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PLENARY SESSION.

Thermoluminescence and lattice defects in alkali halides

J. L. Alvarez Rivas
Junta de Energia Nuclear, Madrid-3, Spain

Abstract. — Recent developments in the study of the thermoluminescence of irradiated alkali halides indicate that many of the observed glow peaks are due to thermoluminescent processes related to the recombination of radiation induced lattice defects. There is a large amount of experimental results which supports that the \( F + H \) recombination is a rather common thermoluminescent process. Under some conditions it has been observed that the \( I + F, I + V_k \) and \( H + \alpha \) recombinations can indirectly induce light emission. No luminescence associated with the \( I + \alpha \) recombination has been found.

The main problem in the study of a thermoluminescent process is to identify the three elements in terms of which these processes are commonly described: the trap, the mobile entity, and the recombination centre [1, 2]. This is sometimes difficult to obtain and most of the available information only concerns the thermal activation energies, the exponential factors, and the kinetics of the glow peaks. In case the mobile entity are either electrons or holes current peaks associated to the glow peaks are observed. The alkali halides seemed to be quite suitable materials to study thermoluminescent processes, because in these either relatively pure or doped materials well defined electron and hole trapped centres are induced by irradiation [3, 4]. However, the correlation among colour centres and glow peaks is still been worked out. Moreover, recent developments have shown that a large number of the thermoluminescent processes observed in these materials are related to reactions among lattice defects [5]. These processes are the subject of this brief review. It will be divided into three parts which correspond to the temperature range in which the samples have been excited.

1. Thermoluminescence below 80 K. — Alkali halide crystals X- or gamma-irradiated near liquid helium temperature exhibit a few glow peaks below 80 K. In this temperature range, only the radiation induced I- and H-centres become thermally unstable as well as some shallow electron traps. Purdy and Murray [6] have observed in KCl samples irradiated at 7 K and then heated at 1.5 K/min. three glow peaks at about 29.5, 37.5, and 50 K respectively. The peak at 37.5 K which is the most intense peak in the spectrum, and the peak at 50 K are simultaneous with annealing steps in the F centre concentration. The spectrum of the emitted light corresponds to that of the relaxed exciton (2.3 eV) at 50 K, but at 37 K a band at 2.92 eV is observed. They have proposed that the thermoluminescent mechanism in the 37 K peak is the \( F + V_k \) recombination and in the 50 K peak it is the \( H + F \) recombination. The formation of self-trapped excitons in the \( H + F \) recombination has received theoretical support [7]. Analogous results have also been obtained in NaCl and KI [8]. NaCl samples X-irradiated at 6 K and heated at 3.4 K/min. show glow peaks and their corresponding F centre annealing steps at about 16, 21 and 37 K. Glow peaks around 22, 30, 40, 55 and 76 K have been found in KI samples but thermal annealing of the F centres was not obtained. The emission spectrum in these glow peaks also shows the bands corresponding to relaxed exciton in these materials: 5.38 (a) and 3.32 (π) eV in NaCl; 4.07 (a) and 3.32 (π) eV in KI.

The material which has been studied in more detail is KBr [8, 9, 10]. The thermoluminescence spectrum of KBr samples X-irradiated at 6 K shows a strong glow peak at 29.5 K as well as two small glow peaks around 41 and 47 K for a heating rate of 3.4 K/min. Thermal annealing steps in the F centre concentration and in the optical density at 380 nm also occur at the temperatures where these glow peaks appear [8, 9]. As well as in the other alkali halides the emission spectrum in these glow
peaks exhibits the $\sigma$ (4.45 eV) and $\pi$ (2.3 eV) bands of the self-trapped exciton in this material [8, 9], some small additional emission bands between 3 and 4 eV have also been observed by Aboltin et al. [10]. These authors have also obtained the thermoluminescence spectrum of KBr samples X-irradiated at 4.6 K and heated at 1 K/min., the glow peaks, in this case, are about 27, 35, 40 and 50 K which occur simultaneously with annealing steps in the F and 380 nm bands. The glow peak at 27 K is about two orders of magnitude larger than the other glow peaks. Most of the I centres decay below 27 K but about 20 % of these centres anneal while the glow peak at 27 K is operative [10]. The spectrum of thermally stimulated currents in this material [10, 11] shows a large peak at the same temperature as the main glow peak. Several very small current peaks were also observed [10].

