[1] N. J. Harrick, Phys. Rev. 125, 1165 (1962).

[2] G. Samoggia, A. Nucciotti, and G. Chiarotti, Phys. Rev. 144, 749 (1966); G. Chiarotti, G. Del Signore, A. Frova, and G. Samoggia, Nuovo Cimento 26, 403 (1962).

[3] G. Chiarotti, G. Del Signore, and S. Nannarone, Phys. Rev. Letters 21, 1170 (1968).

[4] F. C. Allen and G. W. Gobeli, Surface Sci. 2, 402 (1964); Phys. Rev. 127, 150 (1962).

[5] D. R. Palmer, S. R. Morrison, and C. E. Dauenbaugh, J. Phys. Chem. Solids 14, 27 (1960); Phys. Rev. 129, 608 (1963).

[6] D. E. Aspnes and P. Handler, Surface Sci. 4, 353 (1960).

[7] For review of the subject see D. R. Frankl, *Electrical Properties of Semiconductor Surface* (Pergamon, New York, 1967); and A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland, Amsterdam, 1965).

[8] W. Mönch, Phys. Status Solidi 40, 257 (1970).

[9] M. Henzler, Surface Sci. 24, 209 (1971).

[10] V. Heine, Surface Sci. 2, 1 (1964); and M. Henzler, *ibid.* 25, 650 (1971).

[11] F. Garcia-Moliner and J. Rubio, J. Phys. Chem. 2, 1789 (1969).

[12] V. Bortolani, C. Calandra, and A. Sghedoni, Phys. Letters 33A, 193 (1971).

[13] The change of transmitted light during oxidation goes on until an exposure of 10^{-4} Torr min is reached. At the initial pressure of 10^{-10} Torr, no change of transmission is detected in several hours.

[14] I. Bartoš, Phys. Status Solidi 33, 779 (1969).

[15] In order to determine this contribution, the position of the Fermi level at the surface has been evaluated by following the change of surface conductance as the surface is exposed to dry and wet oxygen, until the minimum of conductivity is reached. From the measured value $\Delta\sigma = 170$ μmho per square, a value of $u_s = -11.5kT/e$ is obtained, using $u_B = 0$ and taking for the surface mobilities the experimental values of R. Missman and P. Handler [in *Proceedings of the International Conference on the Physics of Semiconductors, Rochester*, 1958 (Pergamon, New York, 1959)]. The concentration of free holes in the space-charge region thus obtained is 3×10^{12} cm^{-2} for the clean surface, and at least 2 orders of magnitude smaller for the oxidized one. By taking the optical data of W. Kaiser, R. J. Collins, and H. Y. Fan [Phys. Rev. 91, 1380 (1953)] for hole intraband absorption the contribution of free holes to the $\ln(I_0/I)_{\text{clean}}$ of Fig. 2 turns out to be on the order of 4×10^{-3}. [For more details see S. Nannarone and R. Pastore, Nota Interna No. 249 (Istituto di Fisica "G. Marconi," Università di Roma, 1969) (unpublished).]

[16] F. Bassani, in *Proceedings of the International School of Physics Enrico Fermi*, *Course* 34 (Academic, New York, 1966), p. 33.

[17] In the case of Ge, however, hypothesis (iii) can be ruled out from the measured position of the Fermi level at the surface (see Ref. 15).

[18] F. Yndurain (private communication).

[19] See, for example, J. Koutecky and M. Tomasek, Phys. Rev. 120, 1212 (1960); and J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. 34, 2298 (1963).

[20] H. Y. Fan, W. Spitzer, and F. J. Collins, Phys. Rev. 101, 566 (1956); and W. Spitzer and H. Y. Fan, *ibid.* 108, 268 (1957).

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Microwave Magnetoabsorption at Low Temperatures in Semiconducting CdF_2 †*

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Current models for the observed properties of semiconducting CdF_2 differ in their predictions of polaron mass m_p. A peak with magnetic field in the low-temperature microwave absorption of semiconducting CdF_2 has been interpreted in the literature as cyclotron resonance of polarons with $m_p \sim 11 m_e$. If such a heavy mass were appropriate, semiconducting CdF_2 would be unlike any of the conventional semiconductors. The presently reported measurements of microwave absorption as a function of applied magnetic field, impurity concentration, frequency, microwave polarization, and temperature enable us to rule out cyclotron resonance as a possible explanation for the absorption peak. Instead, the effect can be qualitatively interpreted by a model based on covalent bonding between donor impurities.

I. INTRODUCTION

Pure CdF_2 is a colorless insulator with a band gap of 6 eV. Doped with trivalent rare-earth impurities (Re^{+3}), it can be made semiconducting (SC CdF_2) by chemical treatment. At low temperatures, the conduction electrons are localized about the Re^{+3} ions substituted for divalent Cd ions. Above 77 °K, a significant fraction of these donor traps are ionized.

SC CdF_2 has been studied extensively as a physical system exhibiting strong electron-lattice coupling.[1-7] In this paper, we report the results of a study of microwave absorption as a function of applied magnetic field in SC CdF_2 for temperatures between 1.1 and 2.1 °K at $\nu \sim 13$ GHz. The study was undertaken in an effort to resolve the discrepancy concerning the electron effective mass in this system. On the basis of measurements of thermoelectric power and Hall effect, Khosla and Matz[7] have reported a polaron mass $m_p \sim 0.9m_e$ while a value $m_p \sim 11m_e$ has been proposed in order to interpret the observed low-temperature microwave magnetoabsorption in SC CdF_2[1] as a cyclotron-resonance signal.

We have extended the measurements reported in Ref. 1 and are able to rule out cyclotron resonance as an explanation. Instead, the results may be qualitatively explained by a model based on covalent bonding between impurities. We conclude that the low-temperature microwave magnetoabsorption mechanisms in SC CdF_2 are similar to those in more classical semiconductors when they too are doped so as to be in the impurity-banding regime.

Although polaron effects should be manifest in the transport and optical properties of the SC CdF_2 system at low temperatures, they are masked by effects related to the interaction between the electrons and the rare-earth impurities. Transport properties such as resistivity and Hall effect[2] indicate the onset of effects characteristic of impurity banding below 77 °K. Further evidence of donor interactions is contained in EPR studies,[4] far-infrared absorption measurements,[1] and recent near-infrared measurements[4,5] made using highly purified low-concentration samples.[6]

Although it is clear that an analysis of the low-temperature properties of SC CdF_2 must include multitrap effects, such as the hopping of electrons from donor to donor or the coupling by trapped electrons of two or more donors, details of these effects are not well understood.

