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Exciton Structure in Photoconductivity of CdS, CdSe, and CdS:Se Single Crystals

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Exciton-like structure has been observed in the photoconductive spectral response curves of CdS, CdSe, and CdS:Se single crystals at 77 and 4.2°K. It is observed that a number of peaks in the photoconductivity spectra of CdS and CdSe correspond to the exciton spectra identified by other optical measurements. In CdS the photoconductivity peaks corresponding to the $n=1, 2, 3$ states and the series limit of the exciton from the first and second valence bands and the ground state of the exciton associated with the third valence band were observed. For CdSe the peaks corresponding to the $n=1, 2, 3$ states of the exciton from the first and second valence bands were identified. Only the ground state was identified in the solid solutions. Assignment of the observed photoconductivity peaks was carried out by observing optical selection rules in polarized light. Within a given series the peaks form nearly hydrogen-like energy spacings, and it is observed that the exciton absorption lines always corresponded to photocurrent maxima. From the position of the photoconductivity maxima corresponding to the ground states of the excitons from the first and second valence bands, the exciton ground-state energy levels of the solid solutions were estimated and found to vary nonlinearly with composition. The coincidence of photoconductivity peaks and exciton absorption lines clearly suggests participation of excitons in photoconductivity. Several possible mechanisms for production of free carriers via exciton states are suggested.

I. INTRODUCTION

THE fundamental absorption bands for a number of wurtzite compounds have recently been shown to possess a fine structure at low temperature, and this fine structure was explained in terms of exciton formation.[1–3] The observation and interpretation of the exciton spectra give detailed information concerning the electronic band structure of the material. To this end various optical methods such as transmission, reflection and luminescence measurements have been employed. However, very few attempts have been made to interpret the photoconductivity structure near the fundamental absorption edge in terms of the energy band structure.

It is the purpose of this paper: (1) to report on the details of the experimentally obtained spectra of photoconductivity at 77 and 4.2°K; (2) to show how observed photoconductivity spectra can be interpreted on the basis of the present exciton scheme of the wurtzite structure; (3) to show the variation of the ground-state energy of the exciton with solid solution composition; and (4) to suggest possible mechanisms by means of which excitons participate in photoconductivity.

The existence of fine structure in photoconductivity spectra of CdS and CdSe at 77°K has been observed by several workers.[4–6] However, no interpretation was given for the origin of the observed peaks and the observations do not seem to be consistently correlated to the exciton scheme observed by other workers. Gross and Novikov[5] have established the coincidence of photocurrent peaks and absorption maxima from their observation of the photoconductivity spectra of CdS, and they have indicated possible participation of excitons in photoconductivity. However, they found two types of crystals which they classified as Group I and Group II crystals. In Group I crystals the exciton absorption lines coincided with photocurrent maxima, whereas in Group II crystals the exciton lines coincided in position with photoconductivity minima.

Gross, *et al.*,[7] have recently reported the photoconductivity spectra of CdS at 4.2°K, but without identification of the peaks. No work on photoconductivity structure of CdSe and CdS:Se at 4.2°K has been reported. Optical properties of CdS have been extensively investigated, but comparatively little work has been done on the optical properties of CdSe.

Although there is much evidence of fine structure in the absorption edge spectra of CdS, until recently considerable confusion has existed in the description of the band structure and exciton energy levels. For example, impurity lines often have been wrongly attributed to excitons. To correct this situation, Thomas and Hopfield[2] treated the reflection and luminescence spectra

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[1] D. G. Thomas, Phys. Chem. Solids **15**, 86 (1960).

[2] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[3] R. G. Wheeler and J. O. Dimmock, Phys. Rev. **125**, 1805 (1962).

[4] K. W. Boer and H. Gutjahr, Z. Physik **152**, 203 (1958).

[5] E. F. Gross and B. V. Novikov, Fiz. Tverd. Tela **1**, 357 (1959) [translation: Soviet Physics—Solid State **1**, 321 (1959)].

[6] V. V. Eremenko, Fiz. Tverd. Tela **2**, 2596 (1960) [translation: Soviet Physics—Solid State **2**, 2315 (1961)].

[7] E. F. Gross, K. F. Lider, and B. V. Novikov, Fiz. Tverd. Tela **4**, 1135 (1962) [translation: Soviet Physics—Solid State **4**, 836 (1962)].

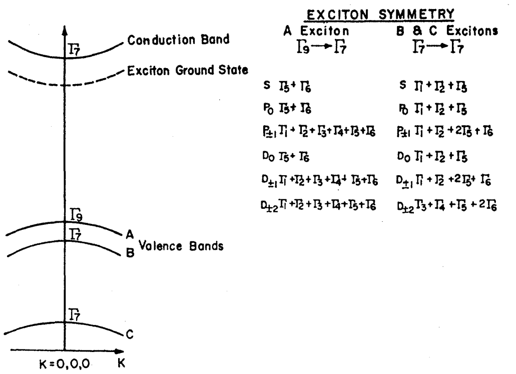

FIG. 1. Band structure and symmetries. A Γ_9–Γ_7 transition is allowed only for $E\perp C$, whereas a Γ_7–Γ_7 transition is allowed for both $E\perp C$ and $E\|C$. Dipole transitions to the Γ_1 and Γ_5 states are allowed with $E\|C$ and $E\perp C$, respectively.

on the basis of Birman's[8] theoretical investigation of the wurtzite band structure. They succeeded in explaining the spectrum of CdS by grouping them into three exciton series, one associated with each of the three valence bands. Each of the bands can give its own group of exciton levels near the conduction band. They have termed the exciton series associated with the first valence band as the "*A*" exciton series, and the series associated with the second and third valence bands as the "*B*" and "*C*" exciton series, respectively.

