Photoluminescence and Thermoluminescence of 4H-CdI₂*

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Photoluminescence (PL) spectra between 1.8 and 3.5 eV in the temperature range 9–215 K and thermoluminescence (TL) spectra between 9 and 150 K of 4H-CdI₂ are reported. At low temperature the PL is due mainly to self-trapped excitons composed of I $5p$ states and Cd $5s$ states. At higher temperature, donors and acceptors also are involved in the luminescence process. The TL shows emission peaks at different temperatures, which are assigned to emission from optically generated donor–acceptor pairs. © 1987 Academic Press, Inc.

Introduction

CdI₂ is a layer compound. The most stable modification 4H-CdI₂ crystallizes in space group $P6_3mc$. The Cd ions occupy slightly trigonally distorted octahedral sites.

The photoluminescence (PL) of CdI₂ in the spectral region 1.8–3.5 eV has been studied by several authors (*1–12*). The PL spectra show strong broad emission bands at 2.16 and 2.50 eV and a number of narrow weak emission lines between 3.0 and 3.5 eV.

Matsumoto *et al.* (*1–4*) interpreted the broad emission bands below 3.1 eV and the emission line at 3.37 eV in terms of relaxed excitonic states of the molecular ion

$(CdI_6)^{4-}$ in a crystal field with D_{3d} symmetry. These authors distinguish two types of such relaxed excitonic states of self-trapped excitons (STEs), one consisting of a hole in the Cd $4d$ levels and an electron in the Cd $5s$ level, and the other consisting of a hole in the I $5p$ levels and an electron in the Cd $5s$ level. However, the distance between the Cd $4d$ level and the Cd $5s$ level is about 13 eV (*13*). This means that the emission bands in the visible and the near UV cannot originate from excitons involving Cd $4d$ holes.

Three very weak emission lines near 3.50 eV, observed at 2 K, were attributed to phonon-assisted radiative decay of indirect excitons (*12*).

The emission lines at 3.23 and 3.12 eV were assigned to the presence of Pb^{2+} impurities because the intensity of these bands increases with increasing Pb^{2+} concentration (*11*). However, Lyskovich *et al.* (*10*) succeeded in preparing from solution CdI₂ crystals that did not show these lines ini-

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tially, but only after heat treatment. This indicates that the emission lines at 3.23 and 3.12 eV are due to intrinsic defects.

In the literature, several studies of the thermoluminescence (TL) of CdI_2 have been reported (10, 14–18). Six TL peaks have been observed (14–17). Using CdI_2 microcrystals of different size, these authors showed that some of the peaks are related to surface traps, whereas other peaks are related to traps in the bulk of the crystals. Four very weak TL peaks were attributed to lattice defects. Three TL peaks of polycrystalline CdI_2 were observed between 350 K and 700 K (18); the authors assigned these peaks to lattice defects.

In this paper we report new measurements of PL and TL spectra of $4H\text{-}CdI_2$. Some of the experimental results were already reported in a preliminary communication (19), but the interpretation given there contains an error with regard to the sign of the Coulomb energy contribution to donor–acceptor energies. In this paper we give a new interpretation of the spectra in terms of free excitons, excitons bound to defects, self-trapped excitons, and donor–acceptor pair recombination.

Experimental Methods

CdI_2 was prepared from high-purity elements. Single crystals were grown with the Bridgman technique. To investigate the influence of the method of preparation on the luminescence, we also prepared crystals of CdI_2 from a solution in H_2O at 75°C and in C_2H_5OH at 50°C.

PL spectra were measured using homebuilt equipment. The light from a 1000-W Xe arc (Oriel 6269) was dispersed with a Jobin–Yvon H.20 UV monochromator. The emitted light was dispersed by means of Jobin–Yvon H.20 VIS monochromator. Spectra were taken with a resolution of about 0.02 eV. The sample was mounted in

an Oxford Instruments MB4 cryostat. The temperature of the sample may be varied between 2 and 300 K.

TL spectra were measured using the same equipment. A polycrystalline sample of CdI_2 was illuminated at 5 K for 15 min, using radiation with an energy of 3.54 eV. After this excitation, the light was switched off, the sample was heated at a constant rate, and the total intensity of the luminescence was measured as a function of temperature. To determine the spectral region within which the TL occurred we used band filters instead of a monochromator because the TL was very weak.

