

Γ -Point Valence-Band Energy Levels in CdS Determined from Excited States of *A*- and *B*-Band Excitons

C. W. Litton, D. C. Reynolds, and T. C. Collins

Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio 45433

(Received 14 March 1972)

Thomas and Hopfield measured the exciton absorption spectrum of CdS in 1961 and identified several of the intrinsic exciton states. The present paper reports the $n=2$, $n=3$, and $n=4$ excited states of intrinsic excitons, whose holes derive from the *B* valence band, as observed in emission spectra of single-crystal CdS platelets at 1.2°K. The energy difference between the $1S \Gamma_{5T}$ ground state and the $2S$ state of the *B*-band exciton is less than the energy differences between corresponding states of the *A*-band exciton by approximately 4 meV. That this deviates from the predicted effective-mass hydrogenic-exciton approximation can be explained by taking into account the details of the valence bands. The binding energies of the *A*- and *B*-band excitons, calculated from the higher excited states, are the same within experimental error in the hydrogenic approximation.

I. INTRODUCTION

Thomas and Hopfield¹ measured the free-exciton reflection spectrum of hexagonal CdS in 1959, from which they identified three separate exciton series whose holes derive from the *A*, *B*, and *C* valence bands at the Γ symmetry point of the zone. This was followed, in 1961, by a definitive magneto-optical study of the intrinsic exciton absorption spectrum, in which they identified several of the higher exciton states from both the *A* and *B* bands.² From these measurements they calculated such important band parameters as the electron, the hole, and the exciton effective masses, exciton binding energies, etc., which still stand as the accepted values of these parameters. These same investigators then extended their intrinsic exciton work to a study of bound excitons³ (impurity and native-defect excitons), a study which has contributed greatly toward our understanding of the complicated defect state in CdS, and, indeed, in all the II-VI compounds.

Although the various free-exciton transitions are not too difficult to observe in the low-temperature reflection and absorption spectra of high-quality CdS crystals, it is usually much more difficult to observe these same transitions in emission spectra. In fact, emission spectra with sufficient detail to resolve the intrinsic exciton excited states can be obtained only from very high-quality strain-free single-crystal platelets, at temperatures near 1°K; also, the intrinsic exciton transitions are weak in emission and are not usually detected, except in long photographic exposures of the spectrum.

In the present paper we report the first work on intrinsic exciton emission spectra from thin CdS platelets. It is the purpose of this paper to report the observation of *A*- and *B*-band intrinsic

exciton states (ground and excited states), as deduced from emission spectra at 1.2°K, and to compare these results with the previously reported absorption and reflection spectra of Thomas and Hopfield.^{1,2} In general, the emission results are in good agreement with those derived from absorption and reflection spectra. In emission, however, the excited configurations are seen in greater detail, as the present data show. A further purpose is to consider a small energy difference (~ 4 meV) which is always observed between the $n=1$ and $n=2$ states of the *A* and *B* exciton series, a difference not to be expected on the basis of a simple hydrogenic approximation, assuming equal masses for the *A*- and *B*-band holes. This observation is illustrated diagrammatically in Fig. 1.

II. EXPERIMENTAL RESULTS

Shown in Fig. 2 is a densitometer trace of a typical, unpolarized, intrinsic exciton emission spectrum of CdS. Clearly resolved are the $n=2$, 3, and 4 peaks of the *A*-band series, followed by the $n=2$, 3, and 4 peaks of the *B*-band series. The $\Gamma_{5L} A$ ($n=1$) and B ($n=1$) exciton ground states are indicated at their appropriate positions on the photon energy scale (although these states are not shown in the spectral trace, their precise spectral positions have been determined and are given in Table I). Based on a binding energy of 0.028 eV,^{1,2} we note that the $n=2$, 3, and 4 states of the *B* band fall at energies above the band gap, a fact which doubtless makes their observation difficult in absorption spectra.