Microwave frequency absorption in samples with high donor concentration ($c = 0.1\%$ molar) exhibits a strong peak with increasing magnetic field, and was first observed by Eisenberger *et al.*[1] and interpreted by them as cyclotron resonance of a very heavy polaron ($m^* = 11m_e$). The peak shifts to lower fields with decreasing concentration and is absent for $c = 0.01\%$. The peak is washed out for $T \gtrsim 2.2$ °K. That no similar peak is observed in the dc magnetoconductivity in this temperature range suggests that the absorption of microwave energy results primarily through induced transitions between close-lying states of the impurity system ($\hbar\omega \sim 0.45$ cm^{-1}). At low temperatures such "direct" processes can be expected to dominate the microwave conductivity when compared to those conduction processes ("indirect") requiring phonon assistance.[8,9] Indirect processes account for the low-temperature dc magnetoconductivity.

Direct absorption by coupled donors in Ge and Si has been studied experimentally[8-10] and theoretically[11,12] from the microwave range through the far infrared in the absence of a magnetic field. The absorption is found to reach a concentration-dependent maximum in the far infrared. The maximum shifts to higher energy as impurity concentration is increased. Kobayashi and Tanaka[13] have investigated direct microwave absorption in heavily doped *p*-type Si as a function of magnetic field up to about 9 kOe. Their results indicate a strong increase in absorption with increasing magnetic field. There is also a suggestion of saturation at their highest fields. Both the magnitude and temperature dependence of the effect they observe are similar to the results in SC CdF_2. Although they offer no explanation for the effect, it appears as though the effect of the magnetic field is to increase the microwave frequency absorption at the expense of high-energy infrared absorptions.

SC CdF_2 exhibits a broad absorption in the far infrared[1] which probably has a significant direct absorption component. In analogy with the above-mentioned effects, an applied magnetic field might be expected to shift this component to lower energy.

In Sec. II, we present our experimental results and show that the cyclotron resonance model is incapable of explaining the data on CdF_2. In Sec. III, we propose a simple model for the microwave conductivity based on direct absorption by coupled donors. Although the model is highly conjectural, it accounts qualitatively for the major features of the data in terms of only one adjustable parameter and a Bohr radius inferred fron near-infrared absorption measurements.

II. EXPERIMENT

The microwave absorption measurements were made with a homodyne K_u-band spectrometer[14] employing balanced-bolometer detection. For studies with linear microwave polarization, a rectangular TE_{101} cavity was used. The small disk-shaped sample of SC CdF_2 about 0.025 in. thick was positioned inside the cavity flush against a broad wall. A small hole in this wall allowed light, passing down a light pipe, to strike the sample. The cavity was fitted with a coupler and a quartz tuning slug to allow matching and frequency tuning. The cavity and sample were immersed in pumped liquid helium.

With and without light incident on the sample, for samples of the size needed to give reasonable signal-to-noise ratios, the cavity exhibited a strong magnetic field–dependent dispersion. The dispersion was greatest for high concentration samples and not present in insulating CdF_2. It was therefore necessary to take data point by point, retuning the cavity to resonance at each value of the magnetic field. Detection of the absorption was facilitated by focusing several microwatts of light from an incandescent source onto the sample. The light was chopped at 980 Hz providing modulation of the absorption mechanism at this frequency.

Under the above conditions, the change in the cavity reflection coefficient at cavity resonance and

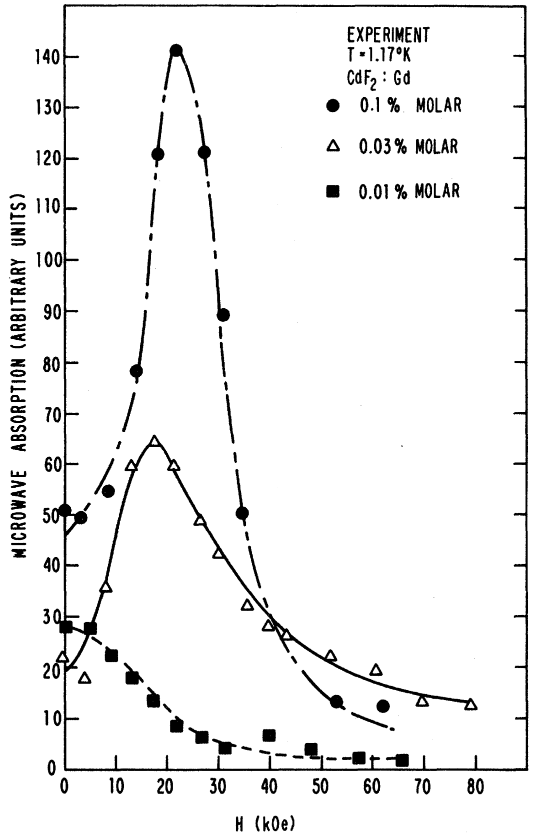

FIG. 1. Microwave absorption vs applied magnetic field at various donor concentrations. $\omega/2\pi = 16.6$ GHz.

critical coupling is[15]

$$\Delta\Gamma = (Q_0\eta_e/2\omega\epsilon^2)\Delta\sigma + jQ_0\delta,$$

where Q_0 is the cavity quality factor, ϵ is the sample dielectric constant, η_e is the filling factor, and $\Delta\sigma$ is the difference between the light-on and light-off conductivity. δ is the fractional difference between the klystron and cavity frequencies. In general, δ will have a component at the light-chopping frequency due to modulation of sample dispersion. This requires that at each value of magnetic field, the spectrometer be set to discriminate against the quadrature component of $\Delta\Gamma$. Once this is done, we may use lock-in phase-sensitive detection to determine $\Delta\sigma$.

Typical results for $\Delta\sigma(H)$ are shown in Fig. 1. The impurity concentrations quoted are those added to the melt. The 0.1% sample shows a pronounced peak at about 23 kOe, shifting to lower fields and decreasing in height with decreasing concentration; it is absent in the 0.01% sample.

There is a very pronounced temperature dependence in the 0.1% case (Fig. 2). The peak height decreases and moves to higher magnetic fields as the temperature is raised. Above 2.2 °K, the signal is below the noise level (Fig. 3). In the 0.01% case, the signal decreases in intensity and shows a weaker magnetic field dependence as T increases (Fig. 4).

