Free-to-Bound and Bound-to-Bound Transitions in CdS

K. COLBOW*

Bell Telephone Laboratories, Murray Hill, New Jersey

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Time-resolved photoluminescence spectra of two green broad emission bands in CdS have been observed as a function of temperature. New structure was discovered in both bands, and has been attributed to tranverse optical phonons. From the wavelength shift of the emitted light with time and temperature, it is concluded that the shorter wavelength band (5130 Å) is due to the recombination of free electrons with bound holes, while the longer wavelength band (5175 Å) is due to the recombination of bound electrons with bound holes. Values for the donor and acceptor binding energies are obtained, as well as the bound-to-bound reaction constant, and an estimate of the donor concentration. The model is supported by independent information from the time decay of the bound-to-bound and the free-to-bound emission intensity, and its correlation with the low-temperature decay of photoconductivity as a function of time after excitation.

I. INTRODUCTION

TWO distinct types of emission occur in the fluorescence of CdS near the band edge. At low temperatures and high excitation intensity, many sharp emission lines in the spectral range from 4860 to 5085 Å are observed. These have been attributed to the decay of free excitons, and to excitons bound to various impurities.[1,2] In addition, two broad bands have been observed[3] between 5100 and 5200 Å, and are repeated at lower energies through the simultaneous emission of one or more longitudinal optical phonons. The origin of these broad bands has been the subject of a great deal of controversy.

Because of the large coupling with the longitudinal optical phonons, radiative recombination of free holes and free electrons through exciton states was first proposed as the responsible mechanism.[4] However, it was shown later that theoretically the phonon replicas of the broad emission can only be understood by a mechanism involving trapped carriers.[5] Lambe et al.[6] proposed at 4°K a free-hole–to–trapped-electron recombination model. Collins[7] showed that after excitation free holes decay much faster than the broad green emission at 77°K and proposed a free-electron–to–bound-hole recombination model. Halsted and Segall[8] interpreted the emission in terms of bound-exciton recombination at a double acceptor level near the conduction band. Razbirin[9] suggested that the emission results from the annihilation of an exciton with simultaneous ionization of a trapped hole.

Pedrotti and Reynolds[3] postulated a bound-to-bound transition at 4°K and a free-to-bound transition at 77°K, with the former occurring at the longer wavelength. Their data show that the bound-to-bound transition predominates at helium temperature when the donors and acceptors will be occupied by electrons and holes, respectively. At nitrogen temperature the shallow donors will become thermally ionized, and the free-to-bound transition predominates. The fact that free electrons rather than free holes are involved at 77°K was further supported by Spear and Bradberry[10] by photoconductivity and luminescence measurements.

Conflicting views about the broad recombination were also expressed by Gross et al.,[11] who postulated that both transitions are of the bound-to-bound type, originating from different shallow donors and terminating on the same deep acceptor. However, one is then left with the dilemma that the higher energy emission predominates at higher temperatures, which implies that the more tightly bound donor electrons become ionized first.

On the basis of thermal quenching of the luminescence, Maeda[12] came to the conclusion that the higher energy emission is of the bound-to-bound type, while his data were insufficient to decide about the lower energy emission.

While there is much controversy about the kinetics of recombination giving rise to the two broad emission bands, there seems to be some agreement now that at the present time nearly all samples of "undoped" CdS contain shallow donor impurities such as Al or Cl (binding energy$\approx$30 meV), partially compensated by deep acceptors (binding energy$\approx$150 meV), which are most likely caused by cadmium vacancies.[13]

* Present address: Simon Fraser University, Department of Physics, Burnaby, B. C., Canada.

[1] D. G. Thomas and J. J. Hopfield, Phys. Rev. Letters 7, 316 (1961). D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).

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

[3] L. S. Pedrotti and D. C. Reynolds, Phys. Rev. 120, 1664 (1960).

[4] F. A. Kroger and H. J. G. Meyer, Physica 20, 1149 (1954).

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

[6] J. J. Lambe, C. C. Klick, and D. L. Dexter, Phys. Rev. 103, 1715 (1956).

[7] R. J. Collins, J. Appl. Phys. 30, 1135 (1959).

[8] R. E. Halsted and B. Segall, Phys. Rev. Letters 10, 392 (1963).

[9] B. S. Razbirin, Fiz. Tverd. Tela 6, 318 (1964) [English transl.: Soviet Phys.—Solid State 6, 256 (1964)].

[10] W. E. Spear and G. W. Bradberry, Phys. Status Solidi 8, 649 (1965).

[11] E. F. Gross, B. S. Razbirin, and S. A. Permogorov, Fiz. Tverd. Tela 7, 558 (1965) [English transl.: Soviet Phys.—Solid State 7, 444 (1965)].

[12] K. Maeda (to be published).

[13] H. H. Woodbury, Phys. Rev. 134, A492 (1964).

