Journal of Luminescence 6 (1973) 245–255. © North-Holland Publishing Company

ELECTRIC FIELD EFFECT ON THE LUMINESCENCE OF KI : Tl *

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Received 23 January 1973

Thermoluminescence of KI : Tl, X- or β-irradiated at $T \leqslant 77^{\circ}$K shows two main peaks at 105°K and 170°K. They are respectively attributed to the recombination of mobile V_K centres with Tl^0 centres and to the recombination of thermally released electrons from Tl^0 centres with Tl^{2+} centres. Similar experiments performed under static electric fields ($E < 40$ kV cm^{-1}) show that the intensity of the second glow peak is strongly reduced. The relative intensity variation is anticorrelated with the intensity of glow peaks occurring at $T > 230^{\circ}$K. We suggest that in the temperature range in which Tl^0 centres are thermally ionised, the effect of the electric field is to favour the retrapping of these electrons on other traps (still unknown). Irradiation doses also play an important role and their effects are studied at $T = 77^{\circ}$K and $T = 200^{\circ}$K.

1. Introduction

Irradiation of alkali halide crystals by ionising particles produces defects either by the displacement of ions out of their normal lattice sites or by the capture of electrons and holes created in the crystal. The latter process is particularly important in crystals doped with impurities. The case of thallium, for instance, is specially interesting since this impurity is known to trap both entities. In this way a high concentration of defects can in principle be frozen in the crystal if the irradiation is performed at sufficiently low temperature.

By heating a previously irradiated crystal at a controlled rate, several thermoluminescence glow peaks are usually observed at well defined temperatures. These photon emissions are associated with the radiative recombination of charges or defects migrating in the crystal following their thermal detrapping. This very sensitive thermoluminescence technique brings important information concerning the nature and the energy depth of the different traps as well as their migration and eventually their recombination kinetics [1].

In KI : Tl crystals [2] X- or β-irradiated at $T = 77^{\circ}$K the hole-type defects frozen in the crystal are essentially the V_K centres. Some Tl^{2+} were also found. The elec-

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* Work supported by the Swiss National Foundation for Scientific Research (FNSRS).

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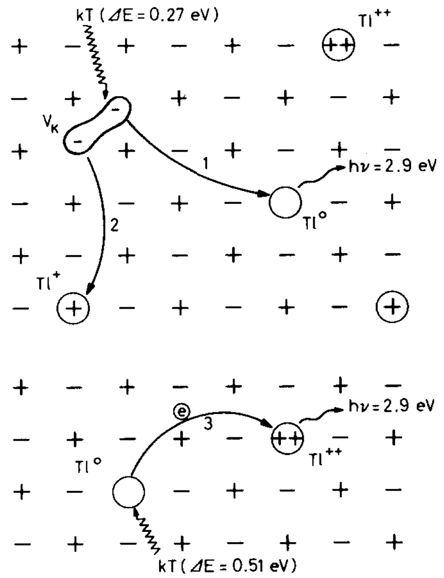

Fig. 1. (A) The two processes associated with the thermal migration of V_K centres (~105°K) in KI:Tl, X- or β-irradiated at $T \lesssim$ LNT; (1) radiative recombination at Tl^0 site ($h\nu$ = 2.9 eV); (2) retrapping at Tl^+ site with formation of Tl^{2+} centres. (B) Process associated with the thermal ionisation of Tl^0 centres (~ 170 °K) in KI : Tl, X- or β-irradiated at $T \lesssim$ LNT; (3) electron radiative recombination at Tl^{2+} centres ($h\nu$ = 2.9 eV).