We have also irradiated polycrystalline CdI_2 with a Molectron UV-400 pulsed N_2 laser at a repetition rate of 10 Hz for 1 hr at 10 K and subsequently heated it to 250 K. The TL spectra taken after this treatment were about 1000 times as intense as those taken before the treatment. This clearly shows that the TL involves optically generated centers.

Experimental Results

The PL spectra of polycrystalline CdI_2 as a function of temperature are shown in Figs. 1 and 2. The excitation energy was 3.54 eV, with a spectral width of 0.02 eV. Generally, the spectra are in good agreement with those reported in the literature (1–4). The observed position and shape of the emission bands do not depend on the way the crystals were prepared; however, the total intensity of the luminescence depends strongly on the degree of perfection of the crystals (7).

TL spectra for polycrystalline CdI_2 are given in Fig. 3. The observed TL corresponds mainly to the emission of light with photon energy between 2.0 and 2.5 eV. Spectra were recorded at different heating rates, B. The temperatures at which the maxima of the TL peaks were observed are given in Table I. We also give the full width
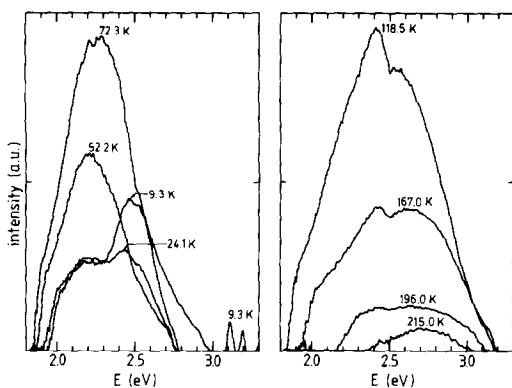
FIG. 1. Photoluminescence spectra of CdI$_2$. The intensity of emission (arbitrary units) from single crystals is given as a function of photon energy. The emission output was corrected for instrumental effects. The excitation energy was 3.54 eV, with a spectral width of 0.02 eV.

at half-maximum, δ, of the TL peaks recorded at the two highest heating rates. We have not given the δ values for the peaks recorded at the lowest heating rate as the TL spectrum in this case is not clearly separated from a continuous background light intensity, probably because of the longer afterglow at lower heating rates.
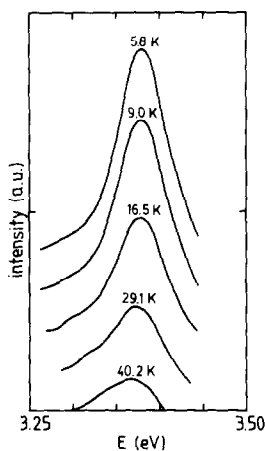

FIG. 2. Emission intensity of the exciton peak at 3.37 eV as a function of temperature. The maximum intensity of this peak is about 10 times that of the emission band at 2.50 eV at 5.8 K.
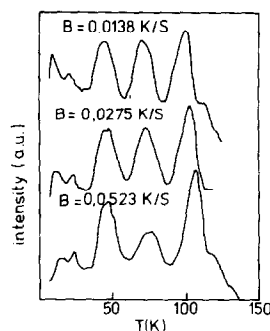

FIG. 3. Thermoluminescence spectra of CdI$_2$ at various heating rates B.

Discussion of Photoluminescence

The valence band states of CdI$_2$ have mainly I $5p$ character; the conduction band states have mainly Cd $5s$ character. Optical investigations combined with band structure calculations (12, 13, 20) show that the smallest energy gap between the valence and conduction band is an indirect gap (3.47 eV at 2 K). The smallest direct gap corresponds to parity forbidden transitions. The direct gap for optically allowed transitions (at the Γ point of the Brillouin zone) is associated with strong exciton peaks X_0, X_1, and X_2, observed in the reflection spectra.

The luminescence spectra of CdI$_2$ are quite reproducible and show the same luminescence peaks as a function of photon energy and temperature, independent of the way the crystals were grown. Moreover, the observed luminescence spectra can be excited only by intrinsic absorption. These arguments suggest that the observed luminescence is an intrinsic property of CdI$_2$, and does not arise from the presence of impurities.