It has been demonstrated in previous work[14,15] that much more detailed information about bound-to-bound transitions may be obtained by studying the emission bands as a function of time after excitation, in addition to observing their dependence with temperature. It will be shown in this paper that the details of the luminescent spectra as a function of temperature and time after excitation may be explained quantitatively by assuming the basic model postulated by Pedrotti and Reynolds.[3] In addition it will be shown that the decay of photoconductivity with time after excitation at low temperatures is consistent with the picture provided by the decay of the free-to-bound and the bound-to-bound light emission.

II. EXPERIMENTAL

The data reported in this paper were obtained from a high-purity CdS crystal,[16] which was further annealed for 24 h at 593.5°C under the equilibrium vapor pressure of Cd at this temperature. This annealing is believed to remove any excess Cd from the crystal.[18] Other crystals, including flake crystals grown by the method of Frerichs,[17] gave qualitatively similar results. The main difference was that at a given temperature, and at a given time after excitation, the relative emission intensity and the intensity ratio between the bound-to-bound and the free-to-bound transitions varied from crystal to crystal.

The experimental arrangement is illustrated in Fig. 1. The sample was mounted in a variable-temperature Dewar and was excited 9 times per sec by a brief (2–3 μsec) flash of band-gap radiation (3000–4500 Å) from an FX 12 xenon flash tube. The luminescence from the crystal passed through a grating spectrometer and was detected by a "gated" photomultiplier for a variable short time interval following a variable time delay after the excitation pulse. The resulting photomultiplier current pulses were fed through a 1-sec RC network, a high impedance dc amplifier, and a 4-sec RC network to a dc X-Y recorder. With a slowly scanning spectrometer the luminescent spectrum will be recorded as a function of wavelength for the time interval after excitation when the photomultiplier is "gated on."

The photomultiplier (S-20 photocathode, EMI model 5865) was gated in the following fashion: In the absence of an excitation flash, two isolated strings of Zener diodes and a dc supply of − 2000 V maintain neighboring pairs of successive dynodes at the same potential, which differs by 200 V from that of the following and the preceding pair. With this potential distribution the photomultiplier will not conduct significantly. With each excitation flash a capacitively coupled pulse triggers
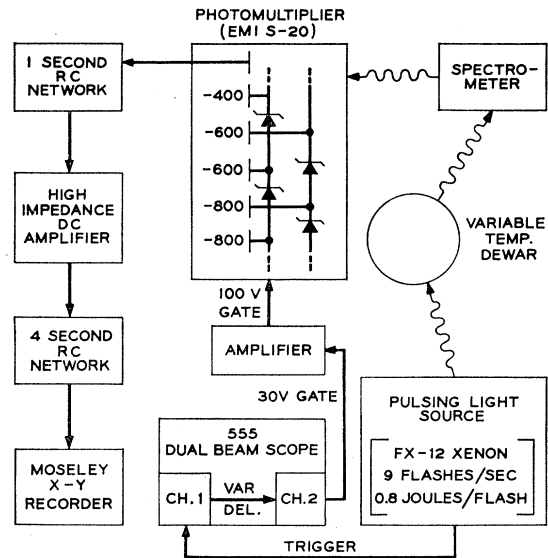

FIG. 1. Block diagram of the experimental arrangement.

the first channel of a Tektronix 555 dual-beam oscilloscope. Using the adjustable sweep time of the second channel, and the variable time delay, an external positive gate of 30 V (of variable duration and starting at a variable time after the triggering pulse) can be obtained. This gate is amplified to 100 V and fed into one string of Zener diodes, thus creating the usual conducting potential distribution, where successive dynodes are at a potential 100 V above the previous one. Hence the photomultiplier will detect light only while the gate is on.

The sample of CdS was kept at 4.2 and 20°K by immersing it directly in liquid helium and liquid hydrogen, respectively. Temperatures between 25 and 75°K were obtained by suspending the sample in the gas of evaporating liquid hydrogen.[12] The temperature was varied by changing the rate of vaporization or by heating the gas. The temperature was measured by means of a thermocouple placed in loose contact with the sample.

The sample was rectangular, with dimensions of 2.41×2.18×0.66 mm. For conductivity measurements Ohmic contacts were made by rubbing gallium with an ultrasonic vibrator on the smallest opposite sides. Room-temperature Hall-effect and resistivity measurements on the sample gave a resistivity of 10.2 Ω cm, a mobility of 410 cm^2 V^{-1} sec^{-1}, and a corresponding free-carrier concentration of 1.5×10^{15} cm^{-3}.[18]

III. THEORY

It has been shown[19] for GaP that for a bound-to-bound transition between a donor-acceptor pair of separation

[14] D. G. Thomas, J. J. Hopfield, and K. Colbow, in *Proceedings of the Symposium on Radiative Recombination in Semiconductors* (Dunod Cie, Paris, 1964), p. 67.
[15] K. Colbow, Phys. Rev. **139**, A274 (1965).
[16] Clevite Corporation, Cleveland, Ohio.
[17] R. Frerichs, Phys. Rev. **72**, 594 (1947).

