computation is required which is beyond the practical limitations of presenting computing equipment. The system studied here represents about the upper limit in size and complexity that can be reasonably handled with present computing equipment.

## ACKNOWLEDGMENTS

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# Exciton Spectrum of Cadmium Sulfide

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The reflectance and fluorescent spectra of hexagonal CdS crystals have been measured at 77° and 4.2°K using polarized light in the region of 5000 A. Structure not previously reported has been found in the reflectivity curves which leads to the identification of three exciton series. These can be understood in terms of the splitting of the valence band into three levels at $\mathbf{k}=0$. The observation of excited exciton states and the polarization properties of the excitons make possible: (1) The determination of two of the three exciton binding energies, (2) the determination of the energy splittings of the three valence bands, (3) the verification of the symmetry assignments of the valence and conduction bands, and (4) correlation of the work of others with the present work, showing that the definite intrinsic effects are consistent both with our observations and our interpretations. The fluorescent experiments strongly suggest that the radiative decay of excitons occurs not directly, but from localized impurity exciton states in agreement with theory.

## I. INTRODUCTION

THERE exists in the literature much evidence of fine structure in various optical effects displayed by CdS at wavelengths near the onset of intrinsic absorption. In spite of these detailed studies the description of the band structure and exciton energy levels in CdS has remained in a state of confusion. The present work represents an attempt to correct this situation and was suggested by the reflectivity measurements of Dutton.[1] From theoretical considerations, together with observations made on ZnO, it was expected that there should occur in the reflectance spectrum two strong peaks in addition to the three already reported. We have therefore remeasured the reflectance at 77°K over a wider range of wavelengths, and have extended the observations to 4.2°K. In order to correlate the various effects, the fluorescence spectrum was also measured at both nitrogen and helium temperatures.

Gross and collaborators,[2–4] and others[5] have studied the absorption spectra of thin crystals at 4.2°K. Gross has pointed out that for wavelengths shorter than 4860 A the absorption lines observed are strong and are an intrinsic property of the crystal, and so are to be ascribed to exciton states. At longer wavelengths the lines are rather weak and vary from one crystal to another. Some lines are independent of the thickness of the crystal and so are connected with surface effects. The weak lines are associated with imperfections, although they cannot be attributed to excited impurity states in the sense that this term is normally understood. They apparently correspond to the formation of excitons in the field of an imperfection which has the effect of slightly lowering the exciton energy. These states may be called impurity excitons. Although Gross has described one set of lines active in light polarized perpendicular to the hexagonal $c$ axis (hereafter denoted by $E\perp c$) between 4855 and 4806 A as being due to the $n=3$, 4, 5, 6 states of a hydrogen-like exciton series with the $n=1$ and 2 states missing, this description is not entirely satisfactory as there are other lines unaccounted for.

The uv-stimulated fluorescent spectra at 4.2°K may be divided into two regions. At wavelengths longer than about 5100 A there is a series of regularly spaced peaks having half-widths of about 10 A, with an energy difference between peaks equal to that of the longitudinal optical phonon.[5,6] This is referred to as the

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[1] D. Dutton, Phys. Rev. **112**, 785 (1958).

[2] E. F. Gross, Suppl. Nuovo cimento **3**, 672 (1956).

[3] Gross, Razbirin, and Iakobson, J. Tech. Phys. U.S.S.R. **27**, 1149 (1957) [translation: Soviet Phys. (Tech. Phys.) **2**, 1043 (1957)].

[4] E. F. Gross and B. S. Razbirin, J. Tech. Phys. U.S.S.R. **27**, 2173 (1957) [translation: Soviet Phys. (Tech. Phys.) **2**, 2014 (1957)].

[5] L. R. Furlong and C. F. Ravilious, Phys. Rev. **98**, 954 (1955).

[6] Lambe, Klick, and Dexter, Phys. Rev. **103**, 1715 (1956).

green emission and arises from the recombination of a trapped carrier with a free carrier, with and without the simultaneous emission of phonons.[7] At shorter wavelengths there is "blue" emission which is of a different character in that the lines are much sharper and irregularly spaced. In general these lines occur in the same wavelength region in which the impurity absorption lines described by Gross occur (that is, 4860–4900 A, although some lines occur at still longer wavelengths). Some authors[5,8] have pointed out an apparent correspondence between the absorption and emission lines in this region, although the emission usually occurs at a slightly longer wavelength than the corresponding absorption. Furlong and Ravilious[5] have observed that this emission is affected by adsorbed air, so surface imperfections are important. Usually the emission is strongly polarized with $E\perp c$, but at longer wavelengths the emission of the less pure crystals appears to be unpolarized.[8]

Near 80°K Dutton[1] observed no absorption lines, possibly because of insufficiently thin crystals, but he did observe three well-defined peaks in the reflection spectrum measured at normal incidence. Such peaks correspond to strong absorption lines, although they are slightly displaced from the absorption lines. One peak occurred at 4874 A for $E\perp c$, and the two other peaks, active in both modes of polarization, occurred at 4844 A.

The photoconductivity[9] at 77°K has been studied under high resolution in polarized light. Considerable structure in the response was found between about 4900 and 4750 A. The interpretation of these results is not clear, although it is likely that the absorption lines already described are significant. The sharp changes in reflectivity described by Dutton should be considered in the interpretation of these data.

The dependence of the intensity of the green and blue emission on the exciting intensity has been studied at 77°K.[10] The results are consistent with the blue emission arising from exciton states, while the green emission must have a different origin. The concensus seems to be that excitons are connected with the blue-wavelength effects, although Balkanski and Waldron[11] have suggested that excitons may be formed at much longer wavelengths. However, the interpretation of Balkanski's experiment has been disputed[12] and there appears to be little evidence that excitons are involved outside the "blue" region.

## II. EXPERIMENTAL PROCEDURE

The reflectance at near normal incidence and the fluorescence of single crystals of CdS have been observed at 77 and 4.2°K. Most of the work has been done with a crystal about 1.5 mm thick cleaved from a large crystal grown at the Wright Air Development Center. Practically identical behavior of the reflectance at 77°K was shown by this crystal and by a thin crystal grown at the RCA Laboratory. The use of a polarizing microscope revealed that the *c* axis lay parallel to striations which occurred on the crystal surfaces. In most experiments the crystals were directly immersed in liquid helium or nitrogen in the tip of a Pyrex Dewar. A piece of polaroid in the path of the reflected or fluorescent light served as a polarizer and also filtered out any scattered 3650 A radiation in the fluorescent experiments. The fluorescence was stimulated by focusing a G.E. H85 Hg lamp filtered with a Corning 7-39 filter onto the face of the crystal from which emission was observed. For reflectance work a tungsten filament lamp was used as a radiation source.

