



Three equal-depth thermoluminescence traps in NaCl crystal

R. Kumar^{1*}, S. Tiwari² and R. Pandey¹

1. Physics Department, Rama University, Mandhana, Kanpur-209217, India

2. Department of Physics, School of Physical and Decision Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow -22602, India

E-mail: rajendrab25@gmail.com

(Received 4 May 2021 ; in final form 20 November 2021)

Abstract

Three equal-depth traps reported in NaCl have been attributed to different defect configurations. In this trio system, the basic trap configuration proposed is the bi-vacancy, the analogy being drawn through observations in KCl crystal. Two other defect configurations that emerged are the derivatives of bi-vacancy with the next nearest neighbor I-V pair and the V_F center which represents a hole linked to a cation vacancy.

Keywords: thermoluminescence, doped NaCl, F-center, bi-vacancy, I-V pairs, V_F center

1. Introduction

In a system like alkali chloride, electrons created through radiation are trapped in the lattice. To observe thermoluminescence (TL), the electrons in the trap are supposed to get excited to the conduction band upon external heating and then fall down to the hole traps or recombination centers [1,2]. The recombination for an electron is also possible without reaching the conduction band. The traps have an important role in the TL process. The electrons situated in traps do not lose energy to drop to the lower available states. There have been numerous studies which characterize the electron traps and their applications in dosimetry [3], but the nature and the physical structure of such traps even in an alkali halide is not yet fully established.

TL studies in a number of alkali halides have been reported by Deshmukh and Moharil [3]. These studies do not, however, yield detailed information about the structure of the traps involved. The TL peaks in melt-grown pure KCl crystals are reported at 135 and 190 °C by Jain and Mahendru [4]. The authors proposed that the two peaks are due to electrons trapped at two different kinds of F-centers with trap depths of 1.05 eV and 1.15 eV respectively. The first type of F-centers is due to vacancies present in the crystal prior to X-ray irradiation and the second type to the vacancies, subsequently generated during X-ray irradiation, possibly near a

defect.

The TL studies in gamma-irradiated Harshaw KCl crystals were also reported by Ausin and Alvarez Rivas [5]. They observed that the area under the TL curve is always proportional to F-center concentration in the sample before heating. They further attribute the role of F-center to the recombination centers in the annealing process. The studies to explore the spectroscopy of traps in powdered KCl are also under taken by Ranita et al. [6] and it was found that the trap depth is proportional to the glow peak temperature (T_m).

The TL studies were further conducted in NaCl and NaCl:Ca²⁺ crystals by Joshi et al.[7]and the role of the latter system in dosimetry has been discussed. Here, the irradiation was done with a gamma ray dose of 2.1×10^4 R. These workers observed three peaks at 97, 175, and 235 °C, in pure NaCl crystals grown from the aqueous solution. However, in NaCl:Ca²⁺ system, two peaks are observed at approximately 75 and 147 °C. For this system, the peak at 147 °C shows a rapid increase in intensity upon gamma irradiation. This peak has been attributed to the electrons trapped at anion vacancy directly linked to divalent cation vacancy dipoles in the crystal.

The two peaks at 170 and 210 °C are observed in the highly pure NaCl crystals, with background impurities not more than 1 ppm by Mahendru and Radhakrishna [8].

