THE STRUCTURE OF THERMOLUMINESCENCE TRAPS IN AQUEOUS GROWN KCl

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Abstract: The results of TL studies in aqueous grown undoped KCl crystals are reported. A de-convolution of TL curve into five component peaks has been performed and trap depths have been obtained. The importance of bi-vacancy has been established as a fundamental trap and its anion vacancy end has also been proposed as a suitable trap for thermoluminescence in KCl crystals. The traps at anion vacancies linked to impurity vacancy I-V pairs have also been envisaged and the shift in the depths of traps is attributed to the electric field of I-V pairs in the lattice caused by inherent divalent ions. Some traps linked to hydroxyl groups have also been identified.

Keywords: Traps, TL, bi-vacancy, I-V pair. stark effect, hydroxyl groups

1. Introduction

A trap, in general, implies an imperfection in the regular spacing of atoms / ions that make up the solid. It can capture and immobilize an electron or hole and prevent its recombination with the carriers of opposite charge as electron- hole pair. Electrons and holes may break free traps quickly, or they may remain there for an extended period. The charge carriers can be released from traps by irradiating the solid with light or by heating it. Traps play a major role in photo conductance, luminescence and also operation of various electronic devices.

Thermoluminescence (TL) involves exciting electrons in traps to the conduction band on heating, and these finally drop to traps or recombination centers (Bos, 2006; Srivastava, 2008). Even if recombination occurs without the electron reaching the conduction band, the requirement of trap is quite necessary to observe the phenomenon of TL. Further, electrons must stay in the traps for sufficient time.

No study seems to be available to discuss the structure of traps even in an elementary system like KCl. In an earlier work TL is reported in pure and impurity doped KBr and NaCl crystals (Mehendru & Radhakrishna, 1969). So far KBr system is concerned, the peaks at 90°C and 150 °C are assigned to first and second type of F-centers respectively for pure as well as doped crystals. But the structure of such centers is not described. Further, TL studies are reported in suprapure RbBr (Sastry &

Sapru, 1979). Two prominent peaks were observed by these workers but no explanation is provided about the structure of corresponding traps. Further, TL studies are available in a number of alkali halides (Deshmukh and Moharil, 1985) without any specific information about the structure of traps.

Other pioneers in the field (Jain and Mehendru, 1965) report two types of defects in pure KCl, giving TL peaks at 135°C and 190°C, but again structure of traps has not been elucidated. TL studies are further provided for Harshaw KCl crystals irradiated with gamma rays (Austin and Alvarez Rivas, 1972) and the role of F-centers as recombination centers is reported in annealing process. Optical and thermoluminescence properties of a NaCl crystal doped with cadmium and manganese ions and exposed to gamma rays are recently reported (Ortiz et.al, 2007). These workers have indicated the role of interstitial defects in creating thermoluminescence through recombination with vacancies. Some headway about the nature of defects for TL is however sought (Benia et. al, 2010; Wosinski, 1989) and TL traps seem to be situated near dislocation sites in the lattice.

Few workers of our group (Pandey et. al, 2017) have reported the importance of bi-vacancy traps in alkali halide crystals through a comparison of TL spectra in nominally pure KCl and that with large manganese content. A theoretical model has also been developed (Pandey et.al, 2021) to highlight the importance of bi vacancy traps in alkali halides.

In the present work, we have made fresh TL studies in undoped KCl crystals grown through aqueous technique. The importance of bi-vacancy is further established. The effect of impurity-vacancy (I-V) pairs in affecting the trap depths is put forth. Further, the role of hydroxyl groups in causing large trap depth centers is highlighted.

