Aside from questions of rigor, two points of interpretation remain unresolved. The first one concerns the real origin of the double periodicity mentioned above. As we have shown, this double periodicity is a feature of Anderson's two-sublattice theory. It appears, however, that it has nothing to do with long-range order, first because it is possible to find models without long-range order which display this double periodicity, and second because the ground state itself is probably not ordered. The second point concerns the number of spin-wave states. In the rigorous case, the spin-wave states, being eigenstates of spin 1, are triply degenerate and correspond to values of $k$ ranging from $-\pi$ to $\pi$. On the other hand, in a two-sublattice model, for each value of $k$, ranging from $-\pi/2$ to $\pi/2$, there are only two spin waves. It is not obvious how these two points of view can be reconciled.

## ACKNOWLEDGMENTS

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# Optical Properties of Bound Exciton Complexes in Cadmium Sulfide

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The absorption and fluorescent spectra of "pure" CdS platelets (impurity concentrations $\sim 10^{17}$/cc) have been studied at low temperatures. In addition to intrinsic exciton lines, many sharp absorption and fluorescent lines were observed at slightly lower energies. Many of these lines are due to transitions involving bound excitons, in which the light creates (or destroys) an exciton bound to a neutral or charged donor or acceptor. Arguments from the known-band symmetries and electron $g$ values permit the identification of the generic centers (neutral donor, neutral acceptor, charged center) with which particular transitions are associated. Transitions in which excitons from the second valence band are bound were also observed, in some cases lifetime broadened by phonon transitions to excitons from the first valence band. States due to neutral donors and neutral acceptors are usually both observed in the same crystal. This nonequilibrium situation is caused by the trapping of holes made by the light which is being used to study the crystal. The "bleaching" of the trapped holes by the application of infrared light during ordinary transmission measurements near the band gap supports the generic transition assignments given. Centers of appropriate symmetries exhibit splittings due to electron-hole and hole-hole j-j coupling. The magnitudes of these splittings agree with crude theoretical estimates. The oscillator strength per center should be directly related to these splittings for the case of excitons bound to neutral impurities. Several different donors are discernible, but only a single acceptor is observed. The generic classification and energies of the observed centers should make possible the combined chemical and optical identification of the corresponding donors and acceptor in doped crystals. The arguments which permit the identification of the centers can easily be generalized to the case of cubic crystals.

## I. INTRODUCTION

EXCITON states represent excited states of a pure crystal. When excitons are studied in real crystals, it is frequently found that many optical effects, such as absorption and fluorescence occur at photon energies less than the exciton energies, yet the character of these effects strongly suggest that they are connected with both excitons and crystals imperfections. Lampert[1] has suggested a variety of models for this type of center in which states are described as being analogous to $H_2$, $H_2^+$, and $H^-$. By observing the fluorescence at low temperatures from silicon crystals of known impurity content, Haynes[2] has identified centers, arising from neutral donors and acceptors, which bear an analogy to $H_2$. This paper describes a number of these "bound" (or "impurity") exciton states which occur in CdS.[3] This material has a particularly simple band structure with band extrema at $k=0$ in the Brillouin zone, and the properties of the intrinsic excitons which arise from these extrema are well known.[4] The CdS crystals which have been used for the present experiments and which, therefore, are of sufficiently good quality to give the sharp lines which will be described, are grown from the vapor without the intentional addition of impurities. The crystals do, however, have many imperfections present which are responsible for the bound exciton

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* Supported in part by the National Science Foundation.

[1] M. A. Lampert, Phys. Rev. Letters 1, 450 (1958).

[2] J. R. Haynes, Phys. Rev. Letters 4, 361 (1960).

[3] D. G. Thomas and J. J. Hopfield, Phys. Rev. Letters 7, 316 (1961).

[4] J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961).

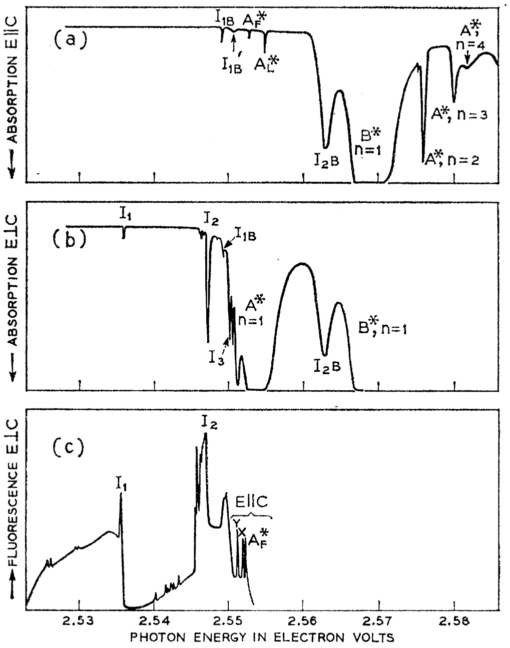

FIG. 1. A schematic diagram of absorption and emission lines seen in selected CdS crystals at 1.6°K. The intrinsic excitons are marked with an asterisk. There is gross distortion in the vertical scale but the energies of the peaks are as indicated. Because of the wide range of absorption coefficients the absorption lines are not all seen in one crystal. The range of crystal thickness used is 5–50 $\mu$. (a) and (b) give the absorption results for $E\|c$ and $E\perp c$, respectively, and (c) gives the fluorescent results. The fluorescence occurs chiefly with $E\perp c$, but the very sharp lines $Y$, $X$, and $A_F$, (seen best at 1.6°K rather than 4.2°K), are seen most clearly with $E\|c$.

states that are observed. The imperfections cannot at present be removed or otherwise identified, and it is necessary to derive as much information as possible from the optical spectra.

Section III gives an account of lines frequently seen in CdS. Some of these lines are associated with phonon effects and are not further discussed. Many of the lines split in a magnetic field due to the spin moments of the ground and excited states. The measured $g$ values can be identified with $g$ values of holes and electrons. If the ground state has the $g$ value of an electron, the line must arise from a neutral donor, and if it has the $g$ value of a hole, then it arises from a neutral acceptor. The simultaneous occurrence of neutral donors and acceptors is surprising, since compensation is expected. This problem is resolved, however, by the results of quenching experiments also described in Sec. III. These experiments reveal other lines which must arise from excitons trapped at ionized centers. Magnetic measurements confirm this identification and give reliable measurements of the zero-magnetic-field energy differences which arise from a type of exchange interaction between a weakly bound electron and hole. In Sec. IV, the group theory of bound excitons is described. Certain simplifications are used in the group theoretical methods which lead to approximate, but nevertheless useful conclusions. The theory of the exchange interaction effects is also discussed, together with lifetime broadening effects which occur for lines derived from excitons made from holes from the second valence band. In Sec. V, it is shown what conclusions about the various observed lines can be drawn from a comparison of theory and experiment.

## II. EXPERIMENTAL

CdS crystals 10–50 $\mu$ thick were grown by flowing purified argon over heated CdS. Distillation took place and the crystals grew in cooler parts of the oven at a temperature near 1000°C. Suitable crystals had to be selected from the resultant growth. The apparatus for optical work consisted essentially of a Dewar vessel with its tip between the pole pieces of a magnet which could produce a field of 31 000 G. Light from the crystal, which was immersed in the refrigerant, was focused onto the slit of a Bausch and Lomb spectrograph which produced a dispersion of 2 Å/mm. The spectra were recorded photographically. For the normal transmission work the crystal was illuminated with a tungsten lamp and for fluorescence, with the ultraviolet light from a high-pressure mercury lamp. For some transmission experiments it was necessary to use the minimum amount of light when observing the absorption lines. To do this, the crystal was illuminated from the exit slit of a Perkin-Elmer monochromator with the wavelength centered on the absorption line. The minimum bandpass of the Perkin-Elmer which was used was about 8 Å. For irradiation of the crystal with infrared light, a tungsten lamp in conjunction with a Corning 7–56 filter was used; this filter passes light of photon energies between about 1.5 and 0.4 eV.

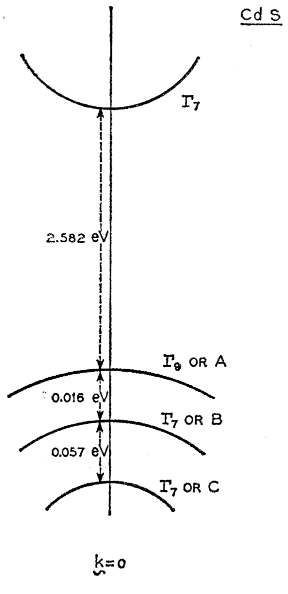

FIG. 2. Sketch of the band extrema in CdS. The $\Gamma_9$ valence band is strongly active only for light with $E\perp c$; the $\Gamma_7$ valence bands interact strongly with both modes of polarization.

