PROPOSED CONFIGURATIONS OF EQUAL DEPTH TL TRAPS IN NaCl

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Abstract

The origin of three almost equal depth energy traps has been explained theoretically. The bi-vacancy has been established as the basic trap configuration. Another variety of trap with slightly lower energy is due to bi-vacancy associated with an I-V pair. Also proposed are the third variety of traps being V_F –center which is a hole linked to the cation vacancy. The earlier reported so called first stage and second stage V_F –centers have been identified and correlated.

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

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1. Introduction

Thermoluminescence (TL) is supposed to occur by excitation of electrons in traps to the conduction band upon external heating and their subsequent falling down to hole traps, or recombination centers as per Bos (2007) and Srivastava (2008). The recombination can also occur without the electron reaching the conduction band. The traps have a key role in TL process and the electrons therein do not loose energy spontaneously. Numerous studies characterized TL emission from traps, but the basic structures of traps are not fully explained.

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. Deshmukh and Moharil (1985) have made numerous studies which characterize the electron traps and their applications in dosimetry, but the nature and the physical structure of suchtraps even in any alkali halide is not yet fully established.

Again, TL peaks in melt grown pure KCl crystals were reported at 135 ^{o}C and 190 ^{o}Cby Jain and Mehendru (1965). They explained the two peaks being due to electrons trapped at two different kinds of F-centers with trap depths of 1.05 eV and 1.15 eV respectively.

The TL studies were further conducted in NaCl and NaCl:Ca^{2+} crystals by Joshi et al(1983)..In this work the irradiation was done with gamma ray of dose of 2.1 x 10^4 R. These workers observed three peaks at 97°C, 175°C and 235°C in pure NaCl crystals, grown from the aqueous solution. However, in NaCl:Ca^{2+}system, two peaks were observed at approximately 75°C and at 147°C. For this system the peak at 147°C shows a rapid increase in intensity upon gamma irradiation dose. 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°C and 210°C were observed in the highly pure NaCl crystals, with background impurities are less than 1ppm by Mehendru and Radhakrishna (1969). The TL peak at 170°C is reported to be due to the first stage F centers, while the peak at 210 ^{o}C is due to the second stage F centers.

Recently, there has been report on the results of TL studies in NaCl and NaCl:Mn^{2+} systems, irradiated with gamma ray dose of 50Gy by Somera et al(2015). For NaCl system TL peaks are observed at 97°C, 145°C and 175°C with trap depths 1.12eV, 1.13eV and 1.15eV respectively. The observation of three equal depth traps is indeed very interesting. The temperatures corresponding to the TL peaks were reported in this work along with the estimated trap depths for the

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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. The present work is towards establishing the structure of various F-center traps in undoped NaCl so as to explain the observed near equal depth traps.

2. Proposed models for traps

2.1 Representation of defects

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

For TL to occur an electron must be captured at a suitable trap. Fig. 1(a) represents an electron trapped at an anion vacancy. Such F-centers have little role in the TL process. Fig. 1(b) however 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 increased life time to the traps as per Pandey et al. (2021) as shown in other components of Fig. 1, are the other types of traps which may also be reflected in the TL spectrum. Fig. 1(c) exhibits arrangement of V_k center linked to anion vacancy. When 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 Fig.1(c) such an electron is shown trapped at an anion vacancy close to Cl_2^- center.

Fig.1 (d), on the other hand is the anti-morph of Fig.1(c). Here, 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 [Fig 1(e)] as per Joshi et al (1983). The Fig.1 (f) shows nn I-V pair linked to anion vacancy and Fig.1 (g) 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 nearest neighbor (nn) or next nearest neighbor (nnn) position with respect to the divalent impurities cation. The electron paramagnetic resonance of $Mn^{2+}$for both types of linkages of cation vacancies with respect to divalent manganese ions were studied in the pioneering work of Watkins(1959).