### Reflection

Quantitative measurements of the reflectivity were made at 77°K by focusing the radiation from the exit slit of a Perkin-Elmer double pass monochromator with a NaCl prism onto the crystal face. The specularly reflected light (which was reflected within about 10° of the normal) was focused onto a 1P28 photomultiplier. Provision was made for determining the beam intensity in terms of the response of the system by positioning the Dewar so that a blank slit was in the position of the crystal. In this work a metal Dewar was used with an outer set of fused quartz windows at room temperature, and an inner set at 77°K to protect the crystal from room-temperature radiation. The crystal was glued at one end to a piece of molybdenum in the vacuum space. This method of support minimized external stresses. The precise position of the reflection peaks were determined from a run in which the crystal was immersed in liquid $N_2$. A resolution of about 2 A was obtained.

The results are shown in Figs. 1(a) and (b) for the two modes of polarization. The absolute values of the reflectivity were obtained by normalizing to Dutton's value at 4800 A (2.58 ev) for $E\perp c$. Dutton[1] obtained his absolute values by adjusting to the reflectivity values in the nonabsorbing region, which are known from the refractive indices. Dutton quotes an accuracy of about 10% for the absolute reflectivity. There is good agreement with Dutton in the observation of three sharp peaks, one, *A* at 2.544 ev (4873 A) occurring only for $E\perp c$, and two, *B* at 2.559 ev (4844.5 A) active in both modes of polarization. However, at slightly higher photon energies, in a region apparently unexplored by Dutton, another broader peak, *C*, is seen, also in both modes at about 2.616 ev. Dutton reported that a polished surface destroyed the reflectivity peaks,

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[7] J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

[8] Bancie-Grillot, Gross, Grillot, and Razbirine, Compt. rend. **248**, 86 (1959).

[9] See, for example, K. W. Boer and H. Gutjahr, Z. Physik **152**, 203 (1958).

[10] G. Diemer and A. J. van der Houven van Oordt, Physica **24**, 707 (1958).

[11] M. Balkanski and R. D. Waldron, Phys. Rev. **112**, 123 (1958).

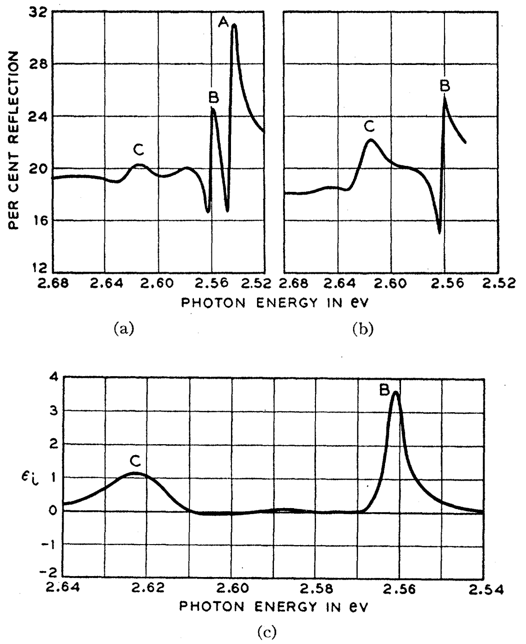
[12] I. Broser and R. Broser-Warminsky, J. Phys. Chem. Solids **6**, 386 (1958); **9**, 181 (1959).

presumably because the crystals were damaged near the surface by the polishing. We found that treating the crystals with HCl or HF tended to diminish the peaks but hot concentrated $H_3PO_4$ at least partially restored the peaks. No accentuation of the structure was attained over an "as grown" or cleaved crystal and so these were used.

Higher resolution than that provided by the prism instrument was attained with a Bausch & Lomb spectrograph equipped with a 4-in.×4-in. grating blazed at 3000 A with 55 000 lines/inch, giving a dispersion of 2 A/mm in first order. Photographs of the reflection and fluorescent spectra were taken and subsequently recorded using a Leeds and Northrup microphotometer. The determination of absolute light intensities with this system is less direct than when a photomultiplier is used, but this disadvantage is offset by the great resolution and sensitivity that can be attained with long exposures. Using 50-$\mu$ slits, a spectral slit width of 0.1 A is achieved.

This instrument revealed no further structure in the reflection spectra at 77°K although the increased resolution showed that the dips in the reflection immediately after the reflection peaks were more pronounced than indicated in Fig. 1.

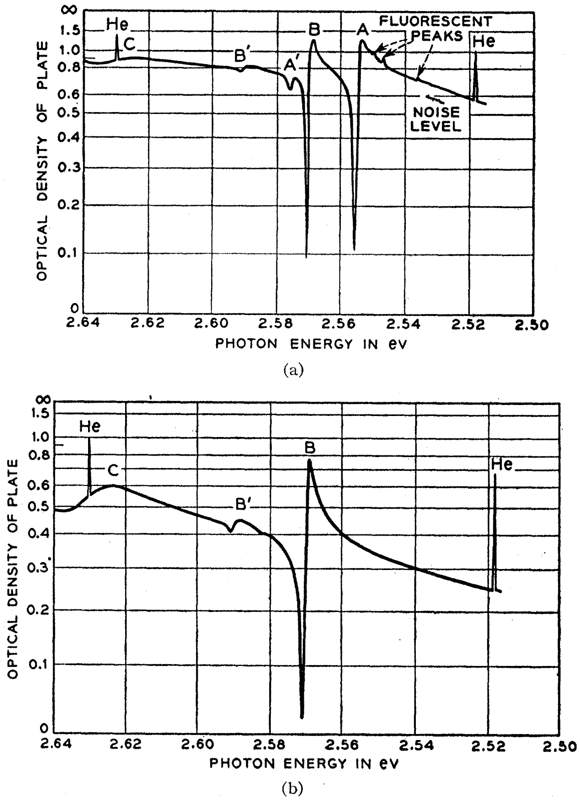
At 4.2°K the reflection spectra become more complex. The microphotometer traces are shown in Figs. 2(a) and (b). The three strong peaks are accentuated and shifted $0.009_3$ ev to higher energies. The first lies at $2.553_3$ ev and the other two at $2.568_4$ ev. Similarly the high-energy broad peaks are shifted about 0.008 ev to higher energies. On the low-energy side of the low-energy peak additional structure is seen; however, this can be ascribed to fluorescent emission stimulated by the tungsten light. This was shown by illuminating the crystal with the tungsten light in such a way that the light was no longer specularly reflected into the spectrograph. The fluorescent lines then stood out strongly from the background. Peak $B$ for light with $E\perp c$ was observed to have an anomalous shape at its maximum point which was not further investigated. The most interesting new structure at 4.2°K consists of fluctuations $A'$ and $B'$ in the reflectivity on the high-energy side of the main peaks $A$ and $B$. These fluctuations may be analyzed in terms of weak oscillators having their resonant frequencies approximately halfway between the reflection maxima and minima. The polarization properties indicate that these weak lines are associated with the strong peaks at lower energies. The separation between the resonant frequencies of $A$-$A'$ is 0.021 ev, and is identical within experimental error with the $B$-$B'$ separation. Approximate analysis reveals that $A'$ and $B'$ have roughly 10% the strength of the corresponding $A$ and $B$ lines.