Within a given series, the lines form nearly hydrogen-like energy spacings. The ground state of each series is the $n=1$ state of the hydrogen-like energy levels, where n is the principal quantum number. The $n=2$, 3, 4, ... states represent the excited states of each exciton series.

The exciton symmetries and selection rules are obtained group theoretically.[3,9] The exciton states are characterized by the symmetry of the electron and hole bands from which the exciton is made and the symmetry of the electron-hole orbit. Excitons belonging to Γ_5 are observable for light polarized perpendicular to the C axis ($E\perp C$), and excitons belonging to Γ_1 are observable in light polarized parallel to the C axis ($E\|C$). From symmetry arguments all other exciton transitions are forbidden. These remarks are summarized in Fig. 1. Here, the exciton states are represented by S-, P-, and D-hydrogenic states. There can be $1S$, $2S$, $2P_0$, $2P_{\pm1}$, $3S$, $3P_0$, $3P_{\pm1}$, $3D_0$, $3D_{\pm1}$, $3D_{\pm2}$, etc. states analogous to the hydrogenic states. The subscripts 0, ±1, etc., refer to the number of units of orbital angular momentum around the C axis (z direction).

The ground state of the A exciton has the symmetry of $\Gamma_5+\Gamma_6$. Since group theory predicts that Γ_5 symmetry is active for light polarized in the $E\perp C$ mode, the optical transition to this state is allowed for $E\perp C$. Correspondingly, the ground states of the B and C excitons have the symmetry $\Gamma_1+\Gamma_2+\Gamma_5$. Since B and C exciton states contain both Γ_1 and Γ_5 symmetries, they are observable for both $E\perp C$ and $E\|C$. Thus, the exciton $1S$ states reflect the symmetries of the bands from which they are formed.

II. EXPERIMENTAL METHOD

The photoconductivity spectra were taken on single-crystal platelets grown from the vapor phase. The crystals used were all in the as-grown condition. In the course of measurements, chemical etching was tried to see whether it had any effect on accentuating the photoconductivity structure. Treating the crystals with hot concentrated HCl did not give added structure over an as-grown crystal. Hence, fresh, as-grown crystal platelets were used throughout the experiments. The platelets varied in size but usually were 100 to 300μ in thickness and 0.5 cm^2 in area.

The photoconductivity was excited by monochromatic light from a 500 mm Bausch and Lomb grating monochromator having a linear dispersion of 16 Å/mm. Indium electrodes were attached to the surface of the as-grown crystals using indium solder with a 25-W Sonobond ultrasonic soldering gun. The photocurrent was measured with a Keithly Model 610R electrometer at field strengths ranging from 50 to 300 V/cm. The photocurrent was recorded on an Electroinstruments Model 500 X-Y recorder. A spectral resolution of 2 to 4 Å was used for all measurements.

The crystals were mounted with rubber cement to a glass base and attached only at one end. This method of mounting minimized external strain on the crystal. (When a CdS crystal was bonded to a glass base over the entire surface, it was noticed that the structure at 77°K showed a displacement of the peaks by as much as 10 Å toward shorter wavelengths compared to corresponding peaks in crystals mounted only at one end, though the separations of the maxima were the same. This effect was not noticed in CdSe.) The crystals were cooled by immersion in either liquid nitrogen or liquid helium.

The spectral response curve of photocurrent for each sample was first determined at room temperature using polarized light. In several crystals of different compositions, both photoconductivity and absorption measurements were made. In every case the photoconductivity maxima at the absorption edge coincided with the absorption maxima. Using these results the band gap energy was inferred for all compositions from the position of the photoconductivity maxima for $E\perp C$. From the band gap energy (inferred from photoconductivity maxima) crystal composition in each solid solution was determined from the previously determined "energy gap versus crystal composition at room-temperature curve."[10] In this curve the energy gap was

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[8] J. L. Birman, Phys. Rev. Letters **2**, 157 (1959); Phys. Rev. **114**, 1490 (1959).

[9] J. J. Hopfield, Phys. Chem. Solids **15**, 97 (1960).

[10] F. Pedrotti and D. C. Reynolds, Phys. Rev. **127**, 1584 (1962).

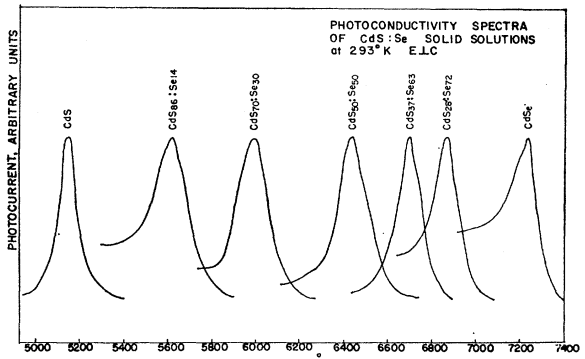

FIG. 2. Photoconductivity spectra of CdS:Se solid solutions at 293°K with $E\perp C$.

determined by absorption measurements, and it shows the nonlinear variation of band gap with composition. In the previous work,[10] the low-temperature A exciton ground-state energy versus crystal composition curve was established by assuming that the deviation of the ground-state energy from a linear variation with composition was proportional to the deviation at room temperature. In the present work the low-temperature curves were established by plotting the photoconductivity peaks as a function of crystal composition using the same crystals for which the room-temperature curve was established as shown in Fig. 8.