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2. Role of Traps In Tl

2.1   Importance of bi-vacancy

The prominent point defects in alkali halides like KCl are of Schottky type i.e. cation and anion vacancies. These should be produced in equal numbers in a KCl 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. In KCl crystal doped with divalent cations an anion vacancy has two options, it could combine with a free cation vacancy to form a bi-vacancy or else link with cation vacancy end of I-V pair. The increase in concentration of I-V pairs due to doping would lead to more anion vacancies getting linked to I-V pairs through their cation vacancy end. The doping of divalent cations would thus decrease the relative concentration ofbarebi-vacancies in an alkali halide. Such a process would proceed effectively during growth of crystals from aqueous solution, wherein the growth takes place at a constant temperature. Such a situation may not be possible in melt grown crystals where growth takes place in a temperature gradient. The decrease in concentration of bivacancy in KCl crystals with appreciable manganese impurity content has actually been verified (Pandey et al., 2017).

A number of workers (Gourary and Adrian, 1957; Herman and Barnett, 1982) were involved in theoretical estimation of energy levels of electrons trapped at anion vacancy sites in alkali halide crystals e.g. NaCl, KCl. Rb Cland KBr etc. with face centered cubic structure. In such crystals positive cations and negative anions are alternately arranged in three dimensional pattern.Fig.1 shows such as arrangement in (001) plane of KCl lattice.

The energies of the levels 1s, 2p and 2s of electron trapped at anion vacancy have been theoretically calculated (Herman and Barnett, 1982). They found the energy of 2s level to be close to the conduction band as -0.277 eV in KCl. Earlier, other workers (Gourary and Adrian, 1957) estimated only two bound states for F-center. Recently, through DFT calculations in a different context it is reported that an s-state of F-center (anion vacancy) in KCl is close to the conduction band (Hoya et al., 2017).

A vacancy-pair as above is a suitable trap for electrons in KCl lattice and helps in forming a cation vacancy coupled F- center. The electrons of such F-centers would not be able to fall to the lower states as in a unique F-center (bare anion vacancy), because normal selection rules for electron transitions may not apply here. This breaking of selection rules is perhaps due to the fact that the field at the anion vacancy site of bi-vacancy is neither Columbic nor a constant spherical well type.   So, a 2s level of such a TL center in KCl is likely to act as an ideal trap for electrons near the conduction band. The TL centers in such ideal traps will exist for a long time and participate in TL emission.

2.2   Role of I-V pairs

The I-V pairs could combine with anion vacancies to form an arrangement linking anion vacancy with ann (nearest neighbor) I-

V pair or else with nnn (next nearest neighbor) I-V pair also termed as Z_1 center (Bushnell, 1964).

When a KCl crystal is irradiated with high energy radiation, electrons liberated could be trapped at free anion vacancy, anion vacancy end of bi-vacancy or at anion vacancy linked to I-V pair combination. The electron trapped at secluded anion vacancy is shown in Fig. 1(a) and that trapped at bi-vacancy is shown in Fig. 1(b). The Figs. 1(c) and 1(d) further describe the two arrangements of electron trapping at anions linked to differently placed I-V pairs.

In a divalent cation doped KCl, there would be plentiful I-V pairs in the lattice. Now if a doped KCl crystal is exposed to ionizing radiations to create F-centers, some of these F-centers would also be under the influence of the electric field of I-V pairs, whether nn or nnn type.
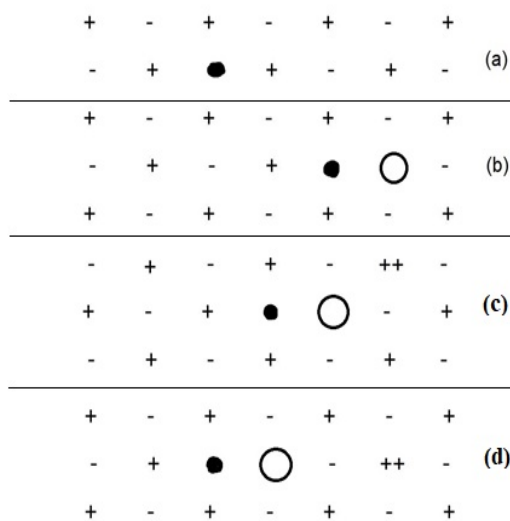
Figure 1. Arrangement of ions in (001) plane of KCl lattice. Alkali ions are shown as +   and negative halide ions as -. The vacant sites are shown as circles. The electron occupying the defect is shown by a dot, possible defects being (a), (b), (c) and (d) viz. (a)secluded anion vacancy (b) bi-vacancy (c) anion vacancy linked to I-V pair at nn position and (d) anion vacancy linked to I-V pair in nnn position.