From these results it has been concluded and it is widely accepted that those of the above indicated glow peaks which have not associated current peaks are induced by the recombination with F centres of mobile interstitial halogen atoms thermally released from H centres. Details of this F + H recombination have been studied and it has been shown that the lowest state of the self-trapped exciton can be formed in this recombination of lattice defects [7]. However, both $\sigma$ and $\pi$ emission have been observed at it has been previously indicated. It is noteworthy that the relative intensity of the $\sigma$ and $\pi$ emissions in these recombinations is different from that observed in radioluminescence measurements [8]. It seems that the emission spectrum of these glow peaks should be studied in more detail. Nevertheless, it is clear that the identification of the F + H recombination as a thermoluminescent process is an important point to study the thermoluminescence of these materials.

Most of the I centre annealing occurs at temperatures where no light emission is observed. It has been concluded that the recombination of interstitial halogen ions with anion vacancies does not induce light emission. There is still some discussion about the nature of the thermoluminescent process involved in the glow peak at 37.5 K in KCl [6] and in the peak at 29.5 K in KBr [8, 9]. The existence of a current peak associated with that glow peak [10, 11, 12] indicates that some other recombination different from the F + H reaction might be involved in this glow peak. In this material, the $V_K$ and H optical absorption bands are strongly overlapped at 380 nm and in the corresponding annealing step at this wavelength might be involved both $V_K$ and H centres. It has proposed that in this glow peak interstitial halogen ions recombine with $V_K$ centres with emission of intrinsic luminescence [10, 12]. Some F + H recombinations might also be involved in this glow peak. Tanimura [8] has found that in this peak the intensity of the $\sigma$ band varies with the decrement of the optical density at 380 nm in a different way that the $\pi$ band does. This might imply that two thermoluminescent processes are operative in this glow peak.

2. Thermoluminescence between 80 and 300 K. The thermoluminescence spectrum of these materials between 80 K and room temperature is more complex than below 80 K. In this temperature range electron and hole traps, most of them related with impurities whose valence states vary under irradiation, are operative. These thermoluminescent processes are correlated with current peaks but the information available on this thermally stimulated currents is still scarce. These processes are not related with recombinations among proper lattice defects and they shall not be treated here.

It is known that in this temperature range, interstitial halogen ions and atoms are released from $I_A$ and $H_A$ centres respectively [5, 13]. Therefore, some thermoluminescent processes related to lattice defect annealing might also occur in this temperature interval. It has been shown that in KBr : Na there are six glow peaks between 100 and 250 K which occur respectively at the same temperature as the $F$ centre annealing steps in this temperature interval [8, 14, 15]. An analogous correlation was also found in KBr : Li. Pulse isochronal annealing measurements also show a one-to-one correspondence among the F centre annealing steps and those of the $V_I$ band which respectively occur around 100, 130-140 and 170-175 K depending on the Na concentration. It was also found in this work that the $I_A$ centre fades out in a single step around 110 K. Since the $V_K$ optical absorption band is overlapped with the $V_I$ band, the thermal annealing of the $V_K$ centres in KBr : Na was obtained by ESR measurements. It was found that the $V_K$ centre concentration grows between 80 and 105 and then annihilates in two stages around 115 and 160 K respectively.

It has been concluded from these results [8, 15] that the glow peaks around 102 and 145 K are caused by the recombination of F centres with mobile interstitial halogen atoms thermally released from $H_A$ centres. The glow peak at 115 K seems to be correlated with the annealing steps of the $V_K$ and $I_A$ centres respectively observed at 115 and 110 K. The defect reactions involved in this glow peak might be as follows : the interstitial ions released from $I_A$ centres recombine with $V_K$ producing free interstitial atoms [12] which are highly mobile at this temperature and they recombine with F centres. This recombination is associated with light emission. The $V_K$ centre growth observed between 80 and 105 K is due to the recombination of some interstitial halogen atoms released while the glow peak at 102 K is operative, with anion vacancies [16]. Note that the $I_A$ centre annealing occurs at higher temperature. Finally, the glow peak at 165 K has been tentatively
adscribed to the recombination of F centres with holes released from $V_K$ centres which are thermally unstable above 160 K in this material [8]. This F + $V_K$ recombination which results in the formation of anion vacancies, has been sometimes invoked to explain some thermoluminescent processes, however, no conclusive results have been shown. The spectrum of the light emission in KBr:Na exhibits the band of the self-trapped exciton and an additional band at 2.9 eV. The intensity of this band depends on the Na concentration.