III. EXPERIMENTAL RESULTS AND ANALYSIS

Spectral response curves of photocurrent for light polarized with $E\perp C$ at 293°K for several crystal compositions are shown in Fig. 2. Here, an attempt is made to display the change in the position of the photoconductivity maxima, hence the band gap with crystal composition along a wavelength scale. The response spectra were not corrected for variation of the incident light intensity with wavelength. Spectral response curves for these crystals are typical of CdS, i.e., beginning with a short wavelength tail, rising to a peak, and falling off rapidly at first and then more slowly toward longer wavelengths.

At room temperature CdS shows two peaks: one at 5146 Å for $E\perp C$ and one at 5107 Å for $E\|C$, the separation between two maxima being 0.018 eV. These agree well with the peaks observed in absorption and reflection spectra. For CdSe two photoconductivity maxima were found: one peak at 7232 Å for $E\perp C$ and another at 7153 Å for $E\|C$; they are separated by 0.019 eV. The separation between the two maxima constitutes the splitting of the two top valence bands. The existence of these two valence bands with a small energy separation gives rise to the absorption dichroism.

The photoconductivity structure of the solid solutions at 293°K exhibited an absorption dichroism similar to pure CdS and CdSe. Therefore, from the position of the maxima observed for $E\perp C$, it was possible to determine the band gap of each composition. The band gap at 293°K is plotted as a function of crystal composition in Fig. 8. At room temperature the band gap rather than the exciton ground state was used, since excitons are not likely to exist at room temperature.

When the crystals are cooled, several distinct peaks stand out in the background in the fundamental absorption region. The structure is more complex at 4.2 than at 77°K. In general, cooling the crystal from 77 to 4.2°K gives rise to narrow and well-defined peaks.

The relative peak heights, as well as the background on which these peaks are imposed, differ widely from sample to sample. In certain samples the peaks constitute only a small addition to a strong background, while in others, a large part of the sensitivity is concentrated in the peaks. This intensity variation is possibly due to defects or surface conditions of the crystal, which would strongly influence the peak intensities making it difficult to establish any definite intensity ratios of the peaks. According to Elliot[11] the intensities should decrease as n^{-3} within a given exciton series. The large variation in the peak sizes prevent verification of this prediction. The peak sizes were not studied in this investigation. In some crystals, impurity peaks are so pronounced that an adjacent intrinsic peak is completely masked, making its identification impossible. Certain crystals showed only a broad continuous background. Therefore, clarification and identification of the peaks could only be accomplished by examining a large number of the crystals.

The results presented in the following section are those of a representative crystal among the crystals examined. The observed peaks summarized in Tables I and II do not correspond to those seen in one particular crystal. A crystal that showed most of the peaks observed in different crystals is chosen for discussion.

TABLE I. A summary of the photoconductivity peaks observed in light polarized perpendicular ($E\perp C$) and parallel ($E\|C$) to the hexagonal C axis in CdS at 293, 77, and 4.2°K.

	$E\perp C$			$E\|C$		
°K	Peaks	Position		Peaks	Position	
		(Å)	eV		(Å)	eV
293		5146	2.409		5107	2.427
77	I_A	4935	2.512	I_B	4905	2.527
	$A, n=1$	4875	2.543	$B, n=1$	4845	2.559
	$B, n=1$	4845	2.559	$B, n=\infty$	4785	2.591
	$B, n=\infty$	4785	2.591	$C, n=1$	4725	2.624
	$C, n=1$	4725	2.624			
4.2	I_A	4868	2.547	Γ_6	4858	2.552
	$A, n=1$	4854	2.554	I_B	4838	2.562
	I_B	4838	2.562	$B, n=1$	4826	2.569
	$B, n=1$	4826	2.569	$A, n=2$	4815	2.575
	$A, n=2$	4815	2.575	$A, n=3$	4810	2.577
	$A, n=3$	4810	2.577	$A, n=\infty$	4800	2.583
	$A, n=\infty$	4800	2.585	$B, n=\infty$	4776	2.596
	$C, n=1$	4719	2.627	$C, n=1$	4719	2.627

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[11] J. Elliot, Phys. Rev. **108**, 1384 (1957).

TABLE II. A summary of the photoconductivity peaks observed in light porized perpendicular ($E\perp C$) and parallel ($E\parallel C$) to the hexagonal C axis in CdSe at 293, 77, and 4.2°K.