Table I. A summary of the properties of the lines described in the text.

| Line | Active for | Energy (eV) ($\lambda$ (Å)) | Approx. apparent width ($10^3$ eV) | Energy below exciton $A$, eV (2.5537 eV) | Energy below exciton $B$, eV (2.5687 eV) | Ground state |
|---|---|---|---|---|---|---|
| $I_1$ | $E\perp c$ | 2.53595<br>(4888.5) | 0.1 | 0.0177 |  | Neutral acceptor |
| $I_2$<br>(Many lines) | $E\perp c$ | e.g., 2.5471<br>(4867.15) | 0.1 | 0.0066 |  | Neutral donor |
| $I_{1B}$ | $E\parallel c$ | 2.54887<br>(4863.7) | 0.1 |  | 0.0198 | Neutral acceptor (trapped exciton from Band $B$) |
| $I_{1B}$ | $E\perp c$ | 2.54914 | 0.1 |  | 0.0196 |  |
| $I_3$ | $E\perp c$ | 2.5499<br>(4861.7) | 0.1 | 0.0038 |  | Ionized donor |
| $I_{1B}'$ | $E\parallel c$ | 2.5504<br>(4860.8) | 0.5 |  | 0.0183 | Neutral acceptor (trapped exciton from Band $B$) |
| $Y$ | $E\parallel c$<br>$E\perp c$? | 2.55127<br>(4859.1) | 0.1 | 0.0024 |  |  |
| $X$ | $E\parallel c$<br>$E\perp c$ | 2.55206<br>(4857.6) | 0.1 | 0.0016 |  |  |
| $I_{2B}$ | $E\parallel c$<br>$E\perp c$ | 2.5626<br>(4837.7) | 1.7 |  | 0.0061 | Neutral donor (trapped exciton from Band $B$) |

## III. RESULTS

### A. Description of Lines

Figure 1 is a composite representation of the various lines seen at 1.6°K which will be considered in this paper. The lines marked with an asterisk are associated with intrinsic excitons. In CdS there are three intrinsic exciton series arising from an electron in the $s$-like conduction band, and a hole in each one of the three $p$-like valence bands (the triple degeneracy of the valence band at $k=0$ is lifted by a combination of the spin-orbit coupling and the hexagonal crystal field). A sketch of the bands is shown in Fig. 2. Selection rules show that the top valence band giving exciton series $A$ is active only for light with its $E$ vector polarized perpendicular to the $c$ axis ($E\perp c$), whereas the other bands are active in both modes of polarization. Thus, the $n=1, 2, \cdots$ states of exciton $A$ are seen strongly for $E\perp c$, and for exciton $B$ in both modes. Dipole selection rules are, however, not rigorous and so weak $A$ lines are seen for $E\parallel c$. Thus, we might expect that bound excitons derived from the $A$ series will also be stronger in $E\perp c$ than $E\parallel c$.

The prominent "impurity" exciton lines which are seen at the same wavelengths in both absorption and fluorescence tend to fall into groups. Nearly all as-grown crystals show an isolated weak line at 2.53595 eV which is called $I_1$. At low temperatures in fluorescence, $I_1$ has a broad continuum at lower photon energies which is peaked about $1\times10^{-3}$ eV below $I_1$, as shown in Fig. 1(c). [In this continuum there are sometimes a number of lines which are, however, not associated with $I_1$. These lines are indicated in Fig. 1(c).] Analogous to the low-energy fluorescent wing of $I_1$ there is a high-energy absorption wing of $I_1$ also peaked about $1\times10^{-3}$ eV away from $I_1$. This does not appear in the absorption curve for $I_1$ in Fig. 1(b), as the absorption is weak. These wings are caused by the electronic transition at $I_1$ going with acoustic phonon emission. At higher temperatures the corresponding phonon absorption processes can be seen.

Nearer to the exciton is a group of lines called $I_2$, active for $E\perp c$. These are usually stronger than the $I_1$ line and show a marked variation from one crystal to another. The fluorescent spectra show that these lines cooperate with acoustic phonons much less strongly than $I_1$.

In crystals in which the background absorption from the tail of exciton $A$ is sufficiently low, other lines may be seen very close to the exciton which behave differently from $I_2$. One such line, seen clearly in absorption, has been called $I_3$. The distinguishing feature of this line is that its strength increases when the crystal is irradiated with infrared light, whereas the strengths of $I_1$ and $I_2$ decrease, as will be described later. There is weak diffuse fluorescence in the region of $I_3$ but no sharp line.

Above exciton $A$ but just below exciton $B$ a broad line (of width about $1.7\times10^{-3}$ eV) is seen in absorption for both modes of polarization. Since exciton $B$ is also active in both modes and since this broad line is approximately the same distance from exciton $B$ as the $I_2$ lines are from exciton $A$, it is reasonable to suppose that the broad line arises from the same impurities as the $I_2$ lines, but from exciton $B$ rather than exciton $A$. Consequently, the broad line is called $I_{2B}$, (in a previous paper[4] it was called $I_4$.) There is no fluorescence associated with $I_{2B}$.

Finally, in absorption in $E\parallel c$, there are two lines below the intrinsic lines $A_F$ and $A_L$. The higher-energy line of these two is broadened and called $I_{1B}'$, the lower-energy line is sharp and called $I_{1B}$. From the infrared quenching behavior and the Zeeman pattern of these lines, it will be shown that they are both derived from the center responsible for $I_1$, and exciton $B$.

In fluorescence as well as the lines described above, very weak, but sharp lines occur between $I_1$ and $I_2$ in $E\perp c$ and will not be further discussed here. Two

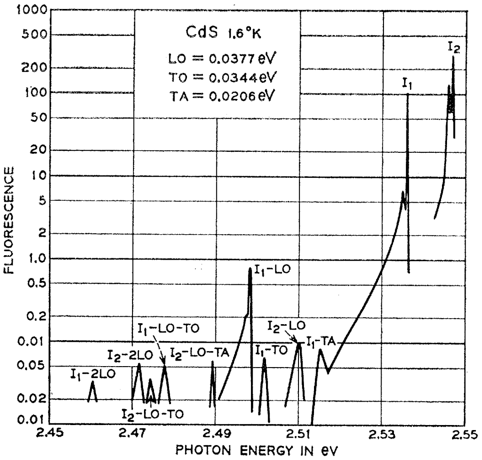

FIG. 3. The fluorescent spectrum of a "good" crystal of CdS at 1.6°K showing the lines derived from the no-phonon lines $I_1$ and $I_2$. All the lines can be accounted for using the 3 phonon energies listed in the figure. The assignment of the *TO* and *TA* phonons is tentative. The cooperation of $I_1$ with low-energy acoustic phonons is seen as a small peak about 0.001 eV below $I_1$; it persists out to the point marked $I_1$–*TA* which presumably marks the energy of the acoustic phonons at the zone boundary. Similar effects occur on the low-energy side of line $I_1$–*LO*. $I_2$, in fact, consists of several lines, and no low-energy acoustic phonon cooperation is seen with these lines.

remarkable, sharp fluorescent lines called $X$ and $Y$ are visible for $E\|c$ at photon energies slightly less than that of exciton $A$. These lines are much weaker at 4.2° than at 1.6°K. $X$ is also active in $E\perp c$ and $Y$ may be as well, but its observation in $E\perp c$ is difficult because of the strong background fluorescence from adjacent lines. $X$ and $Y$ are not seen in absorption. They will not be further discussed as their origin is as yet not understood.

Table I lists most of the lines discussed here and gives their respective energy differences from the excitons from which they are derived. In fact, the exciton energies are not known with high precision because their observed line widths are so great; the values quoted are taken to be the mid points of the broad absorption lines. Also given under the heading "ground state" are the centers to which an exciton is bound, to give rise to the various transitions. The justifications for these assignments are given in Sec. V. Just as for the intrinsic excitons the selection rules are not rigorous so that in thick crystals $I_1$ may be seen in $E\|c$. In addition, the polarization of the fluorescence is not complete, although surface imperfections may be the partial cause of this.

Below $I_1$, a number of fluorescent lines occur which are the $I_1$ or $I_2$ transitions occurring with phonon emission. This is known for the following reasons:

(a) Some of the lines occur at known phonon intervals.

(b) At low temperatures there is no absorption corresponding to the emission.

Figure 3 shows these fluorescent lines, as well as the no-phonon lines from which they are derived, and indicates some phonon energies obtained from the data. The assignment of the *TO* and *TA* phonons is tentative.

