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Excited States of Bound Exciton Complexes in CdS

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The excited states of bound exciton complexes have been studied in CdS, and information relating to donor impurities in this material has been deduced. Donor ionization energies of 0.026 eV were calculated; this value gives a good fit to the experimentally determined ionization energies of the I_5 and I_{2c} neutral donors. A good theoretical fit to the $n=2$ magnetic-field-split levels is obtained, using Wheeler and Dimmock's model. The fit to the $n=3$ states is not as good. This is most likely due to the mixing of high-quantum-number states of different principle quantum numbers through the diamagnetic operator of the Hamiltonian.

I. INTRODUCTION

THE measurement of magnetic field splittings of donor and acceptor impurities in semiconductors allows one to study the ionization energies of these impurities as well as the effective masses of the carriers. Studies of this type have been made on a number of different impurities in Si and Ge.[1–3] These investigations were made by studying infrared absorption in a magnetic field.

The highest-quality crystals obtainable in II-VI materials are platelet-type crystals. These crystals are very thin (0.5–50 μ); as a result they are not suitable for infrared absorption studies. A detailed description of the bound exciton complexes in one of these materials (CdS) has been presented by Thomas and Hopfield.[4] They pointed out that an exciton bound to a neutral donor (or acceptor), upon decaying, could leave the donor (or acceptor) in an excited state. They observed transitions in CdS that were characterized by large magnetic field splittings and negative diamagnetic shifts which they tentatively identified with transitions of this type. Investigations of this type offer another approach to the study of donor or acceptor impurities in a particular host lattice.

It is the purpose of this paper to report on bound exciton transitions in CdS in which the impurity is left in an excited state. The transitions have been associated with donor-type complexes in which the initial state is that of an exciton bound to a neutral donor and the final state is an excited state of the electron on the donor.

In dealing with this type of complex in a material having the wurtzite symmetry, it is possible to examine directly the magnetic field splitting of the electron on the donor. It was previously shown[4] that for the wurtzite symmetry the electron g value is isotropic, (g_e=isotropic). It was further shown that the hole g value is completely anisotropic:

$$g_h = g_{h\|} \cos\theta ,$$

where θ is the angle between the c axis of the crystal and the magnetic field direction. If one does an emission experiment in the orientation $c \perp \mathbf{H}$, then in the upper state (see Fig. 5), the electron spins are paired to give a bonding state and one is left with a degenerate hole spin. For this orientation, the hole g value is zero so there will be no magnetic field effect on this state. In the lower state, since the electron g value is isotropic, the electron will split according to the state it occupies. In the ground state one will observe the usual electron spin splitting. In an excited state one will observe orbital splitting as well. In this configuration one is observing transitions from a singlet upper state to a magnetically split lower state. This provides a direct observation of the ground and excited states of the electron on the donor.

From zero-field measurements we have been able to determine donor binding energies and magnetic-field measurements have permitted the determination of the electron effective mass. Measurements in other orientations ($0° \leq \theta \leq 90°$) have demonstrated the additional multiplicity due to hole splitting.

In this material we have not identified excited state complexes that could be associated with an exciton bound to an acceptor site.

II. EXPERIMENTAL

The crystals used in these experiments were of the platelet type and were grown from the vapor phase.[5] It has been observed that the platelet-type crystals are the highest quality crystals available and are therefore the most desirable for these measurements.

The platelet samples ranged in thickness from 0.5 to 50 μ and were glued on one end (relatively strain free) to a sample holder which was in turn placed in the tip of a glass helium Dewar. The mounting was arranged os that the samples were immersed in liquid He. Provision was made for pumping on the liquid He and the temperature was measured by means of vapor-pressure thermometry, using an oil manometer. All of the experiments were conducted at approximately 1.2°K.

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The Dewar tip was inserted in the air gap of a conventional dc electromagnet, the pole tips of which were separated by $\frac{5}{16}$ in. The maximum field strength of this magnet was 45 000 G. A 500-W Hg lamp (Osram high pressure), equipped with a blue filter, was used for fluorescence excitation. Spectral analysis of the crystal emission was made with a Bausch and Lomb 2-m grating spectrograph. The spectrograph employed a large, high resolution diffraction grating and produced a reciprocal dispersion of approximately 2 Å/mm in first order. With this grating, the spectrographic aperture was about f/16. All of the spectra were photographically recorded on Kodak-type 103 a-F spectroscopic plates.

