Decay Profiles and Spectra of
Stimulated Luminescence in CdI$_2$

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Decay profiles and spectral distributions of the stimulated luminescence in CdI$_2$ crystals have been investigated at liquid nitrogen temperature under high density excitation with a N$_2$-gas laser in the excitonic absorption band. The observed luminescence decay curve consists of two components, fast ($<$ 20 ns) and slow (about 5 μs) ones. The slow component is identical to the main decay component of the spontaneous emission which is observed rather strongly in the case of low density excitation. The fast component is peculiar to the case of high density excitation, and is connected to the stimulated emission. This means that the stimulated luminescence appears in the early stage of the luminescence decay. The spectral distribution of the fast component, namely, the stimulated emission spectrum, consists of eight fine-structures and is different from the usual spontaneous emission spectrum from selftrapped exciton (STE) states. Discussions will be made on the origin of these structures relating it with fine-structures of the STE states.

§ 1. Introduction

Cadmium iodide is a typical ionic crystal of a layer structure with D$_{3d}$ crystal symmetry. Optical absorption and intrinsic luminescence studies on CdI$_2$ have been made by several workers [1-11]. The intrinsic absorption of CdI$_2$ begins at 3.473 eV with indirect excitonic one. Excitation with the UV-light in the intrinsic absorption region gives rise to four emission bands at liquid helium temperature, namely, the Y (at 2.16 eV), G (at 2.57 eV), UV$_1$ (at 3.38 eV), and UV$_2$ (at 3.22 eV) emission bands. It has been

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revealed from experimental investigations on these luminescence that optically created excitons in CdI_2 crystal relax immediately to the STE states through strong exciton-lattice coupling and that the STE states are well described in terms of the excited states of the $[Cd^{2+}I^-{}_6]^{4-}$-complex ions in the D_{3d} crystal field [2,3]. In the case of high density excitation, the luminescence intensity shows superlinear dependence upon the excitation intensity and upon the length of the excited region on the crystal surface. By analyzing the dependence on the excitation length, high optical gain (10^3 to 10^4 cm^{-1}) is obtained. These experimental results indicate that the luminescence under high density excitation is associated with the stimulated emission processes from the STE states [12),13].

In this paper, further studies on the stimulated luminescence have been carried out to investigate the stimulated emission processes from fine-structures of the STE states in the CdI_2 crystal. Luminescence decay profiles and spectral distribution of the stimulated emission were observed at LNT. The results will be discussed on the basis of the excited states of the $[Cd^{2+}I^-{}_6]^{4-}$-complex molecular ions for the STE states in CdI_2 crystal.

§ 2. Experimental

2-1 Samples

Commercially available CdI_2 of special reagent grade contains a considerable amount of Pb^{2+} ions as a residual impurity. In the present work, ultra pure CdI_2 was synthesized in our laboratory from ultra pure cadmium metal of 99.9999 % purity and solid iodine of special reagent grade of 99.8 % purity. Synthesized materials were purified with a method of vacuum distillation. Single crystals of CdI_2 were grown from melt by the Bridgman method. Samples were prepared in a size of $10 \times 10 \times 3$ mm^3. The surfaces perpendicular to the crystal c-axis were obtained by cleaving and the surfaces parallel to the axis were cut and polished with ethyl-alcohol.

2-2. Measurements

The sample crystal was mounted on the copper sample holder and was cooled down to LNT by thermal conduction. Pressure in the cryostat was kept less than 5×10^{-6} Torr.

