satisfactory description of the optical and the transport properties of semiconducting CdF_2. A substantial modification or even a different model is needed.

C. Hydrogenic Model

From the transport measurement, Khosla and Matz[10] and Khosla[11] have calculated that the polaron mass m_p for CdF_2 should be $0.9m_0$ and the bare-band mass $m^* = 0.45m_0$. It is possible that the polaron mass of $11m_0$ measured by cyclotron resonance, measures the mass of electrons in a band other than the conduction band. Then the smaller effective mass from transport data suggests that the impurity states may actually be the hydrogenlike donor states. The hydrogenic model is plausible even if the electron affinity of the 3+ donor ions is somewhat higher than that of Cd^{2+} ions, whereas the tight-binding model requires that Cd^{2+} ions have higher electron affinity. Among the different dopants that have been studied, the values of electron affinity are known[20] only for Y^{3+} and In^{3+}; they are 20.5 and 28.03 eV, respectively, compared with 16.904 eV for Cd^{2+}. Judging from the values of the first and second ionization potentials, the electron affinities of the 3+ rare-earth ions may be close to that of Y^{3+} ions. From the electron affinity point of view, it is plausible that the donor states are hydrogenlike; this point of view also explains the tendency to form In^{2+} centers. Since the difference in electron affinity between In^{3+} and Cd^{2+} ions is three times larger than between Y^{3+} and Cd^{2+}, the donor-electron orbit would be smaller for In^{3+} than for Y^{3+} and the electron may essentially be in an atomiclike state of In.

There are two serious shortcomings in the simple hydrogenic model. With a polaron mass of $0.9m_0$, the effective Bohr radius will be less than one lattice constant, which of course makes the hydrogenic model questionable. Second, from the temperature dependence of the near-infrared absorption, the 178-cm^{-1} far-infrared line, and the 180-cm^{-1} Raman line, it is very clear that the ground state of the donor electrons is split by 0.022 eV, whereas for a simple hydrogenic model the ground state is a singlet except for spin degeneracy. To overcome those difficulties arising from a simple hydrogenic model, we suggest that the conduction band edge in CdF_2 is not located at the center of the Brillouin zone in the k space. In other words, the CdF_2 conduction band has more than one valley. If such a multivalley picture is correct, many of the apparent discrepancies in the experimental results can be resolved. The details are given in the next section.

D. Multivalley Band Model

Earlier work on the intrinsic absorption edge of CdF_2[8,9] has shown that the optical-absorption coefficient was as large as 2000 cm^{-1} at a photon energy of 6.5 eV. The band gap was then extrapolated to be 6.05 eV.[8] Later work on reflectance and on thin-film absorption of CdF_2[21] revealed that the first exciton peak was at 7.6 eV. Such relative energies for the gap and the exciton peak suggest that CdF_2 may have an indirect band gap at about 6 eV and a direct gap near 7.6 eV. Detailed temperature-dependence studies of the band-edge absorption have not been reported for CdF_2. For

CaF_2, measurement on cleaved plates[22] showed that the tail of the absorption edge changed its slope rapidly with decreasing temperature. Although the measurements on CaF_2 covered a limited range and did not permit an unambiguous conclusion, they showed the behavior expected for an indirect-band-gap material. Miyata and Tomiki[23] have measured the ultraviolet reflectance of SrF_2, BaF_2, and CaF_2. They found that the first exciton band of these fluorite-type crystals consisted of five fine lines, instead of the doublet, as observed in the other fluoride crystals with rocksalt structure. These additional lines were interpreted as arising from valence-band to conduction-band transitions near the X point in the Brillouin zone, whereas the doublet was due to transitions at the Γ point. That these fine lines are located in a region of approximately 0.2–0.3 eV strongly suggests that the conduction band near X point is lower in energy than at $k = 0$. The ultraviolet reflectance of CdF_2 is very similar to that of SrF_2, CaF_2, and BaF_2 except that the fine lines have not been resolved. This may be because pure CdF_2 cannot be easily cleaved. Polished and lapped surfaces were used for the reflectance measurement, and these may not show the structure. It is also possible that the lack of fine structure is due to the fact that the measurement was performed at room temperature and the fine structure was washed out by thermal broadening effects. Nevertheless, if one compares CdF_2 with other fluorite-structure crystals, it is reasonable to assume that the conduction band of CdF_2 has its minima away from $k = 0$. If these minima are at the X points, then there are three equivalent valleys in the conduction band. If these minima are located somewhere along (100) directions in the momentum space (Δ) but away from the Brillouin-zone edge (X), there will be six equivalent conduction-band valleys, as in the case of silicon.[24]