CdI$_2$ is a polar crystal, and a strong electron–phonon interaction is expected. Indeed, Matsumoto et al. (1) observed a long exponential tail of absorption below the edge (Urbach's rule) that was due to STEs. The Urbach exponential tail extends to en-

TABLE I

Temperatures (T_m) at which TL Peaks Have Maximum Intensity and the Widths (δ) of
These Peaks

	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5	
	T_m	δ	T_m	δ	T_m	δ	T_m	δ	T_m	δ
B = 0.0138 K/s	9.3		21.9		42.5		66.4		99.5	
B = 0.0275 K/s	12.2	8.6	22.4	8.6	45.9	20.8	71.2	22.0	102.9	17.1
B = 0.0523 K/s	13.5	9.9	24.1	11.1	48.3	16.1	75.2	22.9	106.3	14.8
				E_T						
Eq. (4)	0.002		0.012		0.016		0.050		0.16	
Eq. (3)	0.001		0.02		0.03		0.05		0.16	
	($s \sim 10^{-2}$)		($s \sim 10^3$)		($s \sim 10$)		($s \sim 10$)		($s \sim 10^5$)	

Note. The values of the trap depth, E_T (eV), are calculated from Eq. (3) or (4). The heating rate is B; the frequency factor is s.

ergies far below 3 eV, which indicates that strongly localized STEs with an energy much lower than the energy gap are possible in CdI_2.

Matsumoto et al. (1) assigned the emission at 3.37 eV to a STE. Another possibility is that the 3.37-eV peak is due to bound excitons, as suggested by Bondar et al. (6).

The luminescence band at 3.37 eV is thermally quenched (Fig. 2). The intensity as a function of temperature, $L(T)$, is

$$L(T) = AI/\{1 + C \exp(-E_a/kT)\} \quad (1)$$

where A is a constant, I is the intensity of the exciting light, C is a constant, and E_a is the activation energy. We assumed A to be temperature independent. The observed emission intensity follows closely the temperature dependence predicted by Eq. (1) for E_a = 3.1 ± 0.4 meV (Fig. 4), in good agreement with the value 2.7 ± 0.3 meV reported by Lyskovich and Panasyuk (5). Following Lsykovich et al. (10) we ascribe the sharp weak emission lines at 3.23 and 3.12 eV also to bound excitons.

With the decrease with increasing temperature of the intensity of the 3.37-eV peak, there is an increase in the intensity of the bands at 2.16 and 2.50 eV. We assign these bands to radiative decay of STEs composed of I $5p$ states and Cd $5s$ states. These STEs are formed by a thermally activated process from optically generated free excitons. We try to find arguments for this assignment from data on the polarization of these emission bands, reported by Matsumoto et al. (1). For this it is necessary to
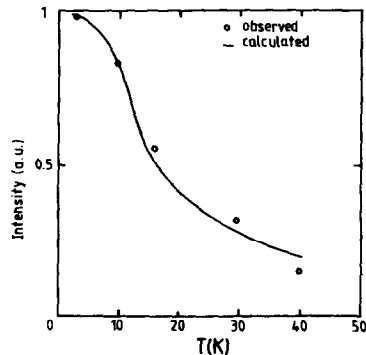

Fig. 4. Observed and calculated intensity of the emission band at 3.37 eV of polycrystalline CdI_2 as a function of temperature.

consider in some detail the nature of the states at the top of the valence band.

The valence band of CdI_2 consists of states of mainly I $5p$ character; the top of the valence band is at the Γ point in the Brillouin zone (13). The crystal field splitting of the valence band states in $(p_x p_y)$ and p_z states is the origin of the difference between reflection spectra of CdI_2 at 4.2 K for light polarized parallel and perpendicular to the crystallographic c axis (1, 20–23) (see Table II). The crystal field splitting at Γ is such that the highest valence band Γ_{6a} has mainly p_z character. If no spin–orbit splitting were present, this would lead to complete polarization of the absorption and emission spectra, with $E \parallel c$ for the Γ_{6a}^-, and $E \perp c$ for the Γ_4^-/Γ_5^- exciton. However, the $5p$ states of I have a large spin–orbit coupling and this causes a strong mixing of $(p_x p_y)$ and p_z states, resulting in a partial polarization. These arguments have been used to explain the polarization of the exciton peaks in $CdCl_2$, $CdBr_2$, and CdI_2 (20). In addition to spin–orbit coupling, there is also an exchange interaction between electron and hole spins in the excitons which also induces mixing of $(p_x p_y)$ and p_z hole states, and therefore also influences the polarization of emission and absorption bands (24, 25).