[18] E. T. Handelman (private communication).
[19] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).

r, the energy of the emitted light is given by

$$E_b = E_G - (E_a + E_d) + E_c \pm nE_p, \qquad (1)$$

for large r. Here E_G is the band-gap energy, E_a and E_d are the acceptor and donor binding energies, respectively, and

$$E_c = e^2/\epsilon r \qquad (2)$$

is the Coulomb attraction between the hole and the electron, where ϵ is the static dielectric constant of the material. The term $\pm nE_p$ represents the simultaneous absorption or emission of $n = 0, 1, 2, \cdots$ phonons of energy E_p.

For the transition of a free electron to the neutral acceptor, the energy of the emitted light is given by

$$E_f = E_G - E_a + E_K \pm nE_p. \qquad (3)$$

Here E_K is the kinetic energy of the free electron. Since the capture cross sections for Coulomb attractive centers are much larger than for neutral centers, the rates of electron capture (R_e) and hole capture (R_h) by the donors and acceptors, respectively, will be initially much larger than the bound-to-bound rate (R_b) and the free-to-bound rate (R_f). The excitation flash of band-gap radiation may be assumed to create sufficient holes and electrons (G) so that at low temperatures (4°K) all the acceptors and donors are neutralized. Excess free holes and electrons may decay rapidly as bound excitons (rate R_x).

For an isolated neutral donor-acceptor pair of separation r, the rate of recombination between the bound electron and the bound hole is proportional to the square of the overlap of the wave functions,[15]

$$W = W_0 e^{-2r/a}, \qquad (4)$$

where W_0 is the reaction constant, and a is the Bohr radius of the less tightly bound carrier, which for $E_d < E_a$ is the electron. This Bohr radius may be obtained through the hydrogenic energy equation

$$E_d = e^2/2\epsilon a, \qquad (5)$$

provided the donor binding energy is known.

Let us assume a random distribution of donors and acceptors; a donor concentration (N_d) much larger than the acceptor concentration (N_a); and no redistribution of electrons or holes from thermal detrapping or tunnelling. The decay of the total bound-to-bound emission is then simply given by the decay of neutral acceptors[14] and has the functional form

$$I(t) = I_0 F(W_0, N_d, E_d, t). \qquad (6)$$

The spectrum of the no-phonon emission[14] may be written in the form

$$I_{E_c}(t) = I_0 E_c^{-4} \exp[-(4E_d/E_c) - W_0 t e^{-4E_d/E_c}]. \qquad (7)$$

Here the zero of energy was taken at $E_G - E_a - E_d$, and use was made of Eqs. (1), (2), (4), and (5).

For comparison with experiment it is desirable to know the shift of the maximum of $I_{E_c}(t)$ with time. This is simply obtained by setting the derivative of $I_{E_c}(t)$ with respect to E_c equal to zero, which gives rise to the expression

$$\ln(W_0 t) = 4E_d/E_c + \ln(1 - E_c/E_d). \qquad (8)$$

For the free-to-bound transition, the rate of recombination of an electron of kinetic energy E_K with a bound hole is given by

$$r_f(E_K) = N_a^0 n(E_K) v \sigma(E_K). \qquad (9)$$

Here N_a^0 is the density of neutral acceptors.

$$v = (2E_K/m_e)^{1/2} \qquad (10)$$

is the velocity of the electron, and $\sigma(E_K)$ is the cross section for radiative capture of an electron with kinetic energy E_K by a neutral acceptor. For a parabolic conduction band, assuming a Boltzmann distribution, the density of free electrons of kinetic energy E_K is given by

$$n(E_K) = CE_K^{1/2} e^{-E_K/kT}. \qquad (11)$$

Assuming a cross section $\sigma(E_K)$ which is independent of kinetic energy, then by Eqs. (9), (10), and (11), the free-to-bound recombination rate is of the form

$$r_f(E_K) = r_f^0 E_K e^{-E_K/kT}, \qquad (12)$$

where r_f^0 is a constant. The maximum of this rate occurs for electrons with kinetic energy

$$E_K = kT. \qquad (13)$$

Since the acceptor binding energy is not expected to vary appreciably with temperature, it follows from Eq. (3) that for the no-phonon free-to-bound transition one might expect a linear temperature variation of the difference between the no-phonon emission peak and the band gap, with slope given by the Boltzmann constant, k. If this is confirmed, one feels justified in using Eq. (3), the known band gap, and the measured position of the no-phonon emission to calculate the acceptor binding energy from

$$E_a = E_G - E_f + kT, \quad n = 0. \qquad (14)$$

Any error in setting $E_K = kT$ will be small at liquid-helium temperature, since E_K will be small.

So far all theory was concerned with the energy (wavelength) of the emitted light, and its variation with temperature and time after excitation. Equation (8) gives at low temperatures the shift of position for the bound-to-bound transition as a function of time after excitation, with the donor binding energy and the reaction constant (W_0) as parameters. Equation (14) gives the no-phonon free-to-bound position in energy as a function of temperature, and leads to an evaluation of the acceptor binding energy, provided the band gap is known as a function of temperature.