2.3   Increased depth of 2s level in bi-vacancy

A secluded anion vacancy cannot be a stable trap as the electron inside would decay via optical and phonon radiations. An anion-cation vacancy pair, also called bi-vacancy is however a suitable trap for electrons in KCl-like lattice which helps in forming a cation vacancy coupled anion vacancy F-center, as shown in Fig.1 (b). In our recent work (Pandey et. al.,2021), it has been theoretically estimated that if we consider a bi-vacancy instead of the single anion vacancy, the electrons in the trap are under the influence of a spheroidal well whose effective potential depth is reduced and simultaneously width is increased, as compared to that of a secluded anion vacancy. This change in the structure of defects is able to explain the observed TL trap depth values.

3. Effect of Internal Electric Field on Tl Center Levels

An impurity vacancy (I-V) dipole would exert an electric field at its neighborhood. In KCl containing divalent cations, there would be plentiful of I-V pairs. If I-V pairs are coupled to a TL center, its energy levels would be affected by the said internal electric field.

Assuming, electric field due to I-V pair to be uniform at the site of anion vacancy, its effect will be zero on the energy levels of electron at TL center, in first order perturbation theory. However, under second order perturbation theory quadratic field effects would be operative and non-zero correction to energy levels are expected (Davydov, 1965). Such a situation would arise for TL center perturbed by internal electric field of I-V pair as per Figs. 1(c) and 1(d).

Now, if an F- center were exactly hydrogen like, its 2s and 2p levels would be degenerate and this condition would lead to creation of three levels under electric field. However, the real situation is different. The site potential over a secluded anion vacancy center is not spherically symmetric but is octahedral due to the effect of charges in the neighborhood in an alkali halide lattice. Nevertheless earlier workers (Herman and Garnett, 1982) obtained certain conclusions about energy levels of F- center.

The 2s and 2p levels are not degenerate in a F- center and the effect of internal electric field (F) has to be considered. In second order perturbation theory (Davydov, 1965), the effect of relevant 2s level would be

$$\frac{<2s|ezF|2p_o><2p_o|ezF|2s>}{E(2s)-E(2p_o)}$$

where the symbols have their usual meanings and $2p_o$ is the 2p level component for m=0 and does contribute to energy shift. The m = ±1, 2p levels do not contribute to all, due to selection rules. The hydrogen atom functions have been used for solving the involved integrals and the energy shift obtained is

$$\frac{4}{9}\frac{(<ezF>)^2}{\Delta E}$$

ΔE being the original energy separation between 2s and $2p_o$ levels. The 2p (±1) levels are unaffected by I-V field. , but $2p_o$ level is shifted downwards. Our present interest is however only on 2s levels, over which the electrons get trapped before TLemission.

4. Experimental

Earlier preliminary studies in KCl system (Pandey et. al., 2017) report two broad peaks in the TL spectrum. The higher temperature peak was completely eliminated on heavy doping. In the present work, experiments are repeated for undoped KCl and the TL curves obtained are de-convoluted and further analysis done. The KCl used was analar grade of Fischer Scientific Co., and contained stray 0.001% divalent cations Ba, Ca and Pb as impurities. All the samples were irradiated with 20 mA, 30kV X-rays at room temperature for production of color centers in them, the irradiation being done for about 900 seconds. For all samples as above, TL measurements were made with a home- built TL apparatus with a heating rate of 30°C /minute.

The TL output was enhanced by IP21photomultiplier tube and resulting signal in terms of charge collected was plotted in a recorder as a function of temperature. The heating rate was the same as in our (Pandey et al., 2017) earlier work and that adopted by other workers (Furetta et al., 1999), while investigating TL of OH- doped aqueous grown alkali halide crystal and gave fine contours for TL plot. Large exposure time of 900 seconds was necessary, so that anion vacancies associated with small number of bi-vacancy I-V pair hybrids due to low impurity concentration could also acquire electrons for TL response.