°K	$E\perp C$			$E\parallel C$		
	Peaks	Position		Peaks	Position	
		(Å)	eV		(Å)	eV
293		7232	1.714		7153	1.733
77	A, $n=1$	6830	1.815	I_B	6807	1.821
	A, $n=2$	6793	1.825	A, $n=2$	6793	1.825
	B, $n=1$	6744	1.838	B, $n=1$	6744	1.838
	B, $n=\infty$	6686	1.854	B, $n=\infty$	6686	1.854
42	I_1	6827	1.816	I_3	6774	1.830
	A, $n=1$	6791	1.825	I_5	6729	1.842
	I_2	6783	1.828	I_6	6721	1.844
	I_4	6764	1.833	B, $n=1$	6710	1.847
	A, $n=2$	6751	1.836	B, $n=2$	6678	1.856
	A, $n=3$	6740	1.839	B, $n=3$	6661	1.861
	I_6	6721	1.844			
	B, $n=1$	6710	1.847			
	$B=2$	6678	1.856			
	B, $n=3$					

Photoconductivity Spectra of CdS at 77 and 4.2°K

In Table I are listed some of the intrinsic photoconductivity peaks and the impurity peaks seen in CdS with $E\perp C$ and $E\parallel C$ at 293, 77, and 4.2°K.

At 77°K six peaks are observed, as seen in Fig. 3. Among these peaks, the peaks at 4935 Å (I_A) and 4875 Å (A, $n=1$) are active for $E\perp C$, while the distinct peaks at 4845 Å (B, $n=1$), 4785 Å (B, $n=\infty$), and 4725 Å (C, $n=1$) are active in both modes of polarization. Above the peak I_A, but just below exciton A, a broad peak at 4905 Å (I_B) is seen for $E\parallel C$.

There is good agreement with Dutton[12] and Thomas and Hopfield[2] in their observation of three sharp reflection peaks, A at 4873 Å active only for $E\perp C$, and B and C at 4844.5 and 4738.7 Å, respectively, active in both modes of polarization.

Two broad peaks observed at the long-wavelength side of the absorption edge show very prominent photoconductivity. They are undoubtedly associated with impurity centers. I_A and I_B may be the bound (or impurity) exciton states. Bound exciton complexes (excitons bound to impurity centers) in CdS have recently been discussed by Thomas and Hopfield.[13] I_A is about 0.031 eV below exciton A and I_B is 0.032 eV below exciton B. Since I_B is energetically as close to exciton B as I_A is to exciton A, it may arise from the same impurity as I_A.

Photoconductivity peaks observed here are very much like those reported by Gross and Novikov.[5] They report an additional peak at 4660 Å in addition to those mentioned above. However, they observed similar impurity peaks only in the so-called "Group II" crystals. In such crystals the exciton absorption lines correspond to photocurrent minima. They termed these long wave maxima as "false" maxima and also they were able to convert Group II crystals to "Group I" crystals by annealing so that the exciton absorption lines then correspond to photocurrent maxima. In our observations, the exciton absorption lines always corresponded to photocurrent maxima.

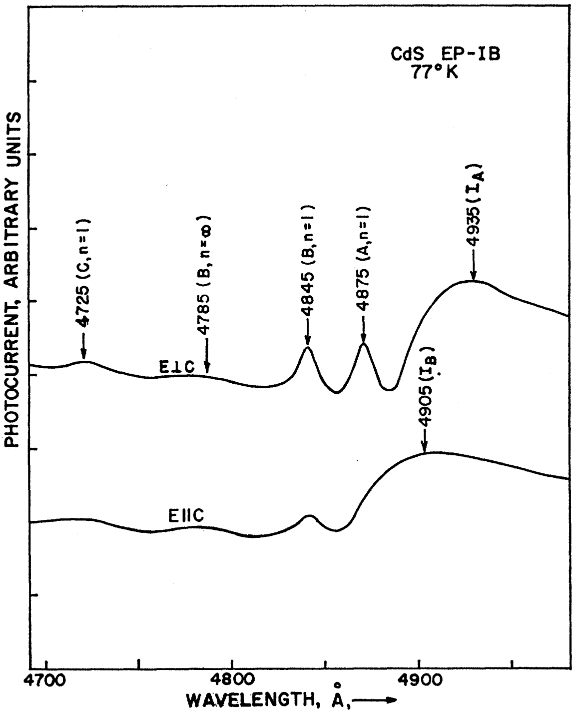

FIG. 3. Photoconductivity spectra of CdS at 77°K in polarized light.

On cooling the crystal from 77 to 4.2°K, the number of peaks is increased and appear more distinct as shown in Fig. 4. Here two crystals are illustrated. One can immediately notice from this Figure the variation of peak intensity and background in two crystals. In the second crystal (lower curves b, b') the impurity peaks seem to be more pronounced than the intrinsic peaks, while in the first crystal (upper curves a, a') the largest part of sensitivity is concentrated in the intrinsic peaks.

The photoconductivity peak corresponding to the $n=1$ state of exciton A is only active in $E\perp C$ and the peaks corresponding to the $n=2$, 3, ∞ states of exciton A are seen in both modes of polarization. Peaks corresponding to the $n=1$ state of exciton B and the $n=1$ state of exciton C are also observed. Two impurity peaks are observed: one at 4868 Å (I_A) active only for $E\perp C$ and the other at 4838 Å (I_B) active for both modes of polarization. I_A is 0.007 eV below exciton A, and I_B is 0.007 eV below exciton B. Absorption peaks at the same wavelength are reported by Thomas and Hopfield.[13] From the behavior of these lines in a magnetic field they identified the lines as transitions arising from exciton A and exciton B bound to neutral donors.

There are two peaks, 4800 and 4776 Å, that are

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

[13] D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).

active in both modes of polarization. From their position, they may correspond to the series limit of exciton A and exciton B. The series limits of exciton A and exciton B, assuming a "hydrogen-like" series, are 4801 and 4772 Å, respectively. In transmission measurements, excited states higher than $n=4$ have not been reported, partly because of weak line strength at higher order and partly due to thickness of the crystal.