Independent correlations may be obtained from the decay of the total light and the photoconductivity with time after excitation. The interpretation is, however, only simple and unambiguous at low temperatures (4.2°K), where no thermal re-excitation occurs. Under the assumption that $N_d \gg N_a$, the decay of the bound-to-bound emission represents the decay of neutral acceptors $(N_a{}^0)$:

$$R_b(t) = AN_a{}^0(t). \tag{15}$$

The free-to-bound emission,

$$R_f(t) = Bn(t)N_a{}^0(t), \tag{16}$$

has a time variation which is the product of the free electron decay $n(t)$, and the decay of neutral acceptors. (A and B are constants.)

The decay of photoconductivity,

$$\sigma(t) = e\mu n(t), \tag{17}$$

gives the decay of free electrons, assuming that the mobility is independent of time and that the conductivity from minority carriers (holes) is negligible. Thus the product of the time variations of the photoconductivity and the bound-to-bound emission at low temperatures should be equal to the time variation of the free-to-bound emission.

IV. EXPERIMENTAL DATA AND CALCULATIONS

Typical luminescence spectra at various temperatures and at various times after photoexcitation are shown in Figs. 2 and 3, respectively. The strongest feature of
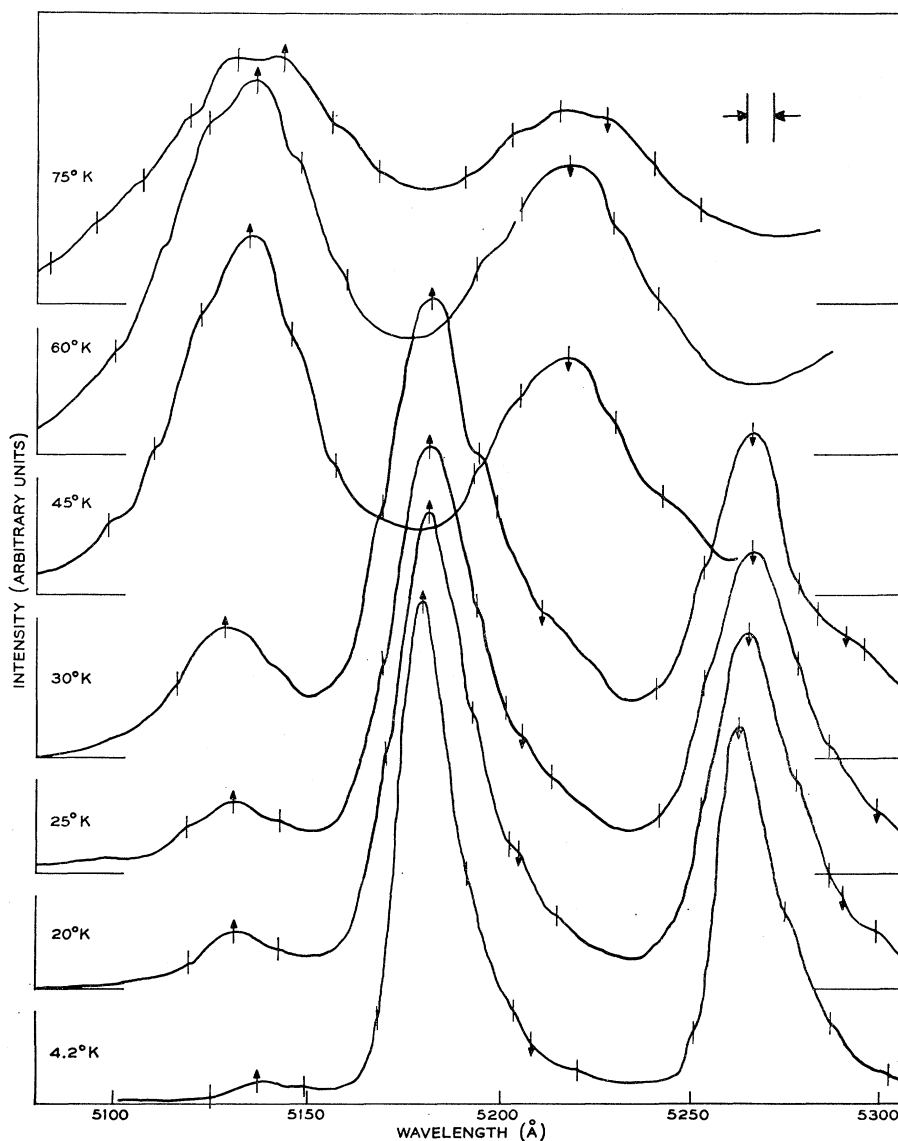