In their preliminary work, Eisenberger *et al.*[1] interpreted the peak as cyclotron resonance of photocarriers. Their measurements were made at 12.7 GHz. A cyclotron resonance peak would occur at a magnetic field obeying $\omega = eH/m^*c$, where m^* is the effective mass of the carrier. We have extended the measurements to 16.6 GHz where one expects, for cyclotron resonance, a shift in peak field of about 35%. Instead, we observe the absorption to be independent of frequency to within experimental error.

As a further check of the cyclotron resonance hypothesis, we have studied the absorption for circularly polarized microwaves. Because electrons and holes rotate in opposite senses in a magnetic field, any particular carrier can absorb energy from a circularly polarized microwave field only if that field is rotating in the correct sense. Thus, if the polarization is held fixed and the direction of the magnetic field is reversed, true cyclotron resonance should show field asymmetry. A circular

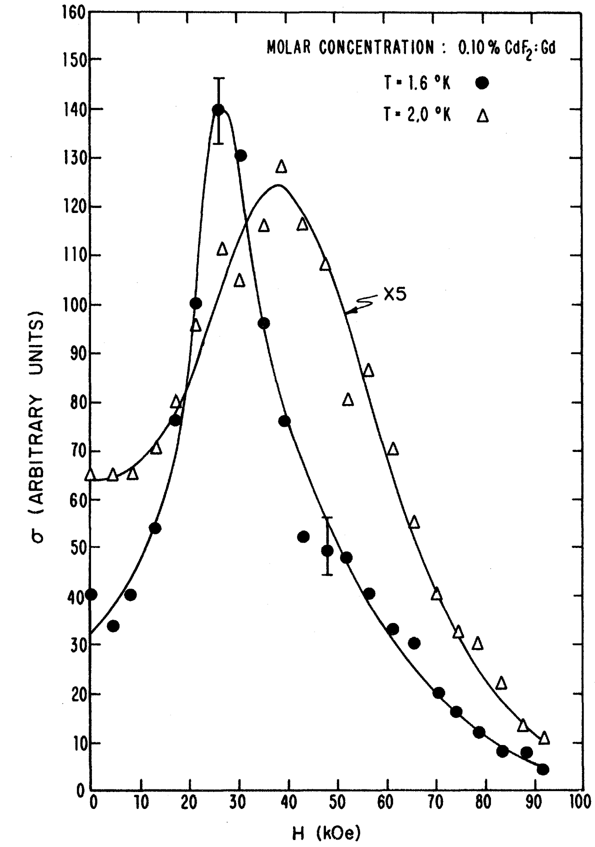

FIG. 2. Microwave magnetoabsorption for 0.1% Gd : CdF_2 at different temperatures. $\omega/2\pi = 13$ GHz.

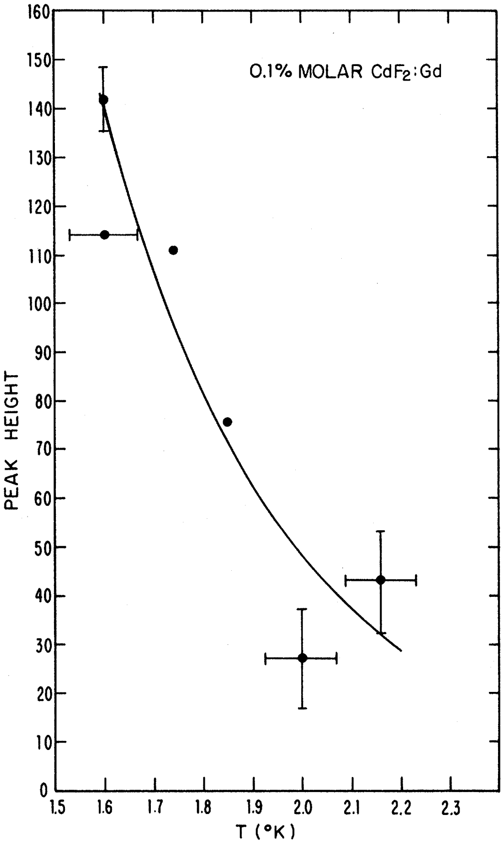

FIG. 3. Temperature dependence of peak height for 0.1% donor concentration.

TE_{111} cavity operating at 13.3 GHz and a turnstile junction circular polarizer[16] have been employed in a search for this asymmetry. A disk-shaped sample is placed axially in the cavity and light enters through a hole in the bottom. Figure 5 shows the electron and hole resonance[17] clearly resolved by the system in oriented intrinsic Ge. The CdF_2 peak, on the other hand, is entirely symmetric.

The evidence indicates that cyclotron resonance is not involved in the phenomenon and that we are observing, instead, impurity-related effects.

III. THEORY

To explain the experimental results, we investigate in detail the microwave absorption mechanism by impurity pairs.[8,9] When CdF_2 is doped with rare-earth ions, the ions in their trivalent state enter substitutionally for Cd^{+2}.[18] Over-all charge neutrality is maintained through compensation by interstitial F^- ions. When the crystal is baked in Cd vapor, the chemical reaction $Cd + 2F^- \rightarrow CdF_2 + 2e^-$ takes place at the surface with the liberated electrons entering the crystal. The F^- vacancies created in the reaction move from the surface into the bulk[19] and annihilate interstitial compensators. The rare-earth ions then act as donors with ionization energy $E_i \sim 0.2$ eV.[5]

Assuming one may approximate individual impurity sites by effective potentials, the depth of the potential well at any one impurity site is influenced by local electric fields due to nearby compensators. Thus, for two nearby impurity sites there will be a difference Δ between the depth of their respective potential wells. For many purposes one may describe the wave function for a single electron trapped at this pair of impurities as a linear combination of the wave functions appropriate to isolated impurities. There are two limiting cases for this: If $\Delta = 0$, the states of the pair will be of the bonding and antibonding type with corresponding energy separation $2W$, where W, the so-called "resonance energy," describes the interaction between sites. Such a pair is termed "homopolar" and has the properties of a covalent diatomic molecule. Transitions can be induced by an external field oscillating at frequency $\omega = 2W\hbar^{-1}$. If, however, $\Delta \gg 2W$, the ground state of the electron remains essentially localized on one site. The first excited state is localized about the second site while higher excited states are not localized to individual sites. The energy required to excite the electron from its ground state can be supplied by a phonon or a photon either of which must have energy $\gtrsim \Delta$. Phonon-assisted hopping is the dominant conduction mechanism in dc fields,[20] while in the ac case, the direct absorption by pairs will be shown to dominate.

