Emission from Excited Terminal States of Bound Exciton Complexes

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Dedicated to Professor H. Gobrecht *on the occasion of his 60th birthday*

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Emission from the excited terminal states of bound exciton-donor complexes has been observed in several II—VI compounds. Studying these optical transitions allows one to determine the donor ionization energies, the electron effective masses as well as the electron *g*-values in these materials. A good theoretical fit to the experimental data was obtained, using the effective mass approximation. Emission from the excited terminal states of bound exciton-acceptor complexes has not yet been observed in these materials. There is no basic reason why such transitions should not occur. Studying transitions of this type would allow one to obtain fundamental information concerning the acceptor impurities in these materials.

Measurements 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[1,2,3]. These investigations were made by studying infrared absorption in magnetic field.

The highest quality crystals obtainable in II-VI materials are platelet type crystals. These crystals are very thin (0.5 μ—50 μ), as a result they are not suitable for infrared absorption studies. Information similar to that obtained from infrared studies can be obtained from studying the transitions to excited states of the bound exciton complexes.

It is the purpose of this paper to report on bound exciton transitions 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 that of 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 ($g_h = g_{h_\parallel} \cos\theta$), 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 $C \perp H$, then in the upper state (see Fig. 2) 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 elctron 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 ($0° \leqq \theta \leqq 90°$) have demonstrated the additional multiplicity due to hole splitting.

I. Experimental

The crystals used in these experiments were of the platelet type and were grown from the vapor phase[5]. It has been

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[1] H. A. Fan and P. Fisher, J. Phys. Chem. Solids 8, 270 (1959).

[2] W. S. Boyle, J. Phys. Chem. Solids **8**, 321 (1959).

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[5] D. C. Reynolds, in: The Art and Sciences of Growing Crystals (ed. by J. J. Gilman), John Wiley & Sons, Inc., New York 1963, p. 62.

observed that the platelet type crystals are the highest quality crystals available and are therefore the most desirable for the 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 so that the samples were immersed in liquid helium. 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. The dewar tip was inserted in the air gap of a conventional dc electromagnet, the pole tips of which were separated by 7,95 mm. The maximum field strength of this magnet was 45000 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 & Lomb 2-m grating spectrograph. The spectrograph employed a large, high resolution, diffraction grating and produced a reciprocal dispersion of approximately 2 A/mm in first order. With this grating, the psectrographic aperture was about *f*/16. All of the spectra were photographically recorded.

II. 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 identified with neutral donors or acceptors[4]. In this experiment five lines were observed in zero field at 2.5214 eV, 2.5220 eV, 2.5235 eV, 2.5254 eV and 2.5262 eV as shown in Table 1. 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. It has further been shown 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.

Lines	Exciton Complex	g_e (electron) g-value isotropic	g_h (hole) g-value $C \parallel H$
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 with terminal excited state	− 1.76	
4908.7 Å		− 1.76	
4912.4 Å		− 1.76	
4915.32 Å		− 1.76	− 1.76
4916.5 Å		− 1.76	− 1.76

Table 1. Bound Exciton Emission Lines in CdS, $T = 1.2$ °K.

In order to relate the energy states of particular series it is necessary to calculate the "hydrogen like" 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 dielectric anisotrophy enteres as a perturbation with the dielectric constant in the x and y directions being equal to ε, and the dielectric constant in the z direction being equal to $\varepsilon\eta$. The effective mass anisotropy which enteres in the free exciton case does not occur in the neutral donor problem because the electron mass is isotropic. The Hamiltonian for the neutral donor problem in the effective mass approximation is:

$$H = H_0 + H_\alpha + H_2 + H_3 , \tag{1}$$

where

$$H_0 = -\frac{\hbar^2 \Delta}{2 m_e^*} - \frac{e^2}{\varepsilon \eta^{1/2} r} , \tag{2}$$