Recent measurements of the thermoluminescence, the thermally stimulated currents, and the thermal stability of the F centres induced by X-irradiation at 80 K in Harshaw KCl [17] and NaCl [18] samples heated at 8.5 K/min. up to 300 K have been presented. Nine first order glow peaks around 100, 120, 145, 165, 200, 220, 235 and 275 K have been found in KCl. The corresponding spectrum of thermally stimulated shows a single peak at about 200 K. It was observed that there is an F centre annealing component associated to each glow peak except for the peak at 200 K. The thermoluminescence (F* emission) and the thermally stimulated current spectra in samples X-irradiated at room temperature and then illuminated with F light at 80 K show six glow peaks and their corresponding current peaks. However, none of these glow and current peaks which are obviously due to electron traps can be identified with the glow and currents peaks observed in samples X-irradiated at 80 K. It has been concluded that the glow peak around 200 K is due to some $V_K + e$ recombination in which the F centres are not involved. The other glow peaks have been ascribed to F + H recombinations. The emission spectrum shows three main bands peaked around 4.06, 2.88 and 2.30 eV whose relative intensity vary with the temperature but they are observed in all the glow peaks. The band at 2.30 eV which is strongly overlapped with the F optical absorption bands, corresponds to the self-trapped exciton. The origin of the other two emission bands is not known but it is interesting to point out that these three emission bands are close to the bands observed at 20 K during X-irradiation [19].

In NaCl samples ten first order glow peaks have been found [18]. The peaks around 89, 98, 118, 210 and 236 K are due to electrons released from traps. Their associated current peaks are observed in both samples X-irradiated at 80 K and in samples F-photostimulated at 80 K after irradiation at room temperature. The emission spectrum at the 210 K glow peak shows a dominant band peaked around 2.70 eV, while in the other four peaks two bands peaked around 4.5-4.8 eV and 3.3-3.4 eV respectively are dominant in the emission spectrum. Around 185 K there is a glow peak which has an associated current peak in X-irradiated samples. There is not either glow or current peak in samples F-photostimulated at 80 K equivalent to the 185 K peak which has been ascribed to a hole trap. This peak as well as the above indicated peaks due to electron traps, are not related with thermal annealing stages of F centres. Glow peaks at 145, 170, 253 and 285 K are correlated with F centre annealing decay but no current peaks associated with them have been observed. It has been concluded that these peaks are caused by F + H recombinations. The emission spectrum at the temperatures where these glow peaks and the glow peak caused by hole release, shows a single band peaked around 2.7 eV which is strongly overlapped with the F absorption band. No intrinsic light emission has been reported at this wavelength in NaCl. It is interesting to point out that the emission spectrum is common to hole and interstitial related glow peaks and that no F centre annealing processes are involved in the glow peaks ascribed to hole release in these alkali halides.

3. Thermoluminescence above room temperature. — The mechanisms involved in the thermoluminescent processes observed in this temperature range have been a rather controversial subject. In some cases the discussion is still open. Nowadays, it is quite well accepted that the F centres are involved in these thermoluminescent processes. It seems, however, that this fact has not been included in the widely studied thermoluminescence of LiF [20].

It has been found that in Harshaw pure KCl [21], KBr, KI, NaCl and NaF [22], there is an one-to-one correspondence among glow peaks and F centre annealing steps. This implies that these centres are involved in the thermoluminescent processes. Some authors have proposed that the F centres act in these processes as electron traps while others are inclined to consider that these centres play the role of recombination centres for holes thermally released from some traps. Finally, it has been also proposed that the F centres act as recombination centres for interstitial halogen atoms released from traps such as impurities and dislocations. At some stage in this recombination an electron-hole recombination takes place and light is emitted [21]. This model in which the mobile entities are halogen atoms instead of electrons or holes, is obviously identical to the model proposed to explain some thermoluminescent processes observed below room temperature. The lattice is restored in these processes. In some cases, it has been also possible to observe M centre annealing steps which occur simultaneously with a glow peak [22].

There are several considerations and experimental results on the thermoluminescence of alkali halides either pure or doped with alkaline-earths, from which one is led to conclude that the F centres do not act either as recombination centres for holes or as electron traps in these thermoluminescent processes.
In these materials six or more glow peaks related with F centres have been observed above room temperature. It does not seem very realistic to assume that there are six or more types of F centres with rather different thermal ionization energies which, on the other hand, does not seem to affect either the halfwidth or the maximum of the F optical absorption band. The preexponential factors found for these glow peaks are usually very far away from the values expected for electron or hole traps [21, 22]. In this model and also in the case that holes recombine with the F centre electrons one should expect to observe current peaks associated to the glow peaks. These current peaks have never been observed. Sometimes it is said that these peaks are too small to be detected on the background of ionic current at this temperature. This is not obvious because there are cases in which the number of F centres annihilated in a glow peak range between $10^{16}$ and $10^{17}$ cm$^{-3}$ at temperatures where the ionic conductivity is still relatively low ($\sim 100 ^\circ C$). It seems sensible to expect that such a large number of electrons or holes released should allow to observe the current peaks associated to the glow peaks at least in some cases. Efforts have recently been made to observe these current peaks without success [22, 23]. The final products of the F centre ionization and of the hole-F centre recombination as well are anion vacancies. The fate of this large number of anion vacancies deserves some explanation which is not usually explicit.