In every crystal investigated a sharp peak at 4858 Å is seen for $E\|C$. This peak is about 0.002 eV below exciton A. Because of limited resolution and experimental uncertainty involved in measurements, it is difficult to say whether this peak is an impurity peak or the Γ_6 $n=1$ state of exciton A described by Hopfield and Thomas.[14] Hopfield and Thomas have reported the Γ_6 exciton at 4857.0 Å active only in $E\|C$. They also report two impurity peaks at 4859.1 and 4857.6 Å, active for both modes of polarization.[13] Since this peak is inherent in all crystals, and observable for $E\|C$, it is likely that the peak is associated with the Γ_6 exciton.

Photoconductivity Spectra of CdSe at 77 and 4.2°K

The photoconductivity peaks observed in CdSe for $E\perp C$ and $E\|C$ are summarized in Table II.

At 77°K, unlike CdS, no impurity peaks were observed in the long-wavelength region as shown in Fig. 5. The photoconductivity peak associated with exciton A at 6830 Å, active only in $E\perp C$, is broader than the corresponding peak in CdS at 77°K. There is a peak at the $n=2$ state of exciton A which appears in both modes of polarization and its intensity is rather strong. The energy difference between this peak and the $n=1$ state of exciton A is about 0.001 eV, which is about $\frac{3}{4}$ of the exciton binding energy (0.015 eV) in CdSe. Since the excitons have a hydrogen-like set of energy levels

$$h\nu_n = E_{\text{gap}} - E_B/n^2,$$

where E_B is the binding energy. Therefore,

$$h(\nu_2-\nu_1)=\tfrac{3}{4}(E_B).$$

There exists a $2P_{\pm 1}$ state which is active in both modes of polarization since it contains Γ_1 and Γ_5 symmetries. Therefore, one would expect to see transitions to this state for both modes of polarization. The photoconductivity peak at the $n=1$ state of exciton B is observed at 6744 Å (B, $n=1$) for both modes of polarization. The $n=2$ state is not observed. Calculations from hydrogen-like levels put this peak at about 6703 Å which is apparently masked by the appearance of the peak at 6686 Å (B, $n=\infty$); in particular, the 6686-Å peak may be either band gap, or the excited states of higher quantum numbers of exciton B. There is one peak at 6807 Å just below (about 0.017 eV) the $n=1$ state of exciton B which is believed to be an impurity exciton. It is a sharp, narrow peak active only for $E\|C$.

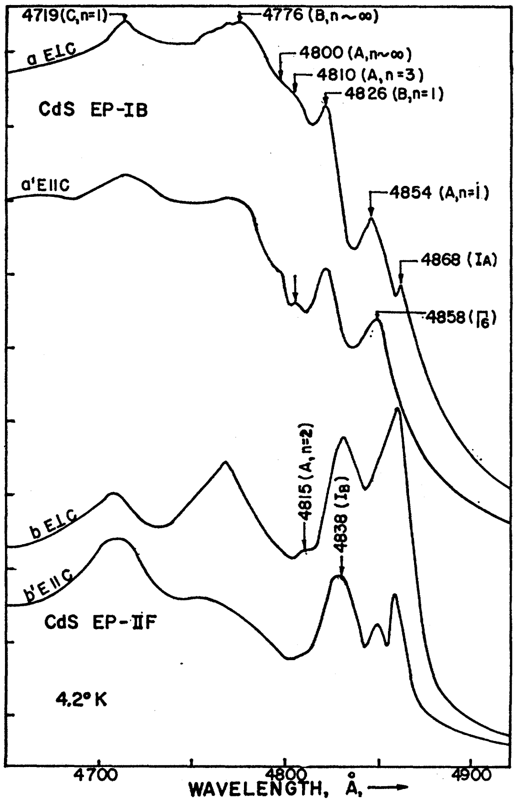

FIG. 4. Photoconductivity spectra of CdS at 4.2°K in polarized light for two crystal samples. In the first crystal (curves a, a') the largest part of sensitivity is concentrated in the intrinsic exciton peaks, while in the second crystal (curves b, b') the impurity peaks are more pronounced than intrinsic exciton peaks.

No conclusive absorption or reflection spectra of CdSe at 77°K are yet available for comparison with the data presented above. (Gross and Sovolev[15] have reported on the observation of lines in the absorption edge of CdSe, but without identification.) Hence, the reflection spectra of the same crystal used for photoconductivity measurements were taken photographically using a grating spectrograph with a linear dispersion of 12 Å/mm. These reflection spectra showed the lines at 6829 and 6740 Å, in good agreement with the respective assignment of exciton A and exciton B from photoconductivity measurements. The line at 6829 Å was active only for $E\perp C$ and the line at 6740 Å was active for both $E\perp C$ and $E\|C$. The photoconductivity structure at 4.2°K is more complex than that of CdS at the same temperature. More impurity peaks were observed. Because of these impurity peaks and their strong intensities, the adjacent intrinsic peaks were often masked, making identification of the intrinsic peaks difficult. In Fig. 6 the structure of a representa-

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[14] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

[15] E. F. Gross and V. V. Sobolev, Fiz. Tverd. Tela **2**, 406 (1959) [translation: Soviet Physics—Solid State **2**, 379 (1960)].