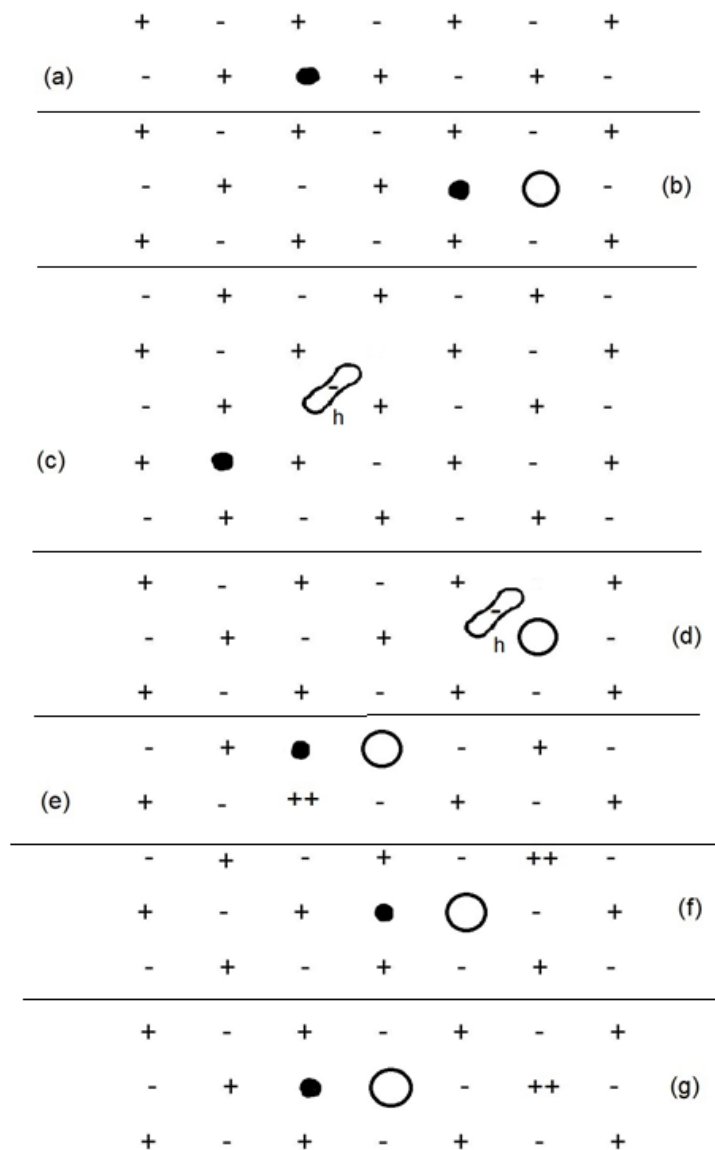


Figure 1. Arrangement of ions in a NaCl lattice: Alkali ions are shown as + and chloride ions as -. The electron occupying anion vacancy is shown by a thick dot. The vacant sites are indicated by circles. The letter h represents a hole in Cl_2^- . Possible defects are indicated by markers (a), (b), (c), (d), (e), (f) and (g) viz. (a) Secluded F-center, (b) bi-vacancy, (c) V_k center linked to anion vacancy, (d) V_F center, (e) Linked divalent cation, (f) nn I-V pair linked to anion vacancy and (g) nnn I-V pair linked to anion vacancy.

In these experiments the irradiation was done with X-rays. The TL peak at 170°C is reported to be due to the first stage F-centers, while the peak at 210°C is due to the second stage F-centers. The first peak at 170°C shows a remarkably fast growth of TL peak intensity. The second peak at 210°C was however not observable until 30 minutes of X-ray irradiation was completed. Again, in analar purity NaCl crystals with background impurities up to 20 ppm, an additional TL peak around 80°C was also observed by these workers.

There has been a recent report by Somera et al. [9] on the TL study of NaCl and NaCl: Mn^{2+} systems, irradiated with a gamma ray dose of 50 Gy. For the NaCl system, TL peaks are observed at 97, 145, and 175°C with trap depths of 1.12, 1.13, and 1.15 eV, respectively. The observation of three equal-depth traps is indeed very interesting. The temperatures corresponding to the TL peaks were reported along with the estimated trap depths

for the deconvoluted TL spectrum, but no explanation was provided about the occurrence of multiple peaks in their samples.

In the literature, thus no attempt has been made to understand the structure of different traps responsible for TL emission in an alkali halide system like NaCl. Our work herewith is towards establishing the structure of various F-center traps in undoped NaCl and identify these to observe near equal depth traps.

2. Proposed models for traps

2. 1. Diagrammatic representation of defects

The following diagrammatic description explains how various anion vacancy sites act as traps for electrons which lead to TL under different situations. The sub-figures 1a to 1g depict important defects structures in a NaCl like alkali halide crystal system. These sub-figures are separated by lines in between.