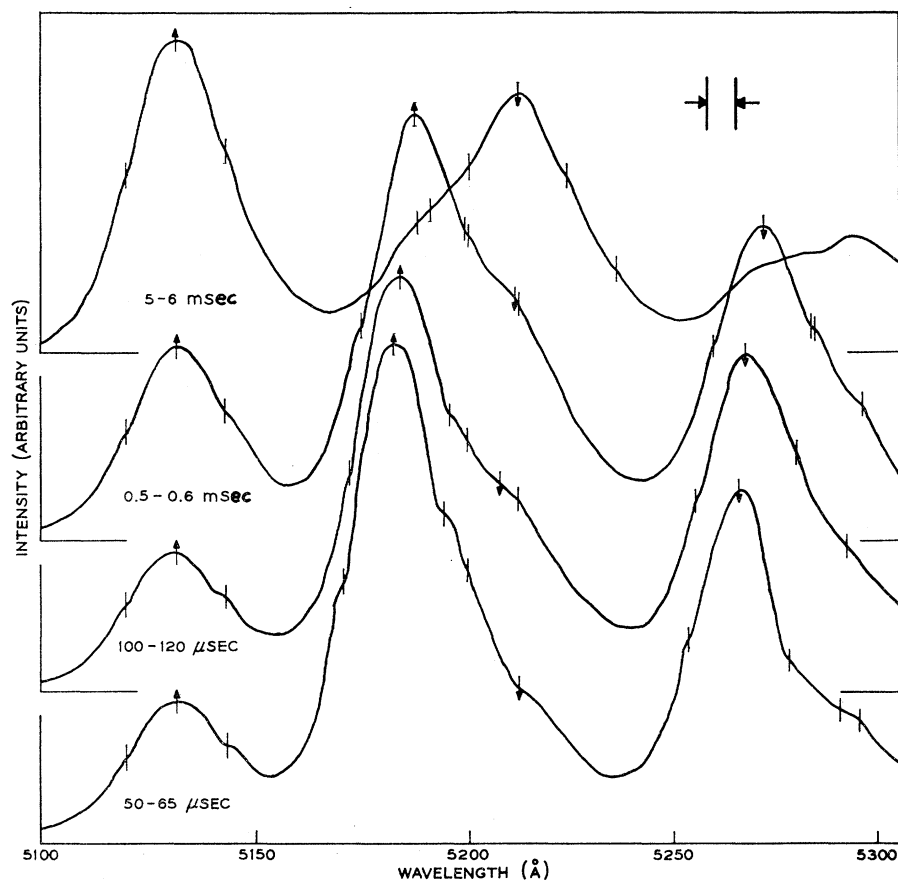FIG. 2. Luminescence spectra at 50–65 μsec after photoexcitation for various temperatures.

FIG. 3. Luminescence spectra at 30°K during various time intervals after photoexcitation.

the spectra is that both the high-energy band (HEB) at about 5130 Å, and the low-energy band (LEB) at about 5175 Å are repeated at lower energies with spacings of 36.8 meV; this repetition has been identified as due to the simultaneous emission of a longitudinal optical phonon,[4] and the spacing is in agreement with independently measured values for the LO phonon energy in CdS.[20] While Figs. 2 and 3 show only the first longitudinal optical (LO) phonon replicas, the simultaneous emission of 2, 3, and 4 LO phonons is easily observable.

TABLE I. Dark conductivity and the decay of photoconductivity at various temperatures.

	$(10^{-4}$ mho cm$^{-1})$		
T (°K)	σ_d	σ_0	n
4.2	0.204	0.154	0.20
20	0.451	0.199	0.18
25	0.714	0.308	0.19
30	2.30	1.51	0.08
35	5.50	5.74	0.03
40	19.5	9.28	0.003

[20] M. Balkanski, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), p. 1023.

With the higher sensitivity obtained through using time resolved spectroscopy and the integrating techniques described in Sec. II a new series of shoulders was observed on both bands and their LO phonon replicas. On each broad band these shoulders are separated by 5.5 ± 0.3 meV, which is believed to be a transverse optical phonon energy (TO$_2$). This value for TO$_2$ is only half as large as the value published by Balkansky,[20] but is in excellent agreement with the value of 5.6 ± 0.4 meV obtained from Raman scattering experiments by Damen, Porto, and Tell.[21]

In Figs. 2 and 3 the upward arrows ($\uparrow$) mark what is believed to be the no-phonon emission, the downward arrows ($\downarrow$) mark the corresponding positions with the emission of LO phonons, and the straight lines ($|$) indicate the shoulders arising from the emission or absorption of one or more TO$_2$ phonons. The assignment of the no-phonon position was made on the assumption that at the lowest temperature TO$_2$-phonon absorption should be unlikely. If this assignment were incorrect in that in all cases the position ($\uparrow$) really marked the one TO$_2$ emission, nothing in the analysis to follow would be changed other than the acceptor binding energy, which should be decreased by TO$_2$.

[21] T. C. Damen, S. P. S. Porto, and B. Tell (unpublished).