There is an interesting phenomenon observed in the thermoluminescence of alkali halides irradiated at room temperature which can not be easily explained either with electron or hole models while it fits well into the interstitial-F centre recombination model. It has been shown [21, 22] that for increasing irradiation dose the intensity of the glow peaks observed at the lower temperatures decreases and they finally vanish. With increasing dose this process affects all the glow peaks initially present in the thermoluminescence spectrum. If electron or hole traps were involved in these thermoluminescent processes one would expect that for increasing doses their corresponding glow peaks might saturate but never that they would fade out. For large enough doses a glow peak at high temperature is observed while all the low temperature glow peaks disappear [24]. In doped samples this effect needs of a dose larger than in pure samples to be observed [23]. These features of the thermoluminescence spectrum are completely consistent with the well known interstitial aggregation processes [5, 25]. The glow peak observed in heavily irradiated samples shows a rather unusual kinetics: at temperatures on the low temperature edge of the peak, the isothermal light decay curves exhibit a maximum which is not observed at higher temperatures [24]. This behaviour might also be consistent with the thermal annihilation of large interstitial aggregates since the interstitial evaporation rate from these large interstitial aggregates might well increase slightly as their initial size decreases. However, the existence of several interacting traps can not be ruled outs. This effect is not observed for small aggregates.

Another result which lends support to the interstitial-F centre recombination as the origin of this thermoluminescence is the one-to-one correspondence found among the glow peaks and the saturating exponential components which form the first stage of the F colouring curve in NaCl irradiated at and above room temperature. The dose rate and temperature dependences of the F colouring curves are completely coherent with interstitial trapping at the traps observed in the thermoluminescence spectrum [26]. It has also been found that plastic deformation which enhances the first stage colourability induces an additional glow peak in the spectrum. A new F centre annealing step corresponding to this glow peak has been observed [27].

Thermal recovery steps of the radiation induced hardening have been published in a few cases. It has been found that samples irradiated in the same conditions as in those cases show dominant glow peaks at the temperatures at which these recovery steps occur [21, 22]. Since the radiation induce hardening is due to the presence of interstitials in the sample [5], this result lends support to the interstitial-F centre recombination model. Additional support to this point also stems from the linear relationship between deformation luminescence and thermoluminescence observed in KCl samples irradiated at room temperature which are then strained and heated till the light emission finishes. During both processes the total light is measured [28].

The spectrum of the emitted light in pure alkali halides exhibits a dominant band which for KCl, KBr, KI, NaCl, and NaF are respectively around 2.82, 2.70, 2.35, 2.92 and 2.10 eV [21, 22]. The origin of this emission band is not well known. However, it is possible that this band might be due to the intrinsic emission of the F + H recombination which is perturbed by a nearby impurity [29, 30] where this recombination occurs [23]. In KCl: Sr and KCl: Ca it has been found that the D$_2$ band due to trapped interstitials shows annealing steps at the same temperature as the glow peaks. In both Ca and Sr-doped samples the dominant emission band is around 2.78 eV and its halfwidth is larger than in pure samples [23]. The average light yield per destroyed vacancy centre in these doped samples is larger than in pure samples but it is affected by the impurity aggregation state. It is noteworthy that in general the light yield is not the same for every glow peak in a sample.

In samples doped with impurities whose valence states vary under irradiation the emission spectrum of the thermoluminescence shows the band observed
in the nominal pure material and bands which are characteristic of the impurities, for example, in NaCl : Mn [31] a band around 2.1 eV is observed. In this work it has been found that both emission bands are operative in all the glow peaks above room temperature. The glow peaks occur at the same temperature as the F centre annealing steps which in turn seem to be correlated with changes in the valence states of the Mn ions as it is shown by ESR measurements. It is suggested that in this case interstitials and holes are captured by the same traps [31]. Further study of the thermoluminescence in samples doped with this type of impurities are needed to clarify this simultaneous release of interstitials and holes. An interesting point in this case is to know the mechanism by which is compensated the effective electrical charge of the cation vacancy associated with the impurity when this traps one or two electrons. Two tentative suggestions are given. In this temperature range the interstitials and the F centres are clustered around the impurity-vacancy pairs [5, 23, 26], if a hole is trapped by the cation vacancy during irradiation it might occur that at the time the F + H recombination takes place some energy is transferred to a nearby hole and this is released. Another possibility is that since the F centres are stabilized close to the impurity-vacancy pair some F centre might be field ionized at the time the impurity valence changes, and a divacancy is formed. In this case hole trapping is not needed. On heating the sample interstitials are released and they recombine with both F centres and anion vacancies. The H + α recombination induces short-living V_K centres [16] which recombine with the electrons at the impurities. Whether or not the F centres are ionized shall depend on parameters such as the size and electron affinity of the impurity ion. It is noteworthy in this context that the formation of Z centres has been only reported in samples doped with impurities whose valence states do not vary by irradiation.