Our samples were prepared through slow evaporation of saturated aqueous solution of KCl at a fixed temperature of 10°C. The number of defect types was small, reflected by fewer numbers of deconvoluted peaks. It may be mentioned that the recent results (Ortiz et al., 2007) of NaCl containing divalent cations in melt grown crystals exhibited complex TL pattern. These authors do expect the role of many more defects needing further explanation.

The TL results for undoped KCl with stray impurities show two broad peaks as given in Fig. 2, there been no TL response above 440 K. The duo of TL curve peak was deconvoluted using the first order Glow Fit software (Puchalaska and Bilski, 2005). This led to five component peaks with FOM of 1.3%. Fig 2 shows composite duo TL curve and five component peaks together in the same figure.
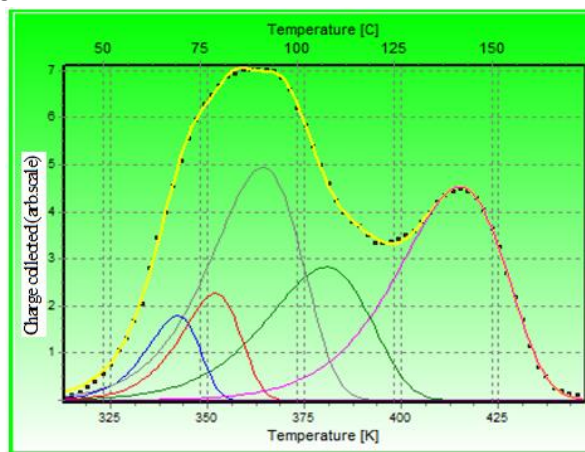

Figure 2. TL Glow curves for KCl systems with stray impurities and irradiated by X-rays. The de-convoluted peaks obtained by Glow Fit program are also seen.

5. Results

The temperatures of all the five component TL peaks and their trap depths are given in Table 1. Along with the TL data for melt grown KCl systems (Jain and Mehendru, 1965).

The peak at 415K is attributed to electrons trapped at an anion vacancy end of bi-vacancy. Such a peak was however, eliminated in samples with heavy doping of divalent cations (Pandey et. al.,

2017). The peaks involving linkage of anion vacancy with nnandnnn I-V pairs are also observed. We also attribute two other peaks to linkage of anion vacancy with OH⁻ ions, the corresponding details being given in the next Sec. 5.2. Such TL peaks cannot be observable in melt grown crystals.

Two TL peaks at 408 K and 463K are reported(Jain & Mehendru, 1965) in pure KCl. The corresponding trap depths are given in Table 1 for comparison.

5.1   Special features of trap assignments

(i)   Bi-vacancy linked traps have a unique presence.
(ii)   This bi-vacancy trap seems to be similar to the first stage F-center as discussed by earlier workers (Jain and Mahendru, 1965).
(iii)   The OH⁻ linked defects are also found.

5.2   Role of hydroxyl ions in blocking the I-V pair formation

Ba²⁺,Sr²⁺ and Ca²⁺ ions have strong affinity for OH⁻ groups. Thus I-V pair anion vacancy link is probably eliminated for such ions through the formation of strong combination chain in the KCl lattice as:

anion vacancy--------H⁺ --------O²⁻ -------AE²⁺
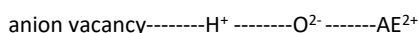
AE²⁺ being an alkaline earth ionwhich perhaps prohibits linking of anion vacancy with AE²⁺ I-V pair due to its own affinity with hydroxyl group. In our work the trap depth observed for OH⁻ sites linked to anion vacancy are quite large. This probably supports earlier conclusions (Dharet. al., 1973) that OH⁻ ions act as deep traps and consequently have a quenching effect on TL peaks. Such peaks have much decreased intensity in TL spectra. Our work thus also supports the role of hydroxyl impurities in TL behavior of LiF (Stoebe et al., 1985).

