Donor-Acceptor Pair Recombination Spectra in Cadmium Sulfide Crystals

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(Received 13 June 1969)

Discrete donor-acceptor pair lines converging to the 5163 Å broad green peak are reported. The lines are characterized in zero magnetic field by spin-exchange splitting which decreases with increasing pair separation. Some of the lines also show zero-magnetic-field splitting due to crystal-field effects. A set of closely spaced lines converging at 2.518 eV is also reported. This set of lines can be interpreted as donor-acceptor pair lines in which the recombination goes to an excited state of the acceptor. A good theoretical fit to the energy profile of the pair lines was not achieved. The density of pair lines can be accounted for by a single donor and acceptor.

I. INTRODUCTION

THE broad green phonon-assisted emission bands in CdS have been investigated by a number of researchers dating back more than 20 years.[1–4] During this time it was shown that the low-energy band could be interpreted in terms of bound-to-bound transitions, while the high-energy band was interpreted as free to bound transitions.[5,6] Thomas *et al.*[7] showed, on the basis of time resolved spectroscopy, that the low-energy band at 5176 Å was due to donor-acceptor pair recombination. At the time isolated pair lines of the type that had been seen[8] in GaP had not been observed in CdS.

More recently, it has been reported[9] that two distinct low-energy bands and two distinct high-energy bands are present in CdS. These bands were designated as X and Y "series." The Y series was interpreted as bound-to-bound transitions with one band occurring at 5179 ± 3 Å and the other band at 5163 ± 3 Å at 4.2°K. Very recently, discrete line donor-acceptor pair spectra have been reported in CdS by Henry *et al.*[10] This work reports a series of discrete lines that converge to the 5176 Å broad green band.

We report here discrete donor-acceptor pair lines that converge to the 5163 Å broad green band. The spectrum differs in some respects from that observed by Henry *et al.* Many more discrete lines are observed, which is partially due to a large number of closely spaced lines converging to approximately 2.518 eV, which we interpret as the donor pairing with an excited state of the acceptor. The zero-field splittings of the various pair lines, resulting from spin exchange, vary appreciably, whereas they were the same for all pair lines reported by Henry *et al.* On the other hand, there is a great deal of similarity between the spectra we observed and those observed in the previous report. The Zeeman splitting of the lines is simple as was previously reported. Splitting is observed in many lines due to crystal-field effects. The observed pair lines are not very well accounted for by a calculation which considers only Coulomb interactions of the hole and electron.

II. EXPERIMENTAL

The crystals used in these experiments were of the platelet type and were grown from the vapor phase. The crystals were not doped with foreign impurities. The crystals ranged in thickness 0.5–50 μ and were mounted strain free in a glass helium Dewar. The samples were immersed in the liquid helium. Provision was made for pumping on the liquid helium, and the temperature was measused by means of vapor-pressure thermometry, using an oil manometer. All of the measurements were made at approximately 1.2°K; however, the pair spectrum was visually observed at 4.2°K. Zeeman measurements were made, using a conventional dc electromagnet, at fields up to 40 000 G. The pair spectra were excited with a 500-W Hg lamp (Osram high pressure), equipped with a filter designed to pass the 3650 Å line of mercury. The emission spectrum was analyzed with a Bausch and Lomb 2-m grating spectrograph. The spectrograph was equipped with a large high-resolution diffraction grating and produced a reciprocal dispersion of approximately 2 Å/mm in first order. All of the spectra were photographically recorded either on Kodak type 103 a-F or Ilford type N. 50 spectroscopic plates.

III. RESEARCH AND DISCUSSION

A. Pair Spectra (Ground State)

Approximately 280 discrete lines were observed in the pair-spectra region. One set of discrete lines converged to the broad green band at 5163 Å. The highest-energy pair line, identified by Zeeman studies (see Sec. III C),

