$$+\frac{H_{(c_2,k_f)(v_4,k_f)}H_{(v_4,k_f)(c_1,k_f)}H_{(c_1,k_f)(v_5,k_f)}}{(-2\hbar\omega)(E_{(c_1,k_f)(v_5,k_f)}-\hbar\omega)}+\frac{H_{(c_2,k_f)(v_5,k_f)}H_{(v_5,k_f)(c_1,k_f)}H_{(c_1,k_f)(v_5,k_f)}}{(-2\hbar\omega)(E_{(c_1,k_f)(v_5,k_f)}-\hbar\omega)}$$

$$+\frac{H_{(c_2,k_f)(v_6,k_f)}H_{(v_6,k_f)(c_1,k_f)}H_{(c_1,k_f)(v_5,k_f)}}{(-2\hbar\omega)(E_{(c_1,k_f)(v_5,k_f)}-\hbar\omega)}\,, \qquad \text{(A5)}$$

where $W_{c_1v_6}$ is the same as $W_{c_2v_5}$ with $c_1$, $c_2$, $v_6$, $v_5$, and $v_1$ replacing $c_2$, $c_1$, $v_5$, $v_6$, and $v_2$, respectively.

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# Study of Two-Electron Transitions of a Donor in CdSe

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Two-electron transitions, in which an exciton bound to a neutral donor decays leaving the donor in an excited state, were measured in CdSe. The donor was not identified. The transition energies from the $1s$ ground state to the $2s$, $2p$, $n=3$, and $n=4$ levels were measured. The transitions were identified by their Zeeman splittings. The spectrum was complicated because a number of the transitions originated from excited states of the three-particle bound-exciton complex. There was a one-to-one correspondence between this spectrum and the two-electron spectrum previously observed in CdS. From these measurements, we deduce that $E_D = 19.5 \pm 0.3$ meV and $m = (0.13 \pm 0.005)m_e$, where $E_D$ is the donor binding energy, $m$ is the measured electron mass, and $m_e$ is the free-electron mass.

## I. INTRODUCTION

An exciton bound to a neutral donor consists of a complex of three particles, two electrons and one hole, bound to the donor impurity. In most cases the exciton is bound by an energy that is small com-

pared to its internal binding energy. One can think of this complex as consisting of an exciton (one electron and the hole) bound to a donor with the other electron in the donor $1s$ state. The $I_2$ line[1] is a bound-exciton transition in which the electron and hole of the exciton recombine leaving the donor electron in the $1s$ state. Two-electron transitions are transitions in which the electron and hole of the exciton recombine and the donor electron is promoted to a higher state. The energy difference between the excited states and ground states of the donor is measured directly from energy separation of the two-electron transitions and the $I_2$ line.

Two-electron transitions were first observed for donors in GaP by Dean *et al.*[2] Soon after, Reynolds *et al.* observed two-electron transitions of donors in CdS[3] and CdSe,[4] and Reynolds and Collins observed two-electron transitions in ZnO.[5] Henry and Nassau[6] studied the two-electron transitions of the Cl donor in CdS in detail and found that a number of two-electron transitions arise from excited states of the three-particle bound-exciton complex. They were then able to properly identify the two-electron transition and accurately determine the donor binding energy. Nassau *et al.*[7] used the two-electron transitions to determine the binding energies of six substitutional donors in CdS. Recently, Malm and Haering[8] confirmed the existence of the excited states of the bound-exciton complex by luminescence excitation experiments in CdS. Merz *et al.*[9] have recently observed two-electron transitions in ZnSe and also find that the spectrum is quite complicated due to transitions originating from excited states of the bound-exciton complex. Finally, Rossi *et al.*[10] have observed two-electron transitions of donors in GaAs.

The earlier experiments of Reynolds *et al.*[4] on two-electron transitions in CdSe were inadequate because the authors were unaware of the complication arising from the excited states of the exciton-bound complex, and also because these authors did not identify the $I_2$ lines associated with these donor transitions. Consequently, they were unable to measure directly the donor transition energies. They did, however, observe Zeeman splittings of the two-electron transitions and thereby measured the electron mass to be $0.13m_e$, where $m_e$ is the free-electron mass. Using this mass and the static dielectric constant, they calculated in the effective-mass approximation that the donor binding energy ($E_D$) in CdSe is 18 meV.