Strictly speaking, the "no-phonon" and the one or more optical-phonon emissions are also broadened by the emission and absorption of acoustical phonons. However, any effects from this interaction will be neglected. That acoustical phonon broadening may be active is supported by the fact that the TO_2-phonon structure did not become better resolved when higher resolution was employed. Using a velocity of sound of about 4×10^5 cm sec^{-1},[22] and an acceptor Bohr radius of about 5 Å, one may expect an acoustical phonon broadening of the "no-phonon" line about equal to the spectral resolution of 3.3 meV used to obtain Figs. 2 and 3.

Figure 4 shows the decay of the total light (excluding LO phonon replicas) as a function of time after excitation
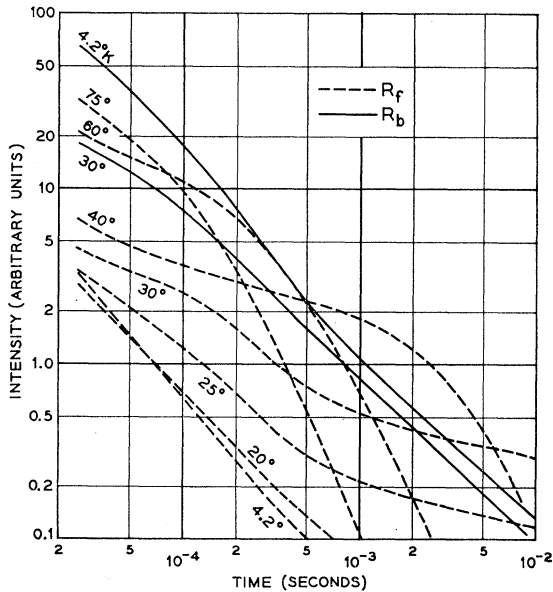

FIG. 4. Decay of the total light after photoexcitation for various temperatures. The full curve shows the decay for the bound-to-bound emission (R_b), and the dashed curve shows the decay for the free-to-bound emission (R_f).

for both the HEB (dashed line) and the LEB (full line). At a given short time after excitation, the LEB changes little in intensity between 4.2 and 20°K and disappears between 35 and 45°K. In contrast, the HEB intensity increases steeply between 20 and 40°K, levels out, and then decreases above 75°K. This is consistent with the interpretation[3] that the HEB is due to a free-to-bound transition, and the LEB to a bound-to-bound transition, as illustrated in Fig. 5 by R_f and R_b, respectively.

It may be seen from Fig. 6 that in the time interval from 10^{-4} to 10^{-1} sec after excitation, the photoconductivity (σ_ν) decays nearly linearly with time on a log-log plot. The total conductivity may then be written in the

[22] H. J. McSkimin, T. B. Bateman, and A. R. Hutson, J. Acoust. Soc. Am. 33, 856 (1961).
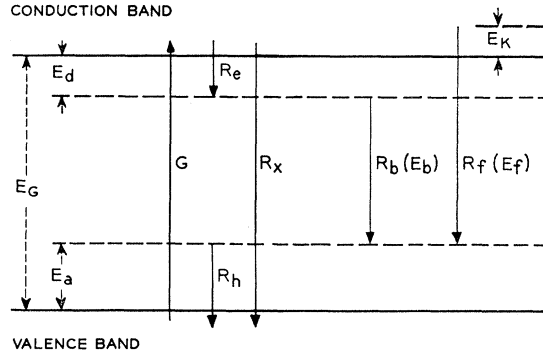

CONDUCTION BAND

VALENCE BAND

FIG. 5. Energy-band diagram illustrating basic model. CdS with band gap E_G contains shallow donors (binding energy E_d), and deep acceptors (E_a). Holes and electrons created by band-gap excitation (G) rapidly neutralize donors (R_e) and acceptors (R_h), with most excess free holes decaying fast by exciton radiation (R_x). A study has been made of the slower decaying bound-to-bound (R_b) and free-to-bound (R_f) transitions, which give rise to photons of energies E_b and E_f, respectively.

form

$$\sigma = \sigma_d + \sigma_0 t^{-n}. \qquad (18)$$

Table I lists the values of the dark conductivity σ_d and the values of σ_0 and n, giving the decay of the photoconductivity $(\sigma_\nu = \sigma_0 t^{-n})$ as a function of temperature. At 4.2°K, the dark conductivity is negligible, and since $n = 0.20$, it follows by Eq. (17) that experimentally the free-electron concentration at 4.2°K varies after excitation as

$$n(t) = n_0 t^{-0.20}. \qquad (19)$$

From Fig. 4 it is found that at 4.2°K the HEB decays as $t^{-1.2}$, which on the basis of a free-to-bound transition implies by Eq. (16) that the product of free-electron concentration and neutral-acceptor concentration decays experimentally like

