found that the attenuation of ultrasonic phonons was due partly to longitudinal thermal phonons and partly to transverse thermal phonons. Lewis and Patterson[22] measured the attenuation of fast transverse waves in $X$-cut and $BC$-cut quartz, and for $\omega\tau_{\rm th}>10$, they found that longitudinal thermal phonons made a negligible contribution to the attenuation. We have ruled out the longitudinal thermal phonon collision term in InAs because it gives a much larger frequency dependence of the attenuation than is observed experimentally.

## ACKNOWLEDGMENTS

We would like to thank W. P. Allred who grew the large crystal used in these experiments, at the Bell and Howell Research Center, and Professor H. J. Yearian of Purdue University for orienting it. We are also indebted to B. B. Chick of Matec, Inc. and Brown University for his many valuable experimental suggestions, and to Professor H. J. Maris of Brown University for providing us with a copy of his thesis. Discussions with R. C. Purdom of Purdue University were very helpful.

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# Exciton Excitation Spectra in CdS

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Optical excitation spectra of exciton emission lines in CdS are presented. It is shown that the center responsible for the $I_1$ emission, an exciton bound to a neutral acceptor, is created by the formation of free excitons which are subsequently trapped or bound to the impurity, or by the direct formation of bound excitons on the impurity site. The centers responsible for an $I_5$ emission line at 4869.5 Å and for an $I_2$ emission line at 4868.3 Å are also created by the formation of free excitons which are subsequently bound to a localized site, but more importantly they are created by direct LO phonon assisted formation of excitons bound to neutral and ionized impurities. It is concluded that the impurity is a donor. Evidence of thermal dissociation of these complexes is also presented.

## INTRODUCTION

The optical properties of CdS have been under investigation for some time. It is now fairly well established that the observed narrow lines in the absorption and reflection spectra at wavelengths less than 4860 Å at helium temperatures are due to intrinsic excitons[1,2] and that many of the sharp lines in the absorption and fluorescence spectra at energies slightly lower than the intrinsic excitons are due to transitions involving bound excitons,[3–5] in which an exciton bound to a neutral or ionized donor or acceptor is created or destroyed.

Nearly all crystals of CdS show a line at 4888.5 Å which has been labeled $I_1$ and which has been shown to be an exciton bound to a neutral acceptor.[4] In emission this line is replicated at lower energies with the spacing between lines equal to the LO phonon energy. At somewhat higher energies there appears a group of absorption and emission lines in the wavelength interval 4867–4870 Å. These lines have been labeled $I_2$ by Thomas and Hopfield,[4] and have been identified by them as arising from excitons bound to neutral donors. Reynolds and Litton[5] have seen an absorption and emission line at 4869.14 Å, labeled $I_5$, which was tentatively identified as an exciton bound to a neutral acceptor, but recent experiments by Reynolds[6] have established that $I_5$ is also an exciton bound to a neutral donor.

The complexes responsible for the emission of lines such as $I_1(I_2)$ involve an electron (hole) and two holes (electrons) bound to an acceptor (donor) impurity. No information is available in the literature regarding the formation of these complexes. It is the purpose of the present study to identify the various modes of formation of bound exciton complexes in CdS.

We shall demonstrate that this identification can be made by an examination of the variation of luminescence efficiency as a function of the wavelength of the exciting radiation, i.e., by the excitation spectra of the emission lines. Although this technique has been previously reported in the literature,[7–12] the present work

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[1] E. F. Gross, B. S. Razbirin, and M. A. Iakobsen, Zh. Tekhn. Fiz. **27**, 1149 (1957) [English transl.: Soviet Phys.—Tech. Phys. **2**, 1043 (1957)].

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

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

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

[5] D. C. Reynolds and C. W. Litton, Phys. Rev. **132**, 1023 (1963).

[6] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **174**, 845 (1968).

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[8] P. J. Dean and J. C. Male, Proc. Roy. Soc. (London) **A277**, 330 (1964).

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[10] Y. S. Park and J. R. Schneider, Phys. Rev. Letters **21**, 798 (1968).

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[12] P. J. Dean, Phys. Rev. **168**, 889 (1968).

represents the first detailed analysis of the formation of bound-exciton complexes.