In this paper we have studied in detail the two-electron transitions of an unidentified donor in CdSe. Two-electron transitions of several other donors were observed and appear to have very similar binding energies. We found as expected that transitions from excited states of the bound-exciton complex were quite important. In fact, there was a one-to-one correspondence between the two-electron transitions observed in CdSe and those found in CdS.[6] This made the interpretation of our data quite simple. These identifications rely heavily on the detailed analysis carried out in Ref. 6. We were able to measure transition energies from the $1s$ state to the $2s$, $2p$, $n=3$, and $n=4$ levels of the donors and find $E_D = 19.5 \pm 0.3$ meV and $m = (0.13 \pm 0.005)m_e$.

## II. EXPERIMENTAL

### A. Spectroscopy

The data were recorded photographically using a 2-m focal-length Bausch and Lomb spectrograph with a dispersion of 0.31 meV/mm. The luminescence was in the deep red where the response of the eye is dropping off rapidly with increasing wavelength, but the bound-exciton transition could be readily observed. The luminescence was excited using the 4880-Å line of an argon-ion laser. After much of the data were taken, it was observed that the lines became much sharper when unfocused laser light was used. The data in Fig. 1 were taken with unfocused laser light at an intensity of 150 mW. The two-electron transitions to the $n=3$ and $n=4$ levels and the sharp $I_2$ line in Fig. 1 could only be observed with unfocused light.

### B. Crystal Growth

Crystals were grown by sublimation in a flowing-gas double-tube quartz apparatus.[11] The source material used was Eagle Pitcher ultrhigh-purity-grade CdSe with extra Cd added. This was held at about 1070 °C and growth occurred at about 880 °C in a gradient of about 13 °C/cm. The carrier gas was forming gas (85% $N_2$, 15% $H_2$). By using a fast flow of gas, 0.7 liter/min, very rapid growth was obtained, the actual growth time in a preheated furnace being about 1 h.

## III. LUMINESCENCE SPECTRA

### A. Spectrum in Zero Magnetic Field

The luminescence shown in Fig. 1 was recorded using exposures of 1 sec for the $I_2$ line and up to 3 min to record the two-electron transitions as indicated in the figure. The $I_2$ line has a wavelength of 6805.13 Å which corresponds to an exciton binding energy of 4.33 meV. In the notation used in Fig. 1, $I_{20}$ is the ground state of the bound-exciton complex and $I_{2a}$, $I_{2b}$, $I_{2c}$ represent excited states of this three-particle bound-exciton complex. This is the same notation that was used by Henry and Nassau[6] to describe the luminescence in CdS. Two-electron transitions are observed to the $2s$, $2p_x$, $2p_y$, $2p_z$, and to the $n=3$ and $n=4$ levels. From the positions of the two-electron transitions, we deduce that $I_{2a} - I_{20} = 0.66 \pm 0.02$ meV, $I_{2b} - I_{20}$