Matsumoto reported measurements of the polarization of the emission bands, P,

calculated from the relation

$$P = (I_\perp - I_\parallel)/(I_\perp + I_\parallel) \qquad (2)$$

where $I_\perp$ and $I_\parallel$ are the intensities of light polarized perpendicular and parallel to the crystallographic c axis, respectively. The degree of polarization is almost independent of the temperature. The emission band at 2.50 eV has a negative P value; the band at 2.16 eV, a positive P value (Table II). The sign of the polarization suggests that the emission band at 2.16 eV is due to a STE of symmetry Γ_4^-/Γ_5^- (corresponding to the X_1 exciton in absorption); and the emission band at 2.50 eV, to a STE of symmetry Γ_{6a}^- (corresponding to the X_0 exciton in absorption). This assignment requires a larger relaxation energy of $3.85 - 2.16 = 1.69$ eV for the X_1 exciton than the value of $3.68 - 2.50 = 1.18$ eV for the X_0 exciton. This is in agreement with the observation that the width of the emission band at 2.16 eV is larger than the width of the emission band at 2.50 eV [0.28 and 0.23 eV at 4.2 K, respectively (1–4)]. Moreover, in layer compounds the E phonons, which modulate the metal–ligand distance in the xy plane, are more strongly polar than the A phonons (26, 27). Therefore, one expects indeed a stronger interaction of $(p_x p_y)$ hole states with the lattice, and as a consequence a larger relaxation energy for excitons with mainly $(p_x p_y)$ hole orbitals. A schematic

TABLE II

ABSORPTION AND EMISSION OF I $5p$–Cd $5s$ EXCITONS IN CdI_2

		Free exciton		STE		
Exciton	Symmetry	Absorption maximum (eV)	P	Emission maximum (eV)	P	Lifetime at 10 K (μs)
X_0	Γ_{6a}^-	3.68	−	2.50	−0.10	6
X_1	Γ_4^-/Γ_5^-	3.85	+	2.16	+0.29	$\left\{\begin{matrix} 6 \\ 20 \end{matrix}\right.$
X_2	Γ_{6b}^-	4.80	+	—		

configuration coordinate diagram for free
and self-trapped Γ excitons is shown in Fig.
5.

The temperature dependence of the in-
tensity of the emission bands at 2.16 and
2.50 eV was analyzed by Matsumoto et al.
(1). The data indicate thermally activated
energy transfer (with activation energy E_b
= 1.84 meV) from the excited state (STE −
X_0) that emits at 2.50 eV to the excited state
(STE − X_1) that emits at 2.16 eV (Fig. 5).

The intensity of the luminescence bands
at 2.16 and 2.50 eV is strongly influenced by
the degree of crystal perfection. The lumi-
nescence is much stronger in crystals with
many dislocations or stacking faults (7). We
ascribe this to a hindered diffusion of free
excitons to luminescence killing centers.
This would lead to a longer lifetime for the
free excitons and to an increased probabil-
ity for the formation of self-trapped exci-
tons.

The relative intensity of the lumines-
cence peaks at 2.16 and 2.50 eV does not
depend on the degree of crystal perfection
(7). This shows that the relative intensity is
not influenced by energy transport in the
crystal, in agreement with our interpreta-
tion in which the relative intensity of the
peaks at 2.16 and 2.50 eV is influenced by
transitions from a STE-X_0 to a STE-X_1
state, which is a local process.