III. RESULTS AND DISCUSSION

A. Identification of Complexes

A number of bound exciton complexes have been observed in CdS,[4,6] and many of them have been

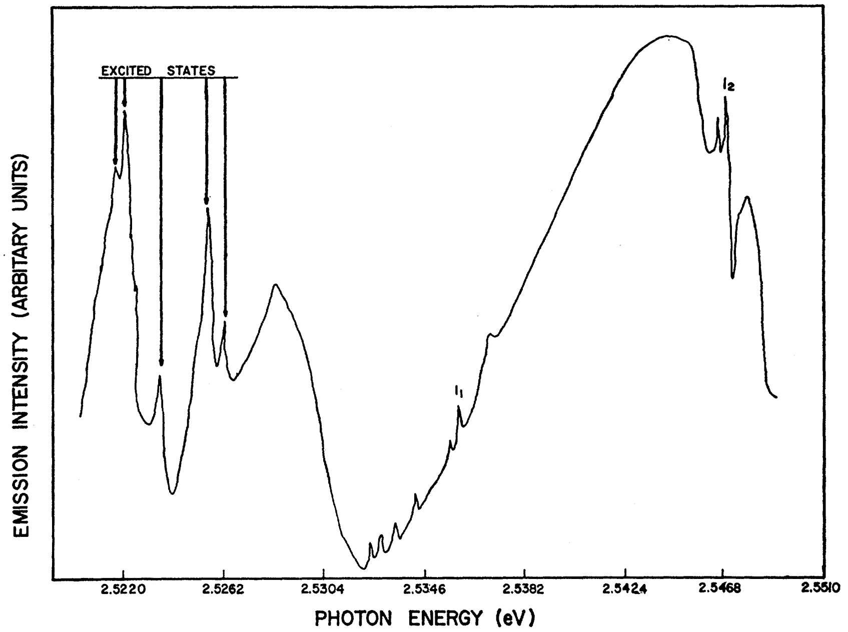

FIG. 1. Emission intensity as a function of photon energy for a Cd-doped CdS platelet. The I_1 line is very weak; the I_5 line is overexposed because of its great intensity. The broad emission in the region of 2.5459 eV is due to the overexposure of the line at that energy. The excited states are well defined.

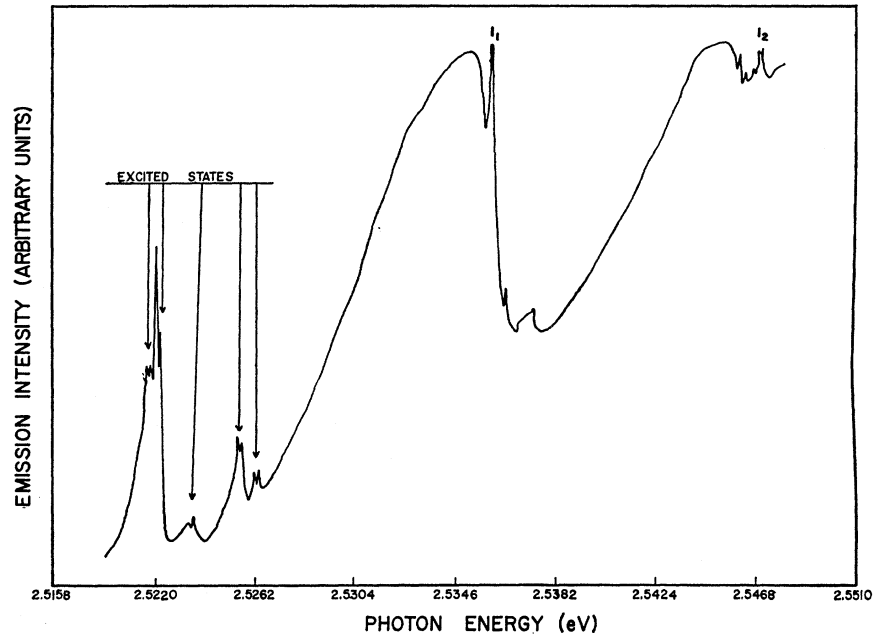

FIG. 2. Emission intensity as a function of photon energy for an "as-grown" CdS platelet. A strong I_1 line with phonon wing is observed. The I_5 line at 2.5459 eV is overexposed due to its great intensity; as a result, its doublet nature is not resolved. The doubling of the I_2 line is apparent, as well as the sharp lines on its low-energy side. The excited-state transitions all occur as doublets.