trical neutrality is insured by the formation of Tl^0 centres (an electron trapped on a substitutional Tl^+) and to a lesser extent by some other unknown electron type defects (fig. 1(A)). All these defects are stable at this temperature. The V_K centres however become mobile around 90°K. By heating a previously X- or β-irradiated crystal at a rate of 3.5 °K min^{-1}, a small thermoluminescence glow peak is observed at 105 °K. Its emission spectrum is centred at 425 nm and is characteristic of the chemical nature of the Tl impurity. This peak is associated with the radiative recombination of mobile V_K centres at the site of Tl^0 centres (process (1), fig. 1(A)):

$$V_K + (kT) + Tl^0 \rightarrow Tl^+ + h\nu \quad (2.9\ eV). \tag{1}$$

However most of the V_K centres are known to be retrapped non-radiatively at Tl^+ impurities (process (2), fig. 1(A)) [3]:

$$V_K + (kT) + Tl^+ \rightarrow Tl^{2+}. \tag{2}$$

Tl^0 centres are thermally ionised around 170 °K and the electron–Tl^{2+} radiative recombination can be observed as an additional thermoluminescence glow peak; its emission spectrum is also centred at 425 nm (process (3), fig. 1(B)) [4]:

$$\mathrm{Tl}^0 + (kT) \rightarrow \mathrm{Tl}^+ + \mathrm{e}^-, \qquad \mathrm{e}^- + \mathrm{Tl}^{2+} \rightarrow \mathrm{Tl}^{+\,*} + h\nu\,(2.9\ \mathrm{eV}). \tag{3}$$

At still higher temperatures a third broad but faint emission has also been observed; no detailed explanation has yet been given.

The effect of an electric field on the radioluminescence and the thermoluminescence of KI : Tl has been scarcely studied. In 1966 Parfianovitch et al. [5] have observed an increase of the radioluminescence under an alternating electric field at 300 °K. Later Denks and Leiman [6] have found at the same temperature a partial quenching of the photoluminescence excited in the C band, which they show to be a direct ionisation of the excited state. Looking at the thermoluminescence glow curves Grigor'ev et al. [7] have reported a partial quenching of the 170 °K peak only, without giving satisfactory explanations.

In this report we present a more systematic and detailed study of the influence of a static electric field on the radio- and thermoluminescence processes in KI :Tl between 4°K and 300°K (section 3). The effects are strongly dependent on the ionising irradiation doses (section 4,5) and can be qualitatively explained in the framework of a charge transfer model.

2. Experimental procedure

The KI crystals used for these experiments were purchased from K. Korth (BRD) and doped either with 200 ppm or 1000 ppm of thallium in the melt. They were first cleaved at approximately 10 × 10 × 1 mm^3, then heated at 400°C and quenched on a copper block. They were clamped on a sample holder which consisted mainly of two frame shape copper electrodes covered by a fine metallic net (100 μm mesh). The first one was fixed and electrically grounded to a variable temperature cryostat (Oxford Instrument L 1085). The high voltage (Brandenburg 807 R, 0–30 kV) was applied to the second mobile electrode which was clamped to the first one by isolated springs and screws specially designed to insure also a good thermal contact. The crystals were usually mounted in a direct contact with the electrodes. However sometimes a blocking electrode configuration, realized by inserting a thin Mylar foil between the net and either one of the two surfaces of the crystals, was also used. The temperature was carefully measured with a Gold Iron–Chromel thermocouple connected to a digital multimeter (Keithley 610). The excitation sources consisted either in a small β source (Sr 90, 8 mCi) or an X-ray generator (Mueller 150 Be tube with a W anticathode) usually operated at 150 kV, 5 mA and filtered by a 1 mm Cu foil. The luminescence was analyzed either by a set of filters (broad band or interference) or by a Leitz prism monochromator and detected with an EMI 6256 S photomultiplier followed by a micro microammeter (Keithley 410 and a recorder (Moseley 680).

3. Electric field effects

KI crystals doped with 200 ppm Tl and irradiated at $T = 77$ °K with the β source or X-rays of extremely low intensity emit a radioluminescence (RL) with the following characteristics:

(a) Almost 90% of its intensity is intrinsic ($h\nu = 3.27$ eV) and corresponds to the radiative recombination of self-trapped excitons. The remaining 10% is characteristic of the Tl impurity ($h\nu = 2.92$ eV).

(b) The intensity of each emission band increases with time to eventually saturate after a long irradiation time.

