conduction band.[4] Such a level would also have Γ_7 symmetry, and hence its polarization perpendicular to the axis is readily understandable.

Copper, on the other hand, appears to be an acceptor, as demonstrated by the sign of Hall and thermoelectric measurement on copper-doped samples,[5] and its emission is best understood in terms of the level depicted in Fig. 2. But, in this case, the copper level or levels should be derived from the valence band, and consequently should have Γ_7 or Γ_9 symmetry. That such is not the case is shown by the polarization emission depicted in Fig. 1. Neither symmetry can explain the existence of radiation parallel to the *c* axis, nor can the situation be saved by assuming copper to lie close to the conduction band rather than to the valence band, as suggested by Klick.[4] It can of course be argued by analogy to germanium and silicon that both copper and silver give rise to deep levels which involve isolated wave functions of symmetries not simply associated with the valence or conduction band.

This is a possibility which is yet to be investigated.

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ZEEMAN SPLITTING OF EXCITON LINES IN CdS†

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During the course of optical studies on cadmium sulfide single crystals, Gross and his coworkers[1] observed at low temperatures many absorption lines near the fundamental absorption edge. In analogy with his work on the excitons in Cu_2O, Gross ascribed some of these lines to exciton absorption, and due to the variations from crystal sample to sample, some lines to impurities and surface defects. The recent work by Dutton,[2] Lempicki,[3] and Thomas[4] on the anomalies of the reflection spectra, when interpreted with the aid of the observed polarizations, as has been done by Birman[5] and Hopfield,[6] indicates that the valence band of cadmium sulfide is split into three bands. The upper two bands are split due to spin-orbit coupling and the remaining lower band due to the crystal field. Interpreting the reflectance data in this light, Lempicki[3] and Birman[5] deduce that the transitions from the valence bands to the single conduction band occur near 4877 A, 4845 A, and 4731 A at 90°K. These deductions assume that the extrema of the bands occur at the same point in the zone; the group-theoretical selection rules are compatible with the experiments if the band extrema lie along $\vec{K}=(0,0,K_z)$[7] in the reduced zone. In light of these developments, one of us[8] extended the group theory to the exciton case, using Birman's symmetry assignments. Considering the exciton spectra originating from the upper two valence bands and the conduction band, the group theory predicts five levels, which are singlet and triplet state excitons. Three of these levels are twofold degenerate, and two of them are nondegenerate.

Both states may be observed, as pointed out by Overhauser,[9] if the spin-orbit energy of *p*-like valence bands is of the same order of magnitude as exciton Coulomb and exchange energies. From the above interpretation of the reflectance measurements and the observed position of the absorption lines, Overhauser's criteria seem to be nearly met.

In order to substantiate this explanation of the absorption spectra in cadmium sulfide, as due to singlet and triplet state excitons, Zeeman data are necessary. Gross[10] has published a Zeeman spectrogram of CdS in a field of 30 kilogauss, indicating that in the region of wavelength greater than 4840 A (that region corresponding to excitons observable from the upper two valence bands) only one line splits, that into two components. Unfortunately his photograph does not include the line at 4888.46 A nor does he indicate the magnetic field direction relative to the crystal axis. Thus it was felt that further Zeeman work was worthwhile in order to substantiate the multiplet explanation.

This Letter is to report on the twofold splitting of three absorption lines in the wavelength region greater than 4840 A. All other lines observed do not split in fields up to 19 kilogauss. The g values of the lines are dependent upon the orientation of the magnetic field with respect to the c axis of the crystal. Also observed is a small shift in the mean position of the split lines which is approximately quadratic with magnetic field strength.

The spectrograph used was a 15 000-lines/inch grating with a 21-foot radius of curvature in a Wadsworth mounting positioned to observe the spectra in the second order. The dispersion was approximately 2.4 A/mm with a measured resolution for emission lines of greater than 60 000. The crystals were immersed in liquid helium between the poles of an electromagnet capable of providing 19 kilogauss in a gap of 15 mm. The crystals used were as described in a previous communication.[8] The observation was always transverse to the field and perpendicular to the c axis of the crystal. It was necessary to use a number of different crystals of varying thicknesses in order to obtain each observed line narrow enough for accurate determination of its splitting.

Typical results, for all split lines, are indicated in Fig. 1, which is a densitometric trace of the absorption line at 4888.46 ± 0.01 A. Figure 2 shows a plot of the splitting of this line as a function of magnetic field strength for both crystal orientations relative to the field direction. From curves of this nature, g values may be obtained for all the lines which split. This information is tabulated in Table I. It is also observed that the mean value of some of these lines shifts slightly with magnetic field strength. This shift is indicated in Fig. 3 for the line at 4888.46 A. One notes that this shift is certainly not linear with field; a quadratic least-squares fit to the data is indicated by the solid line.