Figure 1 shows the experimental set-up for the measurements of the stimulated luminescence. The 337.1 nm light pulses with pulse
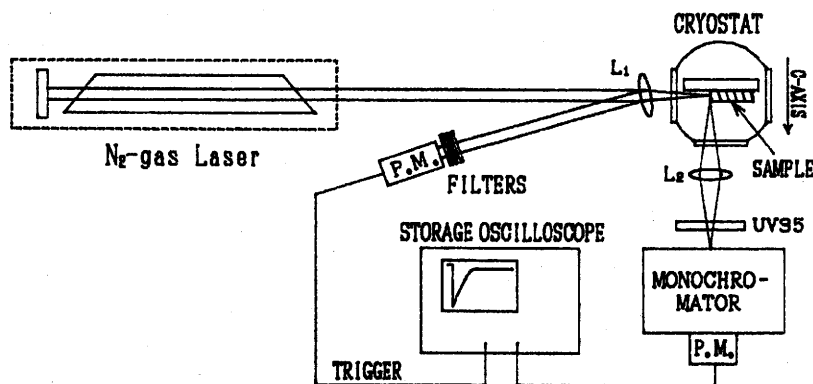
Fig. 1   Experimental set-up for the measurements of the stimulated
luminescence decay and spectrum.   The light pulses from the N_2-gas
laser were focused on the CdI_2 crystal surface with a quartz lens
(L_1).   The luminescence was focused with a quartz lens (L_2) on the
entrance slit of a monochromator through a cut-off filter (UV35).
Analyzed luminescence was detected by a photomultiplier.   Output
signals from the photomultiplier were displayed on the screen of a
storage oscilloscope.   The filter (UV35) was used for the sake of
cutting off intense laser light scattered in the direction of the
measurement.

duration of about 10 ns from a high power N_2-gas laser (> 300 kW)
was used for high density excitation.   The wavelength lies in the
excitonic absorption region of the CdI_2 crystal.   The exciting
light pulse was irradiated in the direction perpendicular to the
crystal c-axis and focused with a quartz lens (L_1) on a crystal
surface parallel to the c-axis.   The degree of focusing was ad-
justed by changing the distance of L_1 from the crystal surface.
The luminescence was focused with a quartz lens (L_2) and monochro-
matized with a NIKON-G250 monochromator through a cut-off filter
(UV35) and detected with a HTV-R955 photomultiplier. The output
signals were led into a 400 MHz storage oscilloscope (Tektronix
7834).

§ 3. Experimental results

   Figure 2 shows oscilloscope traces of the 2.34 eV luminescence
observed at LNT under the various conditions.   (a) The N_2 laser
light was irradiated without focusing.   (b) The laser light was
focused on the crystal surface with a quartz lens.   The irradiated
region was in a straight line of length less than   5 mm   along the
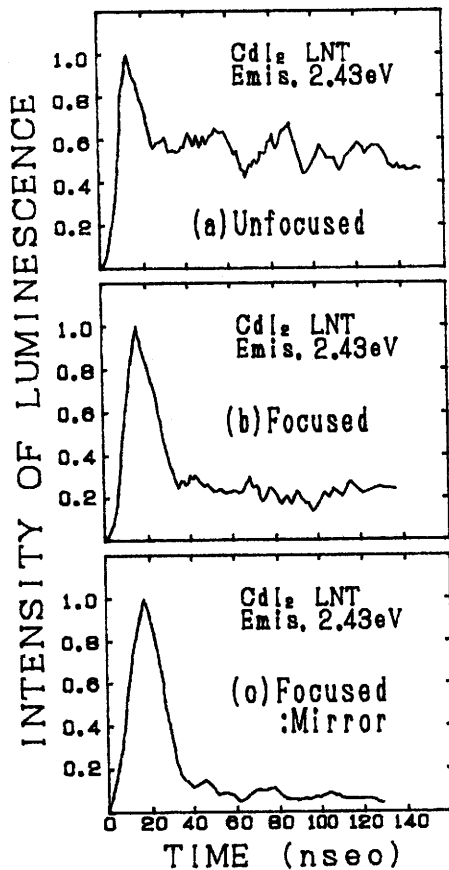crystal c-axis.   (c) The laser light was focused in the same way

Fig. 2 Oscilloscope traces of the 2.34 eV luminescence decay of the CdI_2 crystal at LNT under high density excitation. The experimental conditions are the following : (a) without focusing the laser light, (b) with focused laser light in a straight line on the CdI_2 crystal surface, (c) a plane reflecting mirror perpendicular to the excited line in addition to (b).