If the conduction-band minima consist of six equivalent valleys, the ground state of the donor electrons is then sixfold degenerate, excluding spin degeneracy. The donor ions, which enter the CdF_2 lattice substitutionally for Cd^{2+}, have O_h symmetry. It can be shown that the ground-state wave functions may be reduced into the irreducible representations A_{1g}, E_g, and T_{1u} of the O_h point group. The sixfold degeneracy is partially lifted by the valley-orbit interaction. The lower ground level is a singlet corresponding to the representation A_{1g}. The upper ground level corresponding to $E_g + T_{1u}$ has fivefold degeneracy. With this model, both the infrared transitions and the Raman transitions are allowed between the lower and the upper ground levels. We may now assign the 178-cm^{-1} absorption line and the 180-cm^{-1} Raman line to these transitions. The temperature dependence of infrared absorption can be understood in terms of this ground-state splitting. If, on the other hand, the conduction-band minima were at the X points, the threefold-degenerate ground states would correspond to the representations A_{1g} and E_g, and would be split by the valley-orbit interaction into a singlet and a doublet. In this case, the Raman transitions would be allowed between the two ground levels but the infrared transitions would not be allowed. We therefore think that the model of a conduction band in CdF_2 with six valleys is more appropriate.

Now let us examine the transport data in the context of this model. The polaron mass of $0.9m_0$, given by Khosla and Matz,[10] was calculated from Eq. (1) with the assumption of a simple band. If the band is multivalleyed, however, one should multiply the left-hand side of Eq. (1) by the number of equivalent minima; β will remain the same since the lowest ground state A_{1g} has twofold degeneracy when spin is included. With this modification, the polaron mass for CdF_2 comes out to be $0.27m_0$. To determine the mass from the thermoelectric-power data, Khosla and Matz found that, to be consistent with the mass determined from Hall-coefficient data, the scattering parameter had to have a negative value $\lesssim -\frac{1}{2}$ in the expression[25] for the thermoelectric power Q, where

$$Q = -86.2\left[\ln\left(\frac{4.7\times 10^{15}}{n}\right) + \frac{3}{2}\ln\left(\frac{m_p}{m_0}\right) + \ln N_v + \frac{5}{2} + S + \frac{3}{2}\ln T\right] \quad (\mu V/{}^\circ K). \tag{2}$$

In this expression, n is the number of free carriers, N_v the number of valleys in the conduction band, and S is a scattering parameter defined by a relaxation time $\tau \propto E^s$. From polar optical scattering, Langreth[26] had shown $S \gtrsim 0$, and for acoustic scattering,[25] $S = -\frac{1}{2}$. In the case of a multivalleyed band, the intervalley scattering will also contribute to the relaxation time, and S is a negative value depending on the anisotropy of the band minima.[25] All three scattering mechanisms are important in the temperature range where the thermoelectric power of CdF_2 was measured. As can be seen from Eq. (2), a positive value of S will give smaller calculated mass. In fact, the experimental result shows that the mass will be too small to be consistent with Hall data if S is chosen to be positive. With the multivalley model, a negative value of S becomes more plausible owing to the additional intervalley scattering mechanism. If we use a value $S = -\frac{1}{2}$, the polaron mass for CdF_2 will be $0.22m_0$ from the thermoelectric-power data. In order to obtain a bare conduction-band mass m^* from a polaron mass m_p, we use a formula developed by Langreth[26] which relates the two masses, the dielectric constants, and the phonon energy. Using $m_p = 0.23m_0$, a value of $m^* = 0.16m_0$ is calculated. The formula also gives a coupling constant α of about 1. 9.