The excited states of the *A*-band excitons are shown in the polarized emission spectra of Fig. 3. The solid-line spectral trace was recorded for emission polarized with $\vec{E} \perp \vec{C}$; the dashed-line spectrum is for $\vec{E} \parallel \vec{C}$. We note that the $n=2S$, $n=3S$, and $n=4$ peaks are clearly resolved and

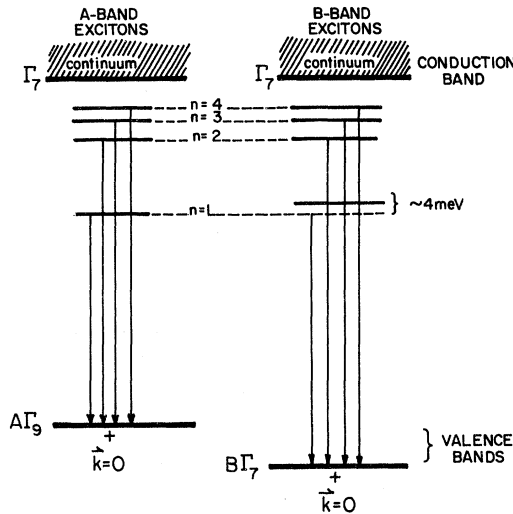


FIG. 1. Energy-level diagram for intrinsic excitons in CdS, A and B valence bands.

that they are the prominent features observed in the $\vec{E} \perp \vec{C}$ mode of polarization. In the $\vec{E} \parallel \vec{C}$ polarization, the $n=2S$, $n=2P$, $n=3P$, and $n=3D$ peaks are observed, as predicted by selection rules. Although the $n=4$ peaks appear in both modes of polarization, and are slightly displaced from one another, the experimental spectral resolution was not sufficient to sort out the $n=4$ excited configurations.

In order to observe the excited states of the B-band excitons it was necessary to use wide spectrometer slits and long photographic exposures. Slit widths ~ 1 mm, with exposure times ranging up to two hours, were required to photograph the emission. Since wide slits were required, one does not observe structure in the excited states as was possible for the A-band ex-

TABLE I. Measured values of ground and excited exciton states in CdS (energies in eV).

A band		B band	
$n=1$	$\begin{cases} 2.55455 \\ 2.5537 \end{cases}$	$n=1$	$\begin{cases} 2.5692 \\ 2.5676 \end{cases}$
$n=2$	$\begin{cases} 2S(2.57458) \\ 2P(2.57521) \end{cases}$	$n=2$	2.5852
$n=3$	$\begin{cases} 3S(2.57841) \\ 3P(2.57891) \\ 3D(2.57923) \end{cases}$	$n=3$	2.5892
$n=4$	$\begin{cases} 2.58018 \parallel \perp \\ 2.57986 \perp \end{cases}$	$n=4$	2.5907

citons. The ground-state B-band excitons are shown in Figs. 4(a) and 4(b). In Fig. 4(a), the emission is shown for $\vec{E} \parallel \vec{C}$; for Fig. 4(b) the polarization is $\vec{E} \perp \vec{C}$. One sees both the longitudinal and transverse excitons. The measured longitudinal-transverse splitting is 1.6×10^{-3} eV. If one assumes for the B-band exciton the same oscillator strength and refractive index that Thomas and Hopfield assumed for the A band, one calculates a value of 1.8×10^{-3} eV for the longitudinal-transverse separation, which agrees very well with the splitting measured in the present results. The experimentally measured energies for the ground and excited states of the A- and B-band excitons are compiled in Table I.