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[6] D. C. Reynolds and C. W. Litton, Phys. Rev. **132**, 1023 (1963).

identified with neutral donors or acceptors.[4] In the present experiment, we observe five lines in zero field at 2.5214, 2.5220, 2.5235, 2.5254, and 2.5262 eV as shown in Table I. The magnetic field splitting of these lines identified them as excited states of bound exciton complexes. Only one of the ground state bound exciton complexes in CdS has been positively identified as an exciton bound to a neutral acceptor complex. This is the I_1 (4888.5 Å) line. It has been shown[7] that the I_1 transition can be removed from CdS by doping with Cd. We show in Fig. 1 that the lines associated with excited state transitions are still present when the I_1 line is practically eliminated by Cd doping. From this it is concluded that the excited states are not associated with the I_1 complex.

It has been previously reported[6] that the I_1 line and the I_2 (4867.17 Å) line appear as doublets in some crystals. Figure 2 shows a crystal in which the I_2 line and other lines near it appear as doublets. It is noted in the same figure that when this occurs the excited state lines also appear as doublets. The lines in the spectral region of I_2 have been identified as excitons bound to neutral donor sites. On the basis of the doubling of the ground-state complexes it seems reasonable to associate the excited state complexes with the donors in the region of the I_2 line. In order to relate the energy states of a particular series, it is necessary to calculate the "hydrogenlike" ground and excited states of a neutral donor. The method chosen is analogous to the one used by Wheeler and Dimmock[8] where they derived the energies of an exciton in an anisotropic crystal. The effective mass of the electron in the neutral donor "hydrogenic" model is assumed to be isotropic; however, the dielectric constant in the z direction is different from that in the x and y directions. This gives the following Hamiltonian:

$$H=H_0+H_\alpha, \tag{1}$$

where

$$H_0=-\frac{\hbar}{2m_e^*}\nabla^2-\frac{e^2}{\epsilon\eta^{1/2}}\left(\frac{1}{r}\right) \tag{2}$$

and

$$H_\alpha=-\frac{e^2}{\epsilon\eta^{1/2}}\left\{(x^2+y^2+\eta^{-1}z^2)^{-1/2}-\frac{1}{r}\right\}. \tag{3}$$

In the above equations, ϵ is the dielectric constant transverse to the z direction and $\epsilon\cdot\eta$ is the dielectric constant parallel to the z axis. H_0 is the hydrogenic operator which is the unperturbed part of the Hamiltonian and H_α, which can be written as

$$H_\alpha=-\frac{e^2}{\epsilon\eta^{1/2}r}\left(\tfrac{1}{2}\alpha\cos^2\theta+\tfrac{3}{8}\alpha^2\cos^4\theta+\cdots\right), \tag{4}$$

is assumed to be accurately calculated by first-order perturbation theory. In Eq. (4)

$$\alpha=1-\eta^{-1}, \tag{5}$$

and in CdS, α has the value of 0.095, so only terms to α^2 are considered.

If one now has an external constant magnetic field in the x direction, two more terms are added to the Hamiltonian of Eq. (1), i.e.,

$$H_2=(\beta_0H_x/m_e^*)\hat{L}_x \tag{6}$$

and

$$H_3=-\frac{1}{8}\frac{e^2}{m_e^*c^2}H_x^2(y^2+z^2). \tag{7}$$

The term in Eq. (6) is linear in magnetic field and is responsible for the linear Zeeman splitting; Eq. (7) gives the diamagnetic or quadratic Zeeman effect. Again, these terms are assumed to be accurately calculated by first-order perturbation theory. Adding the spin momentum interacting with the magnetic field ($\mu^*\cdot H$) to the Hamiltonian given in Eq. (1) and treating as a first-order perturbation one obtains the g values for the electron-spin splittings. The resulting energies obtained from the above Hamiltonian, for the $n=2$ states of the donor complexes, as a function of the magnitude of the magnetic field are given as solid and dashed lines in Fig. 3. It is apparent that there are two overlapping sets of $n=2$ states derived from separate donors. The calculated energy of the $n=2$ state of the donor was matched to the experimentally observed $n=2$ state. From the calculated binding energy of the donor (0.026 eV) one can calculate the ground-state donor energy. Applying this binding energy to the solid and dashed lines of Fig. 2 gives a good fit to the I_5 and I_{2c} (4870.2 Å)[9] levels, respectively.

In the calculated energy levels of Fig. 3 an electron effective mass $m_e^*=0.18m_0$ was used. This gives a good theoretical fit to the experimental data.

