[2] G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. (to be published).

[3] Analysis of the absolute production rates vs bombarding energy for the Si-*J* center indicates a considerably higher threshold energy for divacancy production than that for the single vacancy, as is to be expected. This is in agreement with work by Bemski (to be published), who similarly reports a higher threshold energy for the Si-*C* center formation. As a result of this observation, Bemski independently concluded that the Si-*C* center was to be associated with a multiple defect, suggesting the divacancy as a possibility.

BOUND EXCITON COMPLEXES

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Exciton complexes in which excitons are bound to neutral or charged donors or acceptors have been described by Haynes[1] and Lampert.[2] In crystals with a direct band gap, such states are observable as sharp absorption and emission lines occurring at wavelengths longer than that of the lowest energy intrinsic exciton state. This Letter shows that the Zeeman effect of these impurity complex states can be used to identify which type of center a given absorption line represents. In this way, the g values of donors and acceptors, the binding energies of the various complexes, and even information about the energy levels and g values of excited states of donors and acceptors can be obtained. The electron-hole spin-spin (exchange) interaction can be measured in some of these states. The experimental results discussed are for CdS, but the method of investigation seems to be promising for a wide class of semiconducting crystals. Previous work has established the energies of the intrinsic exciton lines[3] in CdS, but the explanation of the lines occurring at lower energies has remained unsatisfactory.[4,5]

Excitons can be bound to neutral donors or acceptors to form molecular states, or to ionized donors or acceptors to form molecular ion states, as illustrated in Fig. 1. The neutral donors and acceptors are doublet states ($S=\frac{1}{2}$), and this is also true for the complexes formed from these states since the "bonding" electrons or holes must have antiparallel spins. (It is well known that for molecular hydrogen, if the "bonding" particles have parallel spins an unstable system results. Precisely the same considerations apply to the exciton complexes discussed here.) The states considered here are ground states and so have no orbital angular momentum. In a magnetic field the states derived from the neutral centers will split, as shown in Fig. 1, with a g value equal to that of the odd particle in the particular complex. This four-level system gives rise to two pairs of lines, one with a separation controlled by $|g_u - g_l|$ and the other controlled by $|g_u + g_l|$, where u and l refer to the upper and lower states, respectively.

In hexagonal CdS free electrons occupy an S-like $J=\frac{1}{2}\ \Gamma_7$ band, and free holes (from the top valence band) a P-like $J=\frac{3}{2}\ \Gamma_9$ band.[3] The free electron has an almost isotropic g value of -1.7_8. Because the conduction band is simple, this g value will be almost independent of the binding of the electron in a center. Symmetry requires that the g

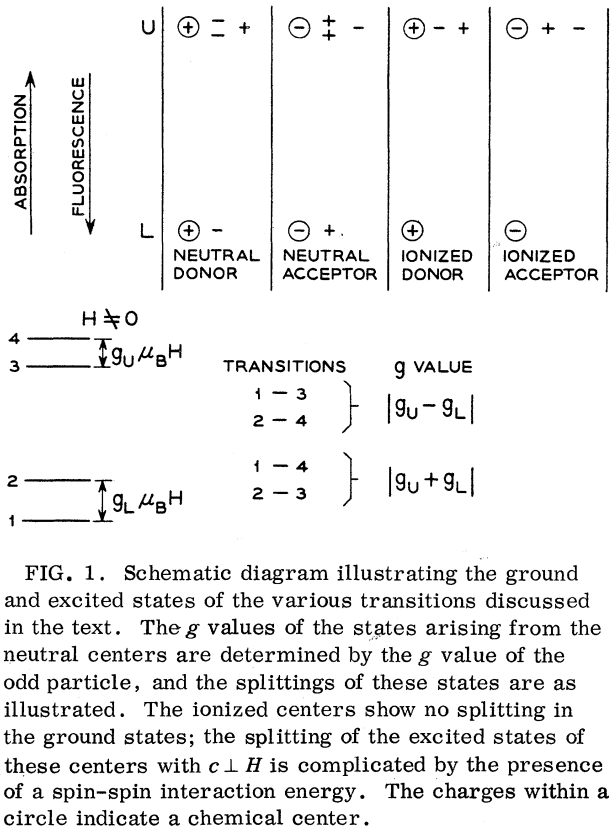

FIG. 1. Schematic diagram illustrating the ground and excited states of the various transitions discussed in the text. The g values of the states arising from the neutral centers are determined by the g value of the odd particle, and the splittings of these states are as illustrated. The ionized centers show no splitting in the ground states; the splitting of the excited states of these centers with $c \perp H$ is complicated by the presence of a spin-spin interaction energy. The charges within a circle indicate a chemical center.