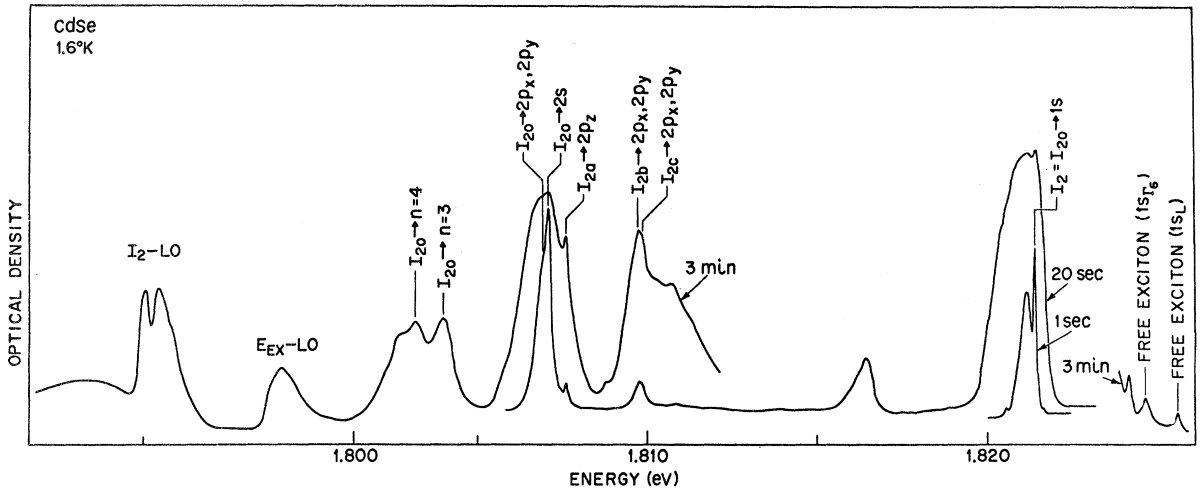


FIG. 1. Edge emission in CdSe. The levels $2s$, $2p_x$, $2p_y$, $2p_z$, $n=3$, and $n=4$ refer to donor states. The levels $I_{20}$, $I_{2a}$, $I_{2b}$, and $I_{2c}$ refer to the ground state and excited states of the bound-exciton complex.

$= 2.74 \pm 0.02$ meV, and $I_{2c} - I_{20} = 2.86 \pm 0.02$ meV.

The strongest two-electron transition is $I_{20} \rightarrow I_{2s}$, from which we determine that $E_{2s} - E_{1s} = 14.22 \pm 0.03$ meV. The $I_{20} \rightarrow 2p$ transition is observed as a shoulder on the $I_{20} \rightarrow 2s$ transition. The transition is observed more clearly when the $2p$ level is split away from the $2s$ level in a magnetic field. Extrapolation to zero magnetic field gives $E_{2p} - E_{1s} = 14.38 \pm 0.04$ meV. Measurement of the broader transition to the $n=3$ and $n=4$ levels gives $E_3 - E_{1s} = 17.41 \pm 0.05$ meV and $E_4 - E_{1s} = 18.26 \pm 0.05$ meV.

The narrow band on the low-energy side of the $I_2$ line is an acoustic-phonon replica similar to the acoustic-phonon replicas observed with bound excitons in CdS.[12] The longitudinal-optical-phonon (LO) replica of the $I_2$ line is also indicated in Fig. 1. The line is structured and broaden due to the electron-phonon coupling. This line shape will be discussed in detail in a separate publication.[13] Finally, the LO-phonon replica of the free exciton is shown in Fig. 1. This replica becomes much stronger if focused laser light is used to excite the luminescence. The second LO-phonon replica of the free exciton is also observed in these crystals. These replicas have the characteristic shape discussed by Segall and Mahan.[14]

### B. Zeeman Splittings

By fitting the Zeeman splittings of the two-electron transitions we confirm our identification of the transitions in zero field. Zeeman splittings are shown in Fig. 2 for $H \parallel c$ axis and in Fig. 3 for $H \perp c$ axis. The $c$ axis is along $z$ in our notation. The analysis of these rather complicated Zeeman splittings was greatly aided by the fact that there was a one-to-one correspondence between these transitions and the transitions previously studied by Henry and Nassau in CdS.[6] In both cases, $I_{2a}$ decays to $2p_z$, $I_{2b}$ and $I_{2c}$ decay to the $2p_x$ and $2p_y$ states, and $I_{20}$ decays to the $2s$. As pointed out by Henry and Nassau,[6] the $I_{20} \rightarrow 2p_x$, $2p_y$, and $2p_z$ transitions are forbidden and occur only because of the finite wave vector of the photon. The direction of the emitted light determines which $I_{20} \rightarrow 2p$ transitions can be observed. For the geometries we used, the $I_{20} \rightarrow 2p_z$ transition is unobservable for $H \parallel z$ (Fig. 2) and the $I_{20} \rightarrow 2p_x$ is unobservable for $H \parallel x$ (Fig. 3). This is described more fully in Ref. 6.

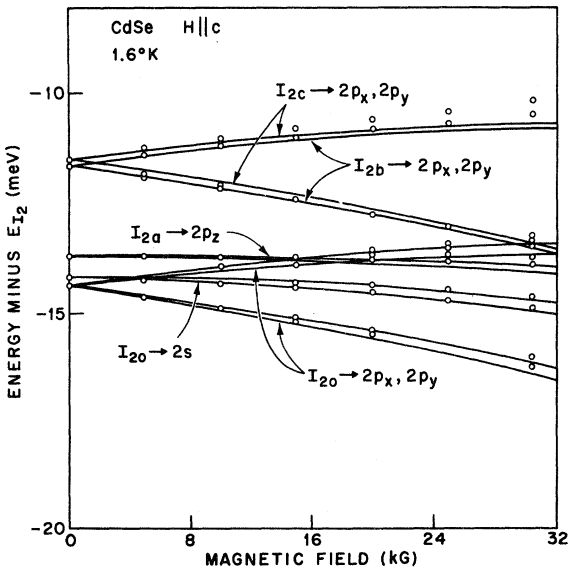


FIG. 2. Zeeman splittings of the two-electron transitions for $H \parallel c$ axis (in $z$ direction). The luminescence traveling in the $x$ direction is detected.