In a recent paper,[3] we discussed the applicability of available continuum theories for isolated hydrogenlike centers in semiconducting CdF_2, and calculated the ionization energies and the effective Bohr radii predicted by such theories in both the adiabatic and the nonadiabatic limit. Those calculations were done assuming a polaron mass of $0.9m_0$ and a conduction-band mass of $0.46m_0$, and led to the conclusion that neither theory was adequate unless one made an assumption that transport data reflected the presence of clusters of donor impurities. With this assumption, a nonadiabatic continuum model seemed to be tenable. However, in view of the revised values of electron mass given in the preceding discussion, this conclusion must be reexamined.

Let us assume that the polaron mass is $0.23m_0$, the bare conduction-band mass $0.16m_0$, and reevaluate the ionization energies based on the continuum model. The simplest case views the electron as a polaron in a medium of static dielectric constant ϵ_0, with kinetic energy less than the lattice phonon energy. In this nonadiabatic limit, the ionization energy is simply $E_a = E_R m_p/\epsilon_0^2$ and the effective Bohr radius of the ground state $r_B = a_0\epsilon_0/m_p$, where $E_R = 13.6$ eV and $a_0 = 0.53$ Å. Using $m_p = 0.23m_0$ and $\epsilon_0 = 7.8$, one obtains $E_a = 0.05$ eV and $r_B = 18$ Å. A more rigorous theoretical treatment of the nonadiabatic limit by Buimistrov[27] yields similar values. The kinetic energy of the polaron in the ground state, $\hbar^2/2m_p r_B^2 \cong 0.05$ eV, is comparable to the LO-phonon energy, suggesting that the nonadiabatic limit is not really applicable. Further, the ionization energy of 0. 05 eV is not confirmed from either the transport or the optical results. The thermal ionization energy, determined from transport studies,[11] is about 0. 1 eV. The optical ionization energy may be estimated by assuming that the sharp absorption line at 0. 129 eV corresponds to the $1s$ - $2p$ transition of the hydrogenlike center. The 1s-to-continuum energy would then be approximately $\frac{4}{3}$ (0. 129) ≅ 0. 17 eV. The nonadiabatic situation, of course, implies no difference between optical and thermal energies.

TABLE I. Characteristic parameters in CdF_2.

ϵ_∞	2.40	Ref. 7
ϵ_0 (300 °K)	8.49	Ref. 6
(80 °K)	7.78	Ref. 6
$\hbar\omega_{\mathrm{LO},\Gamma}$ (300 °K)	47.1 meV	Ref. 7
(80 °K)	50.0 meV	Ref. 6
$\hbar\omega_{\mathrm{TO},\Gamma}$ (300 °K)	25.0 meV	Ref. 7
(80 °K)	27.8 meV	Ref. 6
$\hbar\omega_{\mathrm{R},\Gamma}$	39.9 meV	Ref. 5
Polaron mass m_p	$0.23m_0$	
Conduction-band mass m^*	$0.16m_0$	
Coupling constant α	1.9	

A continuum model in the adiabatic limit has been developed by Kubo[28] and by Simpson.[29] They view the electron as a particle with a conduction-band mass m^* moving in a screened impurity potential $-e/\epsilon^* r$, where ϵ^* is a self-consistently determined dielectric constant. Under these assumptions, the expressions for the ionization energies are

$$E_{\mathrm{opt}} = \frac{e^4 m^*}{2\hbar^2}\left(\frac{1}{\epsilon_0} + \frac{5}{16}C\right)\left(\frac{1}{\epsilon} + \frac{15}{16}C\right), \tag{3}$$

$$E_{\mathrm{th}} = \frac{e^4 m^*}{2\hbar^2}\left(\frac{1}{\epsilon_0} + \frac{5}{16}C\right)^2 \equiv \frac{e^4 m^*}{2\hbar^2}\,\frac{1}{\epsilon^{*2}}, \tag{4}$$

where $C = 1/\epsilon_\infty - 1/\epsilon_0$ and the effective Bohr radius $r_B = a_0\epsilon^*/m^*$. These expressions are independent of any assumption about the nature of the conduction band; they only measure the energy from the donor ground state to the conduction-band minimum.