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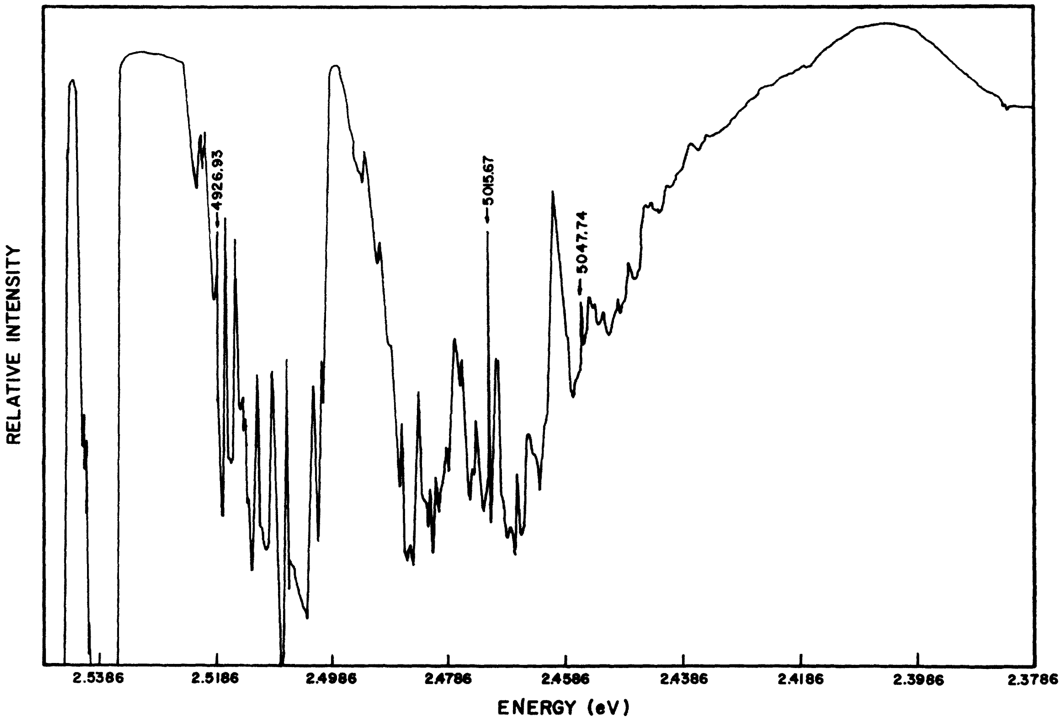

FIG. 1. Emission spectra showing donor-acceptor pair recombination from a CdS platelet.

occurred at approximately 4875 Å. Higher-energy lines, believed due to pairs, could not be identified by Zeeman studies because of interference from bound exciton lines in the same spectral region. The lowest-energy discrete-pair line occurred at approximately 5120 Å. At lower energies the lines could not be resolved.

A densitometer trace of the observed spectra is shown in Fig. 1. Very many of the discrete line spectra were not resolved by the densitometer. Figure 2 is a plot of the observed lines detected with a Gaertener spectroscopic plate reader. The two most intense bound exciton lines present in the spectra are the I_1 (4888.47 Å) line and the I_5 (4869.14 Å) line. The I_1 line has been previously identified as an exciton bound to a neutral acceptor site, and the I_5 line has been identified as an exciton bound to a neutral donor site. The two lines are of approximately the same intensity in these crystals. This would suggest that these two centers play an important part in the donor-acceptor pairs.

From the present work it is not possible to positively

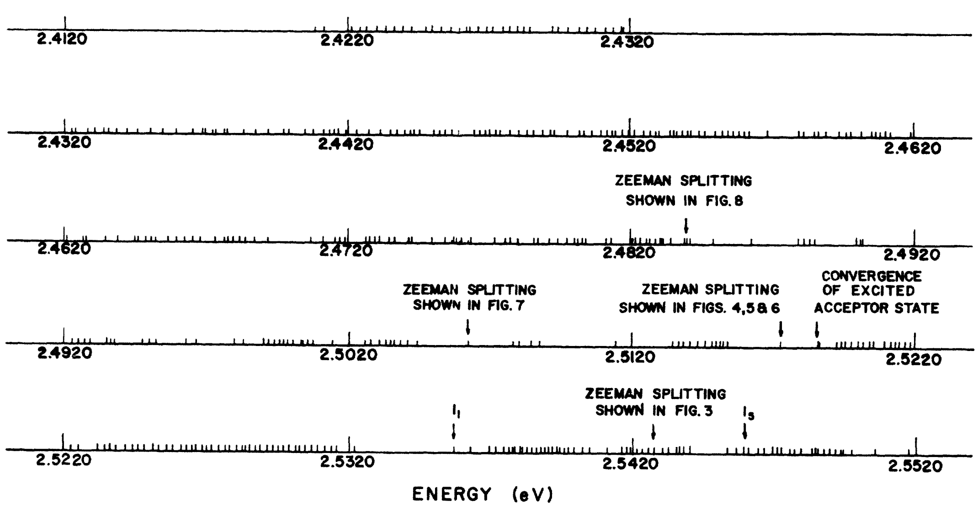

FIG. 2. Plot of the energy position of the donor-acceptor pair lines from the platelet of Fig. 1 detected with a spectroscopic plate reader.

