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## An emission and kinetic study of the impurity-trapped exciton in CdCl<sub>2</sub>:Pb<sup>2+</sup>

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**Abstract.** We have studied the spectroscopic properties of Pb<sup>2+</sup> in a CdCl<sub>2</sub> host crystal. By excitation in the absorption band due to the <sup>1</sup>A<sub>1g</sub> → <sup>3</sup>T<sub>1u</sub> (<sup>3</sup>P<sub>1</sub>) transition, two emission bands are observed. At very low temperature a strong UV luminescence with a very long lifetime (2.5 ms) is detected. As the temperature increases, the lifetime of the UV emission drastically decreases to a few nanoseconds at 100 K, and the UV intensity declines. Meanwhile a strong green fluorescence appears. It is assumed that this emission is of the impurity-trapped exciton type, as in the case of CdCl<sub>2</sub>:Cu<sup>+</sup> and BaF<sub>2</sub>:Eu<sup>2+</sup>. A detailed study of the kinetics of both fluorescences is presented.

### 1. Introduction

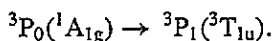
By excitation in the absorption band due to the <sup>1</sup>A<sub>1g</sub> → <sup>3</sup>T<sub>1u</sub> (<sup>3</sup>P<sub>1</sub>) transition, two emission bands are observed in crystals containing Pb<sup>2+</sup> (6s<sup>2</sup> configuration). In a recent review paper, Jacobs [1] discussed the particular emission behaviour of Pb<sup>2+</sup> in alkali halides. In the highest aggregation state, e.g. PbCl<sub>2</sub>, UV emission (UVE) and visible emission (VE) were observed at 3.80 eV (326 nm) and 2.88 eV (430 nm) respectively [2]. There is evidence that PbCl<sub>2</sub> particles can be formed in Pb doped NaCl [3,4] and again two emission bands are observed in the same spectral region as in the PbCl<sub>2</sub> crystal. In CdCl<sub>2</sub>:Pb (0.7%) the VE band was observed at 2.48 eV (500 nm) at 90 K [5]. The band gap for CdCl<sub>2</sub> is about 5.8 eV [6] and the excited states of Pb<sup>2+</sup> lie near or within the conduction band in this crystal. As in the case of CdCl<sub>2</sub>:Cu<sup>+</sup> [5] a thermally activated process of the excited state is likely and the possibility of electron transfer from the excited Pb<sup>2+</sup> levels to an impurity-trapped exciton level is now put forward in order to explain the VE in the CdCl<sub>2</sub>:Pb<sup>2+</sup> system.

### 2. Experimental results

The crystal used in this work was grown by the Bridgman technique. The experimental set-up used to record excitation, emission and lifetime is briefly described hereafter. Measurements of the fluorescence spectra used as the optical excitation source a Q-switched Nd<sup>3+</sup>:YAG pumped dye laser (YAG 481 + TDL IV model from Quantel) associated with frequency-doubling systems. The fluorescence was analysed spectrally with a Hilger computer-scannable 1 m monochromator and detected with a Hamamatsu R1477 PMT followed by an amplifier:discriminator and an Ortec photon counting system connected to a computer. Lifetime measurements were performed with a Stanford SR430 multichannel

analyser with a minimum dwell-time per channel of 5 ns. The excitation spectra were obtained using the synchrotron light source of SuperAco of LURE at Orsay and a 3 m home-made vacuum-UV monochromator.

The excitation spectra of the UVE and VE bands are exactly the same, with two main bands at 285 and 240 nm (figure 1). The emission spectra have been recorded under excitation at 2900 Å into the first absorption band which corresponds to the transition



Several emission spectra at different temperatures are shown in figure 2. For clarity, the different curves have been artificially shifted. The relative intensity of both components is strongly temperature dependent. Below 60 K only the UV emission is detectable; from 60 K to 150 K there is clearly an exchange of intensity between the two emission bands, above 150 K a residual extremely weak UV band is still detectable beside the strong green emission. The UV band is maximum at 3400 Å and the green band at 5000 Å. The UV emission peak shifts to lower energies (about 0.1 eV) as the  ${}^3T_{1u}$  level is thermally populated from  ${}^3A_{1u}$  level as is the case in KCl:Pb<sup>2+</sup> [7].