Using a bare conduction-band mass of $0.16m_0$ in these equations, we can calculate values for E_{opt}, E_{th}, and r_B. The results are $E_{\mathrm{opt}} = 0.17$ eV, $E_{\mathrm{th}} = 0.1$ eV, and $r_B = 16$ Å. These calculated values for the energies seem to be in excellent agreement with the experimental values discussed in the preceding paragraphs. Any higher mass would not give agreement. Therefore, in the framework of this adiabatic continuum model, the assumption of a multivalleyed conduction band gives consistent results. The mass value of $0.16m_0$ also makes the observed room-temperature mobility of 16 cm^2/V sec reasonable. Table I lists the various parameters discussed here for CdF_2.

The kinetic energy in the ground state, in this approximation, is about 0. 09 eV. This kinetic energy is only about twice the LO-phonon energy, which perhaps means that the adiabatic approximation is too extreme. The Bohr orbit of 16 Å also suggests that this simple picture may need some modification.

To fit the near-infrared absorption data to this model, we need to know the anisotropy of the effective mass. The mass we have determined is an average of the longitudinal and the transverse mass. We do not have information on the ratio of the two masses. We shall tentatively assign the energies to the donor levels, on the basis of the absorption spectra of the Y-, Gd-, and Tm-doped samples, as shown schematically in Fig. 5. In the case of silicon and germanium, the absorption for $1s$ - $np_\pm$ transitions was determined to be more intense than that of the corresponding $1s$ - np_0 transitions, both experimentally[30,31] and theoretically.[24] A similar situation may be expected to hold for CdF_2. It is on this basis and on the basis of the relative energies that the assignment is made. We further assign the higher-energy lines, repeated by about every 0.04 eV, as the $1s(A_{1g})$ - $2p_{\pm}$ transitions with the emission of phonons.

V. CONCLUSIONS

We have discussed the donor states of semiconducting CdF_2 in terms of a tight-binding approximation and of a hydrogenlike effective-mass approximation. The tight-binding model explains the large cyclotron mass $\sim 11m_0$, but is inconsistent with all the other optical and transport properties. The hydrogenic model, on the other hand, is consistent with the optical and transport data, but requires a polaron mass of $0.23m_0$. If the measured cyclotron mass of $11m_0$ is indeed the conduction-band polaron mass, then the tight-binding model would be a physically correct picture, and the interpretation of the optical and transport data would have to await new theoretical understanding. In that case, CdF_2 is clearly an interesting material for checking the results of any intermediate-coupling polaron theory. On the other hand, if the cyclotron mass of $11m_0$ turns out to represent the mass of carriers in some other band, then the hydrogenic approximation is a suitable framework within which to describe donor states in CdF_2. We do not have any direct evidence for a multivalleyed conduction band, but the internal agreement of the data shows that this picture is plausible. The form of the conduction band can be probed by measurements of piezoresistance or magnetoresistance. Clearly such measurements would be desirable. Further investigation of the cyclotron resonance is essential. Until the results of such studies are available, any model of the donor states in CdF_2 is subject to some uncertainty.

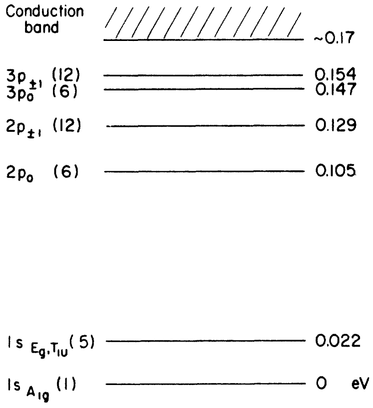

FIG. 5. Schematic diagram of the donor-electron energy levels in CdF_2 with a multivalley, hydrogenlike effective-mass approximation.

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