In a preliminary report of this work,[7] it was shown that the complex responsible for the $I_1$ emission is created preferentially by the production of intrinsic excitons which are subsequently trapped on the impurity. The complex giving rise to the $I_5$ emission at 4869.5 Å was shown to be created directly on the impurity site with the simultaneous emission of LO phonons. These creation mechanisms are confirmed here and further evidence to support Reynolds's identification of the $I_5$ complex as an exciton bound to a neutral donor is given. Additional data on the formation of the complex responsible for the $I_2$ and $I_5$ emission are presented which show that these complexes can also be created via the direct formation of excitons bound to ionized donors with the simultaneous emission of LO phonons. Evidence of thermal dissociation of these complexes is also presented.

The marked resemblance of the $I_2$ and $I_5$ excitation spectra leads us to postulate that these emissions are associated with closely related or identical complexes.

## EXPERIMENTAL

The experimental arrangement is shown schematically in Fig. 1. A high-pressure xenon or mercury 100-W PEK lamp was focused onto the entrance slits of a Spex Model 1700-II spectrometer used in second order where the linear dispersion was 5 Å/mm. Most data were taken with 0.50–0.75-mm slits. The beam splitter (a glass slide) and associated equipment serve to normalize the emission intensity to the intensity of the exciting radiation. The analyzing spectrometer ($\frac{1}{4}m$ Jarrell Ash) has a linear dispersion of 33 Å/mm; all data were taken with 0.1-mm slits, with which the instrumental resolution is 5 Å.

The samples were either immersed in liquid helium or mounted in high vacuum (pressure less than $10^{-6}$ Torr) on the helium finger of a Dewar, the end of which was made of high-conductivity copper.

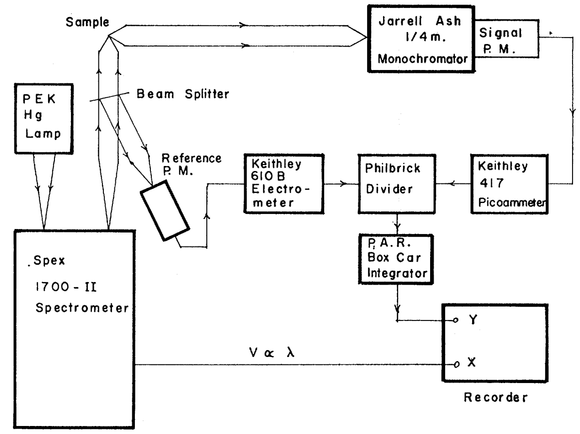

FIG. 1. Schematic of apparatus.

All crystals used were high-purity single crystals obtained from the Eagle-Picher Company. Those crystals whose resistivity was measured showed a room-temperature dark resistivity in excess of $10^7$ Ω cm. In nearly all cases the samples used had been freshly cleaved and mounted with rubber cement or silicon vacuum grease. In some cases the samples were etched at room temperature with concentrated sulphuric acid in which a small amount of $KMnO_4$ had been dissolved.[13] This etch allowed the structure in the excitation spectra to be as sharp and well defined as for cleaved surfaces.

## RESULTS

The portion of the emission spectrum of each crystal which has been studied consists of three sharp lines. All crystals showed the $I_1$ emission line at 4888.5 Å which is replicated at lower energies, the spacing between lines being equal to the LO phonon energy. Crystals 1 and 2 both showed an $I_5$ emission line at 4869.5 Å while crystal $A$ exhibited an $I_2$ emission line at 4868.3 Å, which was normally more intense than the $I_5$ emission from crystals 1 and 2.

### Excitation Spectrum of $I_1$

The excitation spectrum of the $I_1$ emission line in crystal 1 is shown in Fig. 2. Except for some differences in the relative intensities of the different lines, the spectrum is the same for crystal 2 and under certain conditions to be discussed, the same for crystal $A$. The

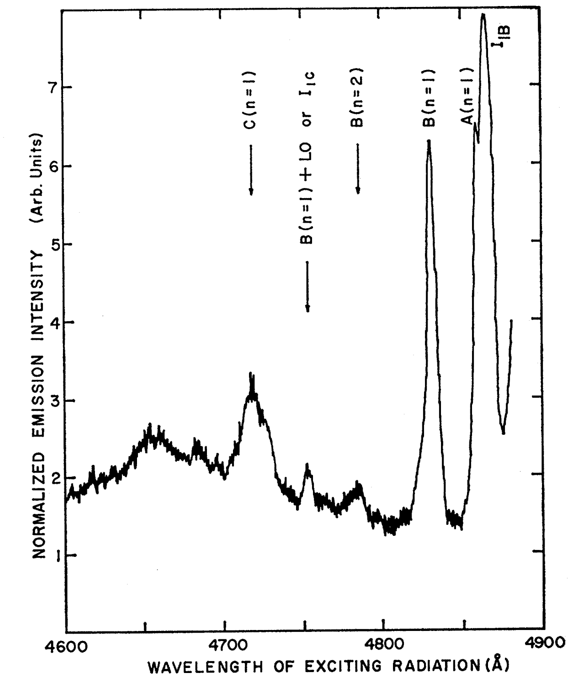

FIG. 2. Excitation spectrum of the $I_1$ emission line in single crystal CdS.

