DIRECT LUMINESCENCE AND THERMALLY STIMULATED LUMINESCENCE OF 4H CdI2

C. Ronda, J. Van Der Meer, A. Van Heuzen, C. Haas

To cite this version:
C. Ronda, J. Van Der Meer, A. Van Heuzen, C. Haas. DIRECT LUMINESCENCE AND THERMALLY STIMULATED LUMINESCENCE OF 4H CdI2. Journal de Physique Colloques, 1985, 46 (C7), pp.C7-463-C7-467. <10.1051/jphyscol:1985782>. <jpa-00225112>

HAL Id: jpa-00225112
https://hal.archives-ouvertes.fr/jpa-00225112
Submitted on 1 Jan 1985

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
DIRECT LUMINESCENCE AND THERMALLY STIMULATED LUMINESCENCE OF 4H CdI₂

C.R. Ronda, J.H. van der Meer, A.A. van Heusen and C. Haas

Laboratory of Inorganic Chemistry, Materials Science Center of the University, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Résumé - Nous présentons les spectres de luminescence directe (LD) du 4H CdI₂ dans la région 1.8 à 3.4 eV, aux températures entre 9.3 et 215 K, ainsi que les spectres de luminescence thermiquement stimulée (LTS) du même composé. Les spectres de LD sont composés de plusieurs larges bandes d'émission qui se recouvrent. Ces bandes sont dues à la recombinaison des électrons localisés avec des trous localisés. Grâce à une théorie simple, qui tient compte de l'interaction électrostatique entre électron et trou nous avons pu expliquer quantitativement la position des bandes spectrales d'émission. Les spectres de LTS montrent des bandes d'émission à plusieurs températures. Ces bandes sont dues à la recombinaison des porteurs de charges initialement piégés. L'énergie d'activation des pièges est calculée en considérant les interactions électrostatiques entre porteurs de charges piégés.

Abstract - Direct luminescence (DL) spectra of 4H CdI₂ in the spectral region 1.8-3.4 eV at temperatures between 9.3 and 215 K and thermally stimulated luminescence (TSL) spectra are reported. The DL spectra consist of several overlapping broad emission bands. These bands are due to radiative recombin-

tion of localized (trapped) electrons with localized (trapped) holes. With a simple theory, which takes into account the electrostatic interaction between electron and hole it was possible to explain the position of the observed emission bands quantitatively. The TSL spectra show emission bands at several temperatures. These bands are due to the recombin-

tion of initially trapped charge carriers. The trap depths can be calculated, by taking into account the electrostatic interaction between the trapped charge carriers.

I - INTRODUCTION

CdI₂ is a layer compound. The most stable modification (4H CdI₂) crystallizes in spacegroup P6₃mc (fig. 1.). The Cd ions occupy slightly trigonally distorted octa-

hedral sites.

Fig. 1. The hexagonal unit cell of 4H CdI₂ and the (110) section. The squares are the octahedral interstitial sites in the van der Waals gap.

The direct luminescence (DL) of CdI₂ in the spectral region 1.8-3.4 eV has been extensively studied by Matsumoto et al. [1-4]. The spectrum shows sharp emission lines at 3.38, 3.23 and 3.12 eV. The emission line at 3.38 eV originates from the emission of the free exciton in CdI₂ and the emission lines at 3.23 and 3.12 eV have been interpreted as due to Pb impurities [5].
The spectrum shows broad emission bands below 3.1 eV with a large Stokes shift. The broad emission bands have been interpreted by Matsumoto et al. [1] as due to localized relaxed excitonic states, belonging to excited states of the molecular ion \((\text{CdI}_2)^{\text{+}}\) in a \(D_{4d}\) crystal field. These authors distinguish two relaxed excitonic states, one consisting of a hole in the Cd 4d level and an electron in the Cd 5s level and the other consisting of a hole in 1 5p level and an electron in the Cd 5s level.

It follows from a recent study [6] that the energy difference between the Cd 4d level and the Cd 5s level is about 13 eV. This means that the DL cannot find its origin in an excitonic state involving the Cd 4d levels.

We report measurements of the DL of \(\text{CdI}_2\) as a function of temperature and show that the broad DL bands of \(\text{CdI}_2\) are due to pair luminescence. We also report thermally stimulated luminescence (TSL) measurements of \(\text{CdI}_2\). The observed trap depths confirm the proposed model.