The energy spacing of the bonding and antibonding states of the homopolar pair is a strong function of R/a [i.e., $W = W(R/a)$], where R is the donor sep-

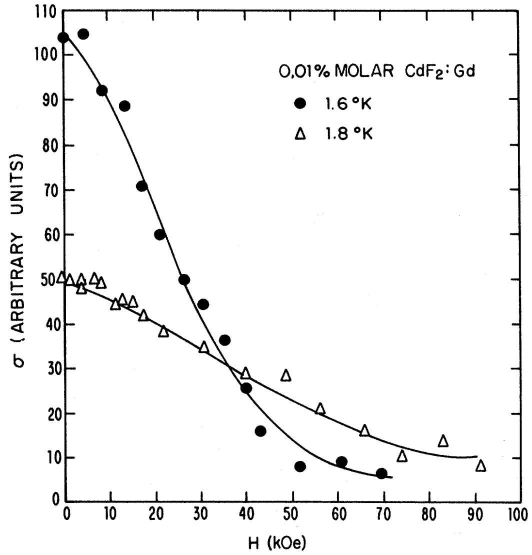

FIG. 4. Microwave magnetoabsorption for 0.01% CdF_2 : Gd at different temperatures. The scale is approximately 2.5 times the scale of Fig. 2. $\omega/2\pi = 13$ GHz.

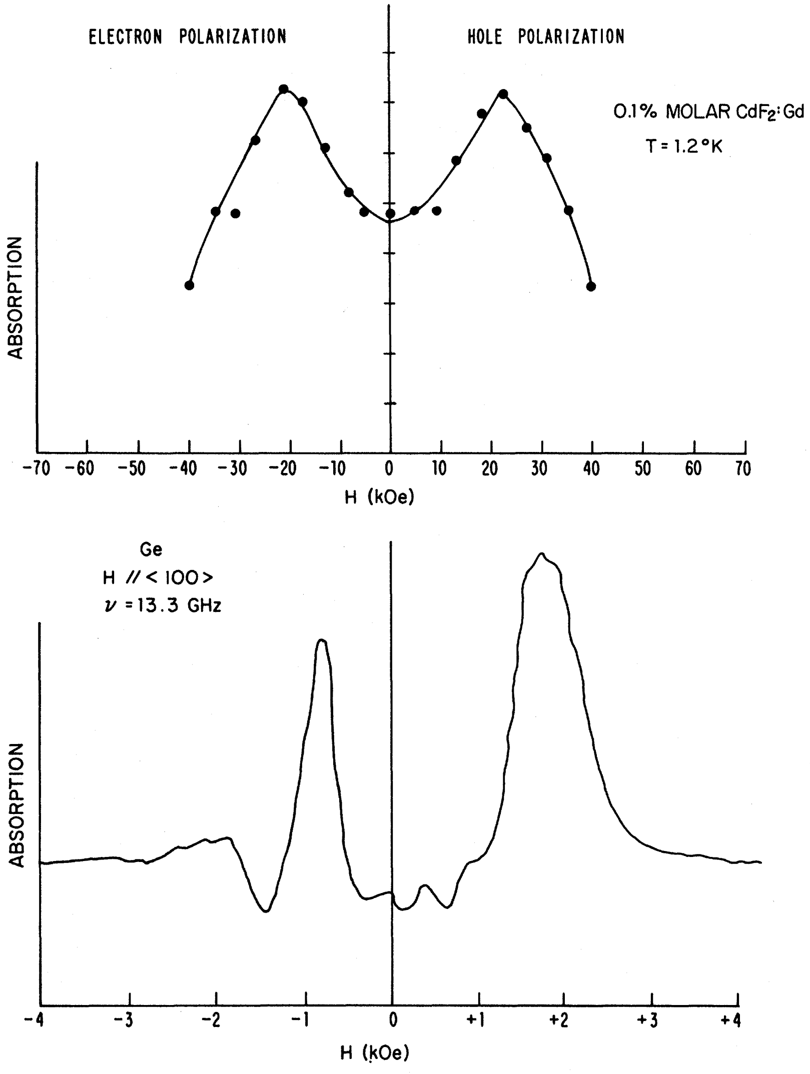

FIG. 5. Circularly polarized microwave absorption vs magnetic field for intrinsic Ge and SC CdF$_2$. The sense of polarization is held fixed and both polarities of magnetic field are swept. The asymmetry in the Ge case is due to the cyclotron resonance absorption of electrons and holes.

aration, and a is the ground-state Bohr radius of the electron. In the absence of an external static magnetic field, radiation at frequency ω will resonate with those homopolar pairs which satisfy $W=\frac{1}{2}\hbar\omega$.

The effect of applying a static magnetic field is to reduce the radius a and, thus, for a given homopolar pair of donors spaced R apart, to decrease W and bring new pairs into resonance. As H is varied, the resonance condition sweeps through the pair distribution function which peaks around some average pair separation $\overline{R}$. The effect is to produce a peak in absorption at a magnetic field whose value depends on the sample concentration.

In the effective-mass approximation the Hamiltonian describing an electron interacting with a donor pair is

$$H_0=\frac{p^2}{2m^*}-\frac{e^2}{\epsilon\,|\vec{r}-\vec{R}_A|}-\frac{e^2}{\epsilon\,|\vec{r}-\vec{R}_B|}+V_a(r), \qquad (1)$$

where ϵ is the dielectric constant, m^* is the effective mass chosen to give a donor ionization energy in reasonable agreement with experiment, and $\vec{R}_A$ and $\vec{R}_B$ are the position vectors of the two donor centers. $V_a(r)$ is the effective potential due to nearby compensators.