(a) (b)

(c)

FIG. 1. Reflection from one surface of CdS at 77°K at near-normal incidence for light polarized (a) perpendicular and (b) parallel to the hexagonal $c$ axis, respectively. (c) The imaginary part of the dielectric constant as calculated from the Kramers-Kronig relation using the data of Fig. 1(b).



(a)

(b)

FIG. 2. Reflection of CdS at 4.2°K for light polarized with (a) $E\perp$ and (b) $E\|$ to $c$. These are traces taken from microphotometer recordings of Kodak 103-0 plates. The noise level is as indicated in Fig. 2(a). The helium calibration lines indicate the resolution used.

## Analysis of Reflectance Data

Oscillator strengths and resonant energy positions were determined by two methods. For very weak reflectance lines, a simple analysis was made using the valid approximation $\Delta R/R \ll 1$. For the stronger reflectance lines ($A$, $B$, and $C$) an analysis was made using the Kramers-Kronig relations.[13]

The Kramers-Kronig inversion was performed on an IBM 704 computer. The program contained a three parameter function to compensate for the effects of truncation of the infinite integral. The parameters were adjusted by the computer to yield zero absorption at energies lower than the absorption edge. The chief causes of inaccuracy in the inversion are the lack of instrumental resolution and the error in normalization of the experimental reflectivity data. The interpretation of the results contained further uncertainties due to the attempt to describe the reflection in terms of bulk crystal parameters. Other calculations with the same computing program under similar experimental circumstances have indicated that the analysis can be relied upon to yield oscillator strengths with an accuracy of about 20%. Relative oscillator strengths can be determined with an estimated accuracy of 10%. The energies of the oscillators can be more accurately established from the $K$-$K$ inversion than from any arbitrary rule of thumb, since the position of the actual energies relative to a reflection maximum depends on many factors such as the line strength, line width, position of nearby lines, etc. For weak reflection peaks, ($\Delta R/R \ll 1$), the oscillator frequency lies to the high-energy side of the reflection maximum at the point of inflection of the reflectivity curve. For strong reflection peaks, ($\Delta R/R \gg 1$), the oscillator frequency lies to the low-energy side of the reflection maximum. In the general case careful analysis of the data is necessary to determine the oscillator frequency. The frequencies of the peak reflectivity, of the maximum absorption, and of the dispersion oscillator are in general all different. The resonant frequencies of the oscillators $A$ and $B$ described in this paper lie approximately at 0.001 ev higher photon energies than the corresponding reflection peaks.

The oscillator strengths[14] and the resonant energies of the oscillators are given in Table I. A typical result of the Kramers-Kronig inversion is given in Fig. 1(c) in which the imaginary part of the dielectric constant is plotted against photon energy for $E \perp c$. (The aggregate effect of the errors previously mentioned is readily apparent.) The areas under the curve are simply related to the oscillator strengths. The relative strengths of the oscillators are probably more accurately known within a single mode of polarization than between the two modes. Because of surface effects, the peak widths are not necessarily the widths characteristic of the bulk crystal. The peak absorption coefficient at 2.561 ev from the $K$-$K$ analysis is $2 \times 10^5$ cm$^{-1}$. The true peak value (corrected for surface broadening) may be somewhat higher. The $K$-$K$ inversion indicates that there exists a pronounced window between the exciton lines, in which the absorption constant is of the order of magnitude of $10^4$ or less at 77°K. This window allows the observation in transmission at 4.2°K of comparatively weak lines at energies above those of peaks $A$ and $B$.[2–4]

## Fluorescence

### 77°K

At 77°K the predominant emission is in the "green" region with the highest energy peak located at about 2.412 ev (5140 A). In the blue region there is weak, rather diffuse emission as shown in Figs. 3(a) and 3(b) for the two modes of polarization of the emitted light. The positions of the reflection peaks $A$ and $B$ at 77°K are indicated in these figures. It is seen that roughly ten times as much light is emitted polarized with $E \perp c$ than with $E \| c$, and that there is a correspondence between the peaks of emission and reflectance, although some additional structure is apparent. The correspondence is emphasized by the observation that the light emitted at the wavelength of peak $A$ is polarized with $E \perp c$ just as peak $A$ is active for $E \perp c$, while the energy at peak $B$ is present in both modes just as peak $B$ is active in both modes.

### 4.2°K

At 4.2°K the "green" emission is not greatly enhanced, although the successive peaks become better defined. The highest energy peak now occurs at 2.398 ev

Table I. Exciton strengths in CdS.[a]

| Line | (Oscillator strengths/molecule) $\times 10^4$ | | | | Width at 77° |
|---|---|---|---|---|---|
| | $E_\perp$ Expt. | $E_{\|\|}$ Expt. | $E_\perp$ Theory | $E_{\|\|}$ Theory | |
| $A$, $n=1$ | 25.6 | 0 | 25.0 | 0 | 0.0049 ev |
| $B$, $n=1$ | 14.2 | 15.7 | 14.2 | 16.4 | 0.0047 ev |
| $C$, $n=1$ | 8.0 | 17.0 | 10.7 (8.2)[e] | 21.7 (16.6)[e] | 0.017 ev |
| $A'$, $n=2$ | 1.5[b] | 0 | 3.1[c] | 0 | |
| $B'$, $n=2$ | 1.4[d] | 1.3[d] | 1.8[c] | 2.1[c] | |
| $C'$, $n=2$ | | | (1.0)[c] | (2.1)[c] | |

[a] The difficulty in estimating the oscillator strengths of the $n=2$ lines is probably compounded by the fact that group theory shows that these lines should be multiplets. The $n=2, 3, \cdots$ states of exciton $A$ can also occur in both modes of polarization of the light.

