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1991 J. Phys.: Condens. Matter 3 8127

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Thermoluminescence induced by x-ray or ultraviolet irradiation at low temperatures in NaCl:Eu²⁺

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Received 15 April 1991, in final form 25 June 1991

Abstract. The thermal recovery processes after 77 K irradiation with x-ray or ultraviolet light lying in the high-energy absorption of the Eu²⁺ ions have been investigated for NaCl:Eu. It has been ascertained that the TL glow curves are essentially the same for both cases. The TL emission spectrum comprises the intrinsic bands as well as the characteristic emission of Eu²⁺ ions. The possible mechanisms for the origin of the light emission and for the glow peaks have been discussed.

1. Introduction

Thermoluminescence (TL) has been widely used as a method to determine the structure of radiation-induced defects in alkali halide crystals. However, most progress in recent years has taken place when various experimental techniques have been used in parallel to understand the mechanisms of TL itself. Those progresses have been reviewed in [1–3].

The TL of alkali halides doped with Eu x-irradiated at room temperature (RT) has been studied by different workers [4–8]. In particular, KCl:Eu has been proposed as an adequate material for solid state dosimeters [8]. Various mechanisms for the TL peaks involving recombination of electrons released from different traps with Eu³⁺ ions formed during irradiation have been proposed [4–6]. On the contrary, the low-temperature TL of KCl:Eu has been ascribed to the thermal activation of H, H_a or V_k centres [9]. As the observed emission corresponds to that of Eu²⁺ ions it was proposed that the energy of the recombining hole (H and V_k type) and trapped electron (F centre) is transferred to a nearby Eu²⁺ ion. In the case of KI:Eu x-irradiated at liquid nitrogen temperature (LNT) it has been observed that the application of an electric field shifts the TL peak towards low temperatures [10]. To explain this result it has been suggested [11] that the kinetics are simultaneously controlled by the diffusion of V_k centres and by the migration of trapped electrons (on divalent-ion-cation vacancy sites). The electrons tunnel to the V_k centres and the field acts on the electron migration from one Eu²⁺ to another.

In recent work [12] it has been observed for various alkali halides doped with Eu²⁺ that illumination with ultraviolet (UV) light at LNT produces luminescence persistence or afterglow (AG) lasting several minutes. The maximum efficiency to excite the AG corresponds to UV light lying in the high-energy absorption band of Eu²⁺ ions (260 nm for NaCl). In spite of the fact that the energy of the UV light is not enough to excite

interband transitions in the crystal, TL peaks were detected after UV irradiation. Moreover, strong photoconductivity was observed during UV irradiation. These results have been explained by considering that the Eu^{2+} ion is ionized by the UV light. Next, the electron becomes trapped and the hole remains at the impurity site as Eu^{3+} . The AG has been attributed to the release of electrons from traps and posterior recombination with Eu^{3+} [12]; even the presence of Eu^{3+} ions was not detected.

This paper reports a systematic study of the TL from LNT to RT of NaCl samples with various Eu^{2+} concentrations. Conjoint measurements of optical absorption and electron paramagnetic resonance (EPR) have been made in an attempt to clarify the mechanisms for the TL. A comparison between the TL induced by x-irradiation and UV illumination in the high-energy absorption of the Eu^{2+} ions has also been carried out.

2. Experimental details

$\text{NaCl}:\text{Eu}^{2+}$ single crystals were grown in our laboratory under a controlled atmosphere (dry argon) using the Czochralski method, from suprapure Merck materials. Doping was achieved by adding to the melt different initial concentrations of EuCl_2 , previously reduced from $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ using standard techniques [13]. The impurity concentration in the samples was determined from their optical absorption spectra following the procedure reported in [14]. In this work samples with 25, 45, 60, 100, 175, 210, 240, 290, 320 and 400 ppm (molar) of Eu have been studied. Quenching treatments were performed by heating the samples at 600 °C for 20 min and then dropping them onto a copper block at RT.

The samples were cooled to LNT in a conventional cryostat where x-irradiation was achieved through an aluminium window 1 mm thick, using a Kristalloflex 2H Siemens apparatus with a tungsten target operating at 50 kV and 30 mA. The UV illumination was done with a 150 W xenon lamp and a Bausch & Lomb high-intensity monochromator.

The instrumentation for the TL measurements has been described in [15]. The linear heating rate for most experiments was 3 K min^{-1} . The wavelength spectra were not corrected for the response of the detection system. The glow peaks were analysed by the whole area method [15, 16].

The optical absorption measurements were performed with a Varian 2415 spectrophotometer in the same cryostat as that for TL measurements. The EPR spectra were obtained at 85 K with a Varian E-12 X-band spectrometer equipped with an E-257 gas flow temperature controller.