### B. Results in a Magnetic Field

We are chiefly concerned with lines $I_1$, $I_2$, $I_3$, and $I_{1B}$. In a magnetic field, these lines all split in a way which depends strongly on the angle $\theta$ between the magnetic field $H$ and the $c$ axis. The diamagnetic shifts of the lines are all extremely small, as they are for the $1S$ states of the intrinsic excitons, and we will neglect this effect although its magnitude shows that the states are derived from exciton ground states, rather than excited exciton states which have much larger diamagnetic shifts.[4]

#### *Lines $I_1$ and $I_2$*

The splittings of the $I_1$ and $I_2$ lines are linear in the magnetic field; (all of the lines grouped together as $I_2$ behave similarly in a magnetic field). The $g$ values of the lines have been reported previously for the geometries $c\|H$ $(\theta=0°)$ and[5] $c\perp H$ $(\theta=90°)$. Under these circumstances the lines split into doublets; although as it turns out, by chance, $I_2$ shows no splitting for $c\|H$. It is found, however, that in general, if $\theta$ lies between 0° and 90°, each line splits into a quartet of lines, the strengths of the lines varying markedly with the value of $\theta$. This splitting into quartets is illustrated for $I_1$ and $I_2$ in Fig. 4 for a field of 31 000 G. The data are taken from the fluorescent lines rather than from the absorption lines, since a weak line is easier to see in fluorescence than in absorption, and also because the fluorescent lines do not show thermalization effects (see below). The absorption lines do, however, split with precisely the same energy separations as the fluorescent lines.

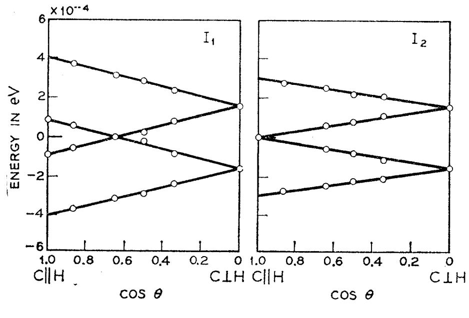

FIG. 4. The splitting of lines $I_1$ and $I_2$ at 31 000 G as a function of $\cos\theta$ at 1.6°K as seen in fluorescence. $\theta$ is the angle between the $c$ axis and the magnetic field. Notice that when $\theta\neq 0°$ or $\theta\neq 90°$ quartets occur. The zero of energy is taken to be at the center of each group of lines. (In a similar figure in reference 3 there was an error. The scale on the vertical axis should have been multiplied by a factor of 2.)

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[5] R. G. Wheeler and J. O. Dimmock, Phys. Rev. Letters 3, 372 (1959).

TABLE II. $g$ values and thermalization results for various absorption lines. $g_u$ and $g_l$ refer to the $g$ values of the upper and lower states, respectively.

| | $I_1$ | $I_2$ |
|---|---|---|
| $c\|\|H$ | $g=-1.03$<br>High-energy line strong<br>Therefore $g_l > g_u$ | No splitting observable<br>Therefore $g_u = g_l$ |
| $c\perp H$ | $g=-1.76$<br>Both lines equal in strength<br>Therefore $g_l=0$ | $g=-1.76$<br>High-energy line strong<br>Therefore $g_l > g_u$ |
| | $I_3$ | $I_{1B}$ |
| $c\|\|H$ | No splitting observable | $g=-2.07$<br>High-energy line weak<br>Therefore $g_u > g_l$ |
| $c\perp H$ | Zero-field splitting of $0.31\times10^{-3}$ eV<br>$g_{\text{eff}}=-1.7_4$<br>No thermalization effects<br>Therefore $g_l=0$ | Zero-field splitting of $0.27\times10^{-3}$ eV<br>$g_{\text{eff}}=-1.8$<br>No thermalization effects<br>Therefore $g_l=0$ |

In fluorescence, we have found that the $I_1$ and $I_2$ multiplets in a magnetic field have line strengths which are independent of the temperature (between 4.2 and 1.6°K), and independent of the magnetic field. In general, this is not so for the absorption lines, where it is noticed that there is sometimes a difference of strength between two lines which increases at constant temperature as the field is increased, or increases at a given field as the temperature is lowered. Since these are absorption results they show that the electrons or holes in the split ground state are coming to thermal equilibrium. By assigning equal statistical weights to the ground-state levels and measuring the intensity ratios at a particular temperature and field, it is, in principle, possible to determine a "thermal" $g$ value $g_t$, which will be the $g$ value of the lower state. In practice, only approximate values of $g_t$ can be determined. The $g$ values and thermalization results are summarized for $I_1$ and $I_2$ with $c\|H$ or $c\perp H$ in Table II. The relative magnitudes of the $g$ values in the upper and lower states ($g_u$ and $g_l$) are readily deduced by observing which line of a pair is stronger and using the four-level model and the selection rules described in Sec. IV.

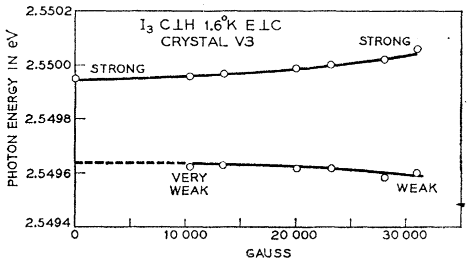


FIG. 5. The splitting of $I_3$ in a magnetic field with $c\perp H$, as seen in absorption. Notice that there is a zero-field splitting but that the lower state involves a forbidden transition and is only seen as it is mixed with the upper state by the magnetic field.

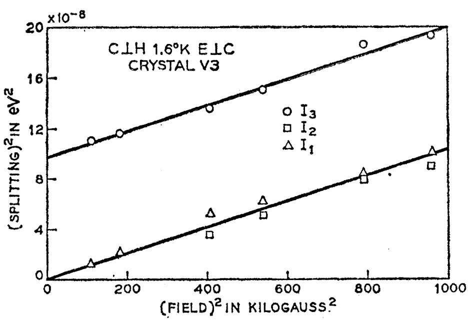


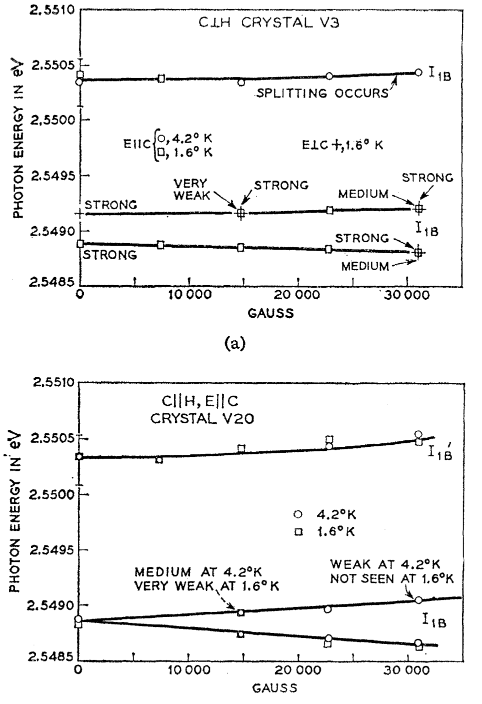
FIG. 6. The splitting of $I_3$ plotted so as to give a straight line from which the zero-field splitting is obtained. Also shown are the splittings of $I_1$ and $I_2$ with no zero-field splitting. Notice that within experimental error the lines all have the same slope which yields the $g$ value of the electron.

The linear splittings of the $I_1$ and $I_2$ lines show that both the excited and ground states have only one unpaired spin (Sec. V). The centers, therefore, arise from excitons associated with neutral donors or acceptors. The ground-state $g$ values will enable one to show that $I_1$ is associated with an acceptor, and the $I_2$ lines with donors.

### *Line $I_3$*

Line $I_3$ is observed only in absorption in crystals of suitable thickness and quality. It is usually necessary to bring its strength up to a convenient level by observing the line with a minimum of band gap light, and increasing its strength with infrared light (see Fig. 8 and the quenching experiments described below). The Zeeman behavior of $I_3$ for $c\|H$ is too small to be detected (indicating a near equality of $g$ values of the electron and hole in the excited state). For $c\perp H$ the Zeeman effect is quite different from that of $I_1$ and $I_2$ in that there is a zero-field splitting between the states which are mixed by the magnetic field. Since one of the transitions is forbidden in zero field, this line does not appear until a high field is applied, whereupon it rapidly increases in strength, and the two lines move apart nonlinearly with field. The results are shown in Fig. 5, and in Fig. 6 the square of the separation between the lines is plotted against the square of the field. The slope of this line gives an effective $g$, $g_{\text{eff}}$, equal to $1.7_4$. The extrapolation of this linear plot to $H=0$ clearly shows the zero-field splitting of $3.1\times10^{-4}$ eV. Also shown in Fig. 6 are the results for $I_1$ and $I_2$ which pass through the origin. It may be noticed that all the results in this figure fall on lines with the same slope. For the same magnetic field, the intensity of the $I_3$ lines does not change with temperature, indicating that $g_t=0$. The results are summarized in Table II.

The magnetic behavior of $I_3$ shows that it arises from an ionized center, since in the upper state it has a zero-field splitting which comes from an exchange interaction of an unpaired electron and an unpaired hole. This conclusion is supported by the observation



(a)

(b)

FIG. 7. The behavior of lines $I_{1B}$ and $I_{1B}'$ in a magnetic field. $I_{1B}'$ is broad, as indicated, and its Zeeman effect cannot be determined accurately; its approximate center of gravity has been plotted. (a) For $c\perp H$, $I_{1B}$ shows no thermalization but has a zero field splitting. (b) For $c\|H$, $I_{1B}$ has a linear splitting but shows thermalization with the low-energy line strong. The width of $I_{1B}'$ and background absorption prevents its observation for $E\perp c$.

that $I_3$ increases in strength when the crystal is irradiated with infrared.