II - EXPERIMENTAL METHODS

\(\text{CdI}_2\) was prepared from the high purity elements. Single crystals were grown with the Bridgman technique. In order to investigate the dependence of the DL characteristics on the way \(\text{CdI}_2\) had been prepared, we also prepared crystals of \(\text{CdI}_2\) from a solution of \(\text{CdI}_2\) in \(\text{H}_2\text{O}\) at 75°C and in \(\text{C}_2\text{H}_5\text{OH}\) at 50°C.

The DL spectra were measured using a home-built equipment. The light of a 1000 W Xe arc (Oriel 6269) is dispersed by means of a Jobin-Yvon H.20 UV monochromator. The emitted light is dispersed by means of a Jobin-Yvon H.20 VIS monochromator. The spectra were recorded with a resolution of about 0.02 eV. The sample is mounted in an Oxford Instruments MB 4 cryostat. The temperature of the sample may be varied between 2-300 K.

The TSL spectra were measured using the same equipment by illuminating \(\text{CdI}_2\) during 15 minutes at 5 K. Thereafter the compound was heated at a constant rate. We used band pass filters instead of a monochromator to determine the spectral region where the TSL occurred because the TSL was very weak.

III - EXPERIMENTAL RESULTS

The DL spectra of \(\text{CdI}_2\) as a function of the temperature are given in fig. 2. The excitation energy was 3.54 eV. The DL characteristics such as position, band shape and intensity of the bands do not depend on the way the \(\text{CdI}_2\) crystals had been prepared.

The TSL spectrum of \(\text{CdI}_2\) (irradiated with the same excitation energy) at a heating rate of 3.14°C/min. is given in fig. 3. The TSL occurs mainly between 2.0 and 2.5 eV.

IV - ANALYSIS OF THE DL AND THE TSL IN TERMS OF PAIR LUMINESCENCE

We ascribe the various observed luminescence bands of \(\text{CdI}_2\) to the pair recombination of localized (trapped) electrons with localized (trapped) holes. The several DL bands correspond to different distances between electron and hole according to the following expression valid for a uniaxial compound [7]:

\[
E_{em} = E_o - \frac{e^2}{\sqrt{\varepsilon_0^\infty \varepsilon_1^\infty}}} + \frac{e^2}{\varepsilon_1^\infty \varepsilon_0} z^2
\]

where \(\varepsilon_0^\infty\) and \(\varepsilon_1^\infty\) are the high frequency dielectric constants for polarization parallel and perpendicular to the c-axis. We remark that we assume in (1) a Coulomb stabilization of the initial state before recombination; this was found to give good agreement with experimental data. The usual model of pair recombination of an electron on a donor with a hole on an acceptor corresponds to a Coulomb stabilization of the final state (a plus instead of a minus sign in eq. (1)); however, this does not explain the observed data for \(\text{CdI}_2\). The DL bands are very broad, indicating that the electronic states are strongly coupled to the lattice. For the maxima of the bands we have to take into account the electron polarization only. This is at variance with the expressions sometimes given in the literature [8,9]. The values of \(\varepsilon_0^\infty\) and \(\varepsilon_1^\infty\) for \(\text{CdI}_2\) are 4.3 and 4.6 respectively. The fact that the DL characteristics do not depend on the way the high purity crystals are grown, in-
Fig. 2. DL spectra of 4H CdI₂ as a function of temperature. The spectra are corrected for the instrumental response. The spectra indicate that any defects involved in the recombination process must be intrinsic. We assume that the recombining electrons and holes are located on interstitial octahedral sites in the van der Waals gap, and on Cd sites, respectively. This completely determines the possible pair distances in the lattice; the first 7 pair coordinates are given in table 1. The values of \( x^2, y^2 \) and \( z^2 \) are obtained from the lattice parameters of 4H CdI₂ (a-axis 4.248 Å, c-axis 13.72 Å). The first DL maximum (at 2.16 eV) is not clearly resolved in the spectra. Matsumoto et al., who measured the luminescence of CdI₂ as a function of time resolved this maximum clearly [1-3]. The DL bands are broad, this makes it difficult to determine the position of the DL maxima accurately. In table 1, the observed DL maxima and the temperature at which they are observed are given and compared with the calculated DL maxima. The overall agreement is quite good. In a coming publication, we will present a more general theory with which we are able to calculate the lineshape of the DL and the observed partial polarization of the emission bands [3]. The trap depths from which the TSL originates have been calculated, using the full profile of the TSL spectrum. If one neglects the retrapping probability, the TSL of a given trap is given by

\[
I(T/B) = n_A \exp \left[ \frac{-E_T}{kT} \right] \int_0^T A \exp \left( \frac{-E_T}{kT} \right) dT
\]