TABLE I. Bound exciton emission lines in CdS at $T=1.2$°K

Line	Exciton complex	g_e (electron) g value isotropic	g_h (hole) g value $c\perp\mathbf{H}$
I_1 (4888.47 Å)	Neutral acceptor	−1.76	−1.03
I_2 (4867.17 Å)	Neutral donor	−1.76	−1.76
I_3 (4861.66 Å)	Ionized donor	−1.74	
I_5 (4869.14 Å)	Neutral donor	−1.75	−1.76
4907.15 Å	Neutral donor	−1.76	
4908.7 Å	with terminal	−1.76	
4912.4 Å	excited state	−1.76	
4915.32 Å		−1.76	−1.76
4916.5 Å		−1.76	−1.76

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[7] C. W. Litton and D. C. Reynolds, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 694.

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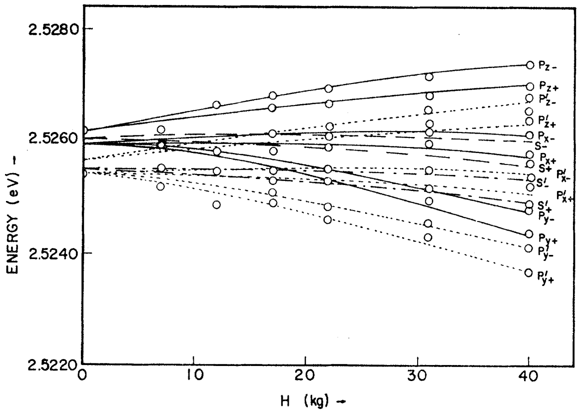

FIG. 3. Photon energy of the $n=2$ excited states of the I_{2c} and I_5 neutral donorbound exciton complexes as a function of magnetic field for the orientation $c\perp\mathbf{H}$.

The calculated energies for the $n=3$ states are shown in Fig. 4. In this calculation the spin was not added for the sake of clarity, likewise only the $n=3$ states of the I_5 donor are included. The fit between theory and experiment is not as good for the $n=3$ states as it is for the $n=2$ states. This probably results from the large radius of the donor causing mixing of states of different principle quantum number, through the diamagnetic term, for larger quantum numbers. It is apparent however that the experimental energies of the $n=3$ states do not come in the region where one calculates them to be, and that they do fit the hydrogenic series for the calculated donor binding energies.

The model used to describe the magnetic field splittings is shown in Fig. 5. It is evident from the model that the lowest-energy transitions result from the highest excited states. The model also demonstrates how the positive diamagnetic shift resulting from Eq. (7) is translated into a negative diamagnetic shift. Negative diamagnetic shifts are observed for the transitions in Figs. 3 and 4. It can be further seen from Fig. 5 that as the c axis of the crystal is rotated with respect to the magnetic-field direction a contribution from the hole spin should be observed. Figure 6 shows the splitting of the zero field lines at 2.5214 and at 2.5220 eV as θ is varied from 0°–90° for a constant magnetic field of 40 kG. For the orientation $c\|\mathbf{H}$ only three lines are observed for these excited states. In the magnetically field split lines of Fig. 6, the outer pair of lines (high and low energy) split as the sum of the g values (g_e+g_h), and the inner pair of lines split as the difference of the g values (g_e-g_h). If the electron and hold g values are nearly equal the inner pair of lines will show no splitting and the outer pair of lines are not allowed by spin consideration. This explains the splitting for the $c\|\mathbf{H}$ orientation in Fig. 6. It was previously shown[6] that the electron and hole g values for the I_2 and I_5 complexes in the ground state were approximately equal.

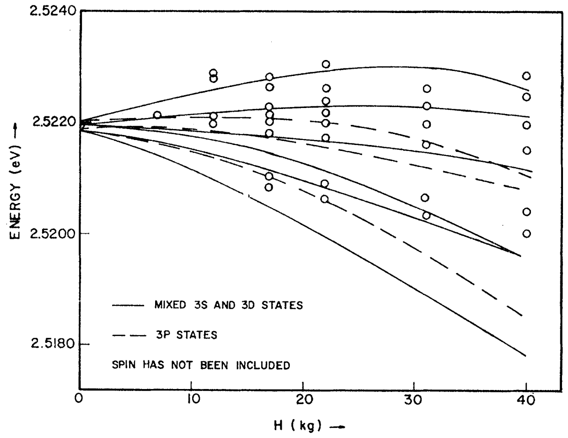

FIG. 4. Photon energy of the $n=3$ excited states of the I_{2c} neutral donor bound exciton complex (spin not included) as a function of magnetic field for the orientation $c\perp\mathbf{H}$.

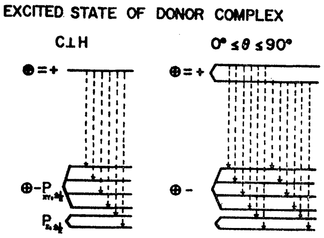

FIG. 5. Model for the decay of a bound donor complex in which the decay of the exciton leaves the terminal state in an excited configuration, in this case a p state.