as the case (b) and an Al-coated plane mirror was inserted perpendicularly to the straight line of the excited region. The excitation light was irradiated on a crystal surface parallel to the c-axis and the luminescence was observed in the direction of the axis. The intensities of the luminescence are normalized to unity at the maximum. All decay curves consist of slow (about 5 μs) and fast (about 20 ns) components. The fast component was found to grow remarkably with increasing the excitation density. The slow decay component is essentially the same as that of the spontaneous emission from the STE states. The fast decay was not observed in the case of the low density excitation. It turns out from the experimental results shown in figure 2 that the relative intensity of the fast component is remarkably enhanced by focusing the laser light (b) and inserting the reflecting mirror (c), while that of the slow component is diminished. The fast component is attributed to the stimulated luminescence from the STE states discussed later.
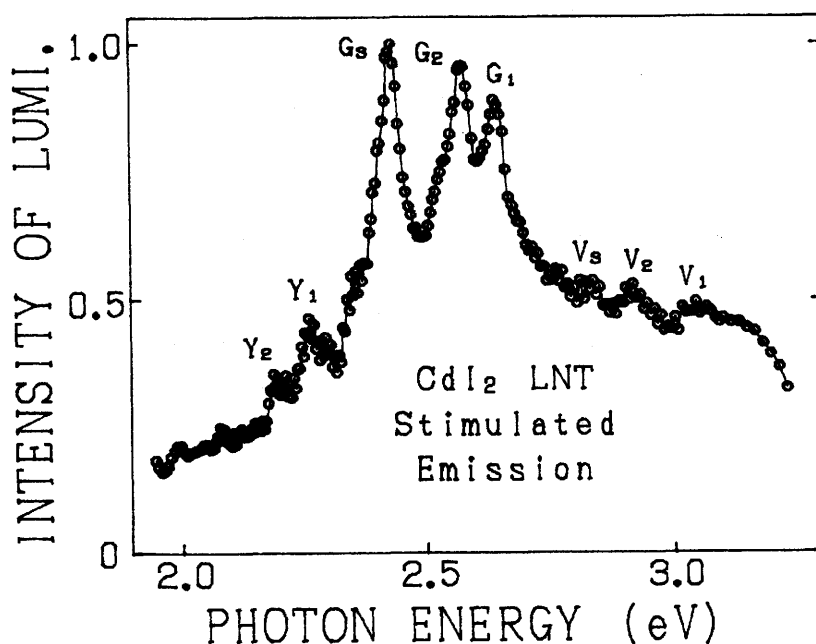
Fig. 3   The stimulated luminescence spectrum of CdI_2 crystal at LNT
under   high density excitation.   The intensity of luminescence is
normalized to unity at the maximum.   This spectrum is obtained by
measuring luminescence decay curves at each emission energy, decompos-
ing them into the fast and slow components and plotting the intensity
of the fast component against the photon energy.

Figure 3 shows the stimulated luminescence spectrum of CdI_2
crystal at LNT.   Decay curves as shown in figure 2 (b) were ob-
served at various emission energies between 2.0 and 3.5 eV.   Each
decay curve was decomposed into two components, the fast and slow
ones, by subtracting the slow component from the observed decay
curve.   The intensities at 20 ns of the fast component were plot-
ted against the emission energy.   The fast component is considered
to be stimulated emission.   Thus, the spectrum obtained by the way
described above is reasonably regarded as the stimulated emission
spectrum.   This stimulated emission spectrum is different from the
usual spontaneous emission spectrum from the STE states which
gives a broad emission   band in the yellow and green region   at
LNT [3].   It has eight fine-structures, namely, three in the region
of the V-emission (V_1, V_2, V_3) three in the region of the G-emis-
sion (G_1, G_2, G_3) and two in the region of the Y-emission (Y_1,
Y_2).   These   structures   can   be connected to the fine-structures
of STE states in the CdI_2 crystal.   This experimental result will

be discussed just later.

§ 4. Discussion

   As shown in figure 2 (b), (c), the fast component which appears
under high density excitation is enhanced in the direction of the
excited straight line.   On the contrary, the slow spontaneous
component is relatively diminished.   These results indicate that
the fast component of luminescence is amplified during passing
through the excited region.   This amplification process is nothing
but the stimulated emission process.   Thus, it would be reasonably
proposed that the fast component of luminescence is attributed to
the stimulated emission.   This proposal is supported by the super-
linear dependence of the luminescence intensity on the excitation
intensity and on the length of the excited straight line region.
In the early stage of the luminescence decay, where the photon
density in the excited region is sufficiently large, the dominant
emission process would be the stimulated process.   On the other
hand, the spontaneous process would be dominant in the later decay
stage because of the low photon density.