[b] This line lies close to peak $B$ which makes the determination of its strength difficult.

[c] Based on an isotropic reduced mass and no central cell correction.

[d] The estimated error for these lines is 50%.

[e] The numbers in parentheses are obtained by adjusting the binding energy of exciton $C$ (see text).

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[13] F. C. Jahoda, Phys. Rev. **107**, 1261 (1957).

[14] There is some ambiguity about the definition of oscillator strengths. The definition used here is the continuum definition, for which the dielectric tensor may be written in principal axis form as

$$\epsilon_l = 1 + 4\pi \frac{e^2}{m} \frac{N}{V} \sum_j \frac{f_{lj}}{\omega_0^2 - \omega^2}.$$

The index $l$ refers to the mode of polarization ($x$, $y$, or $z$); the numbers $f_{lj}$ are the oscillator strengths. The quantity $N/V$ is the number of molecules per unit volume.

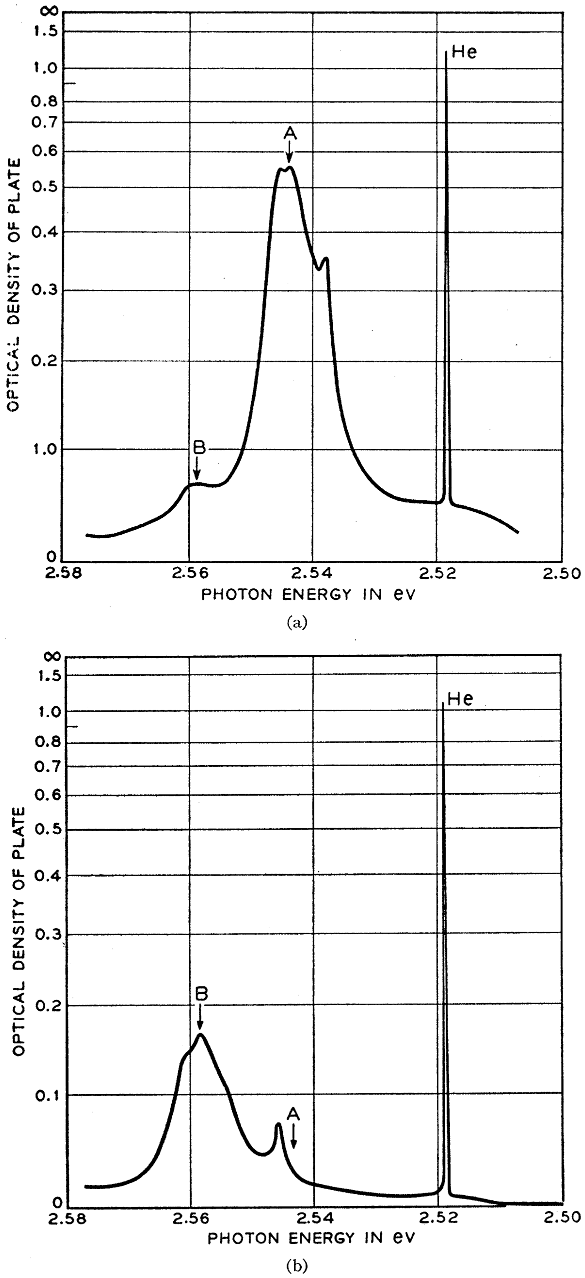

FIG. 3. "Blue" fluorescence of CdS at 77°K as shown by microphotometer records of Kodak 103-0 plates. The emission is polarized (a) $E\perp c$ and (b) $E\|c$. The positions of the reflection peaks are marked.

(5170 A) having been shifted 0.014 ev to lower energies. The difference between the peaks is about 0.040 ev which is nearly equal to the longitudinal optical phonon energy[7,15] (0.038 ev). The blue emission which is now completely polarized with $E\perp c$ has undergone a marked increase in intensity and, as reported by other authors, consists largely of irregularly spaced lines. Figure 4 shows microphotometer traces taken from photographs for various exposure times. With a single exception the lines are all sharp of half-widths of the order of $10^{-4}$ ev; one line is a doublet with a separation of about $1.5\times10^{-4}$ ev. The photographs reveal that the intensity of these lines varies from one part of the crystal to another as may be expected if the lines are associated with impurities which may vary in concentration along the crystal. These differences enable lines to be recognized in an empirical fashion. Long exposure showed that the two strongest lines had weak corresponding lines displaced 0.0379 and 0.0386 ev to lower energies as shown in Fig. 4(c). This displacement is identical to the optical phonon energy and suggests that the fluorescence in this blue region may also take place with the simultaneous emission of a phonon just as can the green emission. It is perhaps surprising that the sharpness of the lines is so well retained in this process. The exceptional broad emission occurs as a band approximately 2 A wide and falls at the highest energy at which fluorescence is observed; its position is very nearly the same as that of the lowest energy reflection peak, $A$, marked by an arrow in Fig. 4. This radiation is much less intense than that associated with the neighboring lines. It was noted above that Ravilious and Furlong,[15] who also observed the line emission, found that it was dependent on impurity effects.

## III. DISCUSSION

In order to identify the intrinsic exciton lines in CdS, it is necessary to separate these lines from impurity lines. A knowledge of the oscillator strengths of the observed lines is of considerable help in the separation. The interpretation of a reflection line can be simpler than the interpretation of an absorption line because of the extreme narrowness of some of the absorption lines at 4.2°K. This narrowness complicates the determination of the oscillator strength of the lines for it requires the use of instruments of high resolving power and very thin crystals. Unless these conditions are met a very strong line which obscures the light will appear hardly different from a weaker line which also obscures the light. If the lines are sharp enough, quite weak lines may have very high peak $\alpha$ values, where $\alpha$ is the absorption coefficient in $\text{cm}^{-1}$. In contrast to the transmission spectrum the dispersion of the refractive index in regions in which the line may cause no absorption can be observed for the more powerful lines by the change of reflectivity, and from this an estimate of the strengths of the lines can be made either by analysis of the reflection curves or by use of the Kramers-Kronig relation.