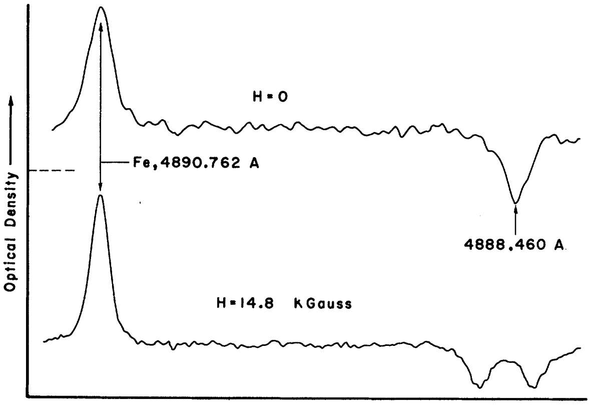

FIG. 1. Densitometric traces of the photographic plates showing the Zeeman splitting of one of the absorption lines in cadmium sulfide; $E\perp c$, $H\perp c$, $T = 4.2$°K.

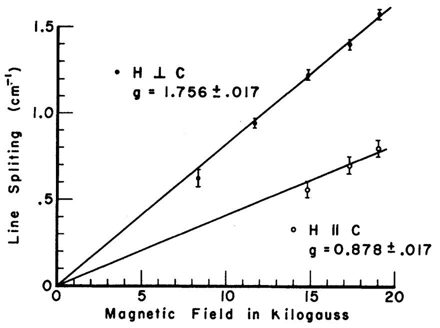

FIG. 2. Line splitting as a function of magnetic field for the absorption line at 4888.46 ±0.01 A.

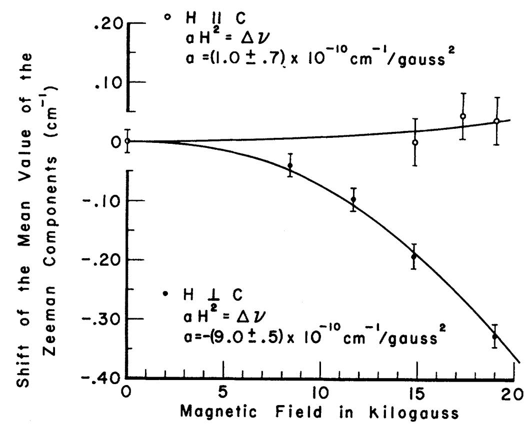

FIG. 3. Line shift as a function of magnetic field for the absorption line at 4888.46 ±0.01 A in zero field. The solid curves are least-squares fits to a quadratic field dependence.

This experiment is consistent with the multiplet interpretation of the exciton absorption spectra. Further, it has identified three lines as excitonic in origin. However, the details of the splittings are not immediately apparent. With the magnetic field oriented either parallel or perpendicular to the c axis, the degeneracy should be removed magnetically. In the parallel case, the group of the wave vector at Γ, A, or Δ is reduced by the magnetic field to the group containing only rotations about the c axis. Thus since this group has only one-dimensional irreducible representations, all degeneracies are removed (excluding any accidental degeneracy).

Table I. Summary of data of the absorption lines near the absorption edge in cadmium sulfide. All lines observed in various samples at wavelengths greater than 4840 A are listed.

Line A	Observed polarization	Line width cm^{-1}	Magnetic field orientation	Number of Zeeman components observed	g value	Shift of mean value of components $\Delta\nu = aH^2$ $a(10^{-10}\ \mathrm{cm}^{-1}/\mathrm{gauss}^2)$
4888.46 ± 0.01	$E \perp c$	0.96	$H \perp c$	2	1.756 ± 0.017	-9.0 ± 0.5
			$H \parallel c$	2	0.878 ± 0.017	+1.0 ± 0.7
4869.13 ± 0.01	$E \perp c$	1.50	$H \perp c$	2	1.80 ± 0.05	<2.0
			$H \parallel c$	1	<0.7	<2.0
4857.09 ± 0.01	$E \parallel c$	0.74	$H \perp c$	1	<0.5	<2.0
			$H \parallel c$	2	2.93 ± 0.03	+2.5 ± 1.5
4852.99	$E \parallel c$	1.45	$H \perp c$	1	0	<2.0
			$H \parallel c$	1	0	+4.5 ± 1.0
4869.66 ± 0.09	$E \perp c$	1.2	No splitting			
4868.30 ± 0.01 faint	$E \parallel c$	0.9	No splitting			
4866.72 ± 0.01	$E \parallel c$	1.4	No splitting			
4865.05 ± 0.01 faint	$E \parallel c$	0.8	No splitting			
4863.86 ± 0.01	$E \parallel c$	1.0	No splitting			
4861.89 ± 0.01 faint	$E \parallel c$	0.7	No splitting			

In the case of the magnetic field perpendicular to the c axis, the group of the wave vector is reduced to the group C_{1h} by the field. This group also has only one-dimensional irreducible representations; thus all degeneracy is removed (again excluding accidental degeneracy). Due to the fact that measurable splitting does not occur in some field orientations for two of the lines, the level structure for the excitons is apparently complex. Further work is underway in order to determine the angular dependence of the g values with crystal orientation.

The shift of the mean value of the Zeeman components should be toward higher energy if it is due to the diamagnetic effects on the exciton orbits. In the case where this shift is the largest, it is toward lower energy. The direction of this shift may indicate a variation in the position of the upper valence band edge with magnetic field strength.

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