### *Lines $I_{1B}$ and $I_{1B}'$*

$I_{1B}$ and $I_{1B}'$ are seen in absorption for $E\|c$; both show Zeeman effects. The broadening of line $I_{1B}'$ however, prevents an accurate determination of its splitting. $I_{1B}$ is also seen for $E\perp c$, although it occurs $0.27\times10^{-3}$ eV above $I_{1B}$ seen for $E\|c$. $I_{1B}'$ is not seen for $E\perp c$ probably because of its breadth and because of other background absorption. For $c\|H$ $I_{1B}$ splits linearly as expected with a $g$ value of 2.07. The pair of lines show thermalization effects with the high-energy line becoming weaker, as the temperature is lowered or the field increased. For $c\perp H$ the behavior of $I_{1B}$ seen in $E\|c$ is nonlinear, with a high-energy component becoming visible at high fields. There is no thermalization effect. The splittings are shown in Fig. 7(a) and 7(b) for $c\|H$ and $c\perp H$. If the squares of the splittings are plotted against the square of the field, linear plots result, which show that for $c\perp H$ there is a zero field splitting of $0.27\times10^{-3}$ eV, and an effective $g$ value for $c\perp H$ of $g_{\text{eff}}=1.8$. The zero-field splitting is equally well determined from a comparison of the $E\perp c$ and $E\|c$ spectra at zero field as mentioned above. The results are summarized in Table II. For $c\|H$ $I_{1B}'$ shows a Zeeman effect consistent with a linear Zeeman effect of the same net $g$ value as $I_{1B}$ but having the low-energy line missing, presumably due to a combination of line width and thermalization with a smaller $g$ value in the excited state than in the ground state.

$I_{1B}$ and $I_{1B}'$ arise from the $I_1$ neutral acceptor state and an exciton formed from a hole in the second valence band. The large zero-field splitting between them of $1.5\times10^{-3}$ eV, comes from the exchange interaction between the two unlike holes.

## C. Quenching of Absorption Lines

The binding energy of an exciton to a neutral center is expected to be different from its binding energy to the same center when ionized, so that different lines will occur depending upon the state of ionization of a particular center. CdS crystals as grown are $n$ type but are usually partially compensated, so that one might expect there to be neutral and ionized donors and ionized acceptors in the crystals. But, as described above, we have suggested that the line $I_1$ originates on a *neutral* acceptor. This apparent paradox may be resolved as follows. Donor binding energies are about[6] 0.032 eV while acceptors are expected to have binding energies of 0.5–1.0 eV.[4] Consequently, at low temperatures and at low concentrations (where tunneling between donor and acceptor neighbors can be neglected), one expects to be able to irradiate the crystal with band-gap light which makes free holes and electrons and that these will react with the ionized acceptors and donors, respectively, to make long-lived neutral centers. Conversely, if a minimum of band-gap light is used for observation of the lines, infrared light of energy equal to or greater than that of the acceptor binding energy might then be expected to liberate a hole from a neutral acceptor, and this hole could react with an electron from a neutral donor to form an ionized donor. Thus, band-gap light might favor neutral centers, infrared light ionized centers.

The conditions described in the experimental section were used to test these predictions. For nearly all the crystals used by us, the quenching effects of infrared could be observed on lines $I_1$ and $I_2$, while simultaneously, the intensity of $I_3$ was increased. Experiments were performed at 20, 4.2, and 1.6°K. The success of the experiments depends upon having a low level of band-gap illumination (as provided by the Perkin-Elmer monochromator), so that the weakly absorbed infrared light has an observable effect. Typical results are shown in Fig. 8. It is often possible to quench the $I_1$ line completely but this is not so with the $I_2$ lines. It might be added that green light of energy slightly less than the band gap is also weakly active in restoring the

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[6] W. W. Piper and R. E. Halsted, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 1046.

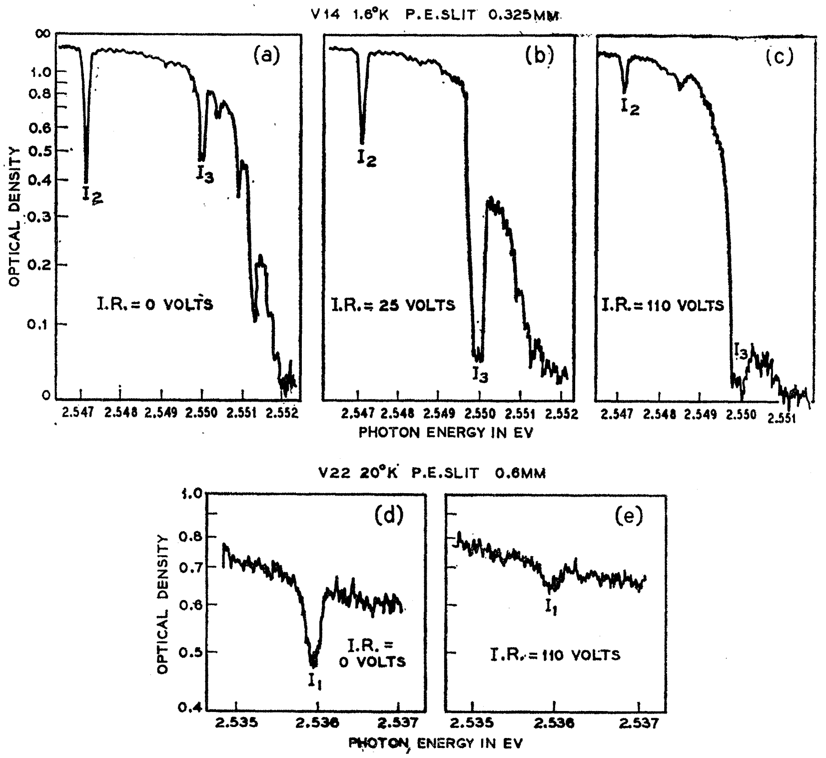

FIG. 8. Microphotometer tracings which show that irradiation of CdS crystals with infrared light quenches the $I_1$ line and the $I_2$ line and enhances the $I_3$ line. The $I_1$ line is shown in *d* and *e* for 20°K but the effect is similar at 1.6°K. The "IR Volts" indicate the voltage to the infrared source. The crystals were illuminated with a minimum of band-gap light from a Perkin-Elmer monochromator the slit width of which is indicated.

intensity of $I_1$ and $I_2$ just as is band-gap light. It may be that this green light is able to remove an electron from an ionized acceptor to the conduction band, and this electron then falls into an ionized donor thereby increasing the concentration of neutral centers. On the basis of these observations, it seems reasonable to suppose that the $I_1$ and $I_2$ lines are associated with excitons trapped at neutral centers, and that the $I_3$ line is associated with an exciton at an ionized center. The lines $I_1$, $I_{1B}$, and $I_{1B}'$ may be observed in the same crystal under the same conditions of illumination by taking a spectrum first with $E\perp c$ and then with $E\|c$. It is found that $I_1$ and $I_{1B}$ (and also $I_{1B}'$, although measurements here are not precise because of the comparatively large width of this line), quench together with infrared irradiation as shown in Fig. 9. This close similarity of quenching behavior is strong evidence for supposing that $I_1$ and $I_{1B}$ arise from the same imperfection.

## IV. THEORY

### A. Introduction

In this section, a general account of the theory of bound excitons in CdS will be presented. The relevant band structure has been sketched in Fig. 2. The discussion will provide a rigorous basis for some of the qualitative assertions already given concerning the nature of the states and the optical-selection rules. The Zeeman effects and energies expected for different types of transitions will also be described, and a comparison of these with the experimental results will enable us to classify the centers responsible for a particular line. In addition, certain lifetime broadening effects will be discussed which arise from a hole in the second valence band relaxing into the top valence band. The general model adopted is that in which an exciton forms a complex which is held together by forces analogous to those that exist in the hydrogen molecule or the

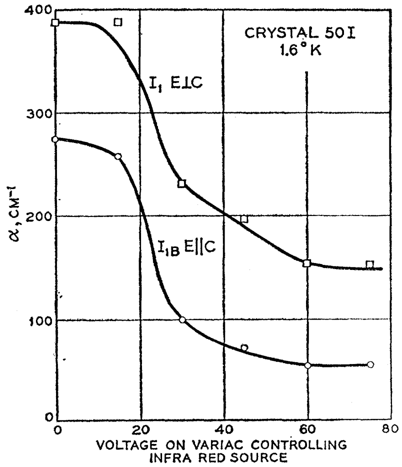

FIG. 9. The simultaneous quenching of line $I_1$ and $I_{1B}$ with infrared light. The similarity of the curves indicate that both lines originate from the same center. The fact that the fractional decrease of both lines is not the same can probably be ascribed to the experimental error involved in measuring the height of a very narrow line.

hydrogen-molecule ion. If there is only one unpaired electronic particle, a simple linear Zeeman effect results. If, however, the angular momenta, ($j$), of the holes or of the electrons in a complex do *not* cancel, then it is found that significant energy differences result from the different possible combinations of the $j$'s and this results in a zero field splitting and a more complex Zeeman pattern.