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[13] J. E. Rowe and R. A. Formann, J. Appl. Phys. 39, 1917 (1968).

TABLE I. Position of peaks in the excitation spectra of the $I_1$ and $I_1$—LO emission lines in CdS.

| Crystal | Emission line | Peak position in excitation spectrum (Å) | Assignment and polarization active in formation of exciton complex |
|---|---|---|---|
| 1 | $I_1$ | 4862.5±2 | $I_{1B}$, $\mathbf{E}\parallel c$ |
| | | 4856.0 | $A(n=1)$, $\mathbf{E}\perp c$ |
| | | 4827.5 | $B(n=1)$, $E\perp c$ and $E\parallel c$ |
| | | 4781.5±5 | $B(n=2)$, $E\perp c$ and $E\parallel c$ |
| | | 4751.0 | $B(n=1)+\mathrm{LO}$ or<br>$I_{1C}$, $E\perp c$ and $E\parallel c$ |
| | | 4715.0 | $C(n=1)$, $E\perp c$ and $E\parallel c$ |
| | $I_1$—LO | 4828.5±2 | $B(n=1)$, $E\perp c$ and $E\parallel c$ |
| | | 4857.5 | $A(n=1)$, $E\perp c$ |
| | | 4865.0 | $I_{1B}$, $E\parallel c$ |
| | | 4890.0 | $I_1$, $E\perp c$ |
| 2 | $I_1$ | 4860 ±2 | $I_{1B}$, $E\parallel c$ |
| | | 4851.0 | $A(n=1)$, $E\perp c$ |
| | | 4827.5 | $B(n=1)$, $E\parallel c$ |
| | | 4826.0 | $B(n=1)$, $E\perp c$ |
| $A$, cooled under uv illumination | $I_1$ | 4862 ±2 | $I_{1B}$, $E\parallel c$ |
| | | 4855 | $A(n=1)$, $E\perp c$ |
| | | 4826 | $B(n=1)$, $E\perp c$ and $E\parallel c$ |
| $A$, cooled in dark | $I_1$ | 4860 ±2 | $I_{1B}$, $E\parallel c$ |
| | | 4862 | $I_{1B}$, $E\perp c$ |
| | | 4827 | $B(n=1)$, $E\parallel c$ |
| | | 4826.5 | $B(n=1)$, $E\perp c$ |

wavelengths of all the peaks are summarized in Table I. The emission is strongly polarized with the electric vector of the light normal to the crystal $c$ axis ($E\perp c$).

From this data it is concluded that the complex responsible for the $I_1$ emission is formed preferentially either directly by the production of a bound $A$, $B$, or $C$ exciton on a neutral acceptor, resulting in the peaks labeled $I_1$ (seen in the phonon replica emission), $I_{1B}$, and $I_{1C}$, or by the formation of intrinsic $A$, $B$, or $C$ excitons which diffuse through the crystal and are subsequently trapped on a neutral acceptor. The designation of intrinsic or free excitons as $A$, $B$, or $C$ excitons corresponds to the designation of the valence band from which the hole originates.[2]

The exciton-impurity complex so formed consists of one electron, a hole from the $A$, $B$, or $C$ valence band, and the hole which neutralized the acceptor. This latter hole is most likely a hole from the $A$ valence band.

Care must be taken in describing the hole of an exciton as being associated with a particular valence band, particularly one of the lower valence bands, because the wave function for such a hole is bound to be an admixture of states from all bands. It is then possible for a "$B$ hole" to change its character and become an "$A$ hole" before the exciton recombines. If this occurs, then the emission will be polarized with $\mathbf{E}\perp c$ irrespective of the nature of the exciton which was created on the impurity site. Such a conversion mechanism has also been proposed by Thomas and Hopfield[4] to account for the broadening of two absorption lines which they label $I_{1B'}$ and $I_{2B}$.