In analogy with the molecular-orbital method, we take

$$\begin{aligned}\psi_{\text{bonding}}&=A_1U_A(r)+B_1U_B(r),\\ \psi_{\text{antibond}}&=A_2U_A(r)+B_2U_B(r),\end{aligned} \qquad (2)$$

where $U_A(r)$ and $U_B(r)$ are hydrogenic wave functions of the ground state of the isolated trap

$$U_A=(\pi a^3)^{-1/2}\,e^{-|\vec{r}-\vec{R}_A|/a}\,. \qquad (3)$$

It follows[9] from Eqs. (1)–(3) that

$$A_1=\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{1/2},$$

$$B_1=\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{-1/2},$$

$$A_2=-\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[-\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{1/2},$$

$$B_2=\frac{1}{\sqrt{2}}\left(1+\frac{\Delta^2}{4W^2}\right)^{-1/4}\left[-\frac{\Delta}{2W}+\left(1+\frac{\Delta^2}{4W^2}\right)^{1/2}\right]^{-1/2}, \tag{4}$$

where

$$\Delta=\langle U_A|V_a|U_B\rangle-\langle U_B|V_a|U_B\rangle>0$$

and

$$\begin{aligned}W&=L-SJ+\langle U_A|V_a|U_B\rangle-S\langle U_A|V_a|U_B\rangle,\\ L&=-\langle U_A|(e^2/\epsilon|\vec{r}-\vec{R}_A|)|U_B\rangle,\\ J&=-\langle U_A|(e^2/\epsilon|\vec{r}-\vec{R}_B|)|U_B\rangle,\\ S&=\langle U_A|U_B\rangle.\end{aligned}$$

The energy difference between the bonding and antibonding state is

$$E=[\Delta^2+(2W)^2]^{1/2}. \tag{5}$$

A simplification results for the case $R \gg a$. Assuming a spherical conduction-band minimum for CdF_2, Moser *et al.*[5] have explained their near-infrared data by taking $\epsilon = 7.78$ and $m^* = 0.92$. This yields $a \sim 4.4$ Å. Eisenberger *et al.*[1] have described the ground-state orbit of the trapped electron as being localized on the shell of 12 Cd^{+2} ions which are nearest neighbors to the impurity, i.e., $a \sim 3.92$ Å. For either model, the majority of the donor pairs satisfy $R/a > 5$ even in our most concentrated samples. In this limit we have[21]

$$W\approx(2e^2/3\epsilon a)\,[R/a]\,e^{-R/a}. \tag{6}$$

Consider now two cases. (i) $2W \ll \Delta$ (polar pair): The wave functions are

$$\begin{aligned}\psi_{\text{bond}}&=U_A(r)+(W/\Delta)U_B(r),\\ \psi_{\text{anti}}&=U_B(r)-(W/\Delta)U_A(r),\end{aligned}$$

and the energy separation between the states is Δ. (ii) $2W \gg \Delta$ (homopolar pair): The wave functions are

$$\begin{aligned}\psi_{\text{bond}}&=(1/\sqrt{2})\,[U_A(r)+U_B(r)],\\ \psi_{\text{anti}}&=(1/\sqrt{2})\,[U_A(r)-U_B(r)],\end{aligned}$$

where the energy separation is $E = 2W$. At $\nu = 13$ GHz, the resonance condition for homopolar pairs can be satisfied with $R/a = 11.7$.

At low temperatures, for which the majority of conduction electrons are trapped at donor sites, absorption of microwave energy can result from two processes: (i) the diffusive conductivity due to thermally activated electrons hopping between traps whose energy difference is comparable to kT, and (ii) resonant absorption by impurity electron complexes.

For moderate concentrations of impurities, the dc conductivity is probably dominated by the thermally activated processes. At microwave frequencies, it is reasonable to expect resonant absorption to dominate, since thermally activated hopping has an associated transition time which can exhibit the exponential behavior characteristic of activated processes. Thus, as $T \to 0$, hopping may not contribute to high-frequency conductivity.

In order to examine this possibility further, we assume the microwave conductance (i.e., the imaginary part of the polarizability for a bound electron) is due to nearest-neighbor impurity pairs and can be approximated as

$$\sigma_p=\int_0^\infty dR\int_0^\infty d\Delta\,G_p(\omega)\,f_p(R,\Delta). \tag{7}$$

The response function for a two-level system $G_p(\omega)$ is taken as[22]

$$G_p(\omega)=\tfrac{1}{3}|P_{12}|^2\,\frac{\omega^2}{kT}\,\frac{1/\tau}{(\omega-\omega_{21})^2+1/\tau^2}\,\rho_1^{(0)}, \tag{8}$$

where[9]

$$|P_{12}|^2=|eRA_1A_2|^2\approx\begin{cases}\tfrac{1}{4}\,e^2R^2\,4W^2/\Delta^2 & \text{for } 2W\ll\Delta\\ \tfrac{1}{4}\,e^2R^2 & \text{for } 2W\gg\Delta\end{cases}$$

and

$$\hbar\omega_{21}=[\Delta^2+(2W)^2]^{1/2}.$$

In Eq. (8), $\rho_1^{(0)}$ is the population of the ground state, and τ is a characteristic relaxation time which will, in general, depend on Δ. The distribution function $f_p(R, \Delta)$ expresses the number of pairs with separation R and energy difference Δ. It is easily shown that if n is the total number of nearest-neighbor pairs, then

$$\int_0^\infty f_p(R,\Delta)\,d\Delta=(3nR^2/\overline{R}^3)\,e^{-(R/\overline{R})^3},$$

where $\overline{R}=(\frac{4}{3}\pi N)^{-1/3}$, and N is the impurity concentration.

The dependence of the function in the integral (7) on Δ is not known, but assuming that the majority of nearest-neighbor pairs are homopolar, Eq. (7) becomes

$$\sigma=C\,\frac{n\omega^2e^2\overline{R}}{8kT}\int_0^\infty\left(\frac{R}{\overline{R}}\right)^4 e^{-(R/\overline{R})^3}\,\frac{1/\tau}{(\omega-\omega_{21})^2+1/\tau^2}\,dR, \tag{9}$$

where $h\omega_{21} \approx 2W(R)$, and C is of order unity.