### B. Group Theory of Bound Complexes

We treat here the group theory of weakly bound localized states in crystals having a direct band gap at $k=0$. For crystals having only one molecule per unit cell and substitutional impurities, the bound impurity states will belong to an irreducible representation of the point group of the crystal. For a substitutional impurity in a crystal of several molecules per unit cell, the symmetry group which leaves the impurity fixed is smaller than the point group, and the symmetries of the states around an impurity will correspond to this smaller group.

In the case of the wurtzite structure with 2 molecules/unit cell, the symmetry group of a point substitutional impurity is $C_{3v}$.[7] The second three representations are, of course, those referring to an odd number of particles, and the first three to an even number of particles. The representations $\Lambda_4$ and $\Lambda_5$ are degenerate by time reversal, and will be jointly referred to as $\Lambda_{45}$. The decomposition of the wurtzite point group into the representations of the impurity point group is as follows:

$$\begin{array}{ll}
\Gamma_1 \rightarrow \Lambda_1, & \Gamma_6 \rightarrow \Lambda_3, \\
\Gamma_2 \rightarrow \Lambda_2, & \Gamma_7 \rightarrow \Lambda_6, \\
\Gamma_3 \rightarrow \Lambda_2, & \Gamma_8 \rightarrow \Lambda_6, \\
\Gamma_4 \rightarrow \Lambda_1, & \Gamma_9 \rightarrow \Lambda_{45}. \\
\Gamma_5 \rightarrow \Lambda_3 &
\end{array}$$

No nonaccidental degeneracy is lifted in this decomposition, since each representation of the point group decomposes into a unique representation of the impurity group.

Simple calculations show that states $\Lambda_3$, $\Lambda_{45}$, and $\Lambda_6$ can have nonzero $g$ values for a magnetic field parallel to the $c$ axis, while only states $\Lambda_3$ and $\Lambda_6$ have a nonzero $g$ value for a magnetic field perpendicular to the $c$ axis. The corresponding possible $g$ values of states for the point group are $g_{\parallel}$ for $\Gamma_5$, $\Gamma_6$, $\Gamma_7$, $\Gamma_8$, and $\Gamma_9$ and $g_{\perp}$ for $\Gamma_7$ and $\Gamma_8$.

For light polarized parallel to the $c$ axis, the optical dipole selection rules are $\Gamma_i \rightarrow \Gamma_i$ and $\Lambda_i \rightarrow \Lambda_i$, etc. For light polarized perpendicular to the $c$ axis, the optical selection rules are:

$$\begin{array}{lll}
\Lambda_1 \rightarrow \Lambda_3, & \Gamma_1 \rightarrow \Gamma_5, & \Gamma_4 \rightarrow \Gamma_6, \\
\Lambda_2 \rightarrow \Lambda_3, & \Gamma_2 \rightarrow \Gamma_5, & \Gamma_3 \rightarrow \Gamma_6, \\
\Lambda_3 \rightarrow \Lambda_1+\Lambda_2+\Lambda_3, & \Gamma_5 \rightarrow \Gamma_1+\Gamma_2+\Gamma_6, & \\
 & \Gamma_6 \rightarrow \Gamma_3+\Gamma_4+\Gamma_5, & \\
\Lambda_{45} \rightarrow \Lambda_6, & \Gamma_7 \rightarrow \Gamma_7+\Gamma_9, & \\
\Lambda_6 \rightarrow \Lambda_{45}+\Lambda_6, & \Gamma_8 \rightarrow \Gamma_8+\Gamma_9, & \\
 & \Gamma_9 \rightarrow \Gamma_7+\Gamma_8. &
\end{array}$$

Some relaxation of selection rules occurs for the group of the impurity. For example, the transition $\Gamma_1 \rightarrow \Gamma_6$ for light polarized parallel to the $c$ axis is forbidden, whereas the corresponding transition $\Lambda_1 \rightarrow \Lambda_3$ is allowed. Similarly, state $\Gamma_5$ has zero $g$ value for $H \perp c$, but the corresponding state $\Lambda_3$, can have a nonzero $g$ value for $H \perp c$.

Consider now any simple optical transition in which an electron bound to an impurity is taken from one band to another. Suppose the initial and final states can be approximately assigned effective mass wave functions. The initial-state wave function can then be written as,

$$f_i(r)u_{i0}(r),$$

where $f_i(r)$ is a slowly varying function of $r$, and $u_{i0}$ is the periodic part of the Bloch function of band $i$ for wave vector zero. Similarly, the final-state wave function can be written,

$$f_f(r)u_{f0}(r).$$

Since $f$ is a slowly varying function, the optical matrix element,

$$\int f_i(r)u_{i0}(r)\mathbf{P}f_f^*(r)u_{f0}^*(r)d^3r,$$

can be approximately written as

$$\left[\int f_i(r)f_f^*(r)d^3r\right]\frac{1}{\Omega}\left[\int u_{i0}(r)\mathbf{P}u_{if}^*(r)d\tau\right],$$

where the second integration is carried out over the unit cell, whose volume is $r$. In this approximation, the only large optical matrix elements will arise when the analogous band-to-band transition is allowed.

A similar argument can be made to show that in this effective-mass approximation, large $g$ values can be expected only when the parent-energy band wave functions exhibit large $g$ values.

It is concluded that in this simple case of weakly bound states at substitutional impurities and for energy bands at $\mathbf{k}=0$ in the wurtzite structure, it is reasonable to describe the states as though they belonged to the point group of the crystal rather than to the group of the impurity. Such a description gives the degeneracy of the states correctly. This description neglects certain optical

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[7] For the character table, see G. F. Koster, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, pp. 187, 243.

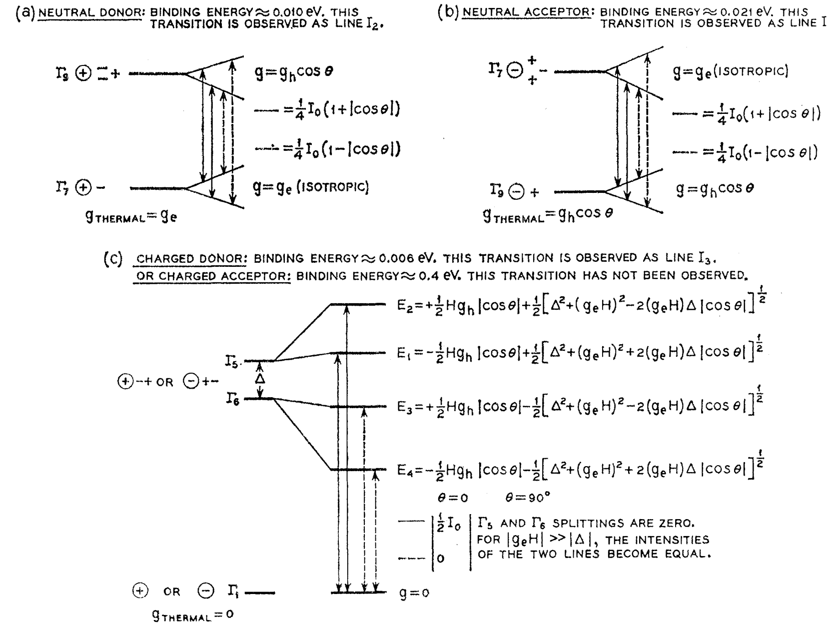

FIG. 10. A schematic representation of the energy levels of complexes which can be formed using holes only from the top valence band. In (a) and (b) linear splittings are observed, but in (c) the splittings are more complex and the energy levels are given. The expressions associated with the dashed or solid lines refer to the intensities of the transitions.

transitions which are technically allowed, but are weak in the effective mass approximation and will set equal to zero certain $g$ values which should be much smaller than usual $g$ values. The advantage of the description is that it neglects these small effects and thus permits the full use of group theory without the clutter of what should be extremely small perturbations (In the case of an odd number of electrons, most of the conclusions which will be drawn regarding $g$ values and selection rules are, in fact, exact for the group of the impurity.)

### C. Application to States Involving the Top Valence Band in CdS

The simplest bound exciton transitions are those occurring in absorption for which the initial state of the transition is a neutral or ionized donor or acceptor, and the final state is an exciton bound to one of these centers; for emission, the roles of initial and final states are, of course, reversed. Since the effective mass of the electron and hole are comparable, "vibrational" and "electronic" parts of the bound exciton wave functions cannot be separated and should have comparable frequencies. We treat only the lowest states of these complexes, in which, when two electrons or holes are present, the spatial symmetry of the presumed ground state will require an antisymmetric spin wave function for the two like particles.