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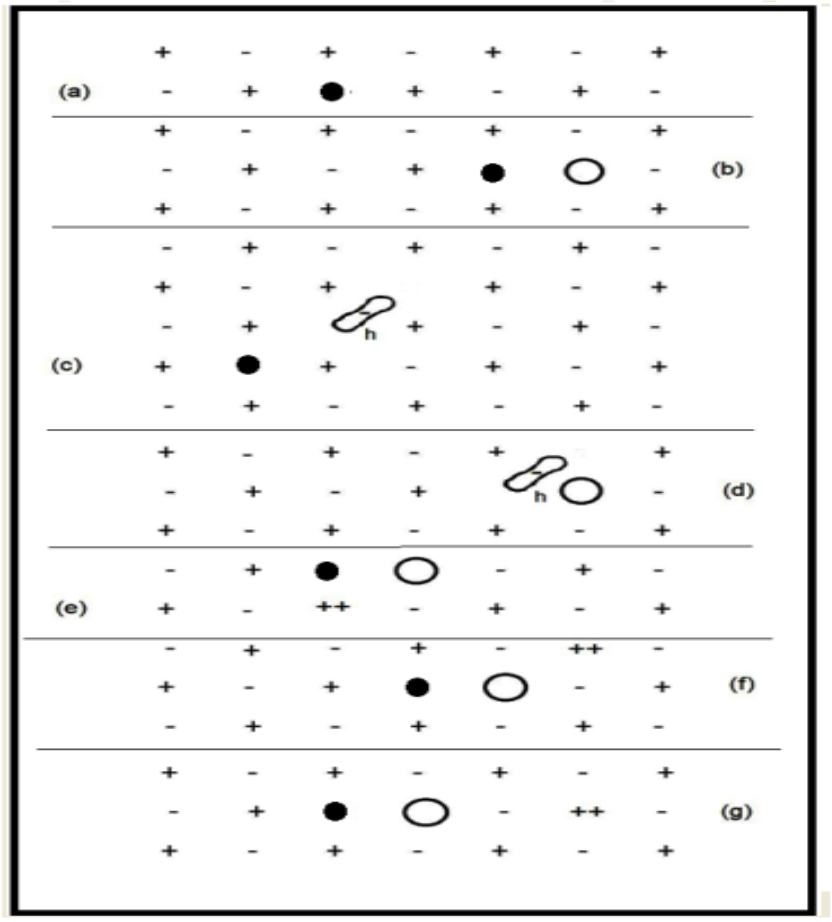

Fig. 1. Arrangement of ions in a NaCl lattice: Alkali ions are shown as + and chloride ions as - .The electron occupying anion vacancy is shown by a thick dot. The vacant sites are indicated by circles. The h represents a hole in Cl_2^-.Possible defects are indicated by markers (a), (b), (c), (d), (e), (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 divalentcation. (f) nn I-V pair liked to anion vacancy and (g) nnn I-V pair linked to anion vacancy.

2.2 The importance of bi-vacancy

As per a theoretical model by Herman and Barnett (1982), it has been estimated that the 2s level of secluded F - center has energy close to the conduction band in NaCl. The 2s energy level thus fits as an ideal candidate for possible electron traps near conduction band in NaCl crystal. It may be mentioned here that the energy of 2s level has been estimated by Hoya et al(2017) 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 (1972). A vacancy pair, also called a bi-vacancy, is also a suitable trap for electrons in NaCl lattice and helps in the formation of a cation vacancy coupled F-center as shown in Fig.1 (b).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

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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 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 2mm x 2mm x 1mm size. For Mn^{2+}doped sample, 1% of the $MnCl_2$ was also added in the mother solution. All the samples were irradiated with 20mA, 30kVX-rays at RT for production of colour centres in them, the irradiation time being kept as 900 seconds. The power of X-ray dose is assessed through accelerating voltage. On the other hand the strength of radioactive dose is measured in Rongten or Gray. The TL measurements were made with a home-built TL apparatus with a heating rate of 30^0C/minute.