All lines in the excitation spectrum have the polarization dependence corresponding to the valence band from which the hole of the exciton originates, although it is not understood why the $I_{1B}$ peak is active only for $\mathbf{E}\parallel c$ and not for $\mathbf{E}\perp c$.

The above excitation spectrum for the $I_1$ emission line is found in crystals 1 and 2 and in crystal $A$ if it is cooled from room temperature with above-band-gap radiation ($h\nu > E_g$) incident on the crystal. If crystal $A$ is cooled in the dark, the peak corresponding to the formation of the intrinsic $A$ exciton disappears and $I_{1B}$ is now active in both polarization modes. This suggests that there is some competition between $I_{1B}$ and the intrinsic $A$ exciton, the relative strength of the two lines depending on the initial conditions of the experiment.

Also, when the excitation spectrum of the $I_1$—LO line is taken, it is found that the intensity of the $I_1$ peak, corresponding to the direct formation of the complex responsible for the emission, is only very slightly more dominant than the peaks corresponding to the formation of intrinsic $A$ and $B$ excitons, so that the formation of intrinsic excitons and subsequent trapping is nearly as efficient as the direct formation of the bound-exciton complex.

### Excitation Spectra of $I_5$ and $I_2$

While the complex responsible for the $I_1$ emission is created preferentially by the production of free $A$, $B$, and $C$ excitons and the creation of $A$, $B$, and $C$ excitons directly on the acceptor site, the complex responsible for the $I_5$ or $I_2$ emission is created predominantly by phonon assisted formation, although each of the three crystals studied has a somewhat different excitation spectrum.

The excitation spectrum of the 4869.5 Å $I_5$ emission line in crystal 1 is shown in Fig. 3. Peaks in the emission intensity are observed whenever the energy of the exciting light differs from $I_5$ by an integral multiple of $\hbar\Omega$, the $k=0$ LO phonon energy. The fact that the spacing of the peaks corresponds to $\hbar\Omega$ rather than to $\hbar\Omega(1+m_c/m_v)$, where $m_c$ and $m_v$ are the conduction and valence-band-electron effective masses, means that the bound-exciton complex is formed directly with the emission of one or more LO phonons. If we were dealing with the formation of electrons and holes with the electron decaying via LO phonon relaxation, the hole, if it is to have the same momentum as the electron, must lose energy $\hbar\Omega m_c/m_v$, and the total energy difference between peaks would be $\hbar\Omega(1+m_c/m_v)$. This latter type of behavior is seen in the photoconductivity spectrum of InSb.[14]

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[14] H. J. Stocker, C. R. Stannard, Jr., H. Kaplan, and H. Levinstein, Phys. Rev. Letters 12, 163 (1964).

A peak in the $I_5$ emission is also seen when the energy of the incident light corresponds to that of the free $B$ exciton. These excitons diffuse through the crystal and are captured by the impurity and recombine emitting light corresponding to $I_5$. This formation mechanism is the same as for the $I_1$ emission except that the impurity is different. Again, since the emission is strongly polarized with $E \perp c$ it would appear that recombination of an electron with an "$A$ hole" takes place. If the $I_5$ emission results from the recombination of an exciton bound to a neutral donor the hole must have changed its character prior to recombination, which was postulated as a possible mechanism in the $I_1$ emission.

The excitation spectrum of the 4869.5 Å emission line in crystal 2 is shown in Fig. 4. This spectrum is the same, within experimental error, as the $I_5$ excitation spectrum in crystal 1, except for the addition of a weak peak at 4838.5 Å and a second series of peaks which are separated from the $I_5 + n$LO peaks by a fixed energy $\Delta E = 3.9 \pm 0.8$ meV. This spacing is, within experimental error, equal to the spacing of the $I_2$ and $I_3$ absorption lines seen by Thomas and Hopfield which they have attributed to excitons bound to neutral and ionized donors.[4] The peak at 4838.5 Å corresponds, by comparison with $I_2$, to the direct formation of a $B$ exciton on the impurity site and is labeled $I_{5B}$.