Figure 10 shows the energy-level structure, magnetic field splittings, and intensities as a function of magnetic field for simple bound states. The electron $g$ value $g_e$ should be very nearly isotropic and, since the conduction band is simple and the $g$ shift of the free electron is small, only weakly dependent on the state of binding of the electron. The hole $g$ value, $g_h$, should be completely anisotropic with $g_h$ equal to zero for magnetic fields perpendicular to the hexagonal axis. It is to be expected that the hole $g$ value will be sensitive to its state of binding, since the different valence bands will be strongly mixed in bound-hole states. All formulas have been written making explicit use of an isotropic electron $g$ value and a completely anisotropic hole $g$ value. In the models of the states, ⊕ and ⊖ represent ionized donors and acceptors, respectively, and + and − represent holes and electrons. The symmetries, strengths, and magnetic moments have been calculated on the basis of the results of Sec. IV B. The magnetic field $H$ makes an angle $\theta$ with the crystal $c$ axis. $I_0$ is the absorption strength of a single line of a given type for zero magnetic field. $\Delta$ is a splitting energy due to the electron-hole exchange interaction.

The quoted binding energies represent the binding energy of an exciton to the center in question. These are theoretical values based on scaling the known binding energies of states of hydrogen ions and molecules to exciton parameters. These values are only qualitative, since this scaling ignores central cell corrections, polaron effects, the complicated valence band structure, and they treat the mass ratio $m_e/m_h$ as very small.

In the case of excitons bound to neutral donors (or acceptors), transitions should also be possible in which the donor (or acceptor) is left in an excited (or ionized) state. Such transitions would produce a photon having the energy of the simple transitions minus the excitation energies of the donor (or acceptor), and produce a 1:1 map of the excitation levels of the donor (or acceptor). Lines have been seen at energies below $I_1$ in fluorescence which have large magnetic splittings and negative diamagnetic shifts and so have been tentatively identified as corresponding to these transitions.

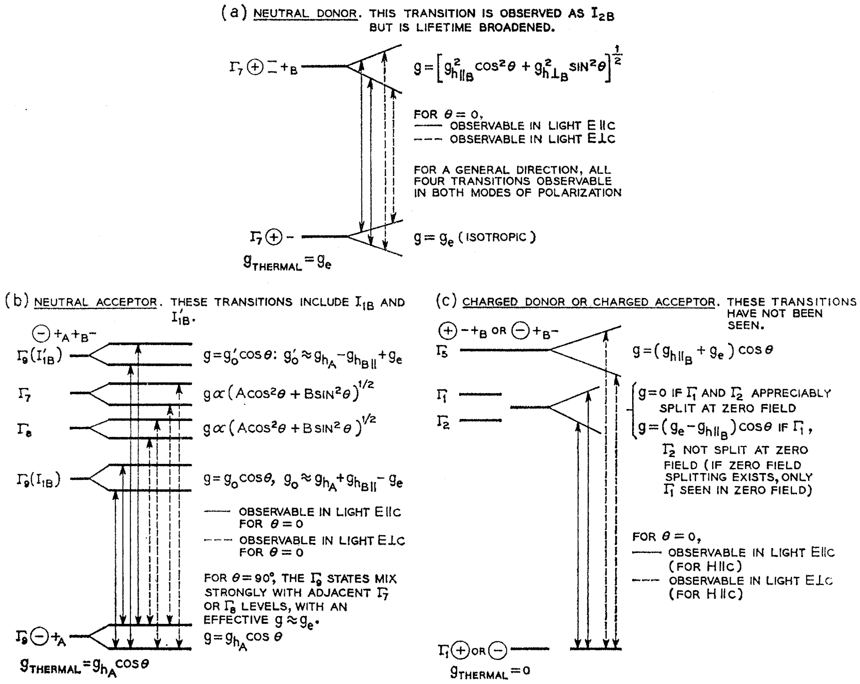

FIG. 11. A Schematic representation of the energy levels of complexes which can be formed using holes from the second, or $B$, valence band as well as from the top, or $A$, valence band.

## D. Application to States Involving the Second Valence Band in CdS

Given a neutral or charged donor or acceptor (taking in the case of the acceptor, a hole in the top valence band), it is, of course, possible to bind to this center an exciton made from an electron plus a hole in the second ($\Gamma_7$) valence band. Such states should lie about 0.016 eV (the splitting of the top two valence bands) above the corresponding bound state involving an exciton from the first valence band. At low temperatures, states involving the second valence band should not occur in fluorescence, but can, of course, occur in absorption. Results analogous to those of Fig. 10 are given in Fig. 11 for states involving a hole from the second valence band.

The case of the neutral donor is very like the case of the neutral donor in Fig. 10 except that now transitions are allowed (with roughly the same oscillator strength) in both modes of polarization. General intensity expressions are, in all cases, somewhat lengthy, so they have not been given.

The case of the charged donor or charged acceptor is complicated, because of the possibility of two splittings in zero field due to the fact that three different states are possible. In the case of the excitons in ZnO, the splitting between the $\Gamma_1$ and $\Gamma_2$ states is negligible, and the $\Gamma_1$ line shows a linear Zeeman effect for $H\|c$. The Zeeman splitting in Fig. 11 is given for both possibilities. The exact form of the Zeeman splittings in $H\perp c$ depends on the size of the exchange splitting between $\Gamma_5$ and the other two states in a fashion qualitatively similar to the charged donor of Fig. 10.

The case of the neutral acceptor becomes much more complicated. Since the holes are in different bands, each hole remains free to orient in two possible spin states and four possible energy levels separated by electron-hole and hole-hole exchange interactions will occur. In this case, it becomes very difficult to gain information from $g$ values since the $g$ value of both holes will depend on the binding. The symmetry restrictions and the $g$ values of all states are given in Fig. 11.

## E. $\Gamma_7 \rightarrow \Gamma_9$ Hole Relaxation and Lifetime Broadening

A free hole at $\mathbf{k}=0$ in the $\Gamma_7$ valence band in CdS can spontaneously emit a phonon and convert itself into a hole in the $\Gamma_9$ band. Since the bands are derived from the same atomic levels, a typical deformation potential of perhaps 2 eV is expected for this hole-conversion phonon interaction. This process is not particularly fast in the case of free holes, for the hole recoil necessitated by the conservation of momentum carries off most of the energy, and the phonon involved is of rather low energy. Bound $\Gamma_7$ holes can similarly convert themselves to bound $\Gamma_9$ holes. In this latter case, the phonon carries off all the energy ($\approx$0.016 eV) and the process is much faster. Accurate calculations of this lifetime are difficult. Estimates indicate that the transition in the case of bound holes is sufficiently rapid so that the lifetime broadening due to this transition could be as large as several electron millivolts.

The observed widths of lines $I_{2B}$ and $I_{1B}'$ which are much greater than the corresponding widths of lines $I_2$ and $I_1$ are attributed to lifetime broadening due to $\Gamma_7 \rightarrow \Gamma_9$ hole conversion with phonon emission.

That $I_{1B}$ should not be broadened by the same mechanism can be understood in terms of the details of deformation-potential coupling for transitions involving hole conversion. There is no change in the *net* charge in any unit cell in this process, but only changes in the charge distribution within each shell. Piezoelectric effects will therefore be rather small. If the wave functions are regarded as being entirely of $P_{3/2}$ parentage, the conversion process is

$$[(P_x+iP_y)\downarrow+\alpha P_z\uparrow]\rightarrow(P_x+iP_y)\uparrow \quad \text{or} \quad (P_x-iP_y)\downarrow.$$

For a simple deformation potential which alters the energies of the $P_x$, $P_y$, and $P_z$ states with respect to each other, of the two possible processes, only the *second* can take place, for the first process involves spin flip. The change in angular momentum around the $z$ axis is 2.

Of the two possible states for $I_{1B}$ and $I_{1B}'$, one has a hole $z$ component of angular momentum $J_z=2$, the other $J_z=1$. *One* of these two orientations has the property that the $\Gamma_7$ hole cannot decay into a $\Gamma_9$ hole and become an excited $I_1$ center because the necessary hole state is already occupied. The other of these two orientations has the necessary hole state vacant and therefore decays.

This argument presupposes that hole-hole $j$-$j$ coupling is the dominant source of the splitting of $I_{1B}$ and $I_{1B}'$. Since the states $I_{1B}$ and $I_{1B}'$, in fact, have the same symmetry, the previous argument is true only neglecting certain kinds of configuration interaction and neglecting weaker phonon couplings. It nevertheless shows why one might expect orders of magnitudes of difference between the lifetime broadening of $I_{1B}$ and $I_{1B}'$.

According to this argument, $I_{1B}'$ corresponds to an excited state in which the two holes have their angular momenta parallel (and parallel to the $c$ axis) and $I_{1B}$ to the holes having their angular momenta antiparallel.