From Fig. 2 one observes that the energy separations between the excited states of the excitons derived from the A and B bands are approximately identical. However the energy difference between the ground-state B-band exciton and its first excited state is less than the energy between the ground-state A exciton and its first excited state. This difference can be accounted for as described

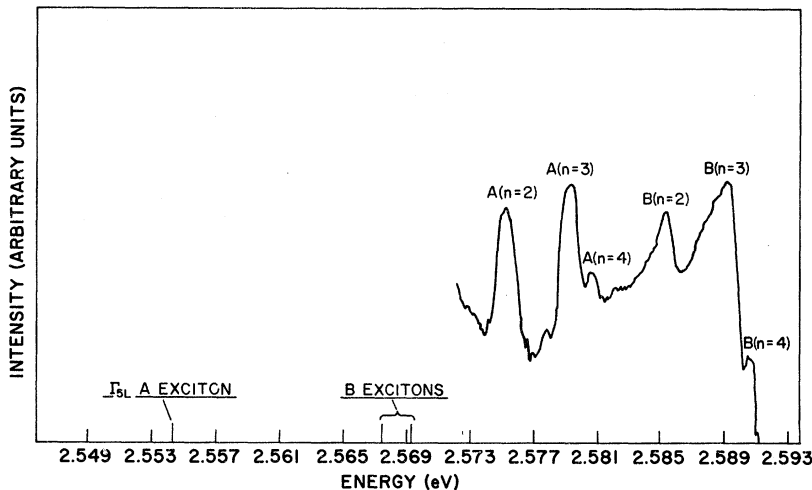


FIG. 2. Densitometer trace of a CdS edge emission spectrum at 1.2°K in the A- and B-band intrinsic exciton region, showing unpolarized emission peaks which correspond to excitons decaying from various ground and excited configurations. (Fluorescence excited by a high-pressure Hg arc lamp.)

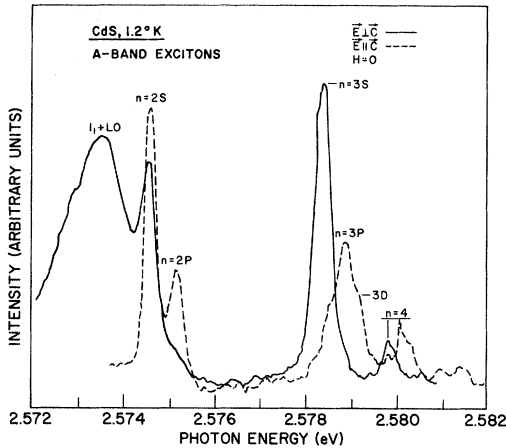


FIG. 3. Polarized intrinsic exciton emission peaks in CdS, showing A-band exciton decay from various excited configurations. The $I_1 + LO$ anti-Stokes peak belongs to the bound exciton emission spectrum.

in Sec. III.

III. DISCUSSION

Before investigating the energy shifts of the $n=1$ states of the A and B exciton, i. e., their deviation from hydrogenic values, let us examine the spin-orbit Δ_{so} and crystal field Δ_{cf} parameters. These parameters have been defined in three different ways⁴⁻⁶; for this report the definition of Ref. 4. will be used. If one assumes that the top of the valence band is p like, for both zinc blende and wurtzite, and that $H_{so} = \Delta_{so} \vec{L} \cdot \vec{S}$, one can write matrices of the form

$$\begin{pmatrix} \Delta_{so} & 0 & 0 \\ 0 & \Delta_{so} & 0 \\ 0 & 0 & -2\Delta_{so} \end{pmatrix} \quad (1)$$

for zinc blende, using $j = \frac{3}{2}$ and $j = \frac{1}{2}$ eigenstates. For wurtzite the basis is rotated so that one has $S + \alpha$, $S - \beta$, $S + \beta$, $-S - \alpha$, $S_z \alpha$, and $S_z \beta$. This basis gives matrices (including crystal field effects) of the form

$$\begin{pmatrix} \Delta_{so} & 0 & 0 \\ 0 & -\Delta_{so} & -i\sqrt{2}\Delta_{so} \\ 0 & +i\sqrt{2}\Delta_{so} & -\Delta_{cf} \end{pmatrix}. \quad (2)$$