### Reflection

At 77°K three reflection peaks are seen; $A$, $B$, and $C$ [see Figs. 1(a) and (b)]. $A$ is active only for light with $E\perp c$ and is roughly twice as strong as $B$ and $C$ which

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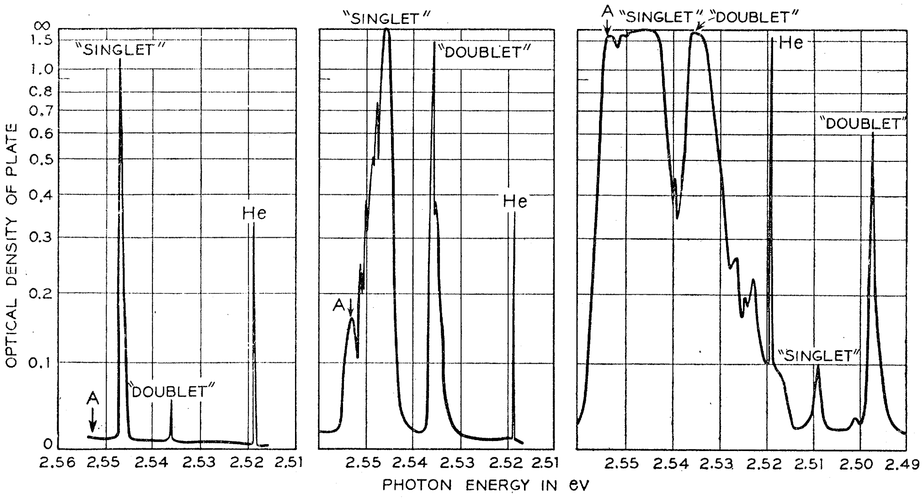
[15] R. J. Collins and J. J. Hopfield (to be published).



(a) (b) (c)

FIG. 4. "Blue" fluorescence of CdS at 4.2°K as shown by microphotometer traces. The emission is completely polarized with $E\perp c$. The position of reflection peak $A$ is marked. The exposures were (a) 30 sec, (b) 5 min, and (c) 31 min.

occur in both modes of polarization. $C$ is broader than $A$ or $B$. These peaks must correspond to the direct allowed excitons as defined by Elliott.[16] The transitions are direct since the absorption occurs as a peak whereas an indirect process involving phonon cooperation would give rise to an absorption edge. The strength of the transitions indicate that the excitons are formed in the ground state by optically allowed processes. The strength and reproducibility of the effects also show that they do not arise from impurities. Indeed it is hard to see what excitation process arising directly from an impurity could give energy states so near to the ionization continuum. The existence of three types of excitons is explained in terms of the splitting of the valence band.

At 4.2°K the lowest energy exciton reflection peak occurs at 2.553 ev (4855 A) so that no intrinsic exciton effects are expected at lower energies than this. This expectation agrees with Gross's observation[4] that intrinsic excitons occur only for $\lambda<4860$ A. The additional structure seen in the intrinsic region at 4.2°K consists of the peaks $A'$ and $B'$. The polarization properties show that these correspond to peaks $A$ and $B$, and it is reasonable to suppose that as $A$ and $B$ correspond to the $n=1$ ground states of the excitons, $A'$ and $B'$ correspond to the $n=2$ excited states. According to Elliott's theory,[16] assuming isotropic masses, $A'$ and $B'$ should have a strength of $1/2^3=\frac{1}{8}$ of the $n=1$ states. Table I indicates that this expectation is only approximately true. There are two chief theoretical corrections to this ratio. An attractive central cell correction increases the strength of the $n=1$ lines relative to the $n=2$ lines. An anisotropic reduced mass also alters the ratio of the $n=1$ and $n=2$ oscillator strengths. It is impossible to tell from the available information whether or not one of these effects is occurring. The separation between the $n=1$ and $n=2$ states for both excitons is about 0.021 ev. If the excitons are hydrogen-like they therefore have an ionization energy, $G$, of $\frac{4}{3}\times 0.021=0.028$ ev. A central cell correction would reduce this figure, but clearly not below 0.021 ev. Assuming a value of 0.028 ev a reduced exciton spherical mass may be estimated from the relation[16]

$$G=e^4\mu/2\hbar^2\epsilon^2=13.5(\mu/\epsilon^2)\text{ ev},\tag{1}$$

where $\epsilon$ is the low-frequency dielectric constant $=9.3$ for CdS.[17] Hence

$$\mu=M_eM_h/(M_e+M_h)=0.18,\tag{2}$$

where $M_e$ and $M_h$ are the effective masses of the holes and electrons in units of the electron rest mass $M_0$. Dexter[18] has tentatively suggested that the hole mass in CdS is 0.07 and the $\mathbf{k}=0$ electron mass is 0.36. These masses would yield a reduced mass of 0.06. The disagreement indicates either that there exists a sizable central cell correction to the exciton binding energy or that Dexter's tentative interpretation of his results should be reconsidered.

If the hydrogenic model is accepted, an exciton radius of 28 A would be obtained. From the exciton radius and a reasonable assumption concerning the band-to-band matrix element it is possible to make a crude estimate of the expected oscillator strength of the excitons. Within the large uncertainty the estimate agrees with observation.

In the presence of spin-orbit coupling, the "$P$" valence bands at $\mathbf{k}=0$ split into three bands,[19] two of which belong to irreducible representation $\Gamma_7$, the third of which belongs to $\Gamma_9$. The conduction band presumably has symmetry $\Gamma_7$ at $\mathbf{k}=0$. Band-to-band transitions are allowed for both modes of polarization of light for $\Gamma_7\rightarrow\Gamma_7$ transitions, but are allowed only

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[16] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

[17] R. J. Collins and D. A. Kleinman (to be published).

[18] R. N. Dexter, J. Phys. Chem. Solids **8**, 494 (1959).