Tanaka *et al.*[9,11] have inferred a value of τ for the homopolar pair in Si on the basis of their measurement of saturation in direct absorption by such pairs. One expects saturation to occur[22] when $|P_{12}|^2(\tau^2/\hbar^2)F_0^2 \geq 10$, where F_0 is the microwave electric-field strength, and $|P_{12}|^2=\frac{1}{4}e^2R^2$. In their samples, $R \sim 130$ Å so that $\tau \sim 10^{-9}$ sec is needed to

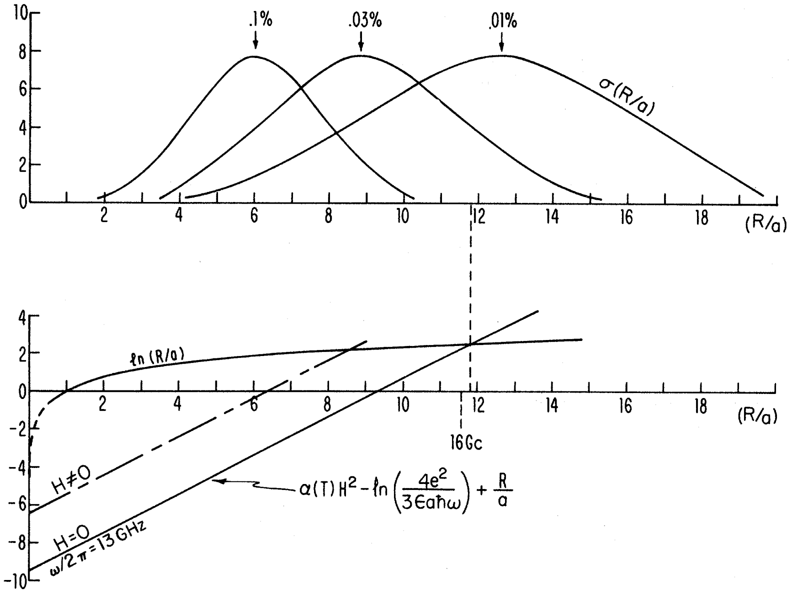

FIG. 6. Graphical solution to the resonance equation for homopolar pairs. Resonant pairs have the separation given by the intersection of the log curve and the straight line. $\sigma(R/a)$ for several concentrations are given for $a=3.92$ Å.

explain their data. For the case of CdF_2, no saturation effects were observed, but since $R \sim 45$ Å in this case, a value $\tau \sim 10^{-9}$ sec is not inconsistent with the data, and we assume $\omega\tau \gg 1$. In this approximation, the integral in Eq. (9) may be evaluated by substituting

$$\frac{1/\tau}{(\omega-\omega_{21})^2+1/\tau^2} \approx \frac{\pi a}{\omega}\, \delta(R-R^*),$$

where, in the absence of a magnetic field, R^* is determined from the condition

$$\hbar\omega = \hbar\omega_{21} \approx 2W(R^*/a). \qquad (10a)$$

Thus,

$$\sigma = C(n\pi e^2 a\bar{R}\omega/8kT)\,(R^*/\bar{R})^4\, e^{-(R^*/\bar{R})^3}. \qquad (10b)$$

Earlier, we suggested that the resonance energy $W(R)$ will vary with magnetic field. We will argue below that experimental results on more conventional semiconductors as well as those for SC CdF_2 suggest

$$W(R^*/a, H) = W(R^*/a)\, e^{-\alpha(T)H^2}. \qquad (11)$$

Equations (6), (10a), and (11) yield

$$\alpha(T)H^2 - \ln(4e^2/3\epsilon a\hbar\omega) + R^*/a = \ln(R^*/a),$$

from which we obtain a graphical solution for R^* as a function of H in terms of the adjustable parameter $\alpha(T)$. This is done in Fig. 6 where we have used $a \approx 4.0$ Å, as previously determined from near-infrared data, and $\epsilon \approx 8$. In Fig. 6, observe that as H increases, R^*/a decreases. Since only the free variable in the expression for σ [Eq. (10b)] is R^*, the conductivity will vary with H as a direct result of the R^* variation.

For a given temperature and concentration of impurities, we may choose a value for $\alpha(T)$ by fitting Eq. (10b) to the observed field dependence. Concentration enters Eq. (10b) through $\bar{R}$. Taking $\alpha(1.17\,°K) = 8.2 \times 10^{-9}\ G^{-2}$ as the value that causes the peak in Eq. (10) to occur at the measured field for a sample of 0.03% impurity concentration, Fig. 7 shows the predicted magnetic field dependence for samples of 0.01 and 0.1% concentration. Equation (10) correctly predicts that the 0.01% conductivity should peak at zero field and comes very close to predicting the actual peak position of the 0.1% sample. It also indicates that there should only be a very weak frequency dependence of the peak position. This in agreement with the experimental observation that, to within experimental error of about 15%, there is no shift with frequency in going from 13 to 16 GHz. The theory attributes the decreasing peak height with increasing temperature (Fig. 3) to thermal depopulation of the bonding state.

To establish the empirical basis for the field dependence of $W(R/a, H)$ suggested above, we have measured the low-temperature dc magnetoresistance of SC CdF_2. The results, shown in Fig. 8, indicate that the data can be fitted by an expression of the form

$$\sigma_{dc} = \sigma_0\, e^{-\alpha_0(T)H^2},$$

where α_0 decreases with temperature.

The same expression can describe the data on more conventional semiconductors in the impurity conduction regime.[23,24] Sadasiv[24] has studied this effect in Ge and found the magnitude of α_0 at a given temperature to depend only on the ratio R/a. His values of α_0 are the same order of magnitude as

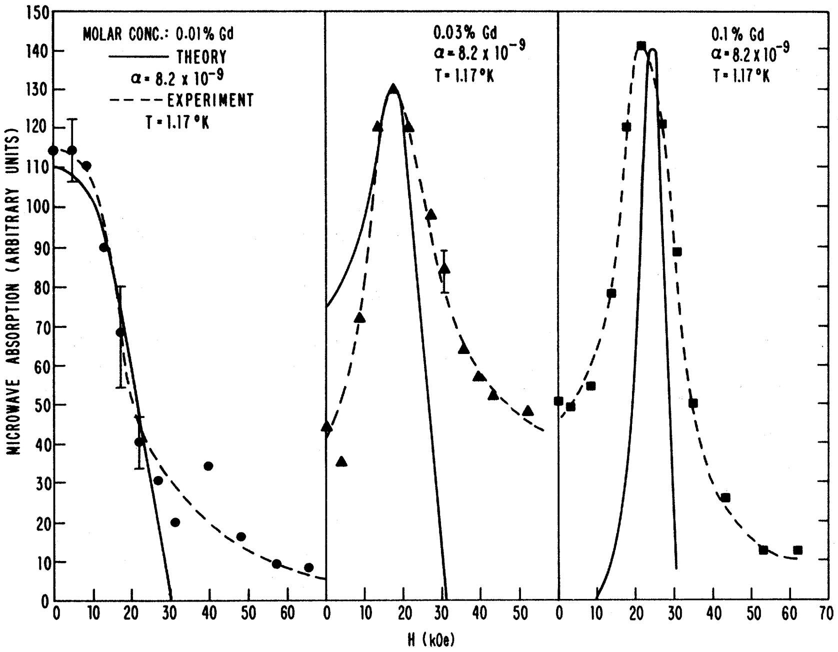

FIG. 7. Theoretical absorption vs magnetic field at various donor concentrations. $\omega/2\pi = 16.6$ GHz.

those we measure.