### F. Electron-Hole and Hole-Hole *j-j* Coupling

As in the case of atoms, bound electrons and holes can be expected to exhibit some weak form of general spin-orbit coupling. Since the atomic spin-orbit coupling is large and is included in the energy band structure, remaining interactions are equivalent to a $j$-$j$ coupling scheme. It is not possible to observe splittings due to such coupling in excitons bound to a neutral donor or in excitons of band $A$ bound to acceptors of band $A$, because of the fact that the exclusion principle forces the two like particles into an antisymmetric state having no angular momentum. In the case of excitons bound to ionized centers ($I_3$), excitons of band $B$ bound to acceptors of band $A$ ($I_{1B}$ and $I_{1B}'$) and free excitons, splittings due to $j$-$j$ coupling should be possible.

For the case of the hole-hole interaction, if the sulfur atom is regarded as being $j$-$j$ coupled, a crude estimate can be obtained for hole-hole $j$-$j$ coupling when the holes are in the same unit cell. This estimate should then be reduced for the bound centers by the probability of finding the two holes in the same cell. When the two holes are on the same atom, the electronic configuration is similar to that of a neutral sulfur atom. By considering the expectation value of the spin-orbit energy for a hypothetical sulfur atom, in which each hole has been arbitrarily constrained to have a particular orbit and spin wave function corresponding to the top two valence bands in CdS, the effective $j$-$j$ coupling of the holes in the top two valence bands can be estimated from the energy levels of the sulfur atom. It is found that this coupling is about 0.4 eV in sulfur and the sign of the coupling is such that if the holes from the top two bands have their $z$ components of angular momentum parallel, the state lies

$$0.4P(0)\text{ eV}$$

*higher* in energy than the state with the $z$ components antiparallel. $P(0)$ is the probability that the two holes in a bound state lie in the same unit cell.

In the case of electron-hole $j$-$j$ coupling, a similar crude estimate can be made based upon the energy levels of the neutral argon atom. This coupling amounts to

$$0.04P'(0)\text{ eV},$$

with the state of highest angular momentum this time lying lowest. The estimate given is for a hole in the top valence band in CdS. In this latter expression, $P'(0)$ is the probability that the electron and the hole lie in the same unit cell. These results give a qualitative explanation of the separation and ordering of the energy levels for an exciton of band $B$ bound to an acceptor of band $A$. The hole-hole $j$-$j$ coupling is largest, so it will be treated first. The two holes put on an acceptor produce two twofold-degenerate states, one of symmetry $\Gamma_5$ and the other of symmetry $\Gamma_6$. The $\Gamma_5$ state, having the $z$ components of hole angular momentum antiparallel, lies lowest. By the arguments of Sec. IV E, it is the $\Gamma_6$ state which can rapidly decay to the two holes in band $A$, and therefore, the upper state which will be lifetime broadened. The extra added electron weakly couples its spin to the resultant hole angular momentum. The wave functions are most easily understood by writing them out explicitly as follows:

$$\begin{aligned}\Gamma_9:&\quad[(P_x+iP_y)\uparrow][(P_x+iP_y)\downarrow+\alpha P_z\uparrow][\downarrow],\\ \Gamma_8:&\quad[(P_x+iP_y)\uparrow][(P_x+iP_y)\downarrow+\alpha P_z\uparrow][\uparrow],\\ \Gamma_7:&\quad[(P_x+iP_y)\uparrow][(P_x-iP_y)\uparrow+\alpha P_z\downarrow][\downarrow],\\ \Gamma_9:&\quad[(P_x+iP_y)\uparrow][(P_x-iP_y)\uparrow+\alpha P_z\downarrow][\uparrow].\end{aligned}$$

The first factor represents the orbital (atomic) wave function of the odd electron in valence band $A$; the second factor that for the odd electron in band $B$; the third for the electron in the conduction band. The arrows represent spin states. Each state is, of course, doubly degenerate by time reversal. The ordering of the states is that determined by the signs of the electron-hole and hole-hole $j$-$j$ couplings.

That the state ordering is correctly given can be seen by the magnetic splitting and shifts for $H \perp c$ (Fig. 7(b)) with $E \| c$ where it is clear that the top $\Gamma_9$ state moves upward and the bottom $\Gamma_9$ state moves downward. The bottom $\Gamma_7$ state also becomes visible by mixing with the bottom $\Gamma_9$ state.

The $g$ values for $H \| c$ given for the two $\Gamma_9$ levels in Fig. 11 were assigned to their particular levels on the basis of the qualitative understanding of lifetime broadening, and the ordering of energy levels on the basis of hole-hole and electron-hole $j$-$j$ coupling.

In the case of $I_{1B}$ and $I_{1B}'$, the bound state is complicated enough that no estimates of $P(0)$ can be reliably made. The observed hole-hole $j$-$j$ coupling of $1.3 \times 10^{-3}$ eV would require a hole-hole $P(0)$ of about $3 \times 10^{-3}$. Since no adequate wave function for such a center exists, no independent estimate of this $P(0)$ exists.

The observed electron-hole $j$-$j$ coupling induced splitting of $I_{1B}$ and $I_{1B}'$ states, and of $I_3$ as well, is about $4 \times 10^{-4}$ eV. $I_3$ shows the same sign of this coupling as do the states around $I_{1B}$ and $I_{1B}'$. As expected the state with the electron and hole $j$'s lying parallel occurs at the lowest energy. This magnitude of coupling would demand a $P(0) \approx 10^{-2}$ for the electron and hole. By way of comparison, the probability that an electron bound to a hydrogenic donor (ground state) is in the unit cell containing the donor atom is about $10^{-3}$.

Clearly, the estimates of the electron-hole and hole-hole $j$-$j$ couplings can be regarded only as qualitative. That these couplings exist is, experimentally, clear. It also appears that these couplings have the sign and rough order of magnitude which can be expected for simple $j$-$j$ coupling which arises from atomic spin-orbit couplings. These atomic couplings will be important only when the electron and hole (for example) are in the same unit cell.

For an exciton bound to a charged donor or acceptor, or for the exciton itself, the oscillator strength per center for simple optical transitions is proportional to the probability that the electron and hole are in the same cell. The electron-hole $j$-$j$ coupling is proportional to the same probability. A relation is thus determined between the integrated absorption, the center concentration, and the $j$-$j$ coupling splitting for states involving only one electron and one hole. It would be of interest to know if this relation is obeyed.

Due to the energy difference between longitudinal and transverse excitons,[4] it has not yet proved possible to evaluate directly the electron-hole $j$-$j$ coupling in the exciton itself.

## V. CONCLUSIONS FROM COMPARISON OF THEORY AND EXPERIMENT

In this section, it will be shown that a number of types of centers which have been discussed in Sec. IV can be identified with many of the experimentally observed lines. This is done chiefly by means of a comparison of the expected and observed Zeeman patterns of the lines. The results of this analysis have been indicated in the last column of Table I.

### Line $I_1$

$I_1$ always shows linear Zeeman effects so that in all probability it has only one unpaired spin in both excited and ground states and so must arise from a neutral donor or acceptor. For $c \perp H$ the absence of any thermalization in the absorption spectrum shows that the ground state has zero $g$ value. For $c \| H$ the thermal $g$ value is nonzero. This magnetic behavior is that expected of a hole in the top valence band of CdS. We may, therefore, conclude that the ground state of $I_1$ is a neutral acceptor, and the excited state is a complex of the neutral acceptor and an exciton, in which the two hole spins pair in an antisymmetric spin state. The $g$ value of the excited state is the isotropic $g$ value of the electron. The inner pair of lines in Fig. 4 give $|g_e - g_h|$, and the outer pair $|g_e + g_h|$. This is known from the allowed transitions for $c \| H$ indicated in Fig. 10, and from the knowledge that only the inner pair are seen for $c \| H$. (The outer pair increase in strength with varying $\theta$ in at least qualitative accord with the expressions of Fig. 10.) The linear relations of Fig. 4 show that the $g$ values are given by

$$g_e \pm g_h = g_{e0} \pm g_{h\parallel} \cos\theta \cdots \tag{1}$$

where $g_{e0} = -1.7_6$, is the isotropic $g$ value of the electron in the complex $\ominus \genfrac{}{}{0pt}{}{+}{+} -$. $g_{h\parallel} = -2.7_6$, is the $g$ value of the neutral acceptor for $c \| H$. It may be noticed that the $g$ value of the acceptors in CdS would be difficult to determine by conventional spin resonance methods, since the hole is derived from an $M_J = \pm 3/2$ band and so demands a $\Delta M = 3$ quantum jump which is, of course, forbidden. The fact that for $c \| H$ the high energy absorption line is stronger than the low-energy line at low temperatures is consistent with the ground state having a larger $g$ value than the excited state, and the holes concentrating in the lower of the two energy levels available to them.

We have only observed one line which behaves like $I_1$, and so we detect only one neutral acceptor state in our crystals. This may be because there is only one acceptor present in appreciable concentration. Another possible reason is that other acceptors have stronger coupling to acoustic phonons, so that the optical strength in the sharp no-phonon part of the line becomes immeasurably small. Because $I_1$ is so constant from one crystal to another, it is tempting to ascribe it to a cadmium vacancy but at present, there is no further evidence for this.