The Δ_{so} and Δ_{cf} have been determined from exciton spectra, assuming that the binding energy of the A, B, and C excitons were the same.¹ From the $n=2, 3$, and 4 exciton energies of the A and B band one obtains an average effective Rydberg of 0.029 eV with little deviation. This implies that the reduced masses for the A and B excitons are approximately equal. This does not appear to hold for the C band. Some insight to the unique character of this lower band can be obtained by examining the calculated band structure of the II-VI compounds.^{7,8} It is found that the lower valence band is quite different from the upper valence band, as shown in Fig. 5. Moreover, the spin-orbit splitting parameter can be calculated to a high degree of accuracy by relativistic orthogonalized plane-wave methods.⁹ Using this method, the value obtained for CdS is $\Delta_{so} = 0.038$ eV. (The energy difference between the Γ_8 and Γ_7 valence bands of zinc blende CdS is 0.114 eV.) This compares with an InP calculated value, $\Delta_{so} = 0.040$ eV, for which an experimental value, $\Delta_{so} = 0.037$ eV, has been measured (obtained from values given in Table IV of Ref. 9).

One can also make comparisons between GaP, InP, ZnS, and CdS spin-orbit parameters. The

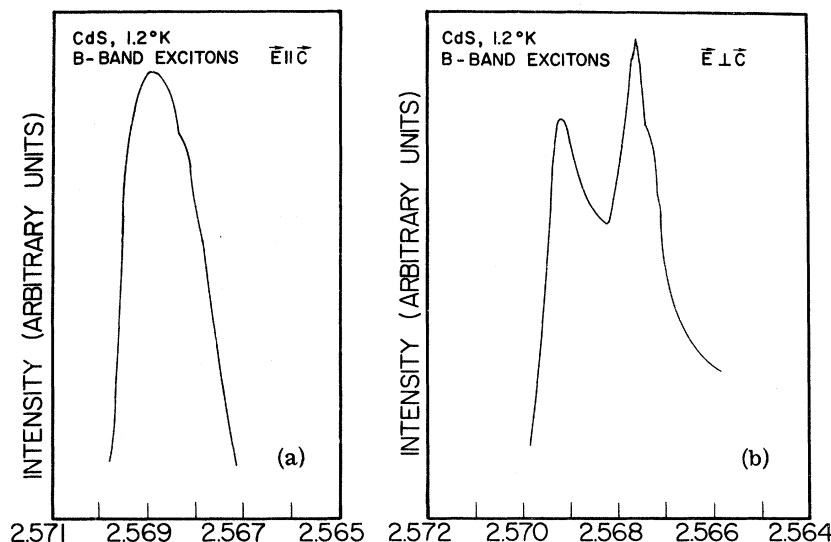


FIG. 4. (a) B-band intrinsic exciton emission in CdS, showing the ground state $B(n=1)$ for $\vec{E} \parallel \vec{C}$. (b) B-band exciton emission peak for $\vec{E} \perp \vec{C}$. Note that the ground state splits into its longitudinal and transverse components in this mode of polarization.

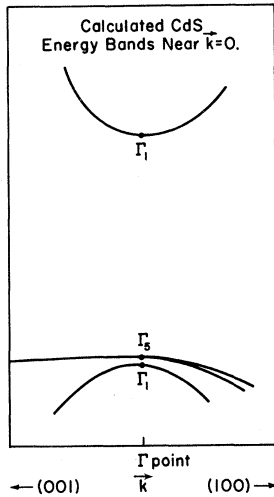


FIG. 5. Calculated energy bands in CdS, showing the shape of the conduction valence bands over a small range of \vec{k} , near $\vec{k}=0$ (after Euwema *et al.*, Ref. 7).

calculated value for GaP is $\Delta_{so} = 0.030$ eV; its experimentally measured value is $\Delta_{so} = 0.033$ eV. In moving along the isoelectronic sequence from GaP to InP, one finds an increase in the spin-orbit parameter. The same type of increase is expected in going from ZnS to CdS. If one uses the old energy differences for the top valence bands in CdS, i. e., $E_A - E_B = 0.016$ eV and $E_A - E_C = 0.073$ eV, one obtains $\Delta_{so} = 0.020$ eV. Using the measured value of the present work for $E_A - E_B$, together with the old value of $E_A - E_C$, one finds that $\Delta_{so} = 0.022$ eV. The experimentally measured values of Δ_{so} for zinc blende and wurtzite ZnS are 0.024 and 0.031 eV, respectively, giving a Δ_{so} for CdS which is less than that of ZnS. If one assumes that the exciton binding energy is the same for excitons which derive from the top three valence bands in CdS (as is sometimes done), one obtains a calculated spin-orbit parameter which is at least 50% too small. Thus using the calculated value for Δ_{so} of CdS and the value $E_A - E_B = 0.011$ eV, one obtains a crystal field parameter of 0.018 eV and $E_A - E_C = 0.120$ eV, as shown in Table I.