[19] J. L. Birman, Phys. Rev. Letters **2**, 157 (1959).

for light polarized perpendicular to the $c$ axis for $\Gamma_9 \rightarrow \Gamma_7$ transitions. Apart from some ultrafine structure effects,[20] a direct parallel exists between selection rules and matrix elements for exciton states formed from an electron in the conduction band and a hole in one particular band, and selection rules and matrix elements for the same band-to-band transition. When the valence bands are spaced a reasonable distance apart compared to the exciton binding energy, it is proper to consider exciton states formed from a single valence band. (Just how far apart the bands must be in order for this concept to be valid depends primarily on the amount of admixture of the different bands that take place in the region of **k**—space from which the hole component of the exciton wave function is taken. It is not necessary that the band separation be large compared to the exciton binding energy, since the kinetic energy of the hole compared to the band splitting is the important parameter.) It is important to note that the selection rules are not modified by band mixing. The model is equally valid if the direct band gap is along the line $A$-$\Gamma$, which has the same symmetry as the point $\Gamma$.

Many parameters relating directly to the band structure can be obtained from an analysis of the properties of the excitons determined from the reflectivity experiments. From $K$-$K$ analysis, the following parameters are obtained (see Fig. 5) at 4.2°K.

$$E_g - E_{\text{exciton } A} = 2.554 \text{ ev},$$
$$E_g - (E_B - E_A) - E_{\text{exciton } B} = 2.570 \text{ ev},$$
$$E_g - (E_C - E_A) - E_{\text{exciton } C} = 2.632 \text{ ev}.$$

$E_{\text{exciton } A}$ here represents the binding energy of exciton $A$ and similarly for $B$ and $C$. The observation of the $n=2$ states of excitons $A$ and $B$ indicates that, within experimental and analysis errors, $E_A - E_{A'}$ equals $E_B - E_{B'}$. If the anisotropies of the reduced masses of these excitons are approximately the same, then $E_{\text{exciton } A} = E_{\text{exciton } B}$ to a high degree of approximation, for the exciton energies are very weak functions of the mass anisotropy. Therefore

$$E_A - E_B = 0.016 \text{ ev}.$$

The energy $E_{\text{exciton } A} = 0.028$ ev in the spherical approximation with possible error of a few millivolts if the bands are noticeably anisotropic or if central cell corrections are important. Therefore, at 4.2°K

$$E_G = 2.582 \text{ ev}.$$

In order to determine $(E_C - E_A)$ it is necessary to compute the binding energy $E_{\text{exciton } C}$ This can be done by using a quasi-cubic model, the details of which will be given in a future paper. The model is based upon the similarity between the wurtzite and zincblende structures. The model leads to a Hamiltonian matrix for $P$-bands in a hexagonal crystal which is closely related to the Hamiltonian matrix of a zincblende structure having a (111) strain. In this model, for the case in which excitons $A$ and $B$ are known to have the same binding energy, the three ratios of oscillator strengths,

$$f_{A\perp}/f_{B\perp}, \quad f_{B\perp}/f_{B\parallel}, \quad f_{C\perp}/f_{C\parallel},$$

are determined by two parameters. One of these parameters is the ratio of two optical matrix elements. This parameter only enters as a multiplicative factor in $f_{B\perp}/f_{B\parallel}$ and $f_{C\perp}/f_{C\parallel}$. The second parameter is a band-mixing parameter $\epsilon$. Since the same ratio of matrix elements appears in $f_{B\perp}/f_{B\parallel}$ and $f_{C\perp}/f_{C\parallel}$, the determination of $\epsilon$ depends only on relative oscillator strengths within the individual modes of polarization, and is not influenced by the possible uncertainty in the ratio of the strengths between the two modes. The only parameter which this uncertainty does influence is the ratio of the two optical matrix elements. Two parameters fit the three ratios within experimental error. (See Table I.) In this table, the theoretical oscillator strength ratios have been normalized to compare directly to the measured oscillator strengths.

The calculated ratio of $(f_{C\perp}/f_{C\parallel})$ agrees with experiment. On the other hand, the individual calculated $f_{C\perp}$ and $f_{C\parallel}$ values should agree with experiment if exciton $C$ had the same binding energy as excitons $A$ and $B$. From the relation between the binding energy and the oscillator strength we conclude that the binding energy of exciton $C$ is 0.915 times the binding energies of

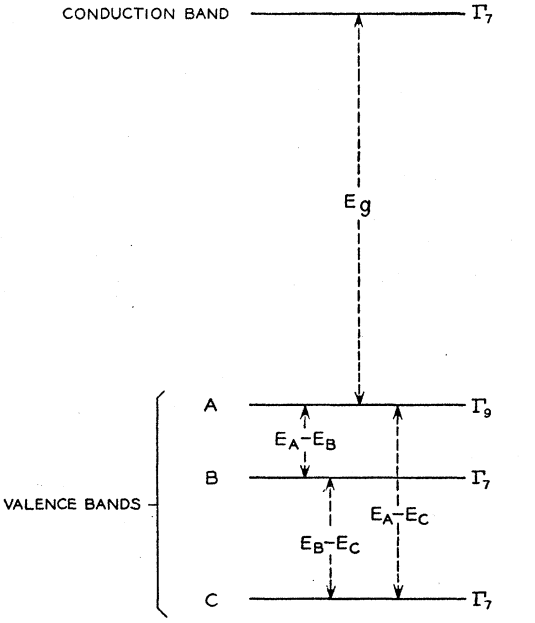

FIG. 5. Energy band structure of CdS at $\mathbf{k}=0$. The levels $A$, $B$, and $C$ refer to the hole bands from which the excitons causing reflections $A$, $B$, and $C$ arise. The band symmetry is given at the right.

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[20] These effects are the analogs of atomic spin-spin and spin-orbit effects, and give rise only to small splittings.