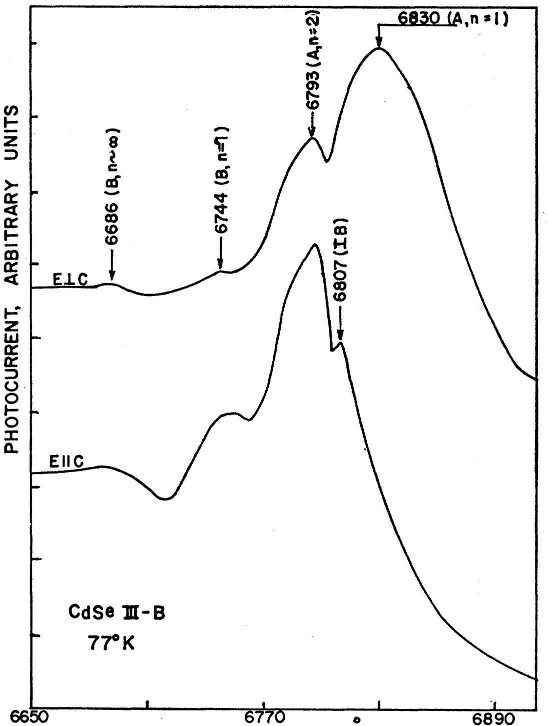

FIG. 5. Photoconductivity spectra of CdSe at 77°K in polarized light.

tive crystal, which showed most of the peaks present in different crystals, is shown. Interpretation of the photoconductivity peaks was facilitated by referring to the absorption spectra obtained by Wheeler and Dimmock.[3] Since the impurity states lying near and associated with one of the band edges are likely to have the same symmetry as the band edge, the transitions involving the impurity states will obey the same optical selection rules. Hence, the behavior of the peaks in polarized light alone would not distinguish the intrinsic peaks from the extrinsic peaks. Also it was found that the impurity peaks themselves formed a hydrogen-like spectrum. Therefore, a criterion for identifying the impurity peaks was based on the fact that the observance of these peaks varied from crystal to crystal. The photoconductivity peaks corresponding to the $n=1$, 2, 3 state of exciton A were found at 6791, 6751, and 6740 Å and were active only in $E\perp C$. The peaks corresponding to $n=1$, 2, 3 states of exciton B were located at 6710, 6678, and 6661 Å in both modes of polarization. They all form nearly hydrogen-like energy spacings within a given series. No peaks corresponding to the exciton C series were detected, and no series limit was observed in either series.

Careful examination shows that there are two series of discrete impurity-center levels. The peaks 6774 (I_3), 6729 (I_5), and 6721 Å (I_6) form one hydrogen-like spectrum, and peaks 6827 (I_1), 6783 (I_2), and 6764 Å (I_4) form another such series. [Peaks 6827 Å (I_1) and 6783 (I_2) are not shown in Fig. 6, but are found in another crystal.] A sharp peak 6807 Å observed at 77°K has apparently the same origin as the peak 6774 Å (I_3), since they are about 0.005 eV above the $n=1$ state of exciton A and 0.017 eV below the $n=1$ state of exciton B at both nitrogen and helium temperature. They are active only for $E\|C$. It has been shown that the energy levels of an imperfection lying near and associated with one of the band edges can be approximated by hydrogen-like levels.[16] The appearance of these photoconductivity excitation bands can be associated with direct ionization of imperfection centers, or they may arise from the bound exciton states.

Photoconductivity Spectra of CdS:Se at 77 and 4.2°K

The photoconductivity peaks coincide with the exciton peaks, observed by other investigators,[2,3] in both pure CdS and CdSe crystals (which constitute two end points of the solid solution). One would expect a similar behavior in the solid solutions, as x-ray data show that CdS and CdSe form a continuous series of solid solutions of the substitution type. Table III summarizes experimental wavelengths of the upper two valence bands of CdS:Se determined from the position of the photoconductivity maxima at 293, 77, and 4.2°K.

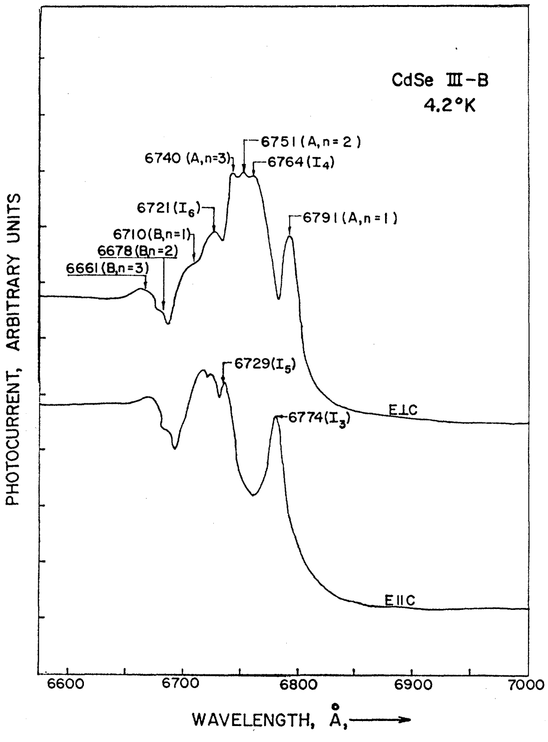

FIG. 6. Photoconductivity spectra of CdSe at 4.2°K in polarized light.