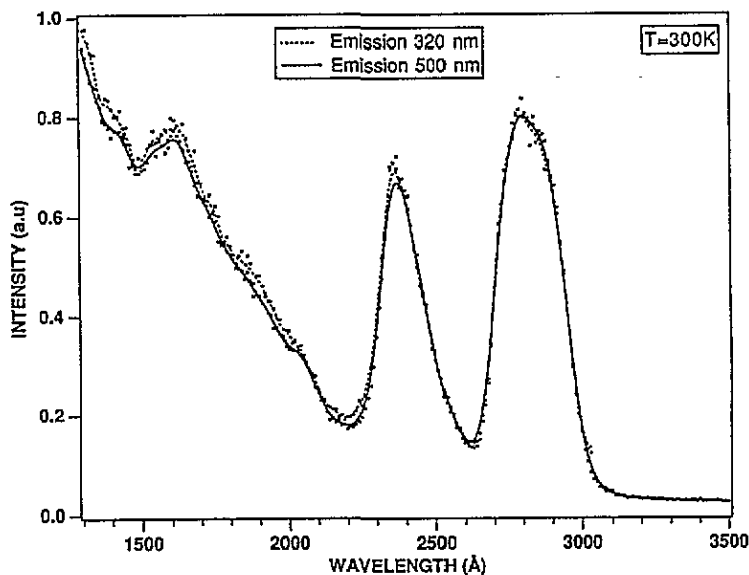


Figure 1. Excitation spectra of the two emission bands of CdCl<sub>2</sub>:Pb<sup>2+</sup> at room temperature. The lower-energy band corresponds to the  ${}^3P_1$  level, the second band to the  ${}^3P_2$  level and the third one to the  ${}^1P_1$ .

The UV emission decay is exponential at all temperatures. Its lifetime is equal to 2.5 ms at liquid He temperature and slowly decreases down to 2 ms at 50 K, then it drastically drops down to 40 μs at 80 K and a few nanoseconds at 140 K (figure 3). The green emission decay is exponential with a risetime of 2 μs at any temperature below 120 K. It varies from 116 μs at 73 K to 1 μs at 170 K. For high temperatures the risetime is no longer detectable.

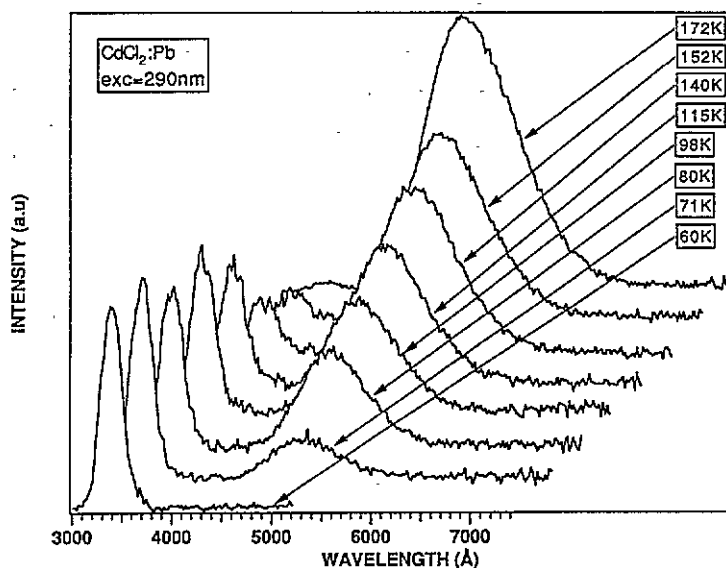


Figure 2. Emission spectra of  $\text{CdCl}_2:\text{Pb}^{2+}$  at several temperatures under excitation in the lowest absorption band at 290 nm. For clarity, the different curves have been artificially shifted.

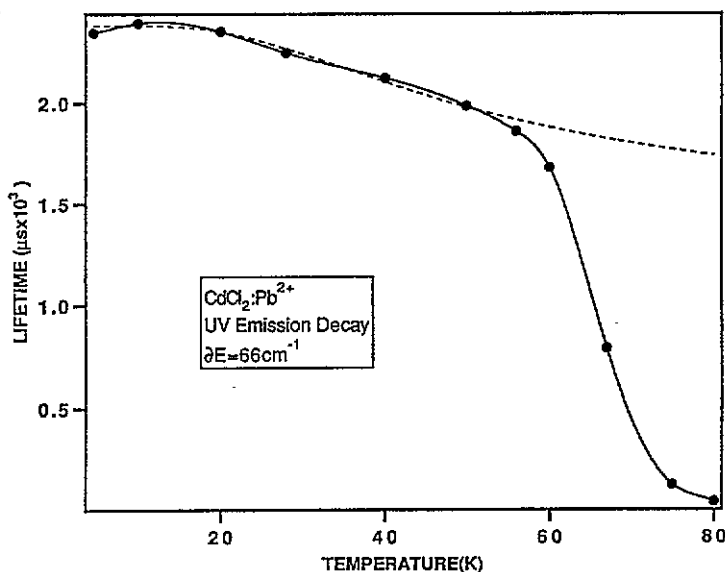


Figure 3. The temperature evolution of the UV emission decay. The dashed line corresponds to the best fit obtained with the three-level scheme in the range 4–60 K.