IV. CONCLUSIONS

The study of the terminal states, after decay of bound exciton complexes, is a technique for gaining information about impurity states in semiconductors. We have

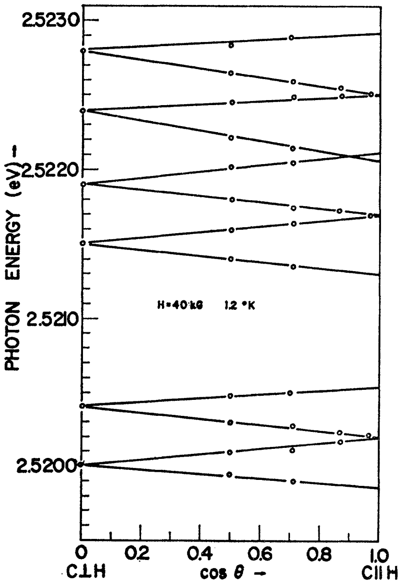

FIG. 6. Magnetic field splitting of the zero-field 2.5220-eV line as a function of cosθ for a constant field of $H=40$ kG.

shown that after exciton decay, the donor electron is left in an excited state in a number of transitions. From the differences in energies of the transitions to various excited states one can determine the donor binding energies. Studying the same excited states in a magnetic field has yielded carrier effective mass information.

In the case of CdS, only excited terminal states were observed for donor complexes. There is no *a priori* reason why similar effects should not be observed for acceptor complexes. The technique should be applicable to any material where well-resolved bound exciton lines are observed.

PHYSICAL REVIEW VOLUME 174, NUMBER 3 15 OCTOBER 1968

Optical Properties of Epitaxial PbSe Films

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Transmission measurements have been carried out on thin films of lead selenide in the energy range 0.5–6 eV. The thicknesses varied from 180 to 550 Å. The index of refraction and the extinction coefficient were calculated by Kramers-Kronig analysis. These show a significant divergence from earlier published values. A splitting of the 4.5-eV absorption peak is observed at low temperatures, which is attributed to spin-orbit splitting in selenium.

INTRODUCTION

The high absorption coefficient of semiconducting materials at energies above the fundamental gap makes it necessary to prepare thin specimens to make transmission measurements. Because of the difficulty in preparing thin epitaxial films of the lead salts, lead sulphide, selenide, and telluride, it was not until quite recently that transmission measurements were made to study the optical properties of these materials in the energy range 1–5 eV. Earlier reflectivity measurements have been carried out by Avery[1] (0.5–3.0 eV) and by Cardona and Greenaway[2] (0.5–25 eV), who have also carried out transmission measurements at energies below 6 eV.

Several reports state that epitaxial films of lead sulphide can be grown on sodium or potassium-chloride substrates.[3–6] This has made it possible for several workers[7–9] to measure optical constants of lead sulphide by both transmission and reflectivity measurements. The values of the optical constants for PbS reported by Cardona and Greenaway[2] differ markedly from those reported by Avery,[1] Schoolar and Dixon,[7] Wessel,[8] and Rossi and Paul.[9]

Since it is not possible to produce thin (200–300 Å) continuous films of PbSe by conventional evaporation methods,[10] we have done this by flash evaporation techniques. Thus we have been able to extend the optical measurements to PbSe to determine the optical constants and compare them with those previously published.

Since it is very hard to make reliable reflectivity measurements on films grown on cleaved NaCl substrates, because of nonflatness of the substrate and cleavage steps, we have used Kramers-Kronig analysis on transmission measurements only.[11]

After the optical measurements, we determined the thickness of the film by multiple interference, looked for pinholes in the film, and checked the crystalline quality of the specimen by transmission-electron microscopy.

EXPERIMENTAL PROCEDURE

The specimens were prepared by flash evaporation in a high-vacuum system capable of producing a vacuum better than 10^{-5} Torr. The lead selenide, which had a grain size between 125 and 250 μ, was evaporated from a heated beryllium-oxide-covered tantalum band, which was kept at a temperature of about 900°C. The substrate, cleaved, prior to pump-down, from optical rocksalt blanks supplied by the Harshaw Chemical Company, was placed in an oven. The temperature of the substrate was monitored by an iron-constantan thermocouple melted into a rocksalt blank of the same dimensions as the substrate crystal itself. A temperature of about 270°C seemed to give good single crystals and all films were grown at this substrate temperature. The

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