3. Results

The majority of measurements in this work were taken from freshly quenched samples. In quenched samples, most Eu^{2+} impurities are dissolved in the lattice and associated with cationic vacancies forming dipoles. The presence of these dipoles can be ascertained by their characteristic EPR spectrum [17] as well as their emission under ultraviolet excitation which takes place at 427 nm in NaCl [18]. The TL glow curves (light intensity versus temperature) were obtained at that fixed wavelength. A few measurements from well aged samples were made for comparison. It is known [19] that in well aged samples the impurities are forming aggregates of dipoles as well as precipitated phases, depending on the impurity concentration and the thermal history of the sample.

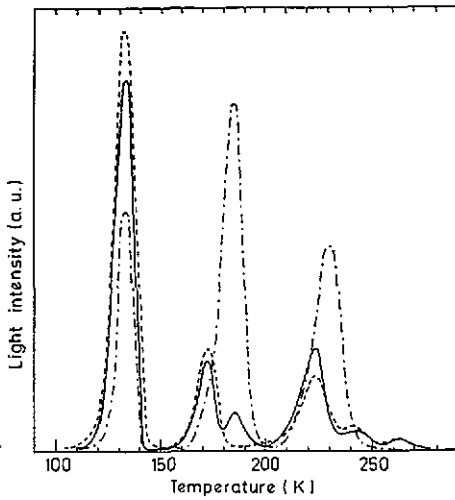


Figure 1. TL glow curves, measured at 427 nm, of NaCl samples doped with various concentrations of Eu²⁺: — · —, 60 ppm; —, 175 ppm; - - -, 240 ppm. All samples were x-irradiated for 10 min at 77 K after quenching.

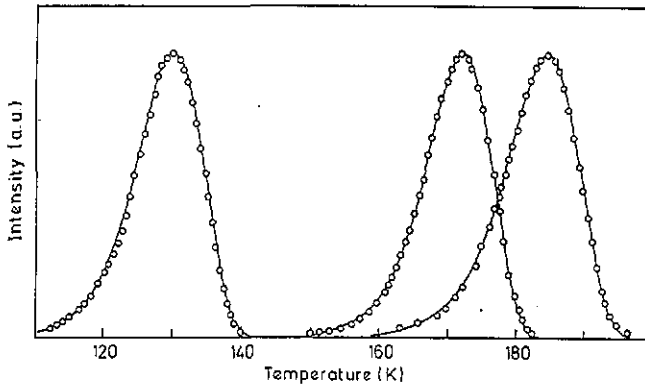


Figure 2. Fitting of the TL peaks at 130, 172 and 184 K: O, experimental values; —, theoretical peaks constructed with the parameters which appear in table 1.

The TL glow curves of quenched samples of NaCl:Eu²⁺ in the temperature range 77–300 K have been measured for samples with different europium concentrations (from 25 up to 400 ppm). As an example figure 1 shows the TL glow curves of three samples (60, 175 and 240 ppm) x-irradiated for 10 min at 77 K immediately after quenching. The glow peaks appear in three temperature zones. The samples containing from 25 to 100 ppm Eu present three strong peaks at 130, 184 and 230 K. The samples containing from 210 to 400 ppm Eu show the second glow peak at 172 K instead of 184 K, and three overlapped peaks at 224 K (intense), 241 K (weak) and 262 K (weak). The sample with 175 ppm Eu (plotted in figure 1) presents both the 172 and the 184 K peaks.

The TL glow peaks were analysed by the total curve-fitting method [15, 16] in order to obtain the activation energy E and the pre-exponential factor S . With both parameters it is possible to reconstruct a theoretical peak and to compare it with the experimental peak. Figure 2 shows three fittings for the peaks at 130, 172 and 184 K. The activation

Table 1. Peak temperatures T_m , activation energies E and pre-exponential factors S of the most intense glow peaks.

T_m (K)	E (eV)	S (s ⁻¹)	Order of kinetics
130	0.30	4×10^9	First
172	0.54	1×10^{14}	First
184	0.54	4×10^{12}	First
230	0.58	2×10^{10}	First

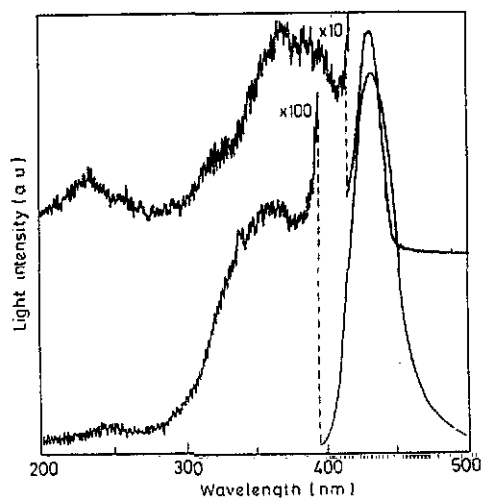


Figure 3. Emission spectrum of the AG measured at 20 K (upper curve) and of the glow peaks (lower curve). Both samples of NaCl:Eu (210 ppm) were x-irradiated for 10 min after quenching.

energies, pre-exponential factors and kinetics orders for the most intense TL glow peaks at 130, 172, 184 and 230 K, are summarized in table 1.