identify the donor or the acceptor involved. It is apparent that the set of pair lines which converge to 5163 Å is different from the donor-acceptor transitions of Henry *et al.*[10] Their lines converged to a peak at 5176 Å. The model of Kingston *et al.*[9] suggests that we are dealing with a different acceptor but the same donor. (The present experiments do not permit one to decide this issue.) Using a donor binding energy of 0.026 eV and the series limit as $R\to\infty$ of the equation

$$E=E_{\mathrm{gap}}-(E_D+E_A)+e^2/[\epsilon_\perp\epsilon_{\|}(x^2+y^2)+\epsilon_\perp{}^2z^2]^{1/2}, \quad (1)$$

one has an acceptor binding energy of 0.155 eV. In this equation E_{gap} is the energy of the fundamental gap, E_D is the binding energy of the donor, E_A is the binding of the acceptor, and $\epsilon_\perp$ and $\epsilon_{\|}$ are the dielectric constants of the perpendicular and parallel directions. One similarity between the spectra of Henry *et al.* and this work is that there is not a one-to-one correspondence between values calculated with Eq. (1) and those observed. However, the density of lines in the discrete line spectral energy range is of the right magnitude. When looking at GaP this is not the case; one gets excellent agreement between calculations and experiment.

Identical pair spectra have been observed for several different crystals, all converging to the 5163 Å green band. This includes the same line positioning as well as relative line intensities. It appears that the spectra are derived from single donor-acceptor combinations.

B. Pair Spectra (Excited States)

Another set of discrete lines composed of a large number of closely spaced energies appear to converge approximately at 2.581 eV. The lines diminish in intensity near the convergence limit. This we believe is due to the lower reaction rate between donor and acceptor as the separation becomes larger. As the lifetime for recombination from the excited state approaches the lifetime of the hole in an excited state, fewer recombinations from the excited state will occur resulting in decreased intensity. This places some uncertainty on the convergence limit; however, it will be very close to 2.518 eV. In the region 2.532–2.536 eV, the lines are obscured by the acoustical phonon wing of the more intense I_1 line. If one assumes, as in the above discussion, that the donor binding energy is 0.026 eV and use Eq. (1) as $R\to\infty$, an acceptor binding energy of 0.038 eV is obtained. This binding energy for a ground-state acceptor is much smaller than the binding energy of any known acceptor in CdS. However, if one assumes that we are observing an excited state of the acceptor, and that it is the hydrogenic $n=2$ state of the previous discussed ground state, a value of 0.039 eV would be obtained. This is very close to the value observed and a plausible explanation for the high-energy series. Although this is the first time an excited state of an acceptor has been seen in CdS, a donor-acceptor pair recombination involving the first excited state of the donor has been previously reported for GaAs.[11] Unfortunately, the Zeeman spectra of these lines could not be resolved because they were so closely spaced. However, they do show magnetic field splittings.

C. Zeeman Splitting of Pair Lines

1. Theoretical Background

The effect of a magnetic field H upon the pair spectra of these crystals can be explained by the theory of Henry *et al.*[10] That is, one assumes an effective Hamiltonian of the form

$$H=\tfrac{1}{2}g_e\beta_0\mathbf{H}\cdot\boldsymbol{\sigma}+g_h\beta_0\mathbf{H}\cdot\mathbf{J}+\alpha_J\mathbf{J}\cdot\boldsymbol{\sigma}. \quad (2)$$