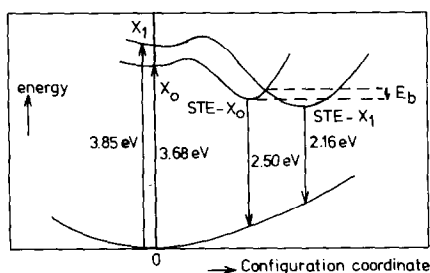At higher temperature ($T > 60$ K) there is

FIG. 5. Configuration coordinate diagram of Γ exci-
tons in CdI_2. X_0 and X_1 are free excitons of symmetry
Γ_{6a}^- and Γ_4^-/Γ_5^-, observed in reflection (20). The corre-
sponding self-trapped excitons STE-X_0 and STE-X_1
are responsible for luminescence at 2.50 and 2.15 eV,
respectively.

an (blue) emission between 2.6 and 3.0 eV,
which increases with increasing tempera-
ture; at the same time the intensity of the
emission bands at 2.16 and 2.50 eV de-
creases. It is not very likely that the blue
luminescence involves impurity ions or
equilibrium native defects. One expects
widely varying impurity ion concentrations
for crystals grown from the melt or from
solutions, and also the concentration of
equilibrium native defects will vary
strongly with the temperature at which the
crystals are grown. This would lead to large
variations in the blue emission intensity,
which are not observed.

We propose that the blue emission of
CdI_2 is due to the presence of optically gen-
erated Frenkel defects, which are intersti-
tial Cd atoms and Cd vacancies. These de-
fects could form as a result of nonradiative
decay of excitons (28). The interstitial Cd
atoms are donors and the Cd vacancies are
acceptors. Further optical excitation pro-
duces electrons and holes that are trapped
at the newly formed donors and acceptors.
The blue emission then results either from
electron–hole recombination at the donors
or acceptors or from donor–acceptor pair
recombination.

The intensity of the luminescence of CdI_2
strongly decreases at temperatures above
120 K and is completely quenched at 225 K.
This thermal quenching of the lumines-
cence of CdI_2 is ascribed to the thermal ion-
ization of the donors and the acceptors and
subsequent nonradiative decay on recombi-
nation centers, for example, I_2^- defects. We
will try to show that the formation of nonra-
diative recombination centers is due to the
partial photolysis of CdI_2 (29). Above about
225 K thermally activated photolysis with
an activation energy of 0.17 eV was ob-
served in $CdI_2 : CuI$ (30). Nearly the same
activation energy (0.18 eV) is reported for
the photolysis of pure CdI_2 (31). This indi-
cates that the rate-determining step of the
photolysis is the same in these two cases.
The photolysis of $CdI_2 : CuI$ produces non-

radiative recombination centers, as was deduced from the observation that optically colored CdI_2:CuI does not show luminescence (30). Therefore we ascribe the thermal quenching of the luminescence of CdI_2 above 120 K to the presence of optically generated nonradiative recombination centers.

Discussion of Thermoluminescence

Thermoluminescence is luminescence induced by the thermally activated release of charge carriers from traps. The trap depth E_T can be calculated from the observed TL spectra. In the case of first-order kinetics, valid if the retrapping probability can be neglected, the trap depth E_T is given (32) as

$$E_T = \frac{skT_m^2}{B} \exp(-E_T/kT_m) \qquad (3)$$

where B is the heating rate, s is the frequency factor, and T_m is the temperature at which the TL peak has maximum intensity. Values of E_T calculated from Eq. (3) are given in Table I. The frequency factor s is approximately given by $s \approx 10^{30} A$, where A is the cross section of the trap in units (m^2) (33). Reasonable values of A range from 10^{-16} to 10^{-26} m^2 (34), indicating that reasonable values of s should range from 10^{14} to 10^4 s^{-1}. Using Eq. (3) we find that only for the deepest trap the value of s falls in this range. We conclude that the only TL process in CdI_2 that can be described by first-order reaction kinetics is the TL process that involves the trap $E_T = 0.16$ eV. For the other traps the retrapping probability cannot be neglected. In that case we can calculate the trap depth assuming that the retrapping probability is much larger than the recombination probability. The trap depth E_T is given by (36)

$$E_T = (2kT_m^2/\delta)f \qquad (4)$$

where δ is the width of the TL peak. The calculated values for E_T are given in Table I. The correction factor f was calculated from the asymmetry of the TL peak; for peaks 1, 2, 3, and 4 we assumed retrapping to be dominant; in all cases we assumed mechanism II, and $\rho = 1$, $\chi \gg 1$, in the notation of (36).