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

$$H_2 = \begin{cases} \dfrac{e\hbar}{2 m_e^* c} H_z L_z & \text{for} \quad H \parallel z , \\ \dfrac{e\hbar}{2 m_e^* c} H_x L_x & \text{for} \quad H \perp z , \end{cases} \tag{4}$$

$$H_3 = \begin{cases} \dfrac{e^2}{8 m_e^* c^2} H_z^2 (x^2 + y^2) & \text{for} \quad H \parallel z , \\ \dfrac{e^2}{8 m_c^* c^2} H_x^2 (y^2 + z^2) & \text{for} \quad H \perp z . \end{cases} \tag{5}$$

In Eq. (1) H_0 is the "hydrogenic" operator and is taken as the unperturbed part of the Hamiltonian. H_α is the anisotropic perturbation operator and

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may be written as

$$H_\alpha = \frac{e^2}{\varepsilon \eta^{1/2} r} \{\tfrac{1}{2}\alpha \operatorname{Cos}^2\theta + \tfrac{3}{8}\alpha^2 \operatorname{Cos}^4\theta + \cdots\} \qquad (6)$$

where

$$\alpha = 1 - \eta^{-1}. \qquad (7)$$

Treating H_α to first order correction, one will have mixing of states $\Delta n = 0$, $\Delta l = \text{even}$, $\Delta m = 0$.

The linear Zeeman term is given by Eq. (4); this term does not mix the hydrogenic states for $\boldsymbol{H} \parallel z$ but mixes states of $\Delta l = 0$, $\Delta m = \pm 1$ for $H \perp z$. The quadratic Zeeman term is given in Eq. (5), this term has non-zero matrix elements between states with $\Delta l = 0, \pm 2$, $\Delta m = 0$. Adding the spin momentum interacting with the magnetic field ($\boldsymbol{\mu}^* \cdot \boldsymbol{H}$) 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 $n = 2$ and $n = 3$ states of the donor complexes for CdS, as a function of the magnitude of the magnetic field are given as solid and dashed lines in Fig. 1. It is apparent that there are two overlapping sets $n = 2$ 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. 1 gives a good fit to the I_5 and I_{2c} (4870.2 Å)[9] levels respectively.

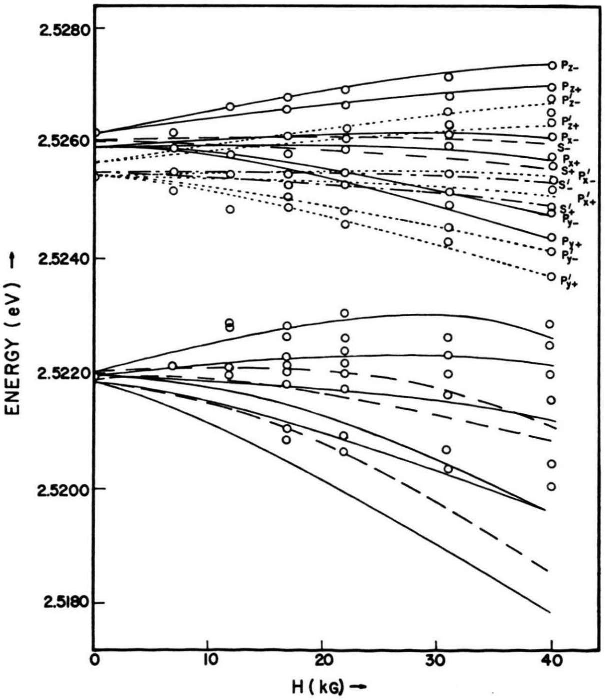

Fig. 1. Photon energy of the $n = 2$ and $n = 3$ states of the I_2 and I_5 neutral donor bound exciton complexes as a function of magnetic field for the orientation $C \perp H$.

In the calculated energy levels of Fig. 1 an electron effective mass $m_e^* = 0.18\, m_0$ was used. This gives a good theoretical fit to the experimental data.