The thermoluminescence of both pure LiF and LiF (TLD-100) have been actively studied because of the interest of this material (TLD-100) for dosimetry purposes. A recent detailed work [32] has shown that the thermoluminescence spectrum exhibits bits about fourteen glow peaks above room temperature. A composite band peaked around 2.95 eV is dominant in the emission spectrum. The thermoluminescence processes in this material have been always ascribed to electron-hole recombinations and no clear role, if any, has been attributed to the F centres [20]. However, recent results obtained in this laboratory and which are still unpublished show that most of the fourteen glow peaks are correlated with F centre annealing stages while the other peaks including the 200 °C peak are correlated with thermal annealing steps in the Z bands [33]. Measurements of thermally stimulated currents did not show any current peaks. For increasing doses the thermoluminescence spectrum varies in the same way as it was indicated for the other alkali halides. The so-called supralinearity is consistent with this effect which is due to the interstitial halides.

4. Conclusions. — The outlined results show that many of the thermoluminescent processes observed in irradiated alkali halides are caused by reactions among lattice defects. The F + H recombination plays a key role in these processes. It has been observed below room temperature that in the light emission stage self-trapped excitons are formed. Both σ and π emission are observed, but it is not still clear whether or not the σ band is also formed in this recombination or by some indirect process. Above room temperature the emission spectrum of each alkali halide either commercially pure or doped with divalent impurities shows a dominant band whose peak position varies little if any with the impurity. The origin of this band is not well known and it is an important point to be worked out. In samples doped with divalent impurities whose valence states change under irradiation an intense emission band characteristic of the impurity is observed. The thermoluminescent processes in these materials need of further study because the valence changes.

There are cases in which the lattice defect recombinations 1 + F, 1 + V_K and H + α can trigger V_K + c recombinations. No luminescence associated with 1 + α recombinations have been observed.

DISCUSSION

Question. — K. Kan’No.

We have found that both the π and σ emission components of the 34 K glow peak in KBr are largely polarized when the crystal has been coloured at 9 K by irradiating with polarized nitrogen laser light. The observed anisotropy is quite similar to that in the case of recombination of released electrons with aligned V_K centers. In our experiments (cf. B-34), the larger part of the anisotropy in the UV absorption band disappears at ~ 15 K, because of disorientation of H centers, and a small amount of dichroism which may be due to the presence of aligned V_K centers, is left behind. Therefore, it is highly likely that recombination of released electrons with V_K centers is responsible for the 34 K glow peak.

Reply. — J. L. Alvarez-Rivas.

The reaction proposed to explain this glow peak is the 1 + F recombination which releases an electron. This electron recombines with a V_K centre and light is emitted. This is consistent with your results.
Question. — Z. Morlin.

I should like to draw your attention to the fact that thermoluminescence is highly structure sensitive. The glow peaks should be essentially of Gaussian type. Every deviation from this is — according to my experiences gained many years ago — partly due to plastic deformation or some defective state.

Reply. — J. L. Alvarez-Rivas.

The thermoluminescence spectrum is affected by plastic deformation either after or prior to irradiation. This introduces a very intense glow peak at high temperature which affects the shape of the low temperature glow peaks [27].

Question. — V. V. Ratnam.

1) For low temperature X-irradiated KCl crystals there is only one STC peak whereas there are many glow peaks. Without the movement of charge carriers how can the peaks be accounted for?

2) One possibility is if they are accounted for by the motion of a neutral species. Another equally strong possibility is the tunneling effect in the movement of charge carriers which we found in Photo-stimulated thermoluminescence.

Reply. — J. L. Alvarez-Rivas.

The glow peaks correlated with F centre annealing steps which are not associated with TSC peaks, are due to F + H recombinations. The TSC peak observed in X-irradiated samples has not been associated with any F centre annealing process.

References