Since the spacing between the two series of peaks corresponds to the $I_2$-$I_3$ spacing, and since theoretical calculations suggest[15–18] that if the electron effective mass is somewhat smaller than the hole effective mass, which is the case for CdS, an exciton can be bound to an ionized donor but not to an ionized acceptor. We identify the center giving rise to the $I_5$ emission as an exciton bound to a neutral donor, in agreement with Thomas and Hopfield[4] and Reynolds.[6]

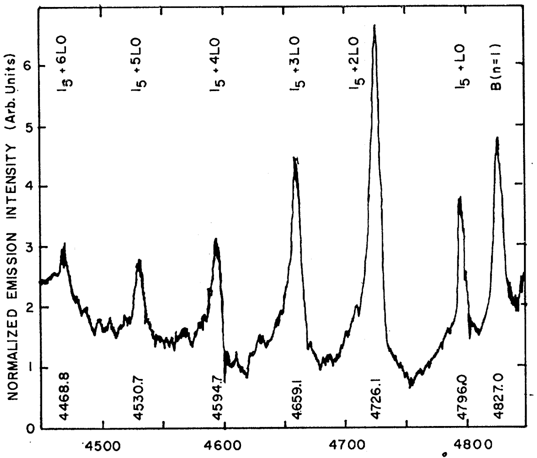

FIG. 3. Excitation spectrum of the 4869.5 Å $I_5$ emission line in CdS crystal 1.

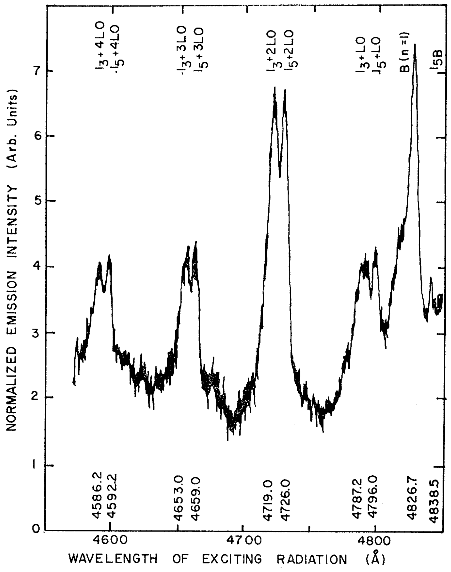

FIG. 4. Excitation spectrum of the 4869.5 Å $I_5$ emission line in CdS crystal 2.

The excitation spectrum of the 4868.3 Å $I_2$ emission line in sample $A$ has been studied as a function of temperature and as a function of the illumination intensity during cool-down from room temperature to 4.2°K.

If this sample is kept in the dark at room temperature and cooled in the dark, the excitation spectrum at 4.2°K, shown in Fig. 5(a), exhibits the same $I_2$-$I_3$ doublet structure in the phonon-assisted creation of the exciton-impurity complex as sample 2. As the helium boils off and the sample temperature rises, the spectrum changes to that shown in Fig. 5(b). The series of peaks based on $I_3$ is now absent and the total intensity of the peaks based on $I_2$ is diminished by a factor of about 5. This is consistent with the onset of rethermalization of excitons bound to neutral and ionized donors.

The binding energy of excitons bound to neutral donors is the energy difference between the free $A$ exciton and the energy of the emitted light. The binding energy of the excitons bound to ionized donors is less than this by the spacing of the peaks in the two series. The binding energies of the two excitons from the spacing of $4.6 \pm 1.1$ meV are shown in Table II.

Thus, the exciton is very weakly bound to the ionized donor and it will not take too large an increase in temperature above 4.2°K ($kT \sim 0.4$ meV) for rethermalization to be important.

Note also in Fig. 5 that as the temperature rises from 4°K, the peak corresponding to the formation of free $B$ excitons disappears and a peak at $I_{2B}$ appears, corre-

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[15] M. Inokuti, K. Katsuura, and H. Mimura, Progr. Theoret. Phys. (Kyoto) 23, 186 (1960).

[16] A. A. Frost, M. Inokuti, and J. P. Lowe, J. Chem. Phys. 41, 482 (1964).

[17] J. J. Hopfield, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 725.

[18] R. R. Sharma and S. Rodriguez, Phys. Rev. 153, 823 (1967).