In the undoped KCl crystals grown from aqueous solution, two TL peaks at 88°C and 140°C have been observed as shown in Fig.2 (a). However, for KCl crystals grown with 1% $MnCl_2$in the mother solution, the 140^0 C peak is eliminated as described in section 2.2.1 and only one peak at 66°C is seen upto the highest measurement temperature. This is shown in Fig 2(b). The 140°C peak has been attributed to the electrons liberated from 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 eliminated upon addition of sufficient amount of Mn^{2+} impurity. Further, the peak at 66°C of Mn^{2+}in Fig.2 (b) is quite prominent, the peak at 88°C of undoped KCl thus getting overshadowed due to effect of excessive Mn^{2+} impurities.

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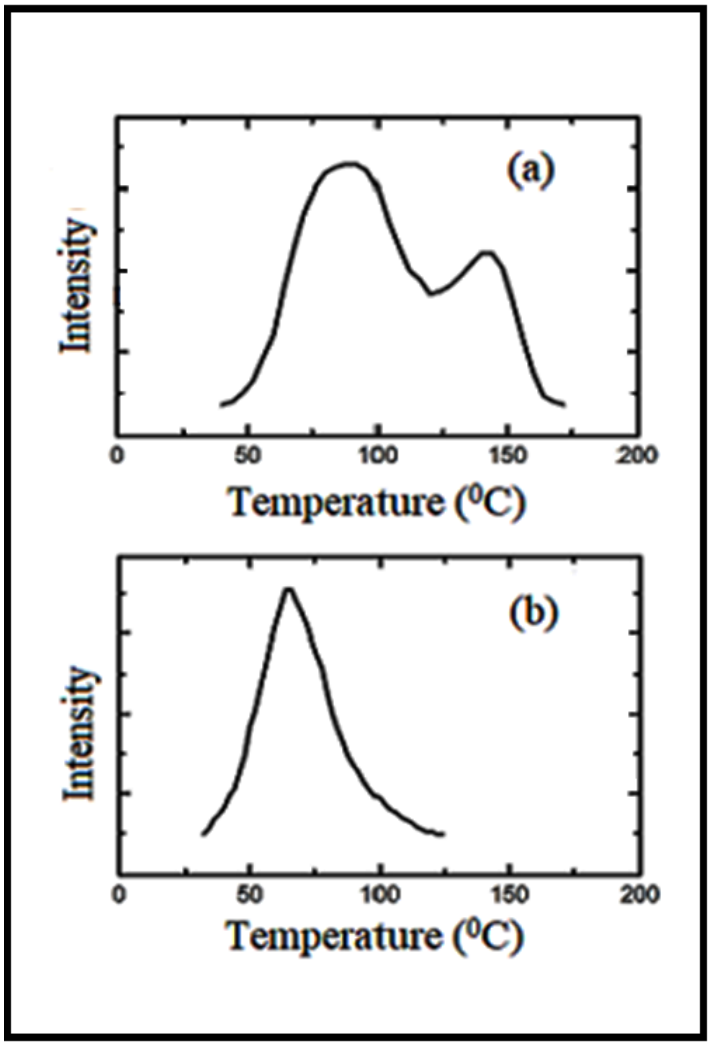

Fig.2 TL spectra for (a) undoped KCl (b) Mn^{2+} doped KCl.

2.3.2 KCl with Eu^{2+}

In the recent work of Kohzuki and Ohgaku (2019), two TL peaks were observed at 97^0C and 177^0C in samples doped with 0.02 mole percent of Eu^{2+}.The higher temperature peak is reduced in intensity due to Eu^{2+} doping; but not completely eliminated as for the case of KCl:Mn^{2+}. This is perhaps due to the fact that impurity content in KCl: $Eu^{2+}$was only feeble compared to KCl:Mn^{2+} system. However, the existence of bivacancy in KCl is justified as per the above experiments.