(2)
in which $\beta$ is the heating rate, $n_0$ is the number of initially trapped charge carriers, $A$ is the recombination cross section and $E_T$ is the trap depth. The thermal excitation energy of an electron from a trap (or hole; we cannot determine whether the electron or the hole is thermally excited) in the presence of a center with the same charge is given by

$$E_T = E_0 - e^2/\varepsilon_{\|}\varepsilon_{\perp} (x^2 + y^2) + \varepsilon_{\perp} z^2$$

in which $E_T$ is the trap depth and $E_0$ is the ionization energy of the isolated trap. $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are the static dielectric constants ($\varepsilon_{\|} = 5.4$ and $\varepsilon_{\perp} = 12.9$ [10]). In Table II the temperatures of the TSL maxima and the values of the Coulomb destabilization energy are given for the first 5 distances together with the calculated trap depths. It follows that the ionization energy of an isolated trap is 0.31 eV, consistent with results obtained in a study of the photoconductivity of CdI$_2$ [11]. Finally, we remark that the origin of the localization of electrons and holes after the photo excitation is not known. A possibility is a localization (self-trapping) of electrons and holes due to a very strong electron-phonon interaction. A recombination of self-trapped electrons with self-trapped holes indeed has a Coulomb stabilization of the initial state, as observed. It is also possible that the trapping involves defects induced optically; photo excitation of the crystal produces free excitons, which relax to self-trapped excitonic states by the displacement of ions in the crystal.

ACKNOWLEDGEMENTS

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

**Table I.** Comparison of observed and calculated maxima of pair DL peaks in CdI$_2$. The calculations are for $E_0 = 3.04$ eV, $\varepsilon_{\parallel} = 4.3$, $\varepsilon_{\perp} = 4.6$ and $z = (1/4)$ c.

<table>
<thead>
<tr>
<th>$\sqrt{(x^2 + y^2)}$ pair</th>
<th>Observed maximum (eV)</th>
<th>Calculated maximum (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.16 ([1-3])</td>
<td>2.13</td>
</tr>
<tr>
<td>(1/3)a/3</td>
<td>2.29 (72.3 K)</td>
<td>2.29</td>
</tr>
<tr>
<td>a</td>
<td>2.46 (9.3 K)</td>
<td>2.46</td>
</tr>
<tr>
<td>(2/3)a/3</td>
<td>2.52 (9.3 K)</td>
<td>2.51</td>
</tr>
<tr>
<td>(1/3)a/21</td>
<td>2.57 (118 K)</td>
<td>2.60</td>
</tr>
<tr>
<td>a/3</td>
<td>2.67 (167 K)</td>
<td>2.64</td>
</tr>
<tr>
<td>2a</td>
<td>2.67 (167 K)</td>
<td>2.69</td>
</tr>
</tbody>
</table>

**Table II.** Calculation of the ionization energy of the isolated trap in 4H CdI$_2$ using the observed trap depths in the TSL experiment. The calculations are for $\varepsilon_{\parallel} = 5.4$, $\varepsilon_{\perp} = 12.9$ and $z = (1/4)$ c.

<table>
<thead>
<tr>
<th>$\sqrt{(x^2 + y^2)}$ pair</th>
<th>trap depths (eV)</th>
<th>Coulomb energy (eV)</th>
<th>Ionization energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.01 (0.01) (13.5 K)</td>
<td>0.33</td>
<td>0.34 (0.01)</td>
</tr>
<tr>
<td>(1/3)a/3</td>
<td>0.02 (0.01) (24.1 K)</td>
<td>0.29</td>
<td>0.31 (0.01)</td>
</tr>
<tr>
<td>a</td>
<td>0.03 (0.02) (48.3 K)</td>
<td>0.25</td>
<td>0.28 (0.02)</td>
</tr>
<tr>
<td>(2/3)a/3</td>
<td>0.05 (0.02) (75.2 K)</td>
<td>0.23</td>
<td>0.28 (0.02)</td>
</tr>
<tr>
<td>(1/3)a/21</td>
<td>0.15 (0.05) (106.3 K)</td>
<td>0.20</td>
<td>0.35 (0.05)</td>
</tr>
</tbody>
</table>

REFERENCES

3 H. Matsumoto, H. Nakagawa and S. Kondo, Memoires of the Faculty of Engineering, Fukui University, 31(1), 53 (1983).