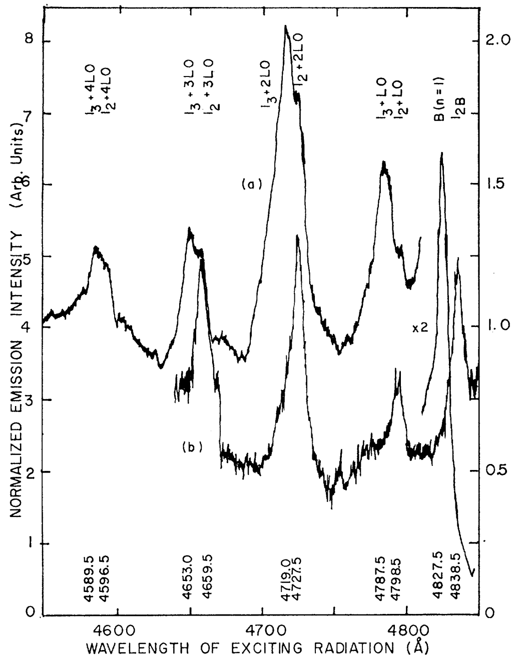

FIG. 5. Excitation spectrum of the 4868.3 Å $I_2$ emission line in CdS crystal *A*. Sample cooled in dark. (a) Spectrum at 4.2°K. Intensity scale on left. (b) Temperature above 4.2°K. Intensity scale on right.

sponding to the formation of *B* excitons directly on a neutral donor.

If sample *A* is cooled under illumination by above-band-gap radiation, only the series of peaks corresponding to the direct phonon-assisted formation of excitons on neutral donors is present and a peak is present corresponding to $I_{2B}$, as shown in Fig. 6. Under these conditions, the $I_1$ emission is absent.

In one experiment, the crystal was allowed to warm up slightly and then was cooled down again. On warming, the peak at $I_{2B}$ shifted gradually to the free *B* exciton and upon cooling remained there. After a period of several hours the $I_2$-$I_3$ doublet structure gradually appeared, and the peak corresponding to the formation of free *B* excitons became very strong (see Fig. 7). Also, the $I_1$ emission grew and became very intense.

Thus, it would appear that the donors which were neutralized by the external light during cooling are metastable in the sense that the neutralizing electron remains on the donor for a long time. After a while the electron is released and the ionized donor density increases allowing the $I_3$ series to appear.

TABLE II. Binding energies of the two excitons.

| | Binding or localization energy |
|---|---|
| $I_2$ | 7.2 meV |
| $I_3$ | 2.6 meV |

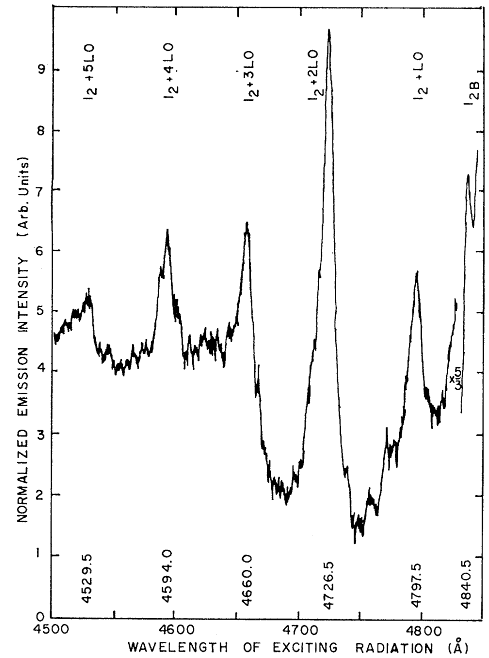

FIG. 6. Excitation spectrum of the 4868.3 Å $I_2$ emission line in CdS crystal *A*. Sample cooled under uv illumination.

## DISCUSSION

### Phonon-Assisted Creation of Exciton-Impurity Complexes

Both crystals 1 and 2 are high resistivity *n*-type crystals, the room temperature resistivity being in excess of $10^7$ Ω cm. The crystals must therefore either be of extremely high purity or, more likely, be compensated with the result that the donors are nearly all

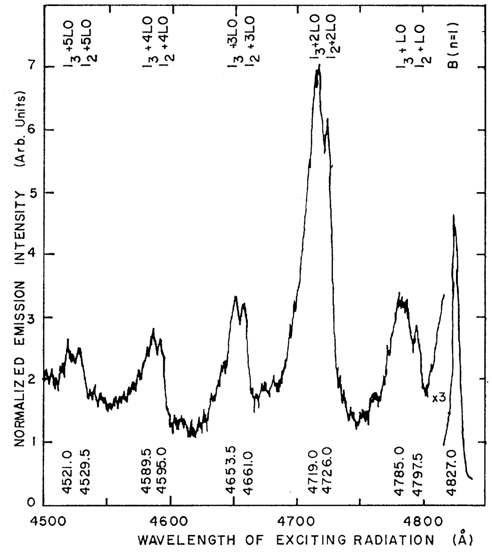

FIG. 7. Excitation spectrum of the 4868.3 Å $I_2$ emission line in CdS crystal *A*. See text for experimental conditions.