   As shown in figure 3, the stimulated emission spectrum has eight
fine-structures and is different from the usual spontaneous emis-
sion spectrum.   In spite of the fatal difference in the spectral
distribution from the usual STE luminescence, the initial states
of the stimulated emission is considered to be the STE states.
This means conversely that the STE states in the CdI_2 crystal
consist of eight fine-structures at least.   In the previous papers
on the STE luminescence in cadmium halides [3], it has been report-
ed that the behaviors of the STE luminescence are well explained
by assuming for the model of the STE states to be the excited
states of the complex molecular ions, $[Cd^{2+}X^-_6]^{4-}$, in the D_{3d}
crystal field, where X^- denotes the halogen ion.   In figure 4 is
shown a schematic energy diagram of molecular orbitals of the
$[Cd^{2+}I^-_6]^{4-}$-complex molecular ions.   In the left side of this
figure are shown the atomic levels of a cadmium ion, where elec-
trons occupy up to the 4d level.   In the right side are shown the
π and σ orbitals composed of the p orbitals of six iodine ions.
In the middle column are shown the molecular orbitals which are
composed of the above orbitals.   The superscripts a, n and b
denote antibonding, nonbonding and bonding orbitals, respectively.
The state symbols represent the irreducible representations in the
O_h symmetry.   Subscripts g and u denote parity.   The $t_{1u}(\pi^n)$ level
belongs to the valence band and the $a_{1g}(\sigma^a)$ level to the conduc-
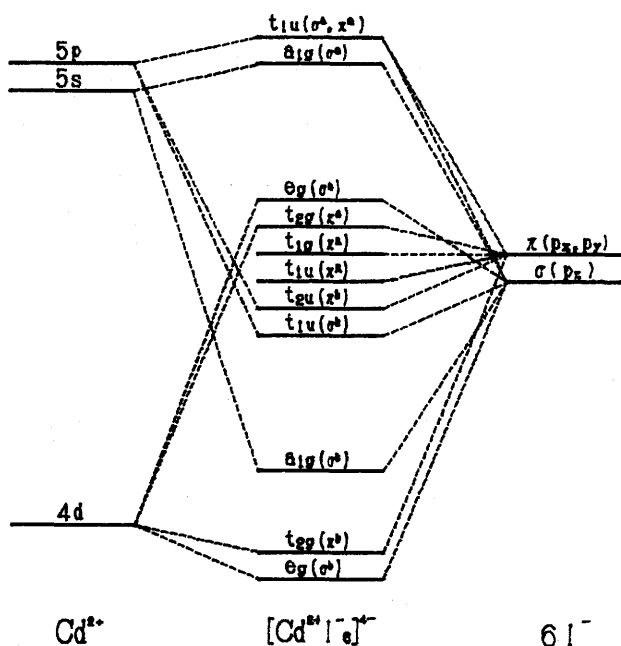
Fig. 4 Schematic energy diagram of single electron molecular orbitals of the $[Cd^{2+}I^-_6]^{4-}$-complex ion. In the left side are shown the atomic levels of the cadmium ion. In the right side are shown the π and σ orbitals composed of the p orbitals of six iodine ions. In the middle column are shown molecular orbital composed of the above orbitals in the O_h crystal field. The superscripts a, n and b denote antibonding, nonbonding and bonding orbitals, respectively. The subscripts g and u denote the parity.