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[16] E. Burstein, G. Picus, and N. Sclar, in *Photoconductivity Conference*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (John Wiley & Sons, Inc., New York, 1956), p. 353.

TABLE III. Experimental wavelengths of the upper two valence bands of CdS:Se determined from the position of the photoconductivity maxima at 293, 77, and 4.2°K.

Crystal Composition mole %Se	293°K Position [λ(Å)] energy (eV)		77°K Position [λ(Å)] energy (eV)		4.2°K Position [λ(Å)] energy (eV)	
	A band	*B* band	*A* band	*B* band	*A* band	*B* band
CdS	5146	5107	4875	4845	4854	4826
	2.409	2.427	2.543	2.559	2.554	2.569
4	5332	5287	5103	5072	5049	5012
	2.325	2.345	2.429	2.440	2.455	2.473
14	5626	5584	5409	5378	5345	5369
	2.203	2.218	2.291	2.305	2.309	2.319
30	5989	5954	5752	5700	5713	5673
	2.070	2.082	2.155	2.175	2.170	2.185
50	6437	6389	6130	6080	6093	6043
	1.926	1.940	2.022	2.039	2.035	2.051
63	6712	6651	6345	6277		
	1.847	1.864	1.954	1.975		
72	6879	6813	6514	6452	6470	6409
	1.802	1.820	1.903	1.921	1.916	1.934
82					6631	6574
					1.869	1.886
85	7128	7054	6722	6637	6669	6608
	1.739	1.757	1.844	1.867	1.859	1.876
CdSe	7232	7153	6830	6744	6791	6710
	1.714	1.733	1.815	1.838	1.825	1.847

From Fig. 9 it is seen that these values agree well with the position of the ground-state excitons observed in transmission measurements. No attempt was made to identify the excited states of each exciton series in solid solutions.

Less structure is observed in the photoconductivity of CdS:Se than that of pure CdS and CdSe. Some compositions show only two maxima corresponding to the ground state of exciton *A* and exciton *B*. Such identification was easily accomplished by observing optical selection rules. Figure 7 shows the photoconductivity spectra of CdS_{50}:Se_{50} at 4.2°K as an illustration. The peak at 6093 Å (A, $n=1$) is active only in $E\perp C$ and 6043 Å (B, $n=1$) in both modes of polarization. The peaks are, in general, broader than the corresponding peaks of pure CdS and CdSe. Although the substitution of Se may be orderly on a macroscopic scale, it is perhaps not surprising to imagine that the distribution of the Se atoms is not uniform in the lattice structure. The spacing between Se atoms is undoubtedly random. This will create nonuniform distribution of defects or impurities at the surface and in the bulk of the crystals. Since the mobility and lifetime of free carriers are influenced by the presence of such defects as recombination and trapping centers, one would expect irregularities in the photoconductivity spectra as a consequence of irregularities in composition.

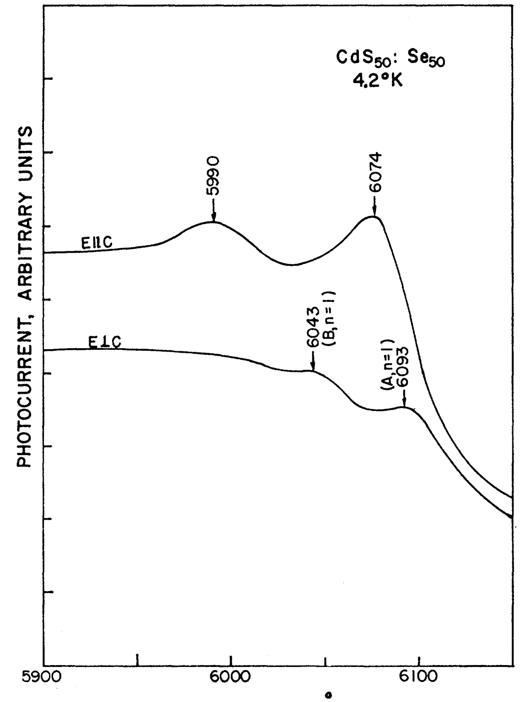

FIG. 7. Photoconductivity spectra of $CdS_{50}Se_{50}$ at 4.2°K in polarized light.

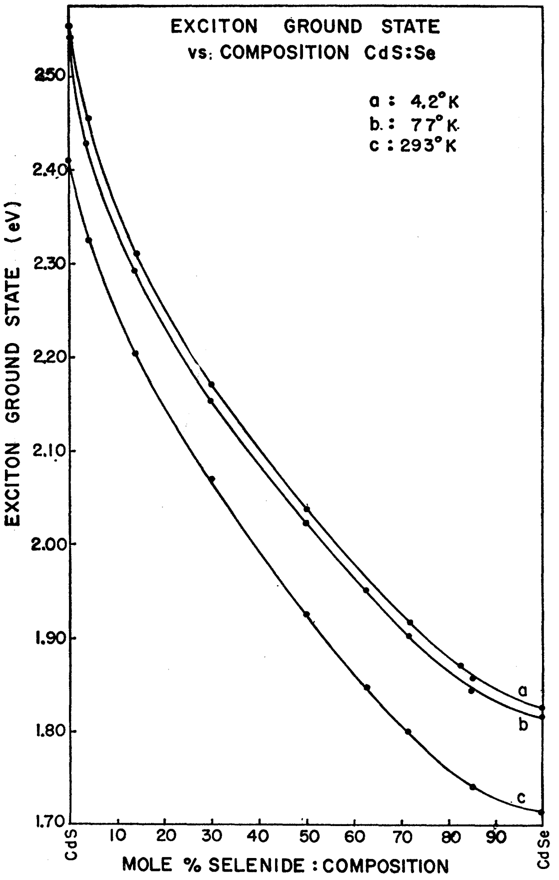

FIG. 8. Variation of ground state of *A* exciton with solid solution composition at 293, 77, and 4.2°K.