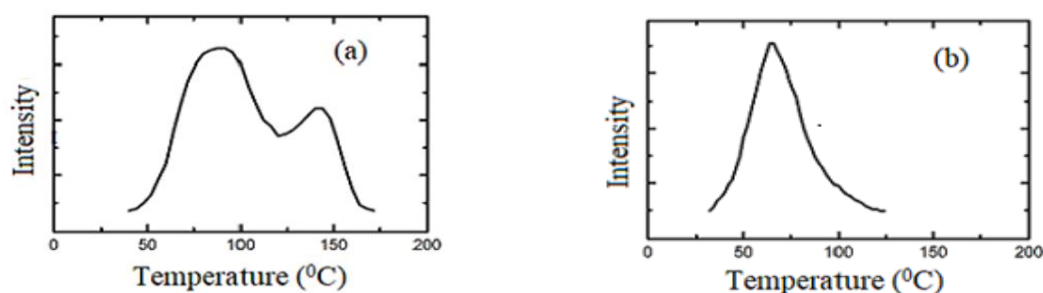


Figure 2. TL spectra for (a) undoped KCl (b) Mn^{2+} doped KCl.

For TL to occur, an electron must be captured at a suitable trap. Figure 1a represents an electron trapped at a secluded anion vacancy. Such F-centers have little role in the TL process. Figure 1b represents the bondage of anion vacancy with cation vacancy, the combination being called a bi-vacancy. The electron gets trapped at an anion vacancy site and accompanied cation vacancy provides an increased lifetime of the trap as per Pandey et al. [10]. Other sub-arrangements of figure 1 are the other types of traps that may be reflected in the TL spectrum. Figure 1c exhibits the arrangement of the V_k center linked to anion vacancy. When the V_k center is formed, an electron leaves $Cl^- - Cl^-$ pair, and we are led to have Cl_2^- arrangement linked to a hole. In figure 1c such an electron is shown trapped at an anion vacancy close to Cl_2^- center.

Figure 1d, on the other hand, is the anti-morph of figure 1c. Here, the electron leaving $Cl^- - Cl^-$ pair is lost somewhere and we have a Cl_2^- linked to a hole (h). Again we may have divalent cations directly linked to anion vacancy (figure 1e) as per Joshi et al. [7]. Figure 1f shows nn I-V pair linked to anion vacancy and figure 1g further shows nnn I-V pair arrangement linked to anion vacancy. When an alkali halide is doped with divalent impurities, a cation vacancy necessary for local charge compensation may be created at the nearest neighbor (nn) or next nearest neighbor (nnn) position to the divalent cation impurities. The electron paramagnetic resonance of Mn^{2+} for both types of linkages of cation vacancies with respect to divalent manganese ions was studied in the pioneering work of Watkins [11].

2. 2. The importance of bi-vacancy

As per a theoretical model by Herman and Barnett [12], it has been estimated that the 2s level of the secluded F-center has energy close to the conduction band in NaCl. The 2s level thus fits as an ideal candidate for possible electron traps near the NaCl conduction band. It may be mentioned here that the energy of 2s level has been estimated [13] to be close to the conduction band in KCl crystals, in a different context.

The electron traps are supposed to be situated at dislocation sites in a crystal lattice, which is supported by the reported works of Benia et al. [14] and Wosinski [15]. A vacancy pair, also called a bi-vacancy, is a suitable trap for electrons in NaCl lattice and helps in the formation of a cation vacancy coupled F-center as shown in figure 1b. The electrons trapped in such bi-vacancy centers cannot fall to the lower energy states as in a

secluded F-center, because the potential at the electron site in a bi-vacancy is neither pure Coulombic nor like a perfect spherical well. Therefore, a 2s energy level of such a bi-vacancy center in pure NaCl is likely to act as an ideal trap for electrons.

2. 2. 1. Decrease in concentration of bi-vacancy due to cation doping

The prominent point defects in alkali halides are of Schottky type i.e. cation and anion vacancies. These should be produced in equal numbers in such a crystal, and could further combine to form cation-anion vacancy pairs, also called a bi-vacancy and equilibrium would be maintained between Schottky pairs and bi-vacancies. When an alkali halide crystal is doped with divalent impurities, additional cation vacancies will be created for local charge neutrality. The impurity vacancy pairs so created are usually termed as I-V pairs. The increase in concentration of I-V pairs due to divalent cation doping would lead to more anion vacancies getting linked to I-V pairs, through their cation vacancy ends. The doping of divalent cations would thus decrease the relative concentration of bi-vacancies in alkali halides. Such a process would proceed effectively during growth of crystals from aqueous solution, wherein the growth takes place at a constant temperature.