### 3. Discussion

$\text{Pb}^{2+}$  ion has a  $6s^2$  configuration. The ground state is  $^1A_{1g}$  and the excited states are  $^3A_{1u}$  ( $^3P_0$ ),  $^3T_{1u}$  ( $^3P_1$ ) and  $^3T_{2u} + ^3E_u$  ( $^3P_2$ ) in order of increasing energy. The transition

$^1A_{1g} \rightarrow ^3T_{1u}$  is partially allowed because of the mixing of the triplet state with the singlet  $^1T_{1u}$  by spin-orbit interaction. The excitation spectrum of  $\text{CdCl}_2:\text{Pb}^{2+}$  resulting from monitoring the UV band is exactly the same as the spectrum obtained by monitoring the green band. Thus the large shift of the UV versus the green emission band, 1.27 eV, is accompanied by absolutely no change in the absorption. Hence, these two emissions must originate in processes beginning at the same excited state and therefore also in the same Pb species.

We propose that the UVE is the normal emission from  $\text{Pb}^{2+}$  and that the VE is of the impurity-trapped exciton type as in the cases of  $\text{CdCl}_2:\text{Cu}^+$  and  $\text{BaF}_2:\text{Eu}^{2+}$  [6–8]. Indeed, the narrow bandgap of the host crystal allows  $\text{Pb}^{2+}$  ions to ionize under UV excitation into their first excited states, which lie near the bottom of the conduction band of the crystal. At low temperature when the  $\text{Pb}^{2+}$  ion is excited into the  $^3P_1$  state it relaxes into the  $^3P_0$  level which then emits in the UV range. At higher temperature a thermally activated ionization process becomes more efficient than the radiative emission process and the green emitter level (i.e. the impurity-trapped exciton) is fed. The green emission is due to the recombination of the delocalized 's' electron with the  $\text{Pb}^{3+}$  ion. The relaxation around the  $\text{Pb}^{3+}$  of the nearest-neighbour  $\text{Cl}^-$  ions causes the shift of the emission towards lower energies.

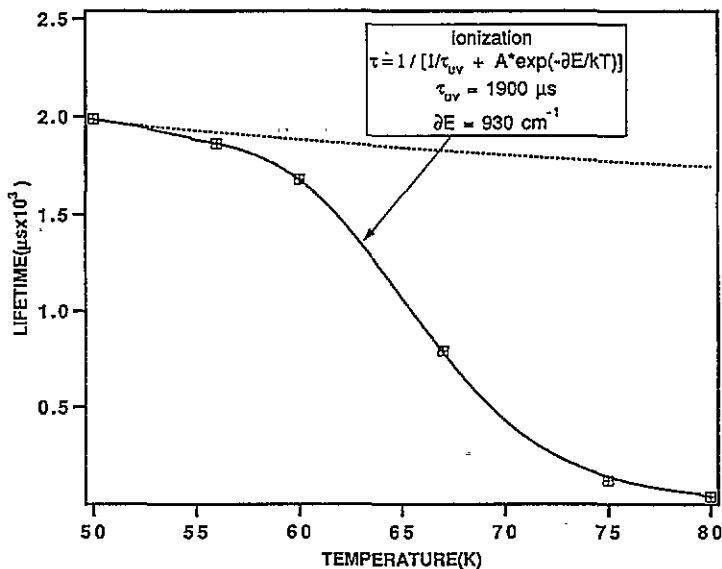


Figure 4. The temperature evolution of the UVE decay above 50 K. The dashed line corresponds to the best fit obtained with the three-level scheme in the the range 4–60 K. The full line corresponds to the fit given by formula (1).

The first part of the evolution of the UVE lifetime can be explained by a three-level scheme with two excited states, the lower one being the metastable level  $^3P_0$  ( $^3A_{1u}$ ) and the higher one the  $^3P_1$  ( $^3T_{1u}$ ). The dashed line in figure 3 corresponds to the best fit obtained with such a system and leads to an energy difference of  $66 \text{ cm}^{-1}$  between the two excited states. Above 60 K the evolution of the UVE lifetime corresponds to the increase of the green emission and is due to the thermal feeding of the impurity trapped exciton responsible