2.4 Theoretical support for bivacancy

A spherical well model was developed by Herman and Barnett (1982) to estimate the energy level values of 2s-trap for a usual secluded F-center in NaCl lattice. They could estimate the total number of bound states as per solution of Schrodinger 3d wave equation, using the well depth V_0 and width of the well '*a*'. Here, V_0 is mainly determined by the positive charges surrounding the anion vacancy.

Our group (2021) has recently extended the above model to estimate the energy of 2s-traps in a bi-vacancy. This is done by assuming the electron to occupy distorted spherical well appropriate to bi-vacancy with reduced well depth ($\frac{5}{6}V_0$) and increased well width (*a*). It may be stated that the values of V_0 and *'a'* determine the position of 2s trap level in the solution of 3d -Schrodinger wave equation for the electron in the bi-vacancy well.

Of course, in the proposed distorted well for the bi-vacancy trap, the well depth value is reduced nearly by a factor of $\frac{1}{6}$ as one

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of six nearest cation neighbours 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 (2021) has justified suitability of bi-vacancy trap in KCl and explained successfully the observed trap depth value of 0.9 eV for 2s level in KCl lattice using 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 Cl_2^- 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 (2006) only upto-93^0C; 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.

A V_k center close to a cation vacancy may represent a V_F center, being depicted in Fig 1(d). Here a hole is under the influence of cation vacancy. Obviously, the energy levels of trapped electrons in a bi-vacancy will resemble the energy levels for $V_F$center arrangement. In this V_F defect, a hole is under the influence of five neighboring anions and thus analogous to the spherical well model appropriate to bi-vacancy; here too V_0 is reduced by a factor of $\frac{1}{6}$ and well width is enhanced giving energy level values for a hole identical to electrons in bi-vacancy. So far position of Cl_2^- is concerned, as per polaron migration concept, this may revolve all around the cation vacancy and appropriate energy level positions could be imagined. One of the trio traps in NaCl is thus probably due to V_F defects.

Through the analysis of paramagnetic resonance spectrum of X-ray irradiated and properly annealed LiF single crystals, Kanzig (1960) established the role of anti-morph of F-center termed as V_F center, which is quite stable and contributes to TL spectrum. The V_F centers in alkali halides are also observed through e.s.r. spectrum. Again Egemberdiev et al.(1982) have also reported TL studies of V_F centers in KCl crystals containing Pb^{++} impurities.

2.6 Divalent cation /I-V pair linked traps

It was attempted to explain the TL data for NaCl: Ca^{2+}system by Joshi et al.(1983) assuming a trap model as shown in Fig. 1(e). 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.(2021) higher trap depths than for both bi-vacancy and V_F center will be anticipated. However, if instead of Fig.1 (e) arrangement one adopts the configuration of Fig.1 (g) in which too 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 I-V pair (nnn arrangement), being far away from the anion vacancy, a trap depth value close to bi-vacancy and V_F center maybe explainable and three equal trap depths are understood.

3. Results & Conclusion

Three trap configurations with near equal trap depths have been identified. The TL peaks observed by Somera et al. (2015) forund oped NaCl system have been assigned these three trap configurations.

Two of the above three trap configurations however involve the role of divalent impurities. Such an involvement may be expected as NaCl samples in the work of Somera et al.(2015) were not extra pure as of earlier workers Mehendru & Radhakrishna (1969). Some stray impurities may well be expected in the works of Somera et al. (2015) above to take care of formation of $V_F$center and anion vacancy linked to I-V pair at nnn position.

Different theoretical and experimented studies of Pandey et al. (2021), Herman & Barnett (1982) & Kanzig (1960) give insight into trap configurations in NaCl and

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help in explaining different TL traps with equal depths and support the idea of bi-vacancy, V_F center and I-V pair linked anion vacancy respectively.

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