The wavelength spectra, in the range 200–700 nm, of the emitted light have been measured during heating in a temperature range near the maximum of each glow peak. An example is displayed in figure 3. The emission spectrum consists of an intense band at 427 nm and two much less intense bands at 360 and 235 nm. The 427 nm band corresponds to the emission of Eu^{2+} ions when they are forming dipoles as well as small dipole aggregates [18]. The two weak emissions agree with the intrinsic self-trapped exciton (STE) emissions of NaCl [20, 21]. The wavelength spectrum of the AG after x-irradiation at 20 K has also been measured for comparison and is included in figure 3. It also presents the same three bands at 235, 360 and 427 nm.

The optical absorption spectrum of NaCl:Eu²⁺ samples has been measured at 77 K. It presents the two structured bands in the UV region which correspond to transitions from the ground state $^8\text{S}(4f^7)$ to states of the $4f^6 5d$ configuration of the Eu^{2+} ion [22, 23]. The x-irradiation at 77 K does not produce an appreciable change in the absorption spectrum, even after 10 h irradiation. We have specifically looked for the Eu^+ and Eu^{3+} absorptions [24, 25] but they were not detected. This behaviour is different from that observed in samples x-irradiated at room temperature [24, 25] where Eu^+ and Eu^{3+} have been detected in heavily irradiated samples.

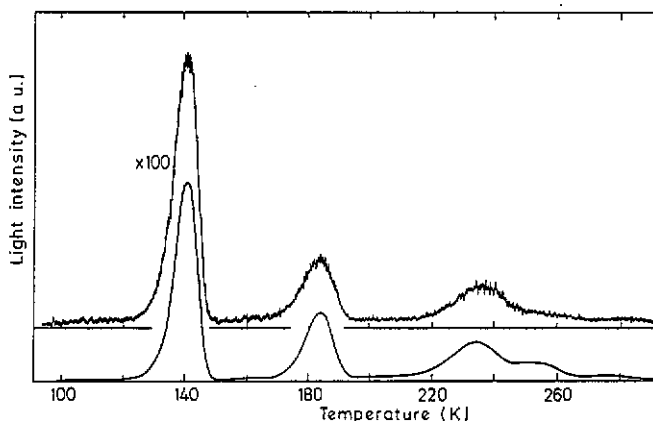


Figure 4. TL glow curves, measured at 427 nm, of NaCl:Eu²⁺ (210 ppm) for a sample UV irradiated for 45 min with 260 nm light after quenching (upper curve) and a sample x-irradiated for 10 min after quenching (lower curve). Both spectra were measured with a faster heating rate than that used in figure 1 (see text).

The EPR spectra have been measured at 85 K before and after x-irradiation at 77 K. They show the well known lines due to the Eu²⁺-cation vacancy dipoles [17]. We have not observed noticeable changes in the spectrum after irradiation. In particular, the spectrum of self-trapped holes (V_k centres) was not detected.

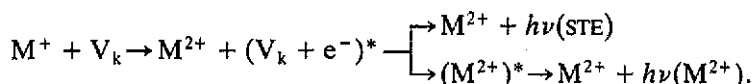
With the aim of comparing the effect of x-irradiation and UV irradiation, the TL induced by UV illumination at 260 nm has been measured. The 260 nm light corresponds to the high-energy absorption of the Eu²⁺ ions, their energy being not enough to excite interband transitions in the crystal. Figure 4 shows the TL glow curves of a quenched sample (210 ppm) after UV or x-irradiation. As the light output after UV irradiation is much weaker (about 100 times) than that after x-irradiation, a faster heating rate (22 K min⁻¹) was used to obtain these spectra. This makes the TL peaks reported above to be at 130 K, 172 K, 184 K, 224 K, 230 K, 241 K and 262 K become displaced to 141 K, 184 K, 197 K, 236 K, 244 K, 256 K and 278 K respectively. It can be observed in figure 4 that the glow peaks are the same in both cases. This is a general behaviour with one exception: the peak at 184 K (197 K) is not observed in precipitated samples for Eu concentrations above 175 ppm when they are UV irradiated, whereas a weak peak is observed in the same samples when they are x-irradiated.