$$n(t)N_a^0(t) = Mt^{-1.20}, \qquad (20)$$

with $M = $ constant. Also at short times after excitation the LEB at 4.2°K decays as about $t^{-1.0}$, which on the interpretation of a bound-to-bound transition by Eq.
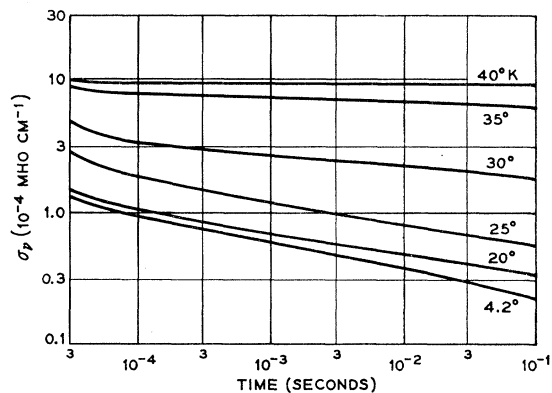

FIG. 6. The decay of photoconductivity after excitation for various temperatures.
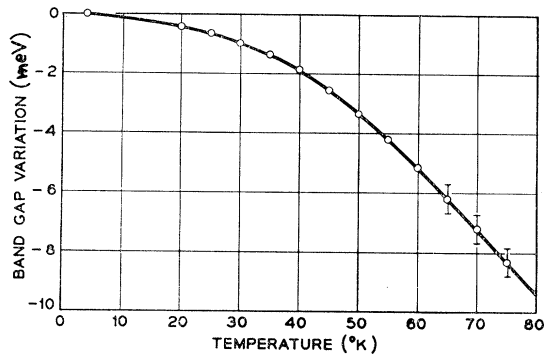
FIG. 7. Band-gap variation with temperature. (Energy shift of bound-exciton emission with temperature.)

(15) gives the decay of neutral acceptors and is consistent with Eqs. (19) and (20).

At a given temperature the wavelength of the HEB is independent of the time after excitation, as one would expect for the free-to-bound transition. In order to investigate whether the shift of the no-phonon emission with temperature obeys Eq. (14), one needs to know the temperature variation of the band gap. This is given in Fig. 7, which was obtained by measuring the energy shift of a sharp emission line at 4869.2 Å at 4.2°K. This line has been called I_5 by Reynolds and Litton[2] and is due to the decay of a bound exciton. The band gap variation in Fig. 7 agrees with previous direct measurements[23] on CdS and is very similar in shape and magnitude to the band gap variation discussed by Mahan[24] for CdTe. The shift of the HEB with temperature minus the band gap variation, as shown in Fig. 8, may be approximated by kT, and may be identified as the kinetic energy of the free electrons just before recombination. Any variation of the experimental points in Fig. 8 from kT (dashed line) may be caused by
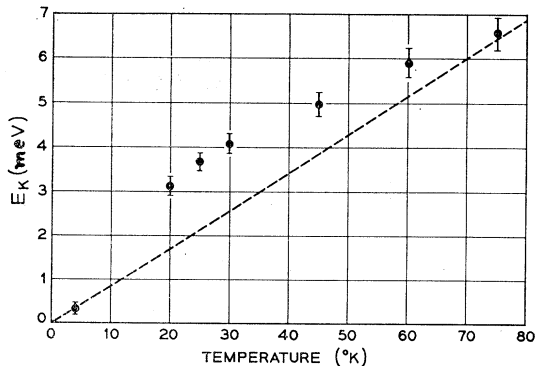

FIG. 8. Shift of high-energy (no-phonon) emission with temperature, after correcting for band-gap variation with T. This is believed to give the most probably kinetic energy of the recombining electrons. The emission energy at 4.2°K (reference point) was fixed on the dashed line, which represents kT.

[23] D. G. Thomas, J. J. Hopfield, and M. Power, Phys. Rev. **119**, 570 (1960).

[24] G. D. Mahan, J. Phys. Chem. Solids **26**, 751 (1965).

an energy dependence of the capture cross section in Eq. (9), and by an approach to degeneracy, which means the Fermi-Dirac function should be used in Eq. (11) instead of the Boltzmann exponential.

At 4.2°K the band gap of CdS is $E_G = 2.5826$ eV,[25] $kT = 0.0004$ eV, and the measured position of the high-energy no-phonon emission is $E_f = 2.4134$ eV. Thus by Eq. (14) one obtains for the acceptor binding energy

$$E_a = 169.6 \pm 0.4 \text{ meV}. \qquad (21)$$

At a given temperature the LEB shifts to lower energies with time after excitation. This is expected for a bound-to-bound transition, since at later times farther separated pairs decay, which contribute a smaller Coulomb energy to the emission. Subtracting from the observed position of the no-phonon bound-to-bound
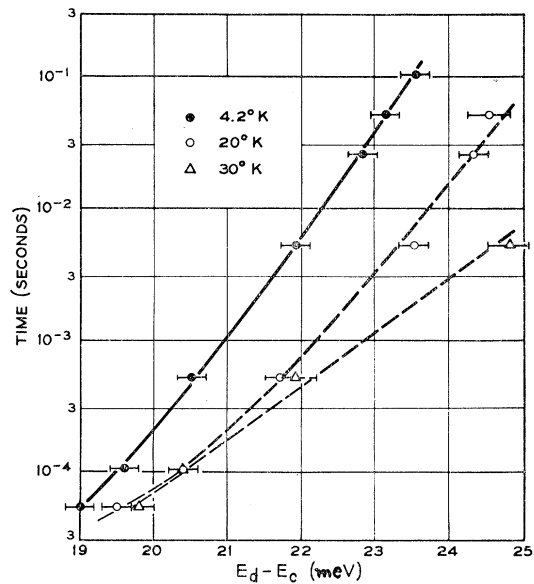