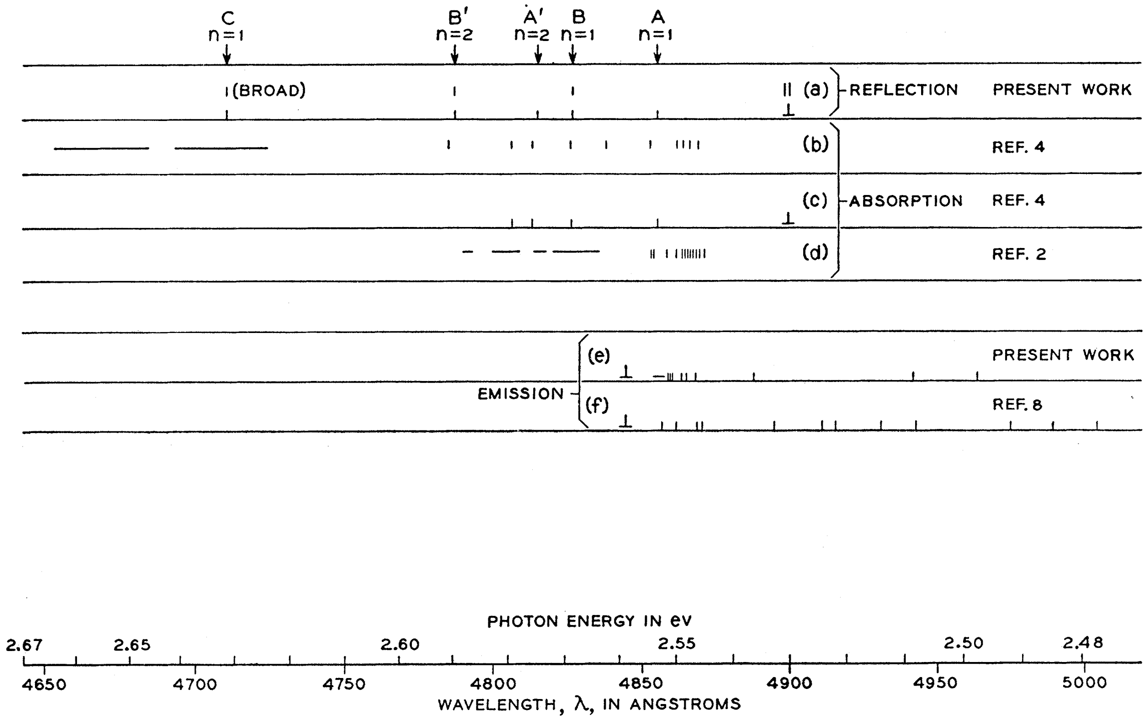

FIG. 6. Schematic diagram summarizing the data on CdS at 4.2°K. Where known the polarization properties of the lines are as indicated. In Sec. (a) the resonant energy positions are marked and are obtained from analysis of the reflectivity data. The exciton classification suggested in this paper is indicated above Sec. A.

excitons $A$ and $B$. This binding energy yields the corrected oscillator strengths given in parentheses in Table I. Thus

$$E_{\text{exciton }C}=0.026\text{ ev},$$

$$(E_A-E_C)=0.073\text{ ev}.$$

Within experimental error the oscillator strengths can also be fitted by $E_{\text{exciton }C}=0.028$ ev, and $E_A-E_C=0.075$ ev. The experimental uncertainty of $E_A-E_C$ as estimated by the range over which a fit can be obtained is therefore about 0.002 ev.

In the quasi-cubic approximation, the ratio of energy splittings depends only on the parameter $\epsilon$, which we have determined only from observed oscillator strength ratios. The quasi-cubic model predicts

$$(E_A-E_B)/(E_A-E_C)=0.215.$$

The experimental value for this ratio is 0.22 which is a strong indication that the quasi-cubic approximation is well justified (the excellent agreement is fortuitous; differences in the computed and measured ratios of 10% might be expected).

The quasi-cubic model yields two parameters which are of direct interest in band structure calculations. The spin-orbit coupling parameter (i.e., the value of the band splitting in the absence of crystal field splittings) is 0.068 ev (with the $P_{\frac{1}{2}}$ states lying lowest, as in germanium). The crystal field splitting parameter (i.e., the value of the band splittings in the absence of spin-orbit interaction) is 0.028 ev (with the $P_x$, $P_y$ states lying highest in the valence band). The admixture of $S$-state (as calculated from the optical matrix elements) in the "$P_z$" valence states is of the order of magnitude of 15%.

The parameter $\epsilon$ would have a value 0 in the absence of spin-orbit interaction, and a value 0.33 in the absence of crystal field splitting. The actual value of $\epsilon$ is 0.22. (It is pure coincidence that this happens also to be the numerical value of the ratio of the band splittings.) The near coincidence of the three exciton binding energies suggests that the electron mass is smaller than the hole masses (and therefore dominates the reduced mass expression).

One striking feature of Figs. 1(a) and (b) is the width of peak $C$, which is approximately four times the widths of peaks $A$ and $B$. We believe this increased width (shortened lifetime) is due to the auto-ionization of the exciton formed from an electron and a hole in band $C$ into a free hole in band $A$ or $B$ and a free electron. This process takes place spontaneously in the absence of lattice defects. It is impossible to evaluate the auto-ionization rate quantitatively for it depends strongly on unknown details of the valence band structure. From the values of the exciton binding energies and band separations observed in CdS, we have obtained the estimate

$$W\approx 4(\mu/m_h)E,$$

where $W$ is the line width, $\mu$ is the exciton reduced mass, $m_h$ is a typical hole mass, and $E$ is the exciton binding energy. The estimate, though extremely crude, does indicate that auto-ionization is a likely source of the width of line $C$. Energy conservation prohibits the auto-ionization of excitons $A$ and $B$. The auto-ionization rate contains a factor $|\psi(0)|^2$, which makes the auto-ionization of the state $B$, $n=2$ (which is energetically possible) considerably less likely than that for state $C$, $n=1$. The factor $|\psi(0)|^2$ enters because the "band mixing" which gives rise to auto-ionization is strongest where the potential is largest.

Having attempted a classification of the exciton peaks on the basis of the reflection data we may compare the results with the absorption spectra as observed by Gross and others.[2–4] Figure 6 is a schematic diagram summarizing various observations at 4.2°K. Section (a) shows the absorption line positions deduced from our reflectivity results together with our exciton assignments. Section (b) shows the absorption results described by Gross and Razbirine for a very thin crystal[4]; the polarization properties of the absorption were not described. Absorption lines can be discerned for all the "$n=1$" states. It is interesting that Gross and Razbirine report that at 4710 and 4660 A there are broad adsorption bands roughly 20 and 30 A wide, respectively. The broad band at 4710 A must correspond to the $C$ reflection peak and the band at 4660 A may result from excited states of this exciton. Weaker lines are seen in approximately the "$n=2$" positions of excitons $A$ and $B$, and a line that may be the "$n=3$" state is seen for exciton $A$. This line falls at 4806 A whereas the "hydrogen-like" position calculated from the $n=1$ and $n=2$ lines is 4805 A. The "$n=3$" state is expected to be too weak to be seen in reflection. The line at 4838 A is reported[4] to be weak and only to occur in certain crystals. This line could be an impurity exciton associated with the $B$ series. Further impurity lines are seen at wavelengths greater than 4860 A. In Sec. (c) of Fig. 6 is plotted the series reported[4] to be active for $E\perp c$, and to correspond with $n=3$, 4, 5, 6 states of an exciton series. In the present scheme these lines are expected to be active for $E\perp c$ and our interpretation of them is apparent from the figure. In Sec. (d) more bands and lines are shown for thicker crystals[2] in unpolarized light. Although reflection shows that line $A$ is the strongest of all, line $A$ will not appear so in transmission if unpolarized light is used since it is active only for $E\perp c$, and thus will only halve the intensity of the transmitted unpolarized light (neglecting reflection corrections).