ionized. Thus, there is a large density of ionized donors on which excitons may be formed. The two series of peaks result from the direct phonon-assisted formation of excitons on neutral and ionized donors. In the case of the series based on $I_5$ or $I_2$, the exciton bound to a neutral donor, the donor must be neutral before the exciton can be created directly on the impurity. The donor is neutral either by virtue of the material being *n* type, i.e., the density of donors exceeds the density of acceptors, or if the material contains a substantial density of ionized donors, the ionized donor first captures an electron, the electron having been excited into the conduction band by the external light source, and the exciton is then created on the neutral donor where it recombines giving off light corresponding to $I_5$ or $I_2$. In the case of the series based on $I_3$, the exciton bound to an ionized donor, the exciton is first formed directly on the ionized donor. This complex then captures an electron which has been excited into the conduction band and emission at the energy corresponding to $I_5$ or $I_2$ can now take place.

The two series of peaks thus result from essentially the same two physical processes, direct phonon-assisted creation of an exciton bound to an impurity and electron capture. Only the order in which the processes occur is reversed.

The peaks at $I_3+n$LO could also result from the direct phonon-assisted formation of an exciton on an ionized donor, followed by tunneling of this exciton to a nearby neutral donor from which radiation ocurs. This tunneling mechanism is similar to that proposed Dean[12] to account for some features in the luminescence excitation spectra of GaP.

All the peaks in the $I_5$ and $I_2$ excitation spectra occur in both polarizations ($\mathbf{E}\perp c$ and $\mathbf{E}\|c$) of the incident light with about equal efficiency except that the peak at $I_5(I_2)+$LO is very weak for $\mathbf{E}\|c$.

On the basis of perturbation theory one would expect the one-phonon line to be the most intense and the other higher-order lines to diminish very rapidly in intensity. The creation of a bound exciton with the simultaneous emission of one phonon is a second-order process, and if we assume perturbation theory to be applicable, then the intensity of the one-phonon peak will involve a summation over a set of intermediate states separated in energy from the ground state by $\sim I_5(I_2)+$LO. If the proper states over which the summation is to be made are one-electron states, then these will be located at $I_5(I_2)+$LO above the *A*-valence-band edge. By coincidence, $I_5(I_2)+$LO is very close to the band-gap energy so that the intermediate states will be those near the conduction-band edge where the density of states is very small, thus causing the one-phonon line to be abnormally weak. The argument that it is these states over which the summation is to be taken is supported by the near absence of a peak at $I_5(I_2)+$LO when the incident light is polarized $E\|c$, since for this polarization the valence-band states for the *A* valence band are only barely active. In view of the extraordinarily strong phonon coupling it is somewhat doubtful whether perturbation theory is applicable.

The direct phonon-assisted creation of the $I_5$ and $I_2$ bound exciton-impurity complexes differs from the mechanisms responsible for the oscillations in the luminescence excitation spectra of diamond,[8] CuBr,[9] ZnSe,[10] and the 4867 Å $I_2$ line in CdS,[10] and in the photoconductivity spectra of CdS,[19–21] CdSe,[19,20] CdTe,[22] InSb,[14] GaP,[23] ZnTe,[24] CuCl,[25] and diamond,[26] where the oscillations are based on an intrinsic exciton, rather than a bound exciton.

### Contributions from Intrinsic Excitons and $I_{2B}$

The observation in sample *A* that the $I_{2B}$ peak is present when the peaks corresponding to $I_3+n$LO are absent and that the intrinsic *B*-exciton peak is present when the $I_3+n$LO peaks are present is intuitively plausible. When the $I_3+n$LO peaks are present a large density of ionized donors exists which must be neutralized before the complex $I_{2B}$ can be created. Equivalently, the density of neutral donors on which to form $I_{2B}$ will be small. On the other hand, the free *B* exciton is created irrespective of the neutral donor density and will diffuse through the crystal until it is captured by an impurity site where it will recombine. When the neutral donor density is large, i.e., when the $I_3+n$LO peaks are absent, the peak at $I_{2B}$ should be enhanced over the case when the $I_3+n$LO peaks are present, which is indeed the case (Figs. 6 and 7). When the $I_3+n$LO peaks are absent, one would expect peaks at both $I_{2B}$ and the free *B* exciton to occur. However, only the $I_{2B}$ peak is present in sample *A*. The reason for the absence of the free *B*-exciton peak in this instance is not understood, although it could arise from differences in the capture cross section for such an exciton by neutral and ionized donors. Alternately, it could be present but it is less intense than the $I_{2B}$ exciton and therefore not resolved, with the relative intensity of the $I_{2B}$ and free *B*-exciton peaks depending on both the relative and the absolute density of neutral and ionized donors.