Since the static dielectric constants are crucial to exciton parameter calculations, it is important to note carefully the values which were used here. The perpendicular and parallel components of the static dielectric constant in CdS have been measured¹⁰ and at room temperatures are given by $\epsilon_{\perp} = 9.35$ and $\epsilon_{\parallel} = 10.33$. At 77°K they are $\epsilon_{\perp} = 8.48$ and $\epsilon_{\parallel} = 9.48$. The ratio $\epsilon_{\perp}/\epsilon_{\parallel}$ for room temperature is 0.905 and for 77°K it is 0.895. Extrapolating these results to 0°K one has $\epsilon_{\perp} = 8.18$, $\epsilon_{\parallel} = 9.19$ and the ratio is 0.890.

Returning now to the corrections to the $n=1$ states of both the A and B excitons, the results of Baldereschi and Lipari,^{11,12} who derived the energy shifts of the 1S levels for both zinc blende and

TABLE II. Valence-band parameters for CdS, past and present work.

	$E_A - E_B$ (eV)	$E_A - E_C$ (eV)	Δ_{so} and Δ_{cf} (eV)	Δ_{cf} (eV)
Present estimate	0.011	0.120	0.114	0.018
Previous estimate ^a	0.016	0.073	0.059	0.020

^aReference 2.

wurtzite structures are applied. In the notation used in Ref. 12, one has

$$\Delta E_A(1S) = R_0 \{ B_1 - A_0 [A_1 S_1(0) + A_2 S_1(E_A - E_B) + A_3 S_1(E_A - E_C)] \} \quad (3)$$

$$\Delta E_B(1S) = R_0 \{ B_2 - A_0 [A_4 S_1(0) + A_5 S_1(E_B - E_C) + A_2 S_1(E_B - E_A)] \} \quad (4)$$

Using the parameters of Table II, one has $S_1(X) > 0$ as well as the A_i 's. Thus to have a decrease between the position of the ground-state excitons as given by Figs. 3 and 4 (i. e., a shift of B 1S exciton state to higher energy), the parameters B_1 and B_2 must take on values different from those obtained in Ref. 12. Both B_1 and B_2 are related to another parameter G which is obtained from four valence band parameters (given in Table I of Ref. 12). In turn these four parameters are not well known but estimates of their relative magnitudes may be made. If one lets the parameter labeled T in Ref. 12 increase in magnitude relative to the others, a fairly good fit to experiment can be obtained. This indicates that Eqs. 3 and 4 are at least of the right form.

IV. CONCLUSION

In this investigation it has been possible to identify the Γ_{5T} and Γ_{5L} exciton states which derive from the B band in CdS. The splitting is almost the same as that predicted by Hopfield and Thomas for the A band, as can be seen from Table I. The energy shift of the ground-state B exciton was found to be different from the A-band ground-state exciton. By using the work of Baldereschi and Lipari it was found that one could explain the results as pointed out in Sec. III. It was also found that in order to obtain the correct spin-orbit parameter for the quasicubic model, one has to use different band parameters and a different binding energy for the C-band exciton.

- ¹D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).
²D. G. Thomas and J. J. Hopfield, Phys. Rev. **122**, 35 (1961).
³D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).
⁴M. Balkanski and J. des Clorzeaux, J. Phys. Radium **21**, 825 (1960).
⁵S. Adler and J. Birman, Gen. Telephone Electron. Res. Develop. J. **1**, 2 (1961).
⁶J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).