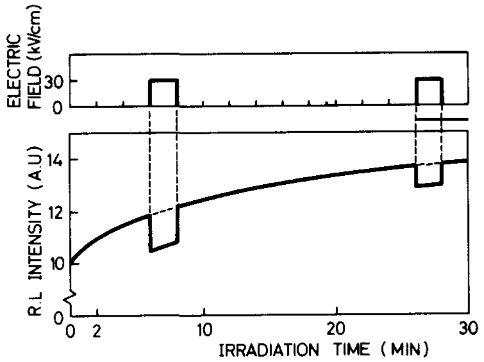

Fig. 2. Time (or irradiation dose) dependence and temporary d.c. electric field effect on the total radioluminescence of a 200 ppm Tl doped KI crystal β-irradiated at 77° K.

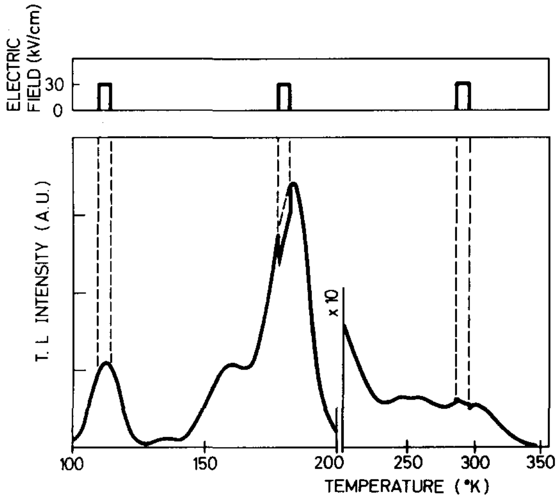

Fig. 3. Temporary d.c. electric field on the thermoluminescence glow curves (constant heating rate of 3.5 °K min^{-1})of a 200 ppm Tl doped KI crystal previously β -irradiated for 30 min at $T = 77$ °K.

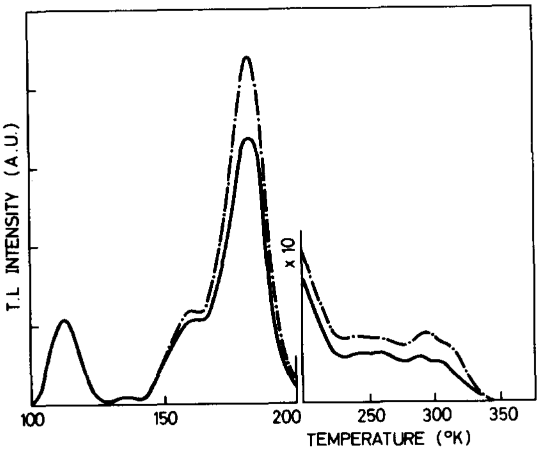

Fig. 4. Thermoluminescence glow curves measured *without* electric field in a 200 ppm Tl doped KI crystal β -irradiated at $T = 77$ °K under the following conditions: —— without d.c. electric field; —·—·— with d.c. electric field ($E = 30$ kV cm^{-1}) (constant heating rate of 3.5°K min^{-1}).

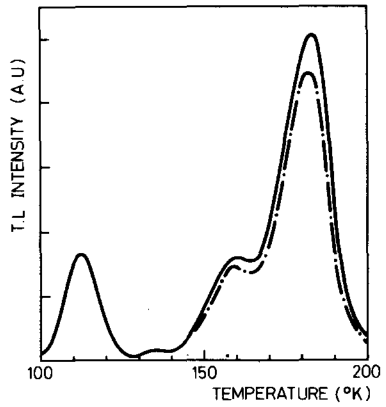

Fig. 5. Thermoluminescence glow curves measured with a constant heating rate of 3.5 °K min^{-1} in a 200 ppm Tl doped KI crystal, β-irradiated at $T = 77$ °K *without* electric field: ——— TL measured without d.c. electric field; —·—·— TL measured with d.c. electric field ($E = 30$ kV cm^{-1}).