In samples 1 and 2, the free *B*-exciton peak in the $I_5$ excitation spectrum is always stronger than the $I_{5B}$

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[23] D. N. Nasledov, V. V. Negreskul, S. I. Radautsan, and S. V. Slobodchikov, Fiz. Tver. Tela **7**, 3671 (1965) [English transl.: Soviet Phys.—Solid State **7**, 2965 (1966)].

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peak. Since in these samples the same excitation spectrum appears regardless of whether the sample is cooled in the dark or under illumination by above-band-gap radiation, it appears that the lifetime of the electrons on the donors is shorter than in sample $A$, the result being that the probability of creating the $B$ exciton directly on the impurity ($I_{5B}$) is decreased.

This may also account for the somewhat lower intensity of the emission in samples 1 and 2 as compared with sample $A$ (The arbitrary units used in the excitation spectra differ from graph to graph).

In a recent paper, Park and Schneider[10] have found that in the excitation spectrum of an $I_2$ emission line at 4867 Å, peaks in the emission appear when the energy of the exciting light corresponds to that of the intrinsic $A$ exciton plus an integral multiple of LO phonons, rather than to the bound exciton plus phonons. This difference in the excitation spectra must be indicative of some physical difference in the centers giving rise to the emission lines seen in the wavelength interval 4867–4870 Å.

## CONCLUSIONS

It has been demonstrated that excitation spectra of emission lines associated with bound-exciton complexes yield definitive information about the formation of these complexes.

From the optical excitation spectrum of the $I_1$ emission line in CdS we find that the complex responsible for this emission is created by the formation of free excitons which are subsequently trapped or bound to the localized site, or by the direct formation of bound excitons on the impurity site.

From the optical excitation spectra of the $I_5$ and $I_2$ emission lines we find that the complexes responsible for these emission lines are also created by the formation of free excitons which are subsequently bound to a localized site, but more importantly, they are created by direct phonon assisted formation of an exciton bound to an ionized or neutral donor.

Evidence has been presented which associates the $I_5$ emission with an exciton bound to a neutral donor. The marked similarity between the $I_5$ and $I_2$ excitation spectra leads us to conclude that the responsible complexes are very similar. The small difference in the emission wavelength is probably due to a difference in the identity of the responsible donor impurity or to a difference in the lattice environment.

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# Theory of the Heat Capacity of Polycrystalline Graphite at Very Low Temperatures—Finite-Lattice Contribution*

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Recent measurements of the heat capacity of polycrystalline graphite at liquid-helium temperatures indicate an abnormal enhancement in the term linear in the absolute temperature with decreasing extent of graphitization. A cause for this anomaly is sought by considering the elastic vibrations of a finite lattice. It is shown that if a platelike crystallite with a thickness of about 100 Å vibrates in the direction perpendicular to the plane of the plate, its contribution to the linear term in the heat capacity at very low temperatures is of the same order of magnitude as the observed excess linear heat capacity. Since polycrystalline graphite is known to be composed of flakelike crystallites, it is argued that an important, and possibly the main, cause of the abnormal enhancement is this oscillation of fine crystallite plates.

## 1. INTRODUCTION

MUCH work, both experimental and theoretical, has been done on the heat capacity of carbon at low temperatures.[1] The behavior of the heat capacity of single-crystal graphite is known to be closely related to its intrinsic layerlike structure: It has a term linear in absolute temperature $T$, and a nonlinear term. The linear term is naturally expected from the conduction electrons; the nonlinear term follows approximately a $T^2$ law between 10 and 50°K, and gradually changes its temperature dependence from $T^2$ to $T^3$ at lower temperatures (1–10°K). The theoretical explanation of this peculiar behavior was attempted by Komatsu and Nagamiya[2] with the aid of the anisotropic model, a

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