tion band. The 4d orbital corresponds to an inner atomic level and lies approximately 8eV below the valence band top. The electrons occupy up to $e_g(\sigma^a)$. The allowed transition from $t_{1u}(\pi^n)$ to $a_{1g}(\sigma^a)$ occurs with UV-light excitation and the created holes in the $t_{1u}(\pi^n)$ orbitals may relax to $t_{1g}(\pi^n)$, $t_{2g}(\pi^a)$ or $e_g(\sigma^a)$. In figure 5 is shown a schematic energy diagram rewritten as the excitonic levels. In this figure, the T_{1u} and T_{1g} states are the excitonic states with a hole on the nonbonding $t_{1u}(\pi^n)$ and $t_{1g}(\pi^n)$ molecular orbitals, respectively, composed mainly of the iodide 5p orbitals and an electron on the antibonding $a_{1g}(\sigma^a)$ orbital composed mainly of the cadmium 5s orbitals. The T_{2g} and E_g states are the excitonic states with a hole on the antibonding $t_{2g}(\pi^a)$, $e_g(\sigma^a)$ molecular orbitals composed mainly of the iodide 5p orbitals and an electron on the $a_{1g}(\sigma^a)$ orbital. Theground state is A_{1g}. As the $[Cd^{2+}I^-_6]^{4-}$-centers have D_{3d} symmetry in the
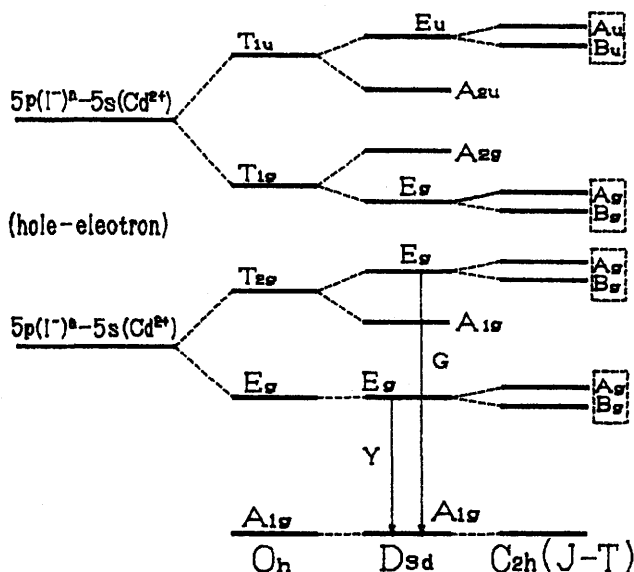
Fig. 5 Schematic energy diagram of the $[Cd^{2+}I^-_6]^{4-}$-complex molecular ion rewritten as excitonic levels. In the left side are shown the possible excitonic states. In the middle column are shown the excited states of the complex molecular ions in the O_h and D_{3d} crystal field, which correspond to the relaxed states of the excitons shown in the left side. These state splits into those shown in the right side in the case of C_{2h} crystal field.
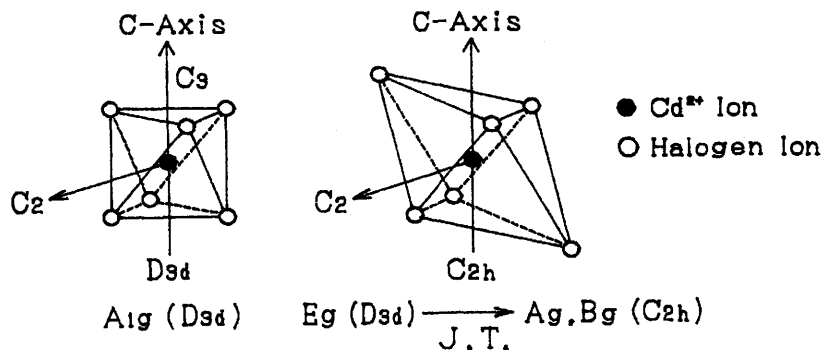

Fig. 6 Jahn-Teller distortions. Since E_g state in the D_{3d} crystal field has twofold orbital degeneracy, the state is expected to split into the A_g and B_g states in the C_{2h} symmetry by Jahn-Teller effect and the $[Cd^{2+}I^-_6]^{4-}$-center are stabilized by lowering the symmetry from D_{3d} to C_{2h}.