A relationship between the dc and microwave conductivities might be inferred by analyzing the thermally activated hopping mechanism that dominates in the dc regime. The average jump rate between sites is given by formulas proportional to W^2.[21]

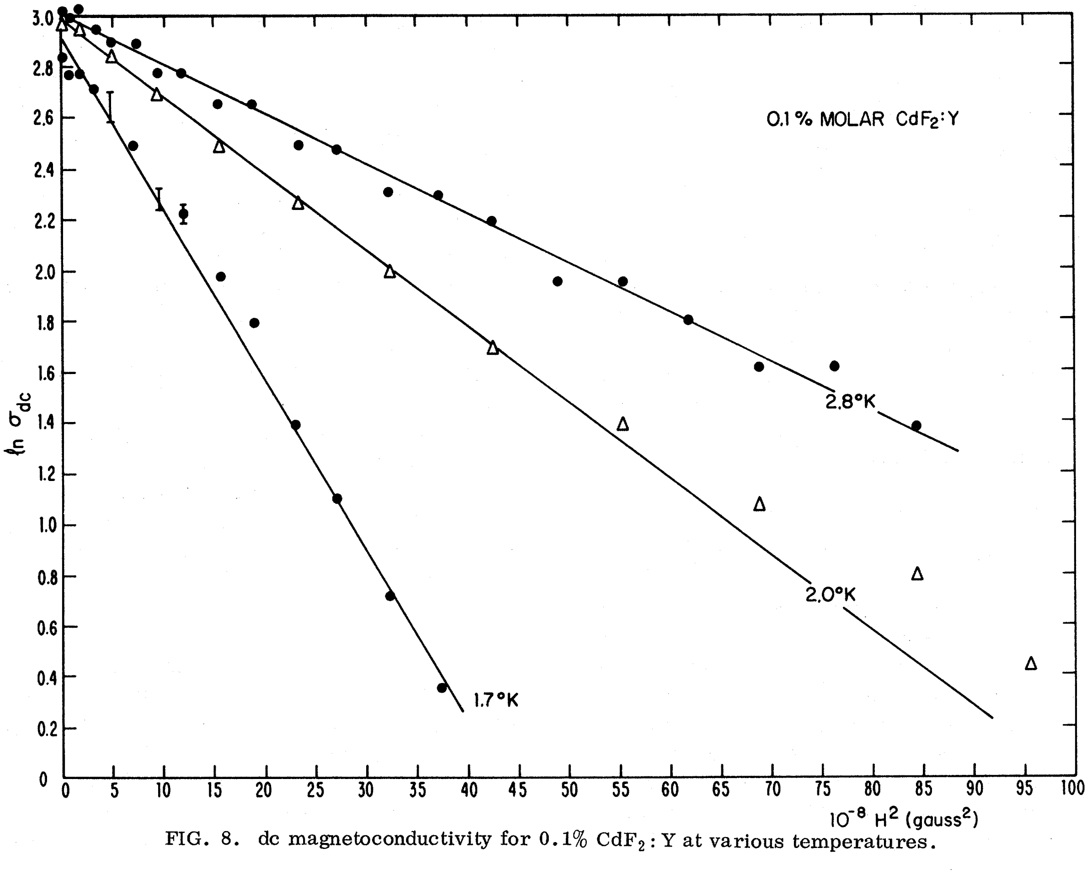

FIG. 8. dc magnetoconductivity for 0.1% $CdF_2:Y$ at various temperatures.

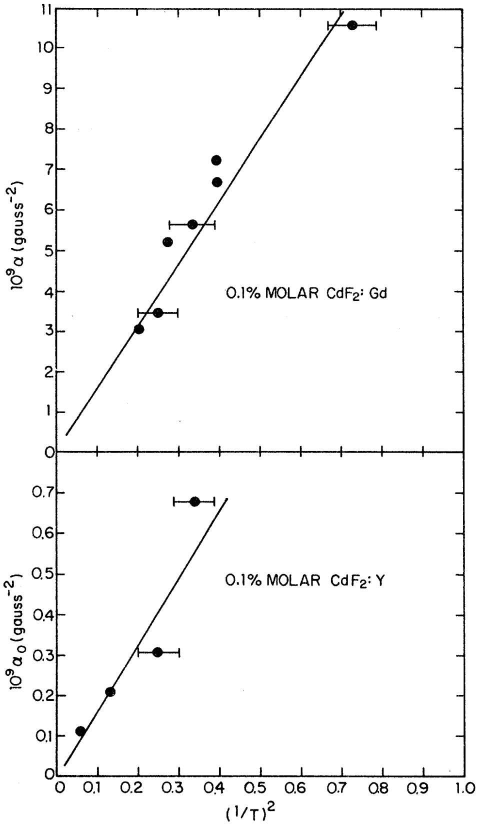

FIG. 9. Temperature dependence of α_0 and α.

According to the dc measurements, $\alpha_0 \sim 1/T^2$ (Fig. 9). Assuming that likewise $\alpha \sim 1/T^2$, we are able to qualitatively account for the peak positions throughout the entire temperature range.

IV. DISCUSSION

Though the model proposed in Sec. III can account for the experimental results qualitatively, it is clearly an oversimplification. The model does not, for example, consider bonding between impurities other than nearest neighbors. Such bonding would be expected to occur if a nearest-neighbor impurity is already compensated and would result in an excess of pairs with large values of R/a. In the experimental situation, this would be especially manifest in high-concentration samples as enhanced low-field absorption and would account for the difference between the low-field portions of the theoretical and experimental line shapes in the 0.1% case. For lower concentrations, the low-field predictions are somewhat better. In the high-field limit, again the greatest difference between the theoretical and experimental line shapes is found at high concentrations. This is probably due to the failure of the model at small R/a.