Table I. CdS – 1.6°K.

Line	Energy (ev)	Energy below exciton A(2.5537 ev) (ev)
I_1	2.53595 (4888.5 A)	0.0177
I_2	2.5471 (4867.15 A)	0.0066
I_3	2.5499 (4861.7 A)	0.0038

value of the hole has the form

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

where θ is the angle between the magnetic field, H, and the c axis. The hole, belonging to a rather complicated and almost degenerate valence band structure, can have a g value sensitive to its exact state of binding. For the free hole, $g_{h\parallel} = -1.1_5$. For $c \parallel H$ selection rules show that the 1-3 and 2-4 transitions will occur optically, resulting in a doublet split with a g value of $|g_u - g_l|$. At an arbitrary value of θ, however, mixing of the states occurs, and a full quartet of lines becomes visible. The additional pair is separated with a g value of $|g_u + g_l|$. From measurements of this type it is easy to derive the individual g values.

Our study of "pure" vapor-grown crystals of CdS of thickness 10-100 μ has been chiefly concerned with three prominent sharp lines listed in Table I. These lines are strongly active for light polarized perpendicular to the c axis, which is also the polarization of the lowest energy exciton, exciton A. At 1.6°K in selected crystals the lines may have a width of 0.6 cm^{-1} or less. They can be seen at 20°K but not at 77°K. I_1 and I_2 are readily seen in both absorption and fluorescence, while I_3 is observed in absorption. I_1 is absent in some crystals. Sometimes other lines appear near I_2, the whole group behaving similarly in a magnetic field. Additional lines also often occur near I_3; some of these behave like I_3 in a magnetic field while others behave like I_2. Many other lines occur, prominent among which are comparatively broad lines (about 6 cm^{-1} wide) seen in fluorescence at photon energies below I_1; some of these correspond to emission taking place with phonon creation.

Lines I_1 and I_2 exhibit linear Zeeman splittings which can conveniently be studied in fluorescence. The splittings of I_1 and I_2 as a function of $\cos\theta$ are plotted in Fig. 2 for $H = 31\,000$ gauss. Quartets are seen when θ has values other than 0° and 90°. Within experimental error there is a linear dependence between the splittings and $\cos\theta$, so the relations

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

must hold, where g_{e0} is an isotropic electron g value equal to -1.7_6 for I_1, and -1.7_1 for I_2. For I_2, $g_{h\parallel}$ equals -1.7; and for I_1, $g_{h\parallel}$ equals -2.7_6. It happens that $g_{h\parallel} \approx g_{e0}$ for I_2. This near equality is the reason that for $c \parallel H$, with the splitting determined by $g_{e0} - g_{h\parallel}$, no Zeeman effect is observed for this line.[5]