The *temporary* application of a d.c. electric field causes a decrease ΔI of the intensity in both spectral regions; the ratio $|\Delta I/I|_{\mathrm{RL}}$ is however a decreasing function of the irradiation dose. The effect disappears after a long irradiation time, i.e. when the intensity of the radioluminescence becomes stationary (fig. 2).

On the other hand the effect of the field on the thermoluminescence glow curves (TL) measured between 77 °K and 200 °K shows that the first peak at 105 °K is not affected, but that the intensity of the 170 °K peak is always depressed (fig. 3). The $|\Delta I/I|_{\mathrm{TL}}$ ratio is constant throughout the peak for a given value of the field and is independent of the field polarity, of the type of the electrodes and of the direction of observation with repect to the field. It, however, decreases with the irradiation dose to eventually disappear after a long irradiation. Results are similar with an a.c. field (50 Hz).

The effect observed on the thermoluminescence glow peaks occurring between 230 and 330 °K corresponds to a small transient increase of their intensities; it is probably due to a local modification of the thermoluminescence kinetics (Gudden-Pohl effect) and will not be discussed in this report.

Although these temporary effects are important and easily observed, they do not allow us to give a clear insight of the physical mechanism involved in these processes. The following observations lead however to the idea that the radio and thermoluminescence electric field effects are intrinsic to the state of the crystal respectively during and at the end of the irradiation and more precisely to the charge state of the different defects present in it.

In fig. 4 we compare the thermoluminescence glow curves recorded after a 30 min β-irradiation realized respectively with and without a d.c. electric field at 77°K. The second peak at 170 °K and to a lesser extent the very faint peaks observed for 200 °K $< T <$ 300 °K, are enhanced. This clearly indicates that the application of the field during the irradiation at 77 °K has favoured the non-radiative trapping of free electrons on Tl^+ sites (formation of Tl^0) and on unknown traps at the expense of the radiative process. In fig. 5 we compare the thermoluminescence glow curves measured with and without an applied d.c. electric field after a 30 min β-irradiation at 77 °K. The first peak is unchanged but the second peak at 170 °K is globally depressed. We see again in this example that the appliction of the field has favoured a non-radiative recapture of free electrons (in this case those thermally ionised from Tl^0 centres) on unknown traps at the expense of the radiative process (process(3), fig. 1(B)).

The fact that no marked variation occurs on the first glow peak ruled out the idea that a d.c. electric field has any influence either on the migration of the self-trapped holes, on their capture by the Tl^0 recombination centres, or on the subsequent recombination process. The effect of the field can only act on charges coming from the conduction band, i.e. the electrons. A Schottky effect in the bound excited state of Tl^+ is rather improbable: if it existed the effect would be temperature dependent. This was never observed experimentally since:

(a) The $|\Delta I/I|_{TL}$ ratio is constant throughout the 170 °K glow peak.

(b) The $|\Delta I/I|_{RL}$ measured for a given irradiation dose is also constant between 4 °K and 77 °K.

(c) The intensity of the 412 nm photoluminescence (2.9 eV) excited in the 236 nm and 286 nm absorption bands does not change under an electric field between 77 °K and 200 °K.

Moreover the electric field does not change the activation energy of the processes (1) and (3) since in this case a temperature shift of the glow curves should have been observed.