### The $I_2$ Lines

Like $I_1$, the $I_2$ lines show linear Zeeman effects. For $c \perp H$ absorption thermalization is present so the states must have an electron in the ground state and arise from neutral donors. Figure 4 shows that the $g_{\parallel}$ value of the hole in the complex $\oplus\ \overset{-}{-}\ +$ has a value of $-1.7$ which is almost exactly equal to $-1.7_1$, the $g$ value of the donor. This accident results in there being no observable splitting of $I_2$ with $c\|H$. The high-energy line being strong for $c\perp H$ is consistent with the ground state having a larger $g$ value than the excited state (which, in this case, is zero). The several $I_2$ lines must arise from a variety of donors, to which the binding energy of the excitons are slightly different. The $I_2$ states all lie within about $1.5\times10^{-3}$ eV of each other. It is possible that, above the group of donor lines near $I_2$, there are other lines which are also associated with donors. Unfortunately, because of the proximity of the strong exciton absorption these cannot clearly be distinguished. It is interesting to notice that the results of $I_1$ and $I_2$ show that the electron has a $g$ value that is, indeed, isotropic and virtually independent of its state of binding. The hole $g$ value, as expected, is completely anisotropic and is sensitive to its state of binding. Thus, the free hole has $g_{\parallel}=-1.1_5$,[4] in the complex $\oplus\ \overset{-}{-}\ +$ it is $-1.7$, and in the acceptor it is $-2.7_6$.

Both $I_1$ and $I_2$ behave as would be expected for neutral acceptors and donors respectively, under the influence of infrared light.

### Line $I_3$

The infrared quenching experiments indicated that this line probably arose from an exciton bound to an ionized donor or acceptor. The position of this line, about 0.0038 eV below that of the exciton from which it is derived indicates strongly that an ionized donor is involved. The reasoning is as follows. Such a center may equally well be regarded as a donor to which is bound a hole. The binding energy of a hole to a neutral donor must be small—of the order of a few milli-electron volts. Consequently, the center would be expected to have an energy equal to that of the forbidden gap less an energy slightly larger than the donor binding energy. The free exciton has a binding energy of 0.029 eV,[4] so that experimentally $I_3$ has an energy 0.033 eV less than the band gap. The donor binding energy is about 0.032 eV.[6] The minimum value for an acceptor binding energy is estimated to be 0.4 eV,[4] and so, had $I_3$ been derived from an ionized acceptor, it would be expected to have an energy at least 0.4 eV less than that of the band gap. Effects due to an exciton bound to the ionized $I_1$ center have yet to be observed.

The magnetic behavior of $I_3$ confirms that it involves an ionized center, for the Zeeman splitting with $c\perp H$ shows that there is a zero-field splitting of $3.1\times10^{-4}$ eV (see Figs. 5 and 6), due to the exchange interaction between the unpaired hole and electron. In accord with the formulas of Fig. 10, the effective $g$ value splitting the $\Gamma_5$ and $\Gamma_6$ states is $1.7_4$, the $g$ value of the electron. For $c\|H$ the $\Gamma_6$ state is not seen and the $\Gamma_5$ state should split linearly with a $g$ value of $|g_e-g_{h\parallel}|$. In fact, no splitting could be detected for $c\|H$ and we conclude that by chance, the $g$ value of the hole and electron in this complex are approximately equal.

### The Lines $I_{1B}$, $I_{1B}'$ and $I_{2B}$

As described above, the position, polarization properties, and infrared quenching behavior of lines $I_{1B}$ and $I_{1B}'$ strongly suggested that they are derived from the neutral $I_1$ center and an exciton including a hole from the second, or $B$ valence band. Similarly, the position of $I_{2B}$ which is as far below exciton $B$ as $I_2$ is below exciton $A$ suggests that $I_{2B}$ is derived from the neutral $I_2$ center and exciton $B$. The expected magnetic behavior of this type of state has been given in Fig. 11. $I_{1B}'$ and $I_{2B}$ are both broadened by a rapid conversion of the $B$ hole into the $A$ hole. This prevents useful Zeeman observations. As discussed in Sec. IV E, this process should not be nearly so rapid for $I_{1B}$. This line does, in fact, remain sharp and Zeeman measurements are possible. $I_{1B}$ and $I_{1B}'$ in zero field are separated by $1.5\times10^{-3}$ eV which essentially represents the energy difference between the two possible combinations of the $j$ values of the two holes. Each of these states can be combined with the two possible orientations of the electron to produce a total of 4 states. The electron-hole interaction is, however, smaller than the hole-hole interaction. This is seen in the $c\perp H$ splitting of $I_{1B}$ shown in Fig. 7(b), where an extrapolation of the lines to $H=0$ gives an energy difference of $0.27\times10^{-3}$ eV which represents the electron-hole interaction energy in this state. This is in agreement with the value determined from a comparison of the $E\|c$ and $E\perp c$ spectra for $H=0$. The effective $g$ value for this splitting is $-1.8$. The $g$ value for the $c\|H$ splitting is $-2.07$. Since the ground state of $I_{1B}$ is the neutral acceptor with a hole from the $A$ valence band there should be no thermalization effects in absorption with $c\perp H$, as is indeed the case. With $c\|H$ thermalization effects occur which show that the excited state has a larger $g$ value than the ground state, which is also the expected result. $I_{1B}'$ seems to indicate the same $g$ value for $c\|H$ as $I_{1B}$, but with a reversed thermalization effect, in accordance with expectation.

## VI. CONCLUSIONS

The study of the Zeeman effect of optical transitions for which the excited state consists of an exciton bound to an impurity has permitted the generic identification of various transitions as being due to a neutral donor, ionized donor, etc. The Zeeman effect alone was capable of making this identification, using in addition only the fact that the $g$ value of the electron in CdS is $\sim-1.8$ and isotropic, and the $g$ value of a hole in the top valence band is zero for $H\perp c$. The general technique will also work in cubic crystals; all that is really needed is an established difference between the valence and conduction-band magnetic effects. In cubic II–VI and III–V components, the fourfold degeneracy of the valence band at $\mathbf{k}=0$ provides such a discrimination.

That (compensated) acceptors could be pumped up to a sufficient level of hole occupancy to produce sizable absorption is not surprising at these low-doping levels. The rate of filling of these levels by tunneling from neutral donors will be small for the large separations involved. The experiments involving "bleaching" of the holes from the acceptors by infrared light gives additional confirmation of the center identifications. The simultaneous presence of both neutral donors and neutral acceptors at concentrations of the order of $10^{17}$ under normal illumination conditions at low temperature points out one of the hazards of trying to identify optical centers by chemistry alone. (Without Zeeman studies, $I_1$ would have been mistakenly assigned, since only ionized acceptors would have been expected.) From the point of view of photoconductivity, it is useful to note that an additional parameter clearly related to infrared quenching of photoconductivity can be measured, namely, the concentration of holes on acceptors.

A wealth of absorption and fluorescent lines were observed which were not described. Some correspond to observed transitions with optical or acoustic phonon cooperation. Others presumably arise from excited molecular configurations.

Transitions in which an exciton from the second valence band was bound to a donor, or acceptor from the first valence band, were also observed. These transitions are lifetime broadened by a process in which the hole changes valence bands with the emission of a phonon to conserve energy. In some cases, however, symmetry considerations tend to forbid this phonon processes, and the lines remain narrow.

Splitting of energy levels by electron-hole and hole-hole *j-j* coupling was observed in the two cases (an exciton bound to an ionized donor, and an exciton from band *B* bound to an acceptor with a hole from band *A*), where the exclusion principle permits such splittings. The splittings have values in order of magnitude agreement with the calculated values. Of particular interest is the electron-hole *j-j* coupling on an ionized donor or acceptor for it should be related to the oscillator strength per center by a proportionality factor independent of configuration.

All symmetry arguments given were based on the point group of wurtzite, although the actual symmetry of substitutional point defects is $C_{3v}$. The use of the higher symmetry group is of definite advantage for the weakly bound centers, for it sets small optical matrix elements and small magnetic moments (which would be zero in the effective-mass approximation) equal to zero, while at the same time describing state degeneracies properly.

The binding energy of an exciton to a neutral acceptor (0.018 eV), a neutral donor (0.007 eV), and a charged donor (*ca.* 0.001 eV) agree remarkably well with simple extrapolations of hydrogen-molecule binding energies for the appropriate configurations. The *g* value of the electron is almost independent of the state of binding. The *g* value of the hole shows a strong effect of binding, presumably because of the almost degenerate valence bands.

Several donors, but a unique acceptor were present in the crystals investigated. It is tempting to ascribe this unique acceptor to a stoichiometric defect, perhaps a cadmium vacancy.

It is hoped that, with these guideposts, it will be possible to identify in doped crystals (in which, because of line broadening and the usual quenching of fluorescence, the bulk of the present experiments would not have been feasible) the chemical impurities which are responsible for the various centers. It is believed that the present assignments are firmly enough based to answer the question of what causes the plethora of sharp, weak, and sample dependent emission and absorption lines near the exciton absorption in CdS.