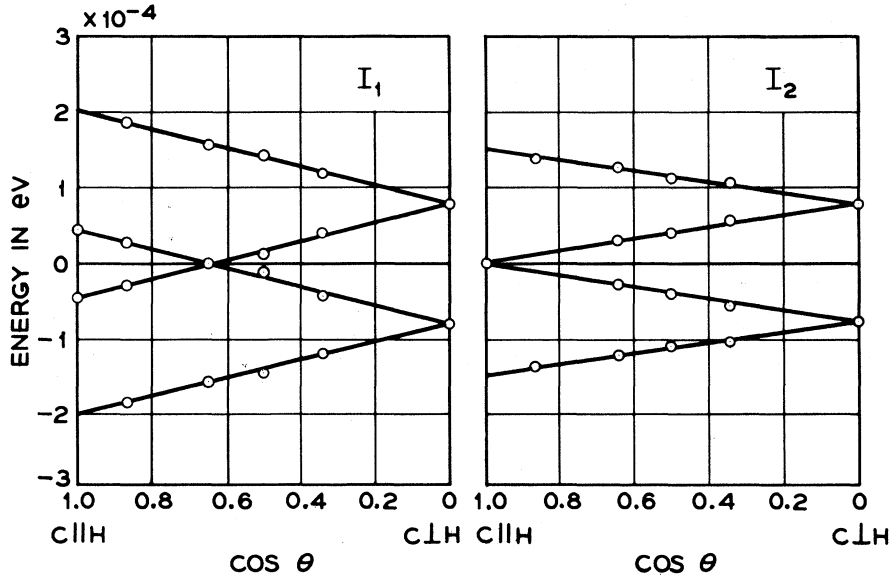

FIG. 2. Splitting of lines I_1 and I_2 at 31 000 gauss as a function of $\cos\theta$ at 1.6°K, as seen in fluorescence. Notice that when $\theta \neq 0°$ or $\theta \neq 90°$, quartets occur. The zero of energy is taken to be at the center of each group of lines.

When I_1 and I_2 are observed in absorption for $c \parallel H$ and $c \perp H$, the two lines in a pair sometimes have different strengths. The differences in strength increase as the magnetic splittings increase or as the temperature decreases, indicating that, for the experimental conditions used, thermal equilibrium of the spins is being approached in the lower states of the complexes. The results are as follows:

	I_1	I_2
$c \parallel H$	High-energy line strong	No splitting observable
$c \perp H$	Both lines equal in strength	High-energy line strong

It is clear that for $c \perp H$ there is thermalization in the lower state of line I_2, but that this does not occur for line I_1. Since $g_{e0} = -1.7_6$ and $g_{h\perp} = 0$, I_2 must arise from a neutral donor, and I_1 from a neutral acceptor. The thermalization results for $c \parallel H$ are consistent with these conclusions when it is remembered that for I_2, $g_{h\parallel} \approx g_{e0}$, and that for I_1, $|g_{h\parallel}| > |g_{e0}|$. It is interesting to note that the free hole has $g = -1.1_5$, but that in the exciton complex $\oplus = +$ the value has increased to -1.7, and in the neutral acceptor it is -2.7_6.

It follows that the other lines described above, which behave magnetically like I_2 also arise from donor states which are, however, chemically different from the center responsible for line I_2. In a similar way, the other lines which behave like I_3 must, as described below, be molecular ion states derived from chemically different centers. It is an interesting fact that we have seen no other lines which behave like I_1. This may be because there is only one acceptor state present in appreciable quantity, but it seems more probable that this is the only "shallow" acceptor state present; deeper lying acceptor states probably give rise to much broader lines as a result of stronger coupling to the acoustic phonons of the lattice.

The fluorescent intensities of I_1 and I_2 show that spin thermalization is not occurring in the upper states, presumably because of the short lifetime of these states.

CdS is normally n type, so acceptors are therefore usually compensated (ionized). On illumination with band gap light, however, free holes and electrons are made. These can be trapped at low temperatures by the ionized acceptor and donors, respectively, to form neutral centers on which the exciton complexes can be formed. It is found that when the lines are observed in absorption using as little band gap light as possible, infrared illumination of the crystal causes I_1 and I_2 to diminish in strength (and in some cases to vanish), while I_3 increases markedly in strength. Since the infrared illumination is of such a wavelength as to ionize the acceptor preferentially, we may conclude that this occurs and that the free hole then ionizes the donors. Thus, the neutral donor and acceptor concentrations are decreased while those of the ionized states are increased. We may therefore conclude that I_3 corresponds to the formation of a molecular ion state.

The magnetic behavior of I_3, although not simple, appears consistent with its assignment as a molecular ion state. For example, no thermalization is observed for absorption, the expected situation for a singlet ground state. In a magnetic field with $c \perp H$, I_3 splits unsymmetrically in the sense that the lines do not shift linearly with H; at low fields only the high-energy member of the doublet is visible, but as the field increases the low-energy line is seen with steadily increasing strength. Extrapolation of the positions of the lines to $H = 0$ shows that there is a zero-field splitting of 3.1×10^{-4} ev. Symmetry arguments show that with $c \perp H$, states with antiparallel spins ($1S\ \Gamma_5$ states) are mixed with states with parallel spins ($1S\ \Gamma_6$ states). The zero-field splitting is therefore ascribed to a spin-spin interaction energy, and since the transition to the $1S\ \Gamma_6$ state is forbidden, it is clear that this state has an energy lower than the $1S\ \Gamma_5$ state. Such an interaction can occur in absorption lines due to excitons bound to ionized donors or acceptors, where the complex involves an odd number of electrons and of holes. It cannot occur in absorption lines due to excitons bound to neutral donors or acceptors, since the spins of the two like particles will be antiparallel. The spin-spin interaction energy of 3.1×10^{-4} ev is surprisingly large. We have, however, evidence from the effect of strain on the intrinsic exciton lines that the free exciton has a similarly large value.