The calculated energies for the $n = 3$ states are shown in Fig. 1. 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 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. 2. 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. (5) is translated into a negative diamagnetic shift. Negative diamagnetic shifts are observed for the transitions in Fig. 1. It can further be seen from Fig. 2 that as the "C" axis of the crystal

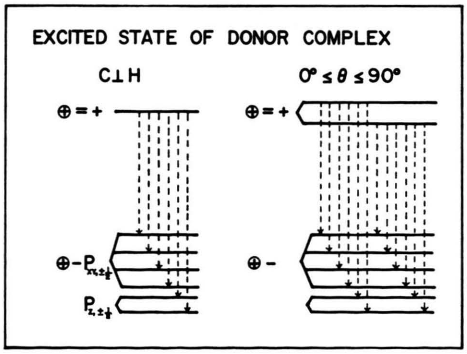

Fig. 2. Model for the decay of a bound donor complex in which the decay of the exciton leaves the terminal state in an excited configuration, in this case a p-state.

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[9] E. T. Handelman and D. G. Thomas, J. Phys. Chem. Solids **26**, 1261 [1965].

is rotated with respect to the magnetic field direction a contribution from the hole spin should be observed. Figure 3 shows the splitting of the zero field lines at 2.5214 eV and at 2.5220 eV as θ is varied from 0°—90° for a constant magnetic field of 40 kG. For the orientation $C \parallel H$ only three lines are observed for these excited states. In the magnetically field split lines of Fig. 3 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 hole 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 $C \parallel H$ orientation in Fig. 3. 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.

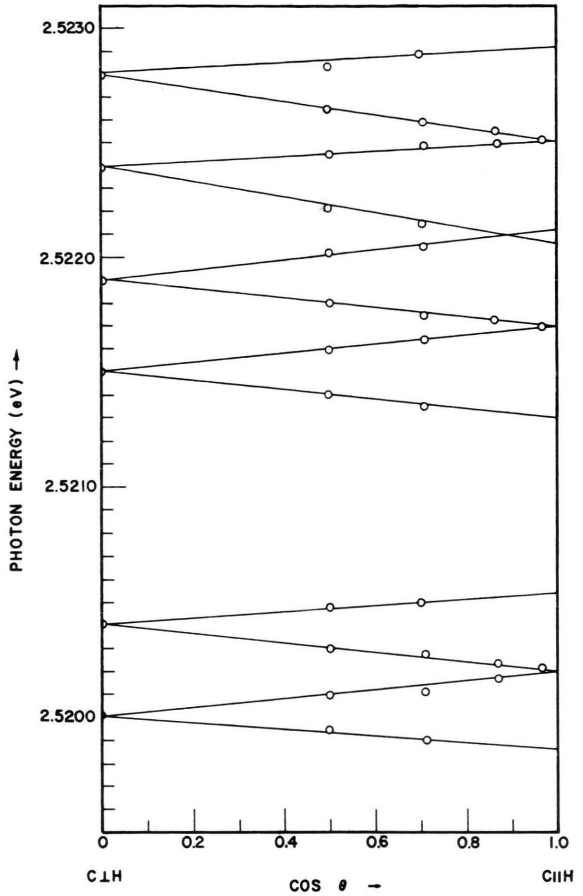

Fig. 3. Magnetic field splitting of the zero field 2.5220 eV line as a function of $\cos\theta$ for a constant field of $H = 40$ kG, $T = 1.2$°K.

A number of bound exciton complexes have also been observed in CdSe [10] however, they have not been identified with donor or acceptor complexes. The magnetic field splitting of the excited states of some of these complexes can positively identify them as excitons bound to neutral donor sites.

In applying the theory to the CdSe data it was found that to obtain the best fit to the experimental results it was necessary to include the mixing of the different principle quantum number states by the diamagnetic term of Eq. (5).