The wavelength spectrum of the TL peaks for UV-irradiated samples shows the 427 nm band. However, the low light output does not permit us to confirm the presence of the bands at 360 and 235 nm.

4. Discussion

Let us first discuss the origin of the light emission. The presence of the typical Eu²⁺ emission is suggestive of a change in the state of charge of Eu²⁺ ions to Eu⁺ (or Eu³⁺) valence by trapping an electron (or a hole) produced by the x-irradiation. In this case, the TL mechanism would consist of the detrapping of holes (or electrons) from different traps and the posterior recombination with Eu⁺ (or Eu³⁺) to generate Eu²⁺ in an excited state (Eu²⁺)*. This excited ion would then relax, giving the characteristic Eu²⁺ emission.

It is important to remember that the wavelength spectrum of the TL glow peaks (figure 3) as well as that for the AG shows (besides the Eu^{2+} emission) two weak bands at 235 and 360 nm which agree with the intrinsic emissions of the STE. This behaviour has been previously observed for other systems such as NaCl:Mn [15, 26] and NaCl:Cu [26] after low-temperature x-irradiation. It has been proposed [26] that the STE is formed in an excited level when an electron tunnels from some trap (for instance Cu^0 , Mn^+ or F^- centre) to a nearby V_k centre. Then the $(\text{STE})^*$ relaxes to its ground state, yielding the intrinsic luminescence or transferring the energy to a nearby impurity which gives the characteristic impurity emission. Such a process can be schematized as follows:



In the present case of NaCl:Eu a difficulty in applying this mechanism arises from the fact that neither Eu^+ nor V_k centres have been detected. As the number of Eu^{2+} ions (measured by optical and EPR techniques) does not change substantially, it is reasonable to think that the number of Eu^+ and V_k defects is below the limit of detection for both the optical and the resonance techniques.

On the other hand, as essentially the same TL peaks are observed for UV-irradiated samples, one has to conclude that the same processes take place in the x- and UV-irradiated samples. Thus, some mechanism is necessary to explain the presence of V_k centres in the UV-irradiated samples. With respect to this, Badalyan *et al* [27] have observed that illumination in the impurity bands at 77 K of various alkali halides doped with Ag^+ or Tl^+ produces V_k centres in the crystal. These workers propose that the impurity is ionized by the light and that Ag^{2+} or Tl^{2+} ions are formed in an excited state; then the hole transforms into a V_k centre before the Ag^{2+} or Tl^{2+} ions relax. It is plausible that this mechanism also takes place in Eu^{2+} -doped samples. The observed photoconductivity [12] confirms the ionization of the Eu^{2+} ions. In conclusion, according to the above arguments, we suggest that the TL emission is a consequence of the recombination of trapped electrons (e.g. in the form of Eu^+) with holes (V_k).

As for the concrete origin of each glow peak, some suggestions can be made. The temperature of the peaks at 184 or 172 K could indicate that one of these peaks is due to the diffusion of the V_k centres as happens in NaCl doped with Mn [15], Tl [28], Ag [28] or Cu [26, 29]. However, that diffusion-limited reaction produces a continuous displacement in the temperature of the maximum of the peak as a function of the impurity concentration. The analysis of glow peaks related to V_k diffusion gives a fixed activation energy and a pre-exponential factor which is proportional to the impurity concentration and leads to a shift in the TL peak maximum [15, 30]. On the contrary, the temperature of the peaks remains constant in our experiments in spite of the fact that the Eu concentration varies in a wide range. Moreover, the activation energy of the peaks at 172 and 184 K (0.54 eV) is clearly higher than that for the diffusion of V_k centres which is 0.37 eV [15, 30].

The glow peak at 184 K takes place for low-doped samples whereas the peak at 172 K appears in samples with a higher impurity concentration. Thus, it is reasonable to think that the 184 K peak is related to isolated dipoles and the 172 K peak to dipole aggregates because it is known that for highly concentrated samples, even after severe quenching, most of the impurities form aggregates [19]. This assignment is in agreement with the non-observance of the peak at 184 K in a well aged sample (where there are no dipoles) after UV illumination, while the peak is detected if the well aged sample is x-irradiated

because it is known that the x-irradiation breaks the precipitates, giving some free dipoles [19].

In summary, we suggest that the mechanisms for the various glow peaks consist in the initiation of tunnelling processes for electron-V_k pairs associated with different defects, these tunnelling processes being temperature dependent. This kind of mechanism has been proposed to explain the effect of an electric field on the recombination processes in alkali halides doped with divalent impurities [11] and is in agreement with the observed first-order kinetics of TL peaks.

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