6.   Discussion

The depth of 2s level in a unique F-center (anion vacancy) with neighbourhood of six positive charges in KCl crystal is 0.277 eV. It however seems that, the absence of one cation from the immediate neighbourhood of anion vacancy as in Fig. 1(b) leads to the increase in the depth of 2s trap level in F-center to 1.05eV; of course if there be no I-V pairs around. This happens for bivacancy trap. The possible I-V pair link lifts the trap due to the effect of electric field as described in section 6.1.

If we compare the trap depths for F-center in KCl as per different workers, we find that 415K glow peak of present work is close to 408K glow peak in earlier work (Jain & Mehendru, 1965), the corresponding trap depths being quite close. In this work a peak was observed at 463K too. Its presence is probably due to the fact that their KCl crystals were grown through melt and are likely to include extra defects which lead to the creation of second stage F-centers with a trap depth of 1.15 eV.

6.1   Observed trap depth changes due to I-V field:

But for traps linked to HO⁻ (written knowingly) groups, depths of traps in our case are found in the range 1.05eV to 0.92eV. Figs. 1(c) and 1(d) show I-V pairs with nn and nnn arrangements respectively. The classical electric field expressions Fnn and F_{nnn} at the site of anion vacancies centers fornn and nnn I-V pair arrangements were derived by us based on point charge model as

$$F_{nn}= K ((2\sqrt{5})/25 - 1) e/ d^2$$
$$\text{and } F_{nnn}=K (-8/9) e/ d^2$$

with $K= 1/ (4\pi\varepsilon_0)$, 'e' as charge of electron and 'd' being the distance between K⁺ and Cl⁻ ion, giving

$$F_{nn}^2 = 0.67K^2e^2/d^4$$
$$F_{nnn}^2 = 0.79K^2e^2/d^4$$

It may be realized here that for nnn disposition of cation vacancy, the anion vacancy is located at the end-on position of I-V dipoles as in Fig 1(d). But, for nn disposition, the situation is quite different as described in Fig 1(c).

However, as seen from Table 1, the effect of I-V field (as in Sec. 3), seems to support the trap depth changes from nn to nnn arrangement; the traps with nnn I- V pairs being shallower than those with nn pairs. The 0.96eV trap depth should thus correspond to nn configuration of I-V pair and 0.92eV trap depth to nnn configuration. The proposed configurations as in Table 1, seem to follow the above behavior due to stray ions as per quadratic Stark effect. It seems alkaline earth ions do not form I-V pairs due to the effect of hydroxyl ions and give TL peaks differently.

Table 1. Observed TL Peak Positions in KCl systems with depths of traps & their structures
(Heating rate being 30˚C/minute in present work)

Sr. No.	Status of Host	Peak Temperatures (⁰K) of sole or de-convoluted Peaks	Trap Depth (eV)	Anion Vacancy linked to
1.	Negligible I-V pairs	415	1.05	cation vacancy
2.	With I-V pairs of stray impurities	342	1.49	OH⁻
		352	1.38	OH⁻
		364	0.96	Pb²⁺I-V pair(nn)
		381	0.92	Pb²⁺I-V pair(nnn)
3.	With first type of F-centers	408	1.05*	
4.	With second type of F-centers	463	1.15*	

* (Jain & Mehendru , 1965)

7. Conclusions

The different configurations of TL traps obtained are as under Unique F-center (anion vacancy), which is probably not much stable.

(i) Bi-vacancy being the main trap configuration.

(ii) Two hybrid configurations of bi-vacancy and I-V pairs.

(iii) In aqueous grown crystals OH⁻ also seems to link anion vacancy with divalent cations and provide new trap.

A good dosimeter must have a large number of traps. In alkali halides the bi-vacancies are natural traps. The traps can be increased by doping alkali halides by divalent cations, when cation vacancy traps coupled to I-V pairs are created. For I-V pairs to exist, their aggregation should be avoided .This may be avoided by doping different kinds of ions at a time. The doping of trivalent ions could further be useful, as one such ion would hold two anion vacancies together. The present work thus also points towards developing good alkali halide dosimeters.

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