IV. DISCUSSION AND CONCLUSION

The position of the photoconductivity maxima in these crystals coincides with the position of the ex-

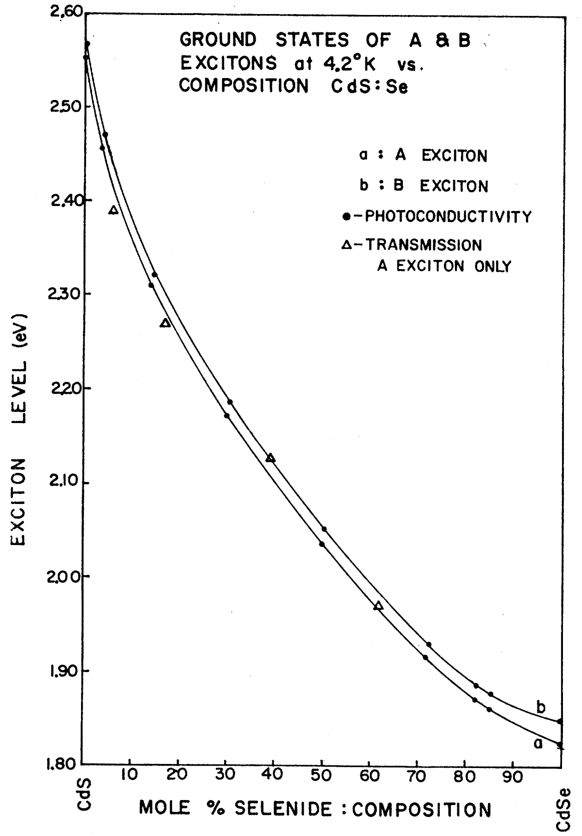

FIG. 9. Variation of ground states of A and B excitons with solid solution composition at 4.2°K. This figure shows photoconductivity as well as transmission data.

citon lines observed from other optical measurements.

From the photoconductivity peaks for $E \perp C$ the ground-state energy of exciton A as a function of crystal composition at 293, 77, and 4.2°K is plotted in Fig. 8. In Fig. 9 the ground-state energy of both exciton A and exciton B at 4.2°K is shown. The variation of exciton ground-state energy with composition at low temperatures deviates from linearity approximately in the same manner as at room temperature.

In the tight-binding approximation, the valence band is assumed to be formed from the p orbitals of the anions, whereas the conduction band arises from the s orbitals of the cations. As the band gap is observed to vary with the content of the selenium atoms, it may be that the principal variation in the band gap results from a shift in the valence band level, while the conduction band remains approximately fixed. The higher atomic states in Se, as compared with those in S, are reflected in the decreased band gap of CdSe as compared with CdS. The band gap (the series limit of exciton A) at 4.2°Kis found to be 2.582 eV in CdS and 1.841 eV in CdSe.[2,3] The binding energy of the exciton in CdS is 0.028 eV and in CdSe it is about 0.015 eV. Therefore, one would expect the variation of the exciton binding energies in the solid solutions to be in the range of 0.028 to 0.015 eV. Unfortunately, experimental data accumulated in this work are not sufficient to corroborate such a variation.

From the appearance of peaks on the spectral curve of photocurrent in the region of fundamental absorption, one can certainly conceive two mechanisms of photocurrent generations: (1) the direct formation of free electrons and holes and (2) the creation of free carriers through excitons. The existence of a background and the observation of the series limit on the spectral curve can be easily comprehended if one assumes a band-to-band transition, i.e., a direct excitation of electrons from the valence band to the conduction band. On the other hand, from the fact that the largest part of the sensitivity is concentrated in the regions of the exciton absorption lines, the contribution of excitons to photoconductivity is apparent and large.

Of course, excitons themselves, having a neutral charge, cannot contribute directly to the electrical conductivity. Excitons must dissociate in order to make a contribution to the photocurrent. The following mechanisms for production of free carriers via exciton states can be envisioned:

(1) The dissociation of excitons through interaction with phonons. The exciton formed by light can be dissociated by absorption of a phonon into a free electron and a free hole. This mode of breakup of the exciton is also applicable to the case of the excitons bound to impurity centers. Such bound excitons can be freed by absorption of a phonon to become a free exciton, with subsequent breakup of the exciton into a free electron and a free hole.

(2) The dissociation of excitons through interaction with impurity centers. When a migrating exciton comes to a site of the impurity center, the exciton can be dissociated by a charge-exchange reaction in which, for example, the electron member of the exciton is captured by a positive ion, the hole being freed into the valence band. Trapped electrons can be excited into the conduction band by means of energy transfer from other excitons.

(3) The dissociation of excitons through interaction with excitons.

For the first mechanism to occur, the excitons need not necessarily be mobile. The second and third mechanisms naturally assume the motion of excitons.