2. 3. Experimental proof for existence of bi-vacancy

2. 3. 1. KCl with Mn^{2+}

We have made TL studies in undoped and Mn^{2+} doped KCl systems. The KCl used was analar grade of Fischer Scientific Co. containing 0.001% divalent cations Ba, Ca, and Pb as stray impurities. The crystals were grown by slow evaporation techniques to yield cuboids of size $2 \times 2 \times 1$ mm size. For Mn^{2+} doped sample, 1% of the $MnCl_2$ was also added to the mother solution. All the samples were irradiated with 20mA and 30kV X-rays at room temperature for the production of color centers in them, the irradiation time being kept as 900 seconds. The power of the X-ray dose is assessed through accelerating voltage. On the other hand, the strength of the radioactive dose is measured in Rontgen or Gray. The TL measurements were made with a home-built TL apparatus with a heating rate of $30^\circ C/minute$.

In the undoped KCl crystals grown from an aqueous solution, two TL peaks at 88 and $140^\circ C$ have been observed (figure 2a). However, for KCl crystals grown with 1% $MnCl_2$ in the mother solution, the $140^\circ C$ peak is eliminated as described in section 2.2.1 and only one

peak at 66°C is seen up to the highest measurement temperature. This is shown in figure 2b. The 140°C peak has been attributed to the electrons liberated from the anion vacancy end of bi-vacancy traps, while the peak at 88°C may be attributed to the electrons liberated from the traps under the influence of I-V dipoles of stray divalent impurities. As above, the peak at 140°C gets completely eliminated upon the addition of a sufficient amount of Mn²⁺ impurity. Furthermore, the peak at 66°C of Mn²⁺ in figure 2b is quite prominent, while the peak at 88°C of undoped KCl thus getting overshadowed due to the effect of excessive Mn²⁺ impurities.

2. 3. 2. KCl with Eu²⁺

In the recent work of Kohzuki and Ohgaku [16], two TL peaks were observed at 97 and 177°C in samples doped with 0.02 mole percent of Eu²⁺. The higher temperature peak is reduced in intensity due to Eu²⁺ doping; but not completely eliminated as for the case of KCl:Mn²⁺. This is perhaps due to the fact that impurity content in KCl:Eu²⁺ was only feeble compared to KCl:Mn²⁺ system. However, the existence of bi-vacancy in KCl is justified as per the above experiments.

2. 4. Theoretical support for bi-vacancy

A spherical well model was developed by Herman and Barnett [12] to estimate the energy level of the 2s-trap for a usual secluded F-center in the NaCl lattice. They could estimate the total number of bound states by the solution of the 3D Schrodinger equation in a quantum well of depth V_0 and width a . Here, V_0 is determined by the positive charges surrounding the anion vacancy. Our group [10] has recently extended this model to estimate the energy of 2s-traps in a bi-vacancy. This is done by assuming the electron to occupy a distorted spherical well appropriate to bi-vacancy with reduced well depth ($5V_0/6$) and increased well width (a). It may be stated that the values of V_0 and a determine the position of the 2s-trap level in the solution of 3D Schrodinger equation for the electron in the bi-vacancy well.

Of course, in the proposed distorted well for the bi-vacancy trap, the well depth is reduced nearly by a factor of 1/6 as one of the six nearest cation neighbors of anionic vacancies is removed, and the increased value of the well width a is determined by the more available space in a bi-vacancy, in contrast to secluded anion vacancy. Our group [10] has justified the suitability of a bi-vacancy trap in KCl and explained successfully the observed trap depth value of 0.9eV for the 2s level in the KCl lattice using the above proposition.

2. 5. V_F center linked traps

Upon irradiation, a Cl⁻ ion in a NaCl lattice would be converted into neutral Cl, which could combine with neighboring Cl⁻ to form a Cl₂⁻ defect, the V_k center. In LiF alkali halide single crystals, in which V_k centers are reported with appreciable thermally stimulated luminescence intensities by Nakonechnyi et al. [17] only upto-93°C; thus free V_k centers will have no role above this temperature. There is thus a need for invoking a new V_F defect in NaCl systems to explain the observed traps.