The reported values for the dielectric constants for CdSe are $\varepsilon = 9.53$ and $\varepsilon\eta = 10.65$ [11]. These constants give a value of 0.105 for the crystal field perturbation parameter. In the calculation for the orientation $C \parallel H$ the best fit to the experimental results was obtained using an effective electron mass of 0.13 m_e. The above values give a donor ionization energy of 0.018 eV and an $n = 2$ state binding energy of 0.0045 eV. The results of the calculation for neutral donor complexes are the solid lines of Fig. 4 and Fig. 5. In these figures the photon energy is plotted as a function of the magnetic field. The experimental energies are plotted as the circles. The zero field calculated energy of the $n = 2$ state of the donor was matched to the experimentally

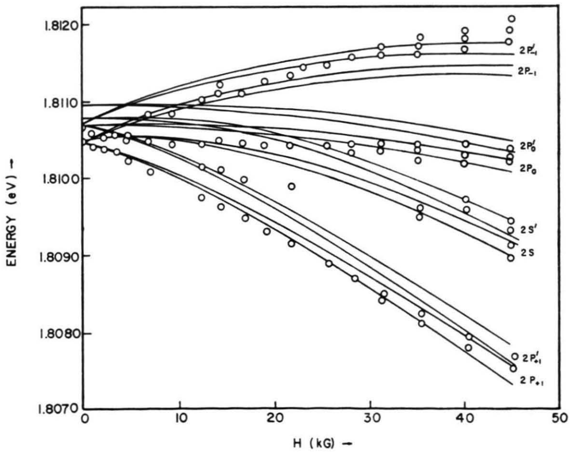

Fig. 4. Photon energy as a function of magnetic field for the I_{8a} and I_{8b} donors for $C \parallel H$. The solid lines are the theoretically calculated energies, the circles are the experimental energies.

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[10] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **156**, 881 (1967).

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observed $n=2$ state. In both Fig. 4 and Fig. 5 the $n=2$ states of two separate donors are observed. At high magnetic fields it is noted that the experimental points lie above the calculated energies for the $2p_{-1}$ states. The chief reason for this difference is that in the calculated energies, only mixing through the $n=3$ state was considered. Some of the $n=3$ states are observed and identified by their diamagnetic shift, however, they are not resolved well enough to permit analyses of their magnetic field splittings.

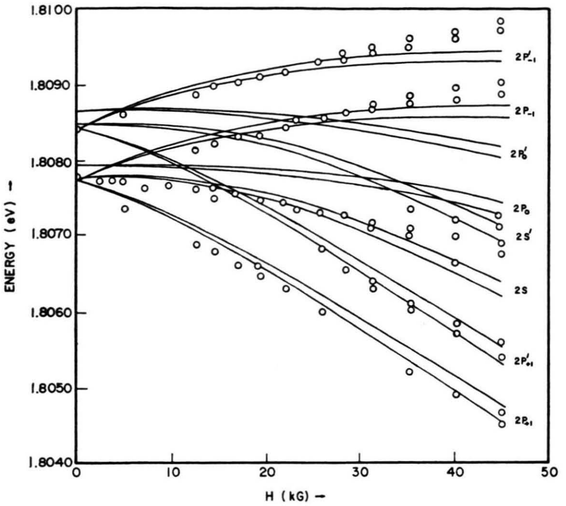

Fig. 5. Photon energy as a function of magnetic field for the I_{9a} and I_{9b} donors for $C \parallel H$. The solid lines are the calculated energies, the circles are the experimental energies.

Another interesting observation is the apparent quenching of the hole spin. One expects the hole spin to be anisotropic ($g_h = g_{h\parallel} \cos\theta$; see Fig. 2). The contribution of the hole spin should be observed for the orientation $C \parallel H$. In the case of CdSe one observes little dependence on the angle θ and also the multiplicity is accounted for at all angles including $\theta=0$ by the orbital and spin splittings of the $n=2$ state electrons.

The excited states of a bound donor excition complex have been observed in ZnO. Using the values $\varepsilon=8.33$ find $\varepsilon\eta=8.84$ the best theoretical fit to the experimental data, for the orientation $C \parallel H$ was obtained with an electron effective mass value of $0.19\, m_e$. The results of the calculation are the solid lines of Fig. 6. In this figure the photon energy is plotted as a function of the magnetic field. The $\mu \cdot H$ term was omitted from the calculation in this orientation. A contribution from the hole spin splitting in the upper state is observed for $C \parallel H$. The allowed transitions are those for $(g_e - g_h)$ and are not resolved but result in broadened lines. The $(g_e + g_h)$ transitions are spin up-spin down transitions and are not allowed. The spin splittings essentially cancel out as far as contributing to additional multiplicity in the optical transitions for $C \parallel H$. The experimental energies are plotted as the circles. The zero field calculated energy of the $n=2$ state of the donor was matched to the experimentally observed $n=2$ state. A good theoretical fit to the experimentally observed 2P-states is observed. The observed 2S-state energies fall somewhat below the calculated values.