Here g_e and g_h are the g factors of the electron and hole, respectively, and β_0 is the Bohr magneton, J is the total angular momentum operator of the hole ($J=\frac{3}{2}$), and σ is the Pauli spin operator of the electron. The first two terms are the Zeeman terms and the last is the j-j coupling operator. In using Eq. (2) the difference between the wurtzite and zinc-blende structure has been ignored. Also, the true exchange term pointed out by Akimoto and Hasegawa[12] as well as other terms which are of higher order are ignored. The effect of the donor field plus the fact that the $J=\frac{1}{2}$ states are split from the $J=\frac{3}{2}$ states are reflected in the hole wave function:

$$|\phi_{\pm3/2}\rangle=|\pm\tfrac{3}{2}\rangle-\frac{1}{\Delta}[|\pm\tfrac{1}{2}\rangle\langle\pm\tfrac{1}{2}|V|\pm\tfrac{3}{2}\rangle \pm|\mp\tfrac{1}{2}\rangle\langle\mp\tfrac{1}{2}|V|\pm\tfrac{3}{2}\rangle], \quad (3)$$

where Δ represents the splitting caused by the wurtzite change from zinc blende and V is the interaction at the acceptor caused by the donor.

From the above, one can obtain the energies of the exciton in terms of g_e, g_h, A, C, and D, where

$$A=-\alpha_J\langle\phi_{3/2}|J_z|\phi_{3/2}\rangle, \quad (4a)$$

$$C=\alpha_J\langle\phi_{3/2}|J_-|\phi_{3/2}\rangle, \quad (4b)$$

$$D=\alpha_J\langle\phi_{3/2}|J_-|\phi_{3/2}\rangle. \quad (4c)$$

Since one finds from experiment that pairs of different orientation have the same Zeeman splittings, C can be set equal to zero.

For $H\|c$, we have

$$E=\tfrac{1}{2}\{A\pm[(g_{h\|}-g_e)^2(\beta_0H)^2+|D|^2]^{1/2}\} \quad (5a)$$

and

$$E=\tfrac{1}{2}[-A\pm(g_{h\|}+g_e)\beta_0H]. \quad (5b)$$

For $H\perp c$,

$$E=\frac{1}{2}\left[[A^2+(g_e\beta_0H)^2]^{1/2} \pm|D|\left(1+\frac{A-(2\alpha/A)(g_e\beta_0H)^2}{[A^2+(g_e\beta_0H)^2]^{1/2}}\right)\right], \quad (5c)$$

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[11] J. Shah, R. C. C. Leite, and J. P. Gordon, Phys. Rev. **176**, 938 (1968).

[12] O. Akimoto and H. Hasegawa, Phys. Rev. Letters **20**, 916 (1968).

$$E=-\tfrac{1}{2}\left[\left[A^2+(g_e\beta_0H)^2\right]^{1/2} \pm|D|\left(1-\frac{A-(2\alpha/A)(g_e\beta_0H)^2}{\left[A^2+(g_e\beta_0H)^2\right]^{1/2}}\right)\right], \quad (5d)$$

where $\alpha=g_{h\parallel}/2g_e$. In some examples it appears that D is also zero. For these cases the magnetic field effect may be explained by the charged donor or charged acceptor energy relations of Thomas and Hopfield[13]:

$$E=\pm\tfrac{1}{2}H_{gh\parallel}|\cos\theta| +\tfrac{1}{2}\left[A^2+(g_eH)^2\mp 2(g_eH)A|\cos\theta|\right]^{1/2}, \quad (6a)$$

$$E=\pm\tfrac{1}{2}H_{gh\parallel}|\cos\theta| -\tfrac{1}{2}\left[A^2+(g_eH)^2\mp 2(g_eH)A|\cos\theta|\right]^{1/2}, \quad (6b)$$

where θ is the angle between H and the c axis.

2. *Measurements*

The magnetic field splittings of the pair lines were investigated in different regions of the spectrum approximately 4875–4990 Å. In particular, the Zeeman splitting of the pair line at 4875.2 Å is shown in Fig. 3. Four states are observed. The two higher-energy states at zero field result from energies described by Eq. (5c). These are allowed states because the spin of the hole and of the electron are antiparallel. The lower-energy states described by Eq. (5d) have the hole and electron spins parallel and constitute an "unallowed" doublet. The zero-field splitting between the allowed and unallowed doublets is due to the parameter A. The zero-field splitting of the allowed doublet is a measure of the magnitude of $|D|$. In Fig. 3 the energy is plotted as a function of the magnetic field for the orientation $\mathbf{H}\perp c$. The circles represent the experimental data while the solid lines are the calculated values. Note that the lower-energy transitions become allowed when the magnetic field is turned on. The fit to experiment gave a value of 0.85×10^{-4} eV for $|D|$ and a value of 2.9×10^{-4} eV for A.