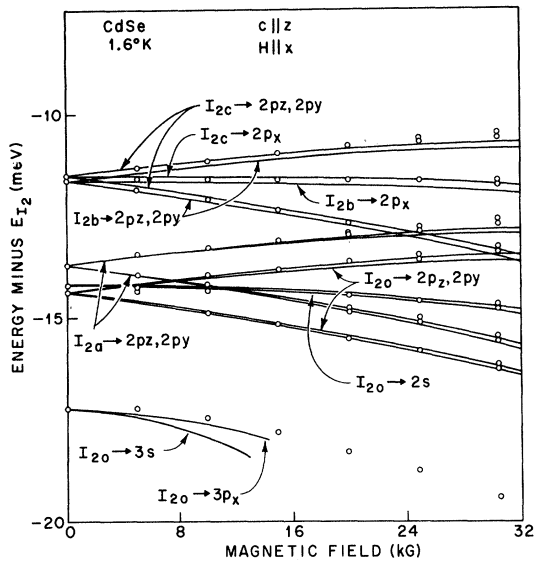


FIG. 3. Zeeman splittings of the two-electron transitions for $H \perp c$ axis; here $H$ is in the $x$ direction. The luminescence traveling the $z$ direction is detected.

The edge emission in CdSe was first studied by Reynolds *et al.*[15] These authors observed the Zeeman pattern of many bound-exciton transitions and found that only one of these transitions gave the simple magnetic behavior for $I_1$ and $I_2$ lines predicted by Thomas and Hopfield.[1] We have recently studied the magnetic behavior of $I_1$ and $I_2$ lines in CdSe.[16] Both of these lines behaved similarly to the corresponding lines in CdS, where the hole $g$ value goes to zero for $H \perp c$ axis. For the $I_2$ line in CdSe we found $g_{h\parallel} = 1.35 \pm 0.02$ and $g_e = 0.52 \pm 0.01$. The spin splittings of the $I_{2o} \rightarrow 2s$, $2p$ transitions were found to be the same as those for the $I_2$ line. Similarly, the spin splitting of the $I_{2a} \rightarrow 2p_z$ transition was found to be the same as that of the $I_{2a} \rightarrow 1s$ transition, which could also be observed. These splittings were used in plotting the theoretical curves in Figs. 2 and 3. No attempt was made to fit the spin splittings of the $I_{2b} \rightarrow 2p$ and $I_{2c} \rightarrow 2p$ transitions because the $I_{2b} \rightarrow 1s$ and $I_{2c} \rightarrow 1s$ transitions were not observed. The best fit for the Zeeman spectra was with $m = (0.13 \pm 0.005) m_e$ and with the $2p_x$ and $2p_z$ states degenerate.

## IV. DETERMINATION OF DONOR BINDING ENERGY

The donor binding energy can be calculated from the preceding information about the transition energies in several ways. First, one can calculate the Rydberg of the donor $E_0$ using a mass of $0.13 m_e$ and a static dielectric constant of 9.53.[17] Then, using

$$E_D = E_{2p} - E_{1s} + \tfrac{1}{4} E_0 , \tag{1}$$

we find $E_D = 19.24$ meV. Second, we may evaluate $E_0$ from the energy difference of the $n = 3$ and $2p$ levels and then determine $E_D$ by

$$E_D = E_3 - E_{1s} + \tfrac{1}{9} E_0 . \tag{2}$$

This yields $E_D = 19.83$ meV. Finally, we may use the energy difference between the $n = 4$ and $2p$ levels to determine $E_0$ and then determine $E_D$ by

$$E_D = E_4 - E_{1s} + \tfrac{1}{16} E_0 . \tag{3}$$

This gives $E_D = 19.55$ meV. This last method is probably most accurate since the correction to the measured energy-level difference is the smallest. In any case, $E_D = 19.5 \pm 0.3$ meV will encompass all three estimates.