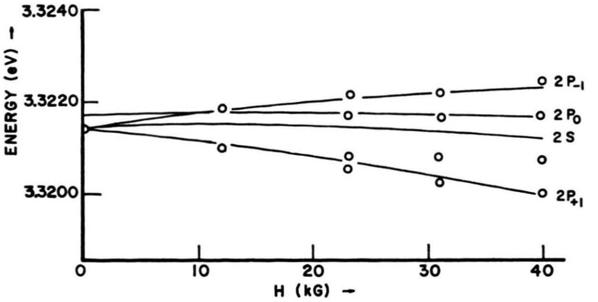

Fig. 6. Photon energy as a function of magnetic field for the I_6 donor excited states for $C \parallel H$ in ZnO. The solid lines are the theoretically calculated energies; the circles are the experimental energies.

In the calculation for the orientation $C \perp H$ an effective mass of $0.19\, m_e$ was again used to fit the experimental results. The results of the calculation are the solid lines of Fig. 7. In this figure the photon energy is again plotted as a function of the magnetic field. The experimental energies are plotted as the circles. The $2P_{x\pm}$ and the $2S_\pm$ states are degenerate

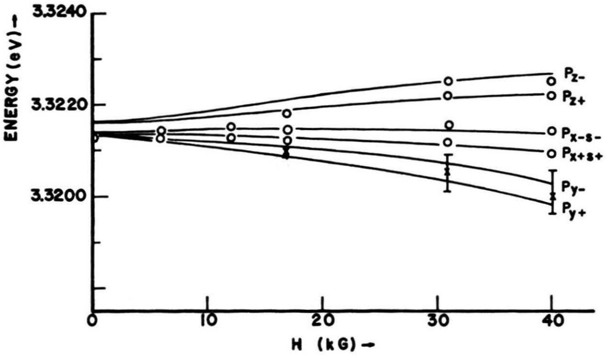

Fig. 7. Photon energy as a function of magnetic field for the I_6 donor excited states for $C \perp H$ in ZnO. The solid lines are the theoretically calculated energies, the circles are the experimental energies.

except at small magnetic fields where the lines cannot be resolved. The $2P_{y\pm}$ state is very weak and is not resolved. The theoretical fit to the experimental data is quite good for an effective mass of 0.19 m_e.

The highest intensity excited state transition is the $2P_{-1}$ transition. The remaining 2P-state transitions are equally as intense as the 2S transitions where comparisons can be made. In the orientation $C \perp H$ the $2P_{x\pm}$ and $2S_{\pm}$ states are not resolved. The P-state excitions represent a parity change whereas the S-state excitations do not. However, the crystals do not have inversion symmetry and therefore parity is not a good quantum number, as was pointed out in the case of GaP[12].

Using the effective mass approximation, the calculated donor binding energy for a mass of 0.19 m_e is 0.035 eV. Experimentally the donor ground state binding energy is 0.052 eV, determined on the assumption that the $n = 2$ excited state is effective mass-like. This agrees well with the donor binding energy of 0.051 reported by HUTSON[13]. It is apparent that the ground state of the donor is not effective mass like. It appears that a central cell connection is necessary as suggested by DIETZ, HOPFIELD, and THOMAS[14].

III. Conclusion

The study of the terminal states, after decay of bound exciton complexes, is a technique for gaining information about impurity states in semiconductors. It has been 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 all cases so far studied only excited terminal states were observed for donor complexes. There is no apriori 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.

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[12] P. J. DEAN, J. D. CUTHBERT, D. G. THOMAS, and R. T. LYNCH, Phys. Rev. Letters **18**, 122 (1967).

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