Again, through the analysis of the paramagnetic resonance spectrum of X-ray irradiated and properly annealed LiF single crystals, Kanzig [18] established the role of anti-morph of F-center termed as V_F center, which is more stable and thus must be considered in the TL spectrum. A V_k center close to a cation vacancy may represent a V_F center, being depicted in figure 1d. Here a hole is under the influence of cation vacancy. Obviously, the energy levels of trapped electrons in a bi-vacancy resemble the energy levels of a V_F center, wherein, a hole is under the influence of five neighboring anions. Thus, analogous to the spherical well model of bi-vacancy; here V_0 is reduced by a factor of 1/6 and well width is enhanced giving holes energy level identical to electrons in bi-vacancy. So far the position of Cl₂⁻ is concerned, as per the polaron migration concept, this may revolve all around the cation vacancy and appropriate energy levels could be imagined. One of the trio traps in NaCl is probably due to V_F defects.

2. 6. Divalent cation /I-V pair linked traps

Joshi et al. [7] attempted to explain the TL data of the NaCl:Ca²⁺ system by assuming a trap model, shown in figure 1e. In this arrangement, electrons in the traps would be surrounded by six unit positive charges, and thus as per the theoretical model of Pandey et al. [10], higher trap depths than for both bi-vacancy and V_F center will be anticipated. However, if one adopts the figure 1g configuration, in which an I-V pair is close to anion vacancy, there would be only five unit positive charges in the close neighborhood of anion vacancy. The divalent cation of the I-V pair (nnn arrangement), being far away from the anion vacancy, a trap depth value close to bi-vacancy and V_F center may be explainable, and three equal trap depths are understood.

3. Conclusions

We have proposed three different trap configurations which are expected to provide near-equal trap depths. The three TL peaks recently observed in the undoped NaCl [9] do seem to be due to the three trap configurations proposed in the present work. The experimental peaks were observed at 97, 145, and 175°C with trap depths of 1.12, 1.13, and 1.15eV, respectively. However, two of the above three trap configurations involve the role of divalent impurities. Such involvement may not be unwarranted as the NaCl samples in the work reported [9] were not extra pure as of earlier workers Mahendru & Radhakrishna [8]. Some stray impurities may well be expected in the works quoted above to take care of the formation of the V_F center and anion vacancy linked to the I-V pair at the nnn position. Different theoretical models [10,11,18] give insight into trap configurations in NaCl and help in explaining three different TL traps with equal depths and support the idea of bi-vacancy, V_F center, and I-V pair linked anion vacancy. It would be interesting if TL spectra for undoped KCl are also analyzed on the above lines. We hope to deconvolute the observed TL spectrum for undoped KCl and reexamine the above defect models.

Acknowledgement

The authors are thankful to Prof. S. D. Pandey of P.P.N.

P.G. center, Kanpur University, India for suggesting the problem and useful discussions during this work.

References

1. J P Srivastava, "Solid State Physics", Prentice Hall (2008).
2. A J J Bos, *Radiation Measurements* **41** (2007) 545.
3. B T Deshmukh and S V Moharil, *Bull. Mat. Sci.* **7** (1985)427.
4. S C Jain and P C Mahendru, *Phys. Rev. A* **957** (1965) 140.
5. V Austin, J L Alvarez Rivas, *J. Phys. C Solid State Phys.* **5** (1972) 82.
6. V Ranita, B A Sharma, and S Singh, *Indian J. Pure and Appl. Phys.* **44** (2006) 308.
7. R V Joshi, *et al.*, *Health Phys.* **44**, 1 (1983) 29.
8. P C Mahendru and S Radhakrishna, *J. Phys. C (Solid State)* **2** (1969) 796.
9. L Somera, *et al.*, ISSSD, Leon, Gto. Mexico. (2015).
10. R Pandey, *et al.*, *Malaysian J. Science* **40**, 1 (2021) 46.
11. G D Watkins, *Phys. Rev.* **79** (1959) 113.
12. Z S Herman and G Barnett, *Rev. Bras. de Ensino de Fis.* **12** (1982) 73.
13. J Hoya, *et al.*, *Comp. Mat. Sci.* **1** (2017) 138.
14. H M Benia, *et al.*, *Phys. Rev. B Condens. Matter Mater. Phys.* **81** (1972) 241415(R).
15. T J Wosinski, *Appl. Phys.* **65** (1989) 1566.
16. Y Kohzuki and T Ohgaku, *Crystals* **9** (2019) 331.
17. S Nakonechnyi, *et al.*, *J. Phys. Condens. Matter* **18** (2006) 379.
18. W Kanzig, *J. Phys. Chem. Solids.* **17**, 1 (1960) 80.