## V. SUMMARY

We have measured the two-electron transitions for a donor in CdSe. The spectrum was complicated due to the presence of transitions originating from excited states of the three-particle bound-exciton complex. There was a one-to-one correspondence between this spectrum and the spectrum of two-electron transitions for a donor in CdS. By using unfocused laser light we were able to observe transitions to the $n = 3$ and $n = 4$ levels as well as transitions to the $2s$ and $2p$ levels. We conclude that the electron mass in CdSe is $(0.13 \pm 0.005) m_e$ and the donor binding energy is $19.5 \pm 0.3$ meV.

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# Excitation Spectra and Piezospectroscopic Effects of Magnesium Donors in Silicon*

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Excitation spectra of magnesium impurities diffused into undoped silicon as well as into silicon doped with group-III acceptors have been measured. In the former, magnesium is a heliumlike neutral donor ($Mg^0$) with excited states similar to those of group-V donors and close to the effective-mass positions; its ionization energy at liquid-helium temperature is $107.50 \pm 0.04$ meV. In specimens containing group-III impurities, with the magnesium partially compensated, excitation spectra are observed similar to those of group-V donors and that of $Mg^0$ except that the spacings between corresponding lines are approximately four times larger and the $1s(A_1) \rightarrow 2p_\pm$ transition is a closely spaced doublet, 0.2 meV apart. These features are consistent with a singly ionized heliumlike magnesium donor ($Mg^+$) and a small chemical splitting of the $2p_\pm$ state; the ionization energy is $256.47 \pm 0.07$ meV at liquid-helium temperature. The excitation spectrum of $Mg^+$ was also observed in specimens containing $Mg^0$ subjected to high-energy electron irradiation. Study of the piezospectroscopic effects shows that both $Mg^0$ and $Mg^+$ occupy a $T_d$-symmetry site with $1s(A_1)$ as the ground state. A value of $8.7 \pm 0.2$ eV has been deduced for the shear-deformation-potential constant $\Xi_u$ of the $\langle 100 \rangle$ conduction-band minima of silicon.

## I. INTRODUCTION

The behavior of group-V impurities as donors and of group-III impurities as acceptors in silicon and germanium represents one of the most extensively studied and best understood aspects of semiconductor physics. The substitutional nature of these impurities, the large dielectric constant of the host, and the effective mass of the bound carrier are the significant features of the model used to explain a variety of phenomena[1-3] associated with these donors and acceptors which are solid-state analogs of the hydrogen atom. It is also now well established that the group-II elements, zinc,[4,5] mercury,[6] and beryllium[7] in germanium and beryllium in silicon,[7] are solid-state analogs of the helium atom in that they are double acceptors; by compensation with group-V donors one can study these double acceptors in their singly ionized state which then are the analogs of singly ionized helium. The group-VI element sulfur when introduced into silicon[8-10] behaves like a heliumlike double donor; several sulfur donor centers have been discovered though the exact structures of these have not yet been established. For example, the electron paramagnetic resonance (EPR) measurements by Ludwig[9] showed that the sulfur centers designated as $D$ centers by Krag *et al.*[8] are isolated $S^+$ at $T_d$ sites, but he could not determine if they occupied the substitutional or the interstitial sites with that symmetry. The group-I impurity copper in germanium,[11] is another element which has been studied to some extent. The acceptor states associated with this impurity are consistent with its being substitutional.

Of the impurities which are interstitial rather than substitutional, the best-known example is that of lithium in silicon and germanium.[12,13] Transition-metal ions in silicon and germanium, both as interstitial and substitutional impurities, have been studied by Woodbury and Ludwig[14] who investigated their EPR spectra. Interstitial aluminum has been reported in electron-irradiated aluminum-doped silicon where interstitial silicon and substitutional aluminum are believed to exchange their roles[15]; it has been shown that these interstitial aluminum impurities are then donors. Recently,[16,17] the group-II element magnesium, when diffused into silicon, has been shown to behave like a double donor rather than a double acceptor. This behavior can be understood only if magnesium is interstitial rather than substitutional. Singly ionized magnesium donors can be produced by diffusing magnesium into