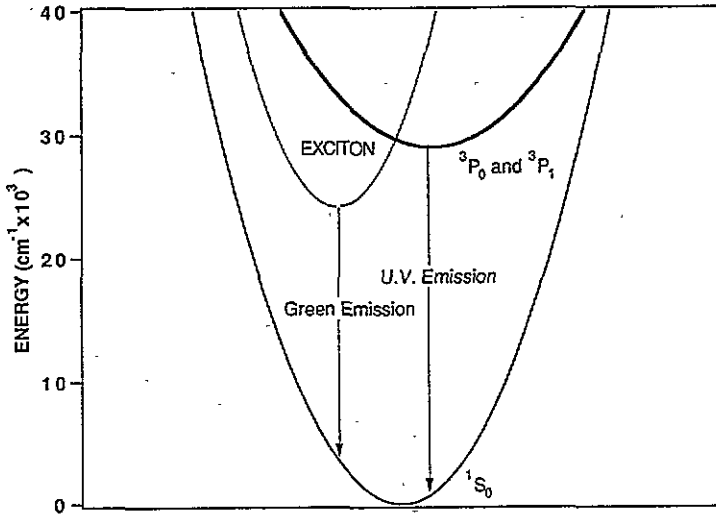


Figure 5. The level scheme of the  $\text{Pb}^{2+}$  ion. The energy difference between  $^3\text{P}_0$  and  $^3\text{P}_1$  ( $66\text{ cm}^{-1}$ ) is too small to be seen.

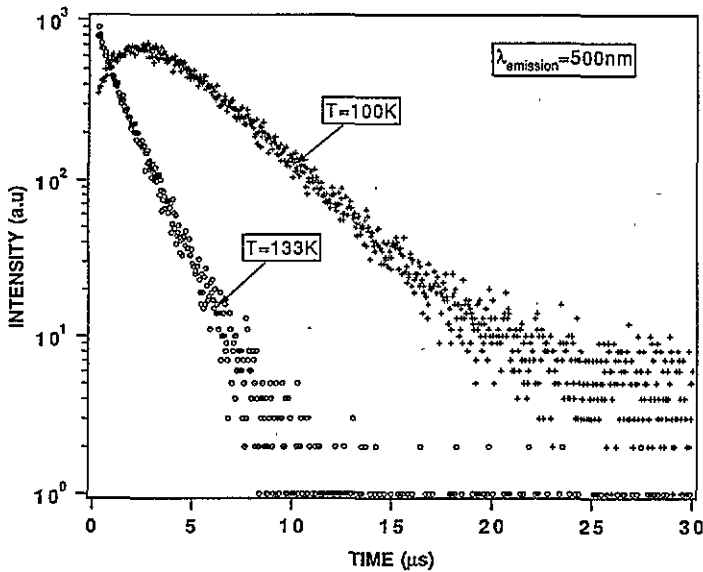


Figure 6. The emission decay of the green fluorescence at two different temperatures under excitation in the lowest absorption band at  $290\text{ nm}$ .

of this green emission. Considering that the  $^3\text{P}_0$  lifetime is approximately constant in this temperature range (the dashed line in figure 4) and that the state may thermally activate an electron into the impurity-trapped exciton level, one can fit the lifetime evolution with the very simple equation (6)

$$\tau_0 = 1/[1/\tau_{uv} + A \exp(-\delta E/kT)] \quad (1)$$

which leads to a potential barrier  $\delta E$  of  $930 \text{ cm}^{-1}$  (figure 4).

The green emission decay is extremely sensitive to the temperature in the range 70–130 K. Below 80 K the decay is exponential and the lifetime corresponds to the UV emission lifetime at the same temperature. Between 80 K and 110 K the green emission decay is still exponential but with a risetime. Above 110 K the decay is shorter and again purely exponential.

If we assume that the trapped exciton state is essentially fed by non-radiative transitions from the  $^3\text{P}_0$  state, the time evolution of the intensity of the VE is given by a simple equation from the system of rate equations of this level scheme (figure 5), where  $\tau_1$  and  $\tau_0$  are the lifetimes of the trapped exciton and of the  $^3\text{P}_0$  states:

$$I(t) = C[\tau_0\tau_1/(\tau_1 - \tau_0)][\exp(-t/\tau_1) - \exp(-t/\tau_0)]. \quad (2)$$

If  $\tau_1$  is smaller than  $\tau_0$  then the risetime of the decay corresponds to the lifetime of the exciton state and the decay to the lifetime of the upper level. This is exactly what we observed between 70 K and 110 K. In this temperature range the lifetime of the exciton state is approximately equal to  $2 \mu\text{s}$  while that of the triplet state is equal to some tens of microseconds. At higher temperature the decay of the green emission becomes exponential without a risetime and decreases like the intensity of the green emission, probably because of a thermal ionization process of the exciton state (figure 6).

Despite the difficulty of obtaining a very clean sample surface because of the hygroscopic character of this crystal, photoconductivity measurements are in progress in order to determine the photoionization threshold.

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