FIG. 9. The difference between the donor binding energy and the Coulomb energy as a function of time after excitation for different temperatures. The data were obtained from the shift of the low-energy (no-phonon) emission.

emission the band gap, and adding the acceptor binding energy of Eq. (21), one obtains by Eq. (1) the difference between donor binding energy and Coulomb energy. This has been plotted in Fig. 9 for three temperatures as a function of time after excitation. Let us concentrate on the 4.2°K results, where the simple theory outlined in Sec. III is expected to hold best. In particular, knowing E_c as a function of time and E_d, one may use Eq. (8) to calculate the reaction constant W_0. Figure 9 gives $(E_d - E_c)$ as a function of time. Thus if one guesses E_d, one may calculate from Eq. (8) the value of W_0. Furthermore if one has made the correct guess of E_d, Eq. (8) should give the same value of W_0 irrespective of the time after excitation at which $(E_d - E_c)$ was

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

determined. Table II gives values of W_0 for various values of E_d, with (E_d-E_c) taken at different times after excitation from the 4.2°K data of Fig. 9. The variation of W_0 with time is seen to be quite large for donor binding energies of 28 and 32 meV, and it becomes even larger for binding energies smaller than 28 and larger than 32 meV. In this way one settles on a donor binding energy of

$$E_d = 30.5 \pm 0.5 \text{ meV}, \tag{22}$$

which is in excellent agreement with the donor binding energy of 32 ± 2 meV obtained by Piper and Halsted.[26]

The value of the reaction constant is then

$$W_0 = (4 \pm 2) \times 10^8 \text{ sec}^{-1}, \tag{23}$$

which is the value required in Eq. (6) to give the proper slope for the low-temperature total bound-to-bound decay at long times (Fig. 4) with a donor concentration of about 10^{16} cm^{-3}. This is thought to be a reasonable value of N_D for the present sample.

With the donor binding energy of Eq. (22) and a dielectric constant of $\epsilon = 10.33$,[27] one finds from Fig. 9 and Eq. (2) that the donor-acceptor pairs responsible for the bound-to-bound emission are about $r = 127$ Å apart at 10^{-4} sec and 199 Å at 0.1 sec after excitation. This seems very reasonable on the basis of what has been learned from GaP.[14,15,16] At a concentration of 10^{16} cm^{-3}, the mean spacing calculated from $(4\pi/3)\bar{r}^3 = 1/N$ is $\bar{r} = 288$ Å.

V. SUMMARY AND CONCLUSIONS

The two broad fluorescent bands which have often been reported previously at about 5130 and 5175 Å were shown to be due to free-to-bound and bound-to-bound radiative recombination, respectively. Both bands shift with temperature and time after excitation in quantitative agreement with the theoretical predictions. At 4.2°K the model is further supported by simple

TABLE II. W_0 (10^9 sec^{-1}) for various values of E_d and times after excitation.

E_D (meV)	Time (sec)				
	5×10^{-4}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
28.0	3.2	3.7	6.1	23	460
30.0	0.66	0.60	0.41	0.39	0.75
30.5	0.46	0.42	0.25	0.19	0.27
31.0	0.36	0.30	0.16	0.11	0.11
32.0	0.22	0.17	0.07	0.03	0.02

correlations between the time decay of the free-to-bound intensity, the bound-to-bound intensity, and the photoconductivity.

New structure was observed in both emission bands and their LO phonon replicas, which was attributed to transverse phonons of energy 5.5 meV.

With a donor level 30.5 meV below the conduction band and an acceptor level 169.6 meV above the valence band, the luminescence data may be explained. The bound-to-bound reaction constant is 4×10^8 sec^{-1}, and the donor concentration is estimated at 10^{16} cm^{-3}.

A surprising result is the large photoconductivity at low temperatures and relatively long times after excitation. Assuming a mobility at 4.2°K of about 2×10^4 cm^2 volt^{-1} sec^{-1} from piezoelectric scattering,[28] one would still have over 10^{13} cm^{-3} photoexcited electrons in the conduction band at 0.1 sec after excitation. This seems only resonable if one postulates in addition to the simple model described a deep trap for holes, which are then not active in recombination, leaving excess free electrons in the conduction band.

ACKNOWLEDGMENTS

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