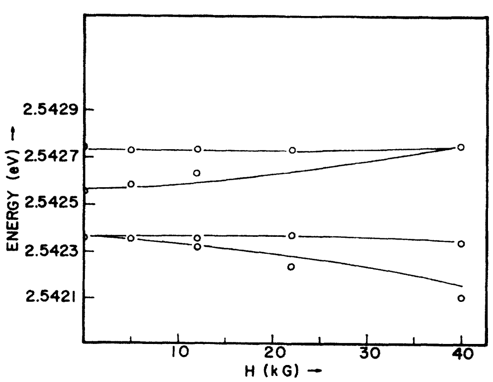

FIG. 3. Magnetic field splitting of the 4875.2 Å line as a function of magnetic field for the orientation $c\perp\mathbf{H}$. The higher-energy solid lines were calculated using Eq. (5c) and the two lower-energy lines were calculated using Eq. (5d). The diameter of the circles represent the experimental uncertainty.

[13] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

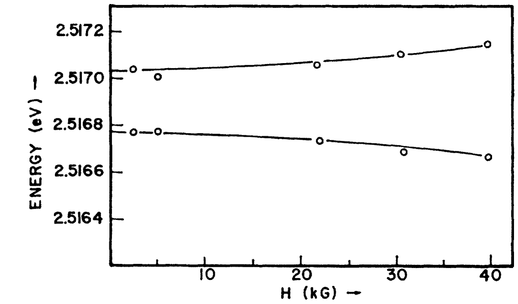

FIG. 4. Magnetic field splitting of the 4925 Å line as a function of magnetic field for the orientation $c\perp\mathbf{H}$. The solid lines in this graph were calculated using Eqs. (6a) and (6b). The circle diameters represent the experimental uncertainty.

The magnetic field splitting as a function of energy for the pair line at 4925 Å for the orientation $\mathbf{H}\perp c$ is shown in Fig. 4. The solid lines in this graph were obtained from using Eqs. (6a) and 6(b). This fit to the experimental data was obtained using the following values for the parameters: $g_e=1.76$, $g_{h\parallel}=2.76$, and $A=2.6\times10^{-4}$ eV. The splitting of this same line as a function of magnetic field is shown in Fig. 5 for $\cos\theta=0.9$. In Fig. 6 the splitting is shown as a function of $\cos\theta$ for a constant magnetic field of 40 000 G. The solid lines in both of these figures were calculated using Eqs. (6). This would indicate that this pair line has essentially the same symmetry as the lattice.

The splitting of the pair line at 4946 Å as a function of magnetic field for orientation $\mathbf{H}\perp c$ is shown in Fig. 7. The calculated energies were again obtained from Eq. 6. The same values for the parameters were used for this line as were used for the 4925 Å line with the exception that $\cos\theta=0.18$ was used rather than $\cos\theta=0.0$. This was performed with $\mathbf{H}\perp c$. It is possible to fit the data with the use of Eq. (5), however, it requires a hole g value of $g_{h\parallel}=6$. This appears to be abnormally

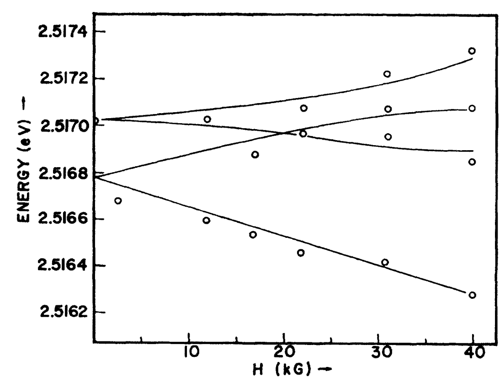

FIG. 5. Magnetic field splitting of the line in Fig. 4 as a function of magnetic field for the orientation $\cos\theta=0.9$. The solid lines were again calculated using Eqs. (6a) and (6b).