In conclusion, the absorption data appear to be consistent with the proposed exciton scheme when account is taken of the many impurity exciton levels that exist.

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Exciting radiation makes free holes and electrons which come to equilibrium at the band minima.[7] At $\mathbf{k}=0$ the intrinsic band gaps may be determined from the ionization limits of the various excitons. It is clear that no radiation is observed in our experiments corresponding to direct band-to-band recombination. At 77°K there are the broad peaks of the "green" emission arising from recombination through an impurity center, and also weak radiation displaying slight structure at wavelengths near the exciton peaks $A$ and $B$, that near $A$ polarized with $E\perp c$ and that near $B$ occurring in both modes. The ratio of intensity of $A/B$ radiation is approximately that to be expected for a Boltzmann distribution of holes between the two valence bands.[15] At 77°K Gross and Iakobson[21] have reported emission in a band at 4805–4813 A which is at shorter wavelengths than peak $B$ (4845 A). This emission might correspond to radiation arising from excited exciton states.

At 4.2°K the radiation is completely polarized with $E\perp c$ as is expected if the holes are entirely concentrated in the $A$ valence band. The "green" emission is not greatly enhanced although its peaks are somewhat sharpened. At the position of reflectance peak $A$ a weak band of radiation approximately 2 A wide is seen. Presumably this represents the "direct" radiative decay of $A$ excitons. Very much stronger radiation is seen occurring as remarkably sharp lines at slightly longer wavelengths in the region in which the impurity absorption lines occur. It was pointed out in the introduction that others have stressed the correspondence between the absorption and emission lines. Since the absorption lines correspond to the formation of impurity excitons it is reasonable to suppose that it is these impurity states which can provide a favorable mechanism for the radiative decay of excitons. Most of these states fall within about 0.015 ev of the main exciton state. At 77°K the impurity states should hardly be occupied, since the entropy term greatly favors the intrinsic exciton state. However, at 4.2°K the impurity states may be occupied and radiation occur from them. A recent paper[22] has predicted that in a perfect crystal excitons will only decay when some imperfection such as a surface or impurity is encountered. This prediction was based upon the resonance between excitons and photons. It was argued that excitons decay only when this resonance is lost, either through the exciton striking the surface (and being converted to a photon on the outside of the crystal) or through the exciton interacting with some impurity to provide a way of violating the conservation of crystal momentum or energy in the exciton-photon system (by enlarging the system). This effect could account for the weakness of the radiation seen at the intrinsic exciton peak.

Figure 6, Secs. (e) and (f) represent emission data found by the present authors and by Bancie-Grillot

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[21] E. F. Gross and M. A. Iakobson, J. Tech. Phys. U.S.S.R. **26**, 1369 (1956) [translation: Soviet Phys. (Tech. Phys.) **1**, 1340 (1957)].

[22] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

*et al.*,[8] respectively. It shows that the radiation is almost entirely associated with the "impurity" region of the CdS spectrum.

In the course of the experiments it was observed (as others have observed earlier) that the green emission shifts to longer wavelengths as the crystal is cooled from 77°K to 4.2°K, whereas the direct band gap shifts in the opposite direction. When the shift in the direct gap of 0.009 ev is subtracted, one finds that the edge emission has shifted 0.023 ev to lower energies between 77°K and 4.2°K. Recently Collins[15] has performed experiments which indicate that the edge emission is associated with the recombination of a trapped hole with a free electron (see Lambe, Klick, and Dexter[6]). Collins' interpretation is, however, consistent with the experimental results of Lambe *et al.* In light of this work, there appear to be only two likely explanations of the shift.

The first possibility is that edge emission is due to the recombination of electrons in valleys not at $\mathbf{k}=0$ with trapped holes. The shift would then be explained by assuming that these valleys move down relative to the $\mathbf{k}=0$ valley as the temperature is lowered. The existence of such valleys is suggested by magnetoresistance experiments.[23] These valleys must not lie very far below the $\mathbf{k}=0$ valley, or Dutton[1] would have observed evidence of indirect absorption processes in his absorption experiments.

The second possibility is that there exists a bound state of the electron in the vicinity of the trapped hole. This bound state would have to lie 0.023 ev below the conduction band. At 77°K, the recombination would be thought of as taking place from the unbound states; at 4.2°K, the Boltzmann factor outweighs all other considerations, and the recombination would take place through the excited state. Other explanations would require extreme coincidences to occur in the valence band structure. Unfortunately there exists no information about the behavior of the edge emission between 4.2° and 77°. Such information would be of great interest since it could distinguish between the two possibilities just considered.

## Addendum

A recent Letter by Wheeler[24] has discussed excitons in CdS at 4.2°K. We wish to point out some difficulties in his interpretation of his data. Group theory predicts the occurrence of five optically observable ground state exciton lines three for $E\perp c$, two for $E\|c$. However, of Wheeler's five lines four are observed in each mode of polarization. Furthermore two pairs of the lines should be degenerate except for spin-spin effects. The minimum separation reported by Wheeler is about $2\times10^{-3}$ ev. This value seems unreasonably large for a hydrogenic exciton. Experiments[25] with ZnO have shown a "linear" Zeeman effect for a nondegenerate exciton having a smaller radius than the excitons in CdS. These experiments place an upper limit on the spin-spin splitting of about $2\times10^{-4}$ ev. We are unable to understand the band edge assignments given by Wheeler.

Many of the lines described by Wheeler we would interpret as impurity excitons. At wavelengths shorter than about 4855 A Wheeler's lines appear to correspond to our assignment of intrinsic exciton levels.

### ACKNOWLEDGMENTS

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[23] T. Masumi, J. Phys. Soc. Japan 14, 47 (1959).

[24] R. G. Wheeler, Phys. Rev. Letters 2, 463 (1959).

[25] D. G. Thomas and J. J. Hopfield (to be published).