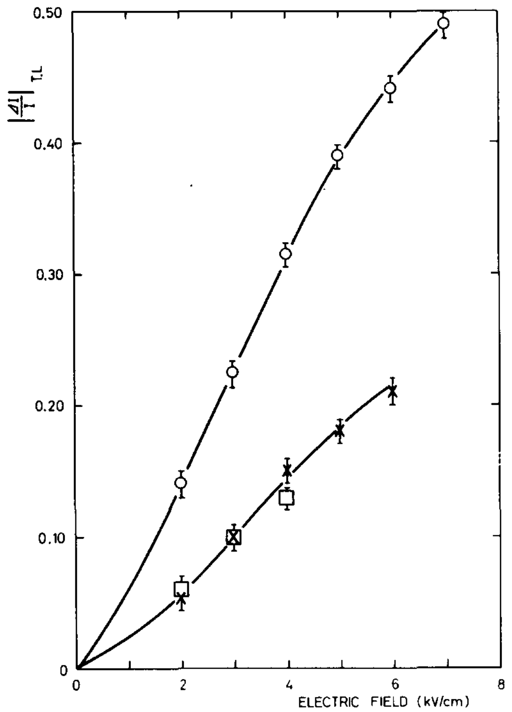

Fig. 6. Relative decrease of the second thermoluminescence glow peak as a function of the applied d.c. electric field in a 200 ppm Tl doped KI crystal, β-irradiated at $T = 77°K$. Curve (1): ○ 3 min β-irradiation; heating rate 3.5 °K min^{-1} ; curve (2): × 30 min β-irradiation, heating rate 3.5 °K min^{-1}; □ 30 min β-irradiation, heating rate 0.6 °K min^{-1}; I error.

We can reasonably assume that the recombination occurs with an initial capture of the electron via hydrogenic excited states close to the conduction band (due to the Coulombic potential of the positively charged recombination centres). Thus as in the case of n-type semiconductors [8], we can expect that in the presence of an external electric field, the electrons which have not had the time to make a transition from these levels to the bound emissive state will be easily retransferred into the conduction band. Therefore the ratio of the electron capture cross-section for positively charged recombination centres (such as V_K, Tl^{2+} centres) to that of neutral electron traps (Tl^+ for instance) is a decreasing function of the applied field. This consequently enhances the rates of electron trapping at the expense of any radiative mechanism.

The relative variation $|\Delta I/I|_{TL}$ as a function of the field strength is shown in fig. 6. This ratio is independent of the heating rate, i.e. of the intensity of the glow peak as long as the other experimental conditions remain the same. The irradiation dose (at low value only) has simply the role of a scaling factor.

4. 200 °K X-irradiation effects

The measurements of electric field effects on KI : Tl crystals have been completed and the interpretation has been confirmed by a systematic study as a function of the irradiation dose at 77 °K and 200 °K.

In the following experiments a sample was first X-irradiated for a given period of time at 200 °K and then immediately cooled down to $T = 77$ °K. At this tempera-

This suggests that the ratio of the electron capture cross-section for positively charged recombination centres to that of neutral (with respect to the crystal) electron traps is reduced by the field. The relative influence of these traps depends on their concentration and it decreases with the irradiation dose. Most of these traps are unstable between 200°K and 300°K, so that the crystal can be regenerated by heating at room temperature. Since the nature of these electron traps is still unknown, a quantitative explanation is as yet impossible. These traps may pre-exist in the crystal but can also be created by the ionising irradiation. The exact knowledge of their nature could be of great practical importance since several optical memory devices are precisely based on reversible inhibited cathodoluminescence mechanisms.

Acknowledgement

The authors are indebted to Prof. F. Bassani (University of Roma) for discussions during his stay in Neuchâtel as a CICP Professor (1972–1973).

References

[1] D.Curie, Luminescence Cristalline (Dunod, Paris, 1960).

[2] W.B. Hadley, S. Polick, R.G. Kaufman and H.N. Hersh, J. Chem. Phys. 45 (1966) 2040.

[3] R.B. Murray and F.J. Keller, Phys. Rev. 150 (1966) 610.

[4] J. Bonanomi and J. Rossel, Helv. Phys. Acta XXV (1952) 725.

[5] I.A. Parfianovitch, V.V. Pologrudov and E.N. Karnaukhov, Proc. Intern. Conf. on Luminescence, Budapest, 1966.

[6] V.P. Denks and V.I. Leiman, Soviet Phys. Sol. State 10 (1968) 1426.

[7] V.A. Grigor'ev, V.K. Lyapidevskii and I.M. Obodovskii, Soviet Phys. Sol. State 11 (1969) 849.

[8] G. Ascarelli and S. Rodriguez, Phys. Rev. 124 (1961) 1321.