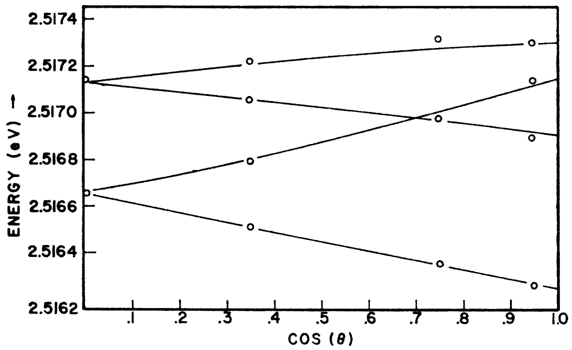

FIG. 6. Magnetic field splitting of the line shown in Fig. 4 as a function of $\cos\theta$ for a constant magnetic field of 40 000 G. The solid lines were calculated using Eqs. (6a) and (6b).

large in view of the fact that $g_{h\parallel}=2.76$ was used for all other lines.

Figure 8 shows the splitting of the 4990 Å line as a function of H for the orientation $\mathbf{H}\perp c$. The solid lines in Fig. 8 were obtained from Eqs. (5c) and (5d). The following values for the parameters were used:

$$A=1.7\times 10^{-4}\,\mathrm{eV}, \quad |D|=0.3+10^{-4}\,\mathrm{eV},$$
$$g_e=1.76, \quad g_{h\parallel}=2.76.$$

It is noted that A decreases as one goes from the high-energy pair lines to the low-energy pair lines. This would be expected as the pair separation becomes larger and the overlap of the electron and hole wave functions become smaller. The magnitude of D shows a random variation with energy and probably reflects the orientation of the pair with respect to the crystal c axis. $|D|$ should be a maximum (for the same R) when the pair is oriented normal to the c axis and a minimum when the pair is oriented along the c axis. One would expect the pairs responsible for the line at 4925 Å to be oriented along the c axis thus giving an effect of zero $|D|$ value. This is somewhat contradicted by the fact that this is a relatively intense line, while the number of equivalent pairs for a given pair separation is a minimum along the c axis.

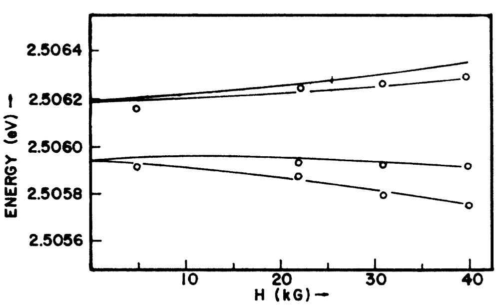

FIG. 7. Magnetic field splitting of the line at 4946 Å as a function of magnetic field for the orientation $c\perp H$. The solid lines were calculated using Eqs. (6a) and (6b) with a value of $\cos\theta=0.18$. The diameters of the circles represent the experimental uncertainty.

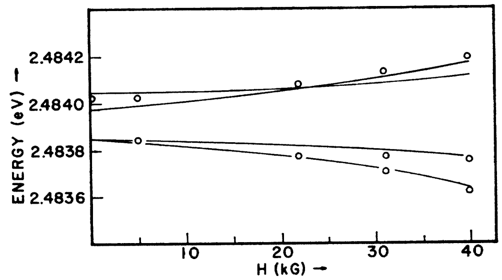

FIG. 8. Magnetic field splitting of the 4990 Å line as a function of magnetic field for the orientation $c\perp H$. The solid lines were calculated using Eqs. (5c) and (5d). The diameters of the circles represent the experimental uncertainty.

IV. CONCLUSIONS

The magnetic field splittings of all of the lines were accounted for with $g_e=1.76$ and $g_{h\parallel}=2.76$, in agreement with the pair spectra observed by Henry *et al.*[10] The Zeeman patterns of all of the pair lines were simple again in agreement with Ref. 10. None of the lines were observed to split into more than four components which are accounted for by having $C=0$. This is indeed remarkable since there can be as many as 12 equivalent pairs for a given pair separation having different orientations in the lattice. One should reasonably expect different magnetic field splittings for the different orientations. This has not been observed. The set of lines converging at 2.518 eV is of great interest. To account for a convergent set of lines in this energy region due to donor-acceptor pair recombination requires a shallow acceptor ($\sim$0.04 eV). Acceptors of this kind have never been reported in CdS. Recombination to the first excited state of the acceptor giving rise to the donor-acceptor pair lines converging at 5163 Å fits the data quite well.

ACKNOWLEDGMENT

We wish to thank Dr. C. H. Henry for valuable discussions during this investigation.