One must exercise caution in the quantitative application of the model since the results are very sensitive to the Bohr radius used. On the experimental side, the impurity concentration cannot be known to better than a factor of 2, and we might expect that the quantitative agreement between theory and experiment is somewhat fortuitous.

As mentioned, we are unable to account for the size or temperature dependence of either α_0 or α by applying available theories. This is exactly the same failure that has occurred in more conventional semiconductors. The conclusion we draw is that SC CdF_2 should not be considered significantly different from conventional semiconductors, and the difficulties encountered with those materials occur in SC CdF_2. In his model of an isolated hydrogenic impurity in a magnetic field, Miller[25] has shown that at low fields the Bohr radius becomes

$$a_H = a[1 - \tfrac{1}{2}(\epsilon a^3/m^* c^2) H^2]. \qquad (12)$$

Substitution of Eq. (12) into Eq. (6) yields an expression of the form of Eq. (11), where $\alpha \sim 10^{-16}$ G^{-2} and is temperature independent. A modification of Eq. (12) which could account for the temperature dependence results if one replaces H with M where M is an induced magnetization. Such a magnetization might result if excited states of the coupled system have nonvanishing off-diagonal matrix elements of magnetic dipole moment. In that case, one has[26]

$$M = (\chi_0/T) H.$$

In order for M to dominate H, however, χ_0 would have to be anomalously large.

It should be pointed out that polaron effects have been included in the model only to the extent that they influence m^* at $H = 0$. In general, we must specify the lattice coordinates in a description of the ground state of an impurity pair. This has not been done because the lattice oscillator states are separated by an energy $\hbar\omega_{LO} \sim 400$ $cm^{-1} \gg \hbar\omega_{21}$. The effect of the lattice may, however, be more important in the characteristics of an isolated trap in a magnetic field; induced shrinkage of a may be enhanced in a temperature-dependent manner.

In summary, measurements of microwave absorption in SC CdF_2 enable us to rule out cyclotron resonance as a possible explanation for the phenomenon observed. A simple semiphenomenological model based on covalent bonding between impurities can account qualitatively for the data.

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[1]P. Eisenberger, P. S. Pershan, and D. R. Bosomworth, Phys. Rev. 188, 1197 (1969).

[2]R. P. Khosla, Phys. Rev. 183, 695 (1969).

[3]P. Eisenberger and M. G. Adlerstein, Phys. Rev. B 1, 1787 (1970).

[4]P. Eisenberger and P. S. Pershan, Phys. Rev. 167, 292 (1968).

[5]F. Moser, D. Matz, and S. Lyu, Phys. Rev. 182, 808 (1969).

[6]T. H. Lee and F. Moser, Phys. Rev. B 3, 347 (1971).

[7]R. P. Khosla and D. Matz, Solid State Commun. 6, 859 (1968).

[8]S. Tanaka and H. Y. Fan, Phys. Rev. 132, 1516 (1963).

[9]S. Tanaka, M. Kobayashi, E. Hanamura, and K. Uchinokura, Phys. Rev. 134, A256 (1964).

[10]R. C. Milward and L. J. Neuringer, Phys. Rev. Letters 15, 664 (1965).

[11]K. Uchinokura and S. Tanaka, Phys. Rev. 153, 828 (1967).

[12]J. Blinowski and J. Mycielski, Phys. Rev. 140, 1024 (1965).

[13]M. Kobayaski and S. Tanaka, J. Phys. Soc. Japan 19, 1246 (1964).

[14]G. Feher, Bell System Tech. J. 36, 449 (1957).

[15]L. C. Kravitz, Harvard University Technical Report No. HP-9, 1963 (unpublished).

[16]M. A. Meyer and H. B. Goldberg, Trans. IRE MTT-3, 40 (1955).

[17]G. Dresselhaus, A. P. Kip, and C. Kittel, Phys. Rev. 100, 618 (1955).

[18]J. D. Kingsley and J. S. Prenner, J. Chem. Phys. 38, 667 (1963).

[19]Y. T. Tan and D. Kramp, J. Chem. Phys. 53, 3691 (1970).

[20]N. F. Mott and W. D. Twose, Advan. Phys. 10, 107 (1961).

[21]A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960).

[22]R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).

[23]R. J. Sladek and R. W. Keyes, Phys. Rev. 122, 437 (1961).

[24]G. Sadasiv, Phys. Rev. 128, 1131 (1962).

[25]A. Miller, Ph.D. thesis (Rutgers University, 1960) (unpublished).

[26]C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1966), p. 628.

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Excitons Bound to Ionized Impurities: Calculation of the Binding Energies of Exciton–Ionized-Donor Complexes*

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The method given by Pekeris for the helium atom and generalized recently by Frost for the three-particle system has been developed extensively to apply to complexes of excitons bound to ionized impurities in semiconductors. Haken's exciton potential is generalized for the complex, and the dielectric constant between the different particles is a function of the interparticle distances. This potential is different from that given by Schroder and Birman, where the ionic polarizability has been neglected. An elaborate general recursion relation is obtained. The application of this relation to the case of ionized donors shows the importance of the corrections introduced due to the polarizability of the potential between the particles. The calculations also show that the critical mass ratio below which the system is stable depends not only on the wave function, but also on the distances between the particles as well as on the fundamental constants: the optical and static dielectric constants, the effective masses of the electron and the hole, and the longitudinal vibrational frequency of the lattice. The results for exciton–ionized-donor complexes in CdS, CdTe, ZnSe, ZnTe, and ZnO give better agreement with experiment than those reported by the previous authors where the polarizabilility has been neglected. The calculations also confirm the existence of such a complex for 6H SiC. The exciton binding energies calculated for TlCl and TlBr are in better agreement with experiment than those given previously.

I. INTRODUCTION

In semiconductors, experimental evidence[1–34] has shown the existence of excitons bound to ionized donors and acceptors. Using the variational-principle technique, different authors have calculated the binding energies of these complexes.[35–42] These binding energies are a function of the variable $\sigma = m_e^* / m_h^*$, where m_e^* and m_h^* are, respectively, the effective masses of the electron and the hole. A critical value σ_c is usually found below which the system is stable. Unfortunately, the theoretical results in Refs. 35–42 do not agree with each other, and different values of σ_c have been reported. Thus, it is of interest to carry out some exact calculations for these complexes. The method given by Pekeris[43] for the helium atom and generalized recently by Frost[44–46] for the three-particle system