We ascribe the observed TL peaks to the presence of donors in the vicinity of ionized acceptors, or to acceptors in the vicinity of ionized donors. The donors and acceptors are generated optically, as indicated by the strong increase in TL with previous irradiation with a N_2 laser. The donors are probably Cd atoms located on interstitial octahedral sites in the van der Waals gap and the acceptors are Cd vacancies. This completely determines the possible donor–acceptor pair distances; the first seven pair coordinates are given in Table III.

The thermal excitation energy of an electron from a trap (or a hole; we cannot determine whether the electron or the hole is

TABLE III

CALCULATIONS OF THE IONIZATION ENERGY E_0 OF THE ISOLATED TRAP, USING THE OBSERVED TRAP DEPTH E_T OF A TRAP AT (000) IN THE VICINITY OF A CENTER WITH CHARGE $-ne$ AT POSITION (xyz)

$\sqrt{x^2 + y^2}$	Coulomb energy, E_c (eV)	Observed trap depth, E_T (eV)	Calculated ionization energy of isolated trap, E_0 (eV)
		$-e$	
0	−0.325	0.002	0.33
$(1/3)a\sqrt{3}$	−0.295	0.01	0.31
a	−0.254	0.02	0.27
$(2/3)a\sqrt{3}$	−0.239	0.05	0.29
$(1/3)a\sqrt{21}$	−0.201	0.16	0.36
$a\sqrt{3}$	−0.190		
$2a$	−0.172		
		$-2e$	
0	−0.650		
$(1/3)a\sqrt{3}$	−0.590		
a	−0.508	0.002	0.51
$(2/3)a\sqrt{3}$	−0.478	0.01	0.49
$(1/3)a\sqrt{21}$	−0.402	0.02	0.42
$a\sqrt{3}$	−0.380	0.05	0.43
$2a$	−0.344	0.16	0.50

thermally excited from the trap) in the presence of a center with charge $-ne$ is given by

$$E_T = E_0 - E_c$$
$$= E_0 - ne^2[\varepsilon_\parallel^\circ \varepsilon_\perp^\circ(x^2 + y^2) + \varepsilon_\perp^{\circ2}z^2]^{-1/2} \quad (5)$$

where E_T is the trap depth and E_0 is the ionization energy of the isolated trap. The distance between the two centers is $(x^2 + y^2 + z^2)^{1/2}$; $\varepsilon_\parallel^\circ$ and $\varepsilon_\perp^\circ$ are the static dielectric constants of CdI_2 [$\varepsilon_\parallel^\circ = 5.4$ and $\varepsilon_\perp^\circ = 12.9$ (37)]. The values of x, y, and z are obtained from the lattice parameters of CdI_2 ($a = 4.248$ Å, $c = 13.72$ Å, for z we take $z = \frac{1}{4}c$).

In Table III we have given the values of the Coulomb energy, E_c, of the final states for different donor–acceptor pairs. Because interstitial Cd and Cd vacancies are double donors and acceptors, respectively, the charge on the centers can be $-e$ or $-2e$. From Table II we find that on the basis of TL data, we cannot decide between these two possibilities. However, a study of the photoconductivity of CdI_2 showed traps with an ionization energy of 0.31 eV (38). This is consistent with our results if the center has a charge of $-e$ (or $+e$). We conclude that the thermoluminescence in CdI_2 is due to the thermal excitation of electrons (or holes) from a center in the vicinity of a single charged acceptor (or donor).

Conclusion

We have ascribed the PL and TL of CdI_2 to intrinsic processes, not involving impurities or defects present in the crystal prior to the luminescence experiment. Energy transport proceeds via free electrons and holes or free excitons. These carriers have a finite lifetime due to the formation of localized self-trapped excitons, as a result of strong electron–phonon interactions. At higher excitation densities the formation of Frenkel defects (interstitial Cd and Cd vacancies) due to the decay of the self-

trapped excitons becomes important. These optically generated defects, which play a role as electron or hole traps in TL, are a precursor to the photolysis of CdI_2.

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