CdI_2 crystal, these states further split into the levels shown in

the middle column of the figure. These states become the initial states of the STE luminescence. Apart from the UV-emission which is not observed at LNT, G- and Y-emission are connected with parity forbidden transitions from the $E_g(T_{2g})$ and the $E_g(E_g)$ states to the ground $A_{1g}(A_{1g})$ state in the above model, respectively. The parity forbidden rule may be partially lifted by some odd parity perturbations, such as odd parity lattice vibrations. When a molecule lies occasionally in an orbitally degenerate state, it would remove the degeneracy by lowering the symmetry to be more stable energetically (Jahn-Teller effect) [14-16]. The $[Cd^{2+}I^-_6]^{4-}$-complex molecular ion is expected to be held in D_{3d} symmetry when the system is in the orbital singlet A_{1g} state and to be distorted into C_{2h} symmetry when the system is in the orbital doublet E_g state as shown in figure 6. Therefore, as shown in the right side of the figure 5, the E_g states, the orbital doublet states, would further split into A_g and B_g. The Jahn-Teller distortion from D_{3d} to C_{2h} symmetry has been confirmed in the angular dependence of ESR spectra for the $[Cu^{2+}X^-_6]^{4-}$ and the $[Ag^{2+}X^-_6]^{4-}$-complex ions in cadmium halide crystals [17,18]. Taking the above described STE model into consideration, the eight fine-structures in the stimulated emission spectrum are connected to the eight parity forbidden transitions in the $[Cd^{2+}I^-_6]^{4-}$-center of the C_{2h} crystal field. The three structures in the region of V-emission correspond to the parity forbidden transitions from $A_{2g}(A_{2g})$, $A_g(E_g)$ and $B_g(E_g)$ to $A_{1g}(A_{1g})$, the three structures in the region of G-emission to the transitions from $A_g(E_g)$, $B_g(E_g)$ and $A_{1g}(A_{1g})$ to $A_{1g}(A_{1g})$, and the two structures in the region of Y-emission to the transitions from $A_g(E_g)$, $B_g(E_g)$ to $A_{1g}(A_{1g})$.

In the case of low density excitation, only a broad spectrum is observed in the region over Y and G emission. There is no indication of the sharp fine-structures and of luminescence in the V-emission region. These facts seem to be inconsistent with the assumption that the same STE states are the initial states for both spontaneous and stimulated emissions. There are several reasons, however, for the assumption. Firstly, there is no emission band or peak except the STE luminescence in the concerned energy region in the ultra-pure CdI_2 crystal. If the stimulated emission is of the other origins, such as impurity or defect centers, their characteristic steady spontaneous emission should be observed under low density steady excitation. Secondarily, there is a distinct correlation between the fast stimulated compo-

nent and the slow spontaneous component with regard to their relative intensity as described in § 3. Enhancement of the stimulated component would bring about the decrease in the STE population and the diminishing of spontaneous component is resulted. Thirdly, the peak positions of the sharp structures in figure 3 have fairly good correspondence with the fine-structures of the STE states shown in figure 5.

Decay curves observed in the region of Y- and G-emission under low density excitation condition consist of two or three exponential decay components, the life-time of the main component of which is 5 μs. By decomposing these decay curves, five emission bands were resolved according their life-times. It was found that their peak energies agree with the sharp peak positions of the stimulated emission in the Y and G region. Forthly, good agreement is obtained between the decay curves observed under high density excitation condition and the calculated ones from a non-linear rate equation including both spontaneous and stimulated emission processes from the STE state. Fifthly, optical gains of the luminescence obtained by the dependence of luminescence excitation intensity on the length of the excited region, show high values of the order of 10^3 over the wide STE emission region from 2.0 to 3.5 eV.

Unfortunately, it is not possible at present to give any reasonable explanation on the appearance of the sharp structures only in the stimulated emission spectrum. It may be related to the stimulation of luminescence during exciton relaxation processes among various semi-stable STE states in the initial stage of luminescence decay.

§ 5. Conclusion

Under high density excitation was found the fast decay component of luminescence which was not observed in the case of low density excitation. This component is attributed to the stimulated emission process from the STE states in the CdI_2 crystal. The spectral distribution of the fast component, namely, the stimulated emission spectrum shows eight sharp structures in the region between 2.0 and 3.5 eV. These structures are connected to those in the STE states, that is, those in the excited states of the $[Cd^{2+}I^-_6]^{4-}$-complex molecular ions. It is not possible at present to explain the reason of appearance of sharp structures in the stimulated emission spectrum only.

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