The methods described here could be of help in determining the types of impurities present in many 2-6 semiconductors. Information is also derived about the donors and acceptors, as illustrated here by the determination of the g value of the hole on the acceptor (a value that would be hard to obtain by paramagnetic resonance since $\Delta m = 3$ for a spin transition in the $J = \frac{3}{2}$

band). The dethermalization of the lower state population by microwave pumping should be easily detected optically. Donor and perhaps acceptor g values can therefore be measured with microwave precision on crystals too small to investigate with normal microwave techniques. Finally, there is evidence in the fluorescent spectra for transitions which leave neutral donors or acceptors in excited states. Such transitions provide a means of measuring donor and acceptor excited state energies and magnetic splittings.

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M-SHELL, RELATIVISTIC ELECTRON WAVE FUNCTIONS*

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The effects of screening and finite nuclear size on M-shell electron wave functions have been calculated numerically. The ratio of the corrected M-shell wave functions to the corresponding point-nuclear values (evaluated at the finite nuclear radius) is presented here in Fig. 1 for their application in evaluating M-capture transition probabilities.[1,2] In the past, these orbital capture transitions were corrected empirically for screening. The results presented here indicate the necessity for including such corrections and, in addition, indicate wide variations between the correction factors for different M subshells.

The correction factors were derived from wave functions which were calculated as part of a program for obtaining M-shell internal conversion coefficients. The wave functions are available in tabular form[3] for points outside the nuclear surface for atomic numbers 55 through 90 in steps of 5.

For the evaluation of these wave functions, a uniform charge distribution was assumed inside the nucleus, and power series solutions[4] were obtained for f and g (small and large component) of Dirac's equations. These series solutions were evaluated at the nuclear radius[5] to give starting values for a numerical solution of the equations in the external region. Here the potential due to the nucleus and orbital electrons was represented by a Thomas-Fermi-Dirac (TFD) potential[6] and is given by

$$V = \alpha Z \varphi / r + D.$$

In this equation α is the fine structure constant, φ is the screening function taken from Umeda's tables,[7] D is the Dirac exchange term,[6] Z is the atomic number, and r is the radial distance. The outer boundary condition for $f(a)$ and $g(a)$ is given by

$$f(a)/g(a) = -[(1-W)/(1+W)]^{1/2},$$

where W is the trial energy eigenvalue and a is the value of r for which φ vanishes. Trial values of W were varied until the solutions matched both the boundary condition at $r=a$ and that at the nuclear surface, and possessed the correct number of nodes in the interval.

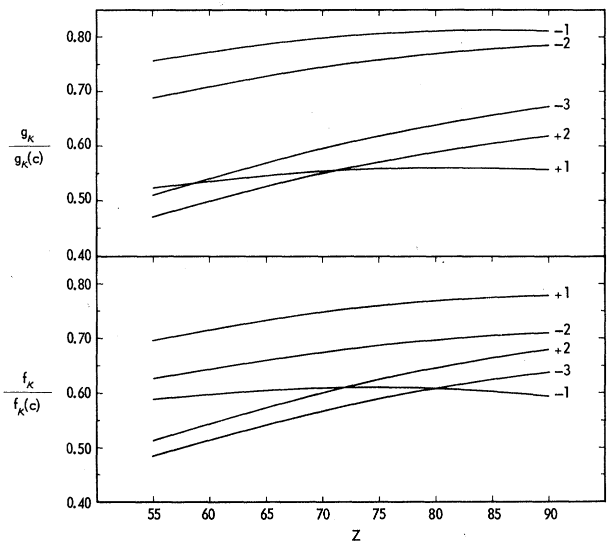

FIG. 1. $f_\kappa/f_\kappa(c)$ and $g_\kappa/g_\kappa(c)$ are the ratios of the screened, finite nuclear size functions to the corresponding analytic point-nuclear functions[7] evaluated at the nuclear radius and plotted as a function of the nuclear charge Z. The numbers to the right of each curve give the value of κ as defined in the text.