- ⁷R. Euwema, T. Collins, D. Shankland, and J. DeWitt, Phys. Rev. **162**, 710 (1967).
⁸D. Stukel, R. Euwema, T. Collins, F. Herman, and R. Kartum, Phys. Rev. **179**, 740 (1969).
⁹G. Wepfer, T. Collins, and R. Euwema, Phys. Rev. B **4**, 1296 (1971).
¹⁰D. Berlincourt, H. Jaffee, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).
¹¹A. Baldereschi and N. O. Lipari, Phys. Rev. B **3**, 439 (1971).
¹²N. O. Lipari, Phys. Rev. B **4**, 4535 (1971).

PHYSICAL REVIEW B

VOLUME 6, NUMBER 6

15 SEPTEMBER 1972

Pressure Dependence of the Refractive Index of Amorphous Lone-Pair Semiconductors*†

Marc Kastner‡

Department of Physics, The University of Chicago, Chicago, Illinois 60637

(Received 22 May 1972)

The pressure dependence of the refractive index (dn/dP) of several amorphous chalcogenide semiconductors is reported. dn/dP is positive for materials containing group-VI elements in twofold coordination (lone-pair semiconductors), whereas it is negative for tetrahedral semiconductors. Furthermore, dn/dP is the same for the amorphous and crystalline phases of a given semiconductor. Although a one-oscillator (Penn) model adequately predicts dn/dP for tetrahedral semiconductors, a similar approach does not predict the positive dn/dP of lone-pair semiconductors. Local-field corrections appear to be the cause of the positive dn/dP . The Lorenz-Lorentz description of the local field predicts dn/dP in agreement with experiment for most molecular lone-pair materials. It fails, however, for materials containing large concentrations of group-IV elements. The limitations of the local-field correction in describing dn/dP of partially molecular semiconductors is discussed.

INTRODUCTION

The pressure dependence of the refractive index of semiconductors is related to the pressure-induced shifts of the principal interband absorption processes. For tetrahedral semiconductors and compounds of the $A^N B^{8-N}$ type, Phillips¹ describes the principal interband absorption by a single-oscillator model, with an oscillator of energy E_σ , a modified Penn gap.² The value of E_σ is actually determined from the refractive index n by

$$n^2 - 1 = (\hbar\omega_p/E_\sigma)^2, \quad (1)$$

where $\omega_p = (4\pi Ne^2/m)^{1/2}$ is the plasma frequency. N is the density of valence electrons participating in the principal interband absorption. The plasma frequency changes with pressure as the reciprocal volume. For group-IV elements the dependence of E_σ on interatomic spacing a follows the empirical relation

$$E_\sigma \propto a^{-2.5}. \quad (2)$$

With this information, Van Vechten³ calculated the strain dependence of the refractive index. He obtained good agreement with the experimental

values for the group-IV elements. One obtains the same value of $(1/n)(dn/dP)$ for the amorphous and crystalline phases of the same substance.

Thus one can use n as a measure of E_σ which is associated with the strength of the chemical bond. The volume dependence of n can test to what extent this association is valid. The simple approach of Phillips and Van Vechten is especially attractive in the case of amorphous semiconductors where the physical properties cannot be described by band theory, and one might hope to relate observed physical properties to the chemical bonding.

Phillips's theory has been limited to $A^N B^{8-N}$ compounds. Most amorphous semiconductors are, however, lone-pair (LP) semiconductors⁴—those containing group-VI elements in twofold coordination. These, of course, are not $A^N B^{8-N}$ materials. The purpose of this work is to determine to what extent n is a measure of bond strength in amorphous LP semiconductors.

This paper reports measurements⁵ of the pressure dependence of the refractive index n or of the optical path length nl (l is the sample thickness) of amorphous layers of As_2S_3 , As_2Se_3 , $GeSe_2$, $GeSeTe$, and of the alloy glass $Ge_{16}As_{35}Te_{28}S_{21}$. We find that $(1/n)(dn/dP)$ is positive for these