CHAPTER 2

RÉSUMÉ ON DEFECTS IN ALKALI HALIDES

In this chapter, an attempt will be made to survey the present day conceptions regarding the imperfections in alkali halides, with a special stress on their bearing on the mechanism of luminescence in KCl:Tl.

The majority of the alkali halides crystallize in the rock salt structure, and potassium chloride belongs to this group. Each potassium ion (cation) is surrounded by six nearest - neighbour chlorine ions (anions) and each anion, by six nearest - neighbour cations. The cations and anions are each situated on the points of separate face centred cubic lattices, and these two lattices are inter-leaved with each other.

2.1 Energy Levels in KCl

A neutral chlorine atom possesses five 3p electrons, while a negative chlorine ion has six 3p electrons. In a crystal of KCl, consisting of N negative Cl^- ions and N positive K^+ ions, these 3p levels of the Cl^- ions give rise to bands containing 6N levels which will be completely filled by the 6N electrons at absolute zero temperature.

At the same time, whereas a neutral potassium atom has one 4s valence electron, a positive K^+ ion has a vacant 4s level. In the crystal, the vacant levels of the N potassium ions combine to form a band of levels which will be completely empty at absolute zero temperature. Between the highest occupied level and the lowest vacant level in the crystal there is a zone of forbidden energy[11]. The large width of the forbidden gap in alkali halides (8.5eV for KCl), distinguishes them from other solids, and affords greater facility for the study of defects by optical methods, not possible in the case of good conductors.

The only energy levels that can possibly be localized in the forbidden gap, and which are characteristics of a perfect ionic lattice are the exciton levels.

2.2 Point Defects

On raising its temperature, the crystal departs from the idealised structure, owing to the thermal vibration of the lattice. This thermal energy creates the point defects - vacancies and interstitials. The free energy of a crystal at high temperature is reduced by the presence of the vacancies inside the crystal. In other words, the thermal equilibrium of a crystal at any temperature demands the creation of a finite number of vacancies in the crystal. The equilibrium number of vacancies will therefore be temperature-dependant.

Schottky defect consists of a pair of positive-ion vacancy and a negative-ion vacancy without the compulsion of their being in the immediate neighbourhood. Frenkel defect arises when a positive or negative ion is displaced from its normal site and made interstitial. While vacancies can be formed in crystals of all structures, interstitial atoms or ions require suitable interionic or interatomic voids for their formation. As the ionic radii of alkali ions (K = 1.33 A°) and halide ions (Cl = 1.81 A°) are nearly equal, interstitials are not encouraged in NaCl and KCl. Nevertheless, Frenkel defects are suggested to be created along with Schottky defects, in KCl or NaCl during bombardment with high energy particles[12], at temperature of liquid helium.

2.3 Production of Point Defects

At high temperatures, the number of vacancies in thermal equilibrium is large. One method of producing vacancies in a crystal is by quenching it from a high temperature. During the quench, the defects which are in equilibrium at the high temperature are retained or "locked" inside the crystal. Consequently the concentration of vacancies at the lower temperature, to which the crystal is quenched, will be greater than the equilibrium number corresponding to that temperature.

The above defects can also be produced by processes such as plastic deformation or exposure to ionizing radiations.

On deforming the crystal, while the lattice retains its general crystalline nature, numerous defects are introduced into the specimen. Of the two types of dislocations resulting from plastic deformation, the edge dislocation and the screw dislocation, the former one is more relevant for ionic crystals.

The distortion in the otherwise perfect structure may be visualised to have been due to the introduction of an extra half-plane of ions somewhere into the body of the crystal, perpendicular to a slip plane. Most of the distortion is concentrated along the edge of this half-plane,and the internal boundary of this plane is known as the dislocation line. As the region near the edge of the dislocation line does not possess the regularity of the perfect lattice, it is possible for extra ions of both signs originally situated at points in the perfect region, to get attached to the edge, thereby shifting the region of irregularity inward. This results in the movement of the dislocation line towards the interior of the crystal. In short, during dislocation climb when the dislocation line moves into the crystal, it creates vacancies in the crystal, and when it moves out of the crystal it absorbs vacancies present in the crystal. The vacancies formed due to the above mechanism are free to diffuse into the bulk of the crystal at room temperature.

It is possible that the dislocation line, instead of being in one specific plane of ions, crosses over to the next plane of ions. The point at which this jump occurs is known as a 'jog'. For an edge-type dislocation therefore, the length of the extra half-plane of ions associated with it, differs by one interionic distance on opposite sides of the jog.[13]. Jogs can act as perfect sinks for point defects. Point defects, once attracted to an arbitrary dislocation site, will migrate along it towards the nearest jog to be absorbed. Interaction of vacancies with dislocation jogs will be especially important in ionic and polar crystals. Since a jog can have an effective charge of either sign, it can have a strong electrical interaction with the point defects.

Dislocations can influence the concentration of lattice defects to a large extent, either by the dynamic moving-jog mechanism or by their activity as static generators of point defects. According to Seitz[14], "dislocations apparently are of primary importance in one of the most vital properties of the alkali halides, namely, their ability to darken under the action of ionizing radiations".

2.4 Effect of Ionizing Radiations on Potassium Chloride

A comparison of the absorption spectrum of an alkali halide crystal before and after exposure to radiations like ultraviolet rays or x-rays, show that strong absorption bands are introduced into the crystal by the irradiation. The character of the absorption spectrum is very much dependant on the temperature at which the crystal is irradiated. Absorption bands, produced during irradiation below room temperature, do not appear if the irradiation is performed at room temperature. The localised defect centres situated within the forbidden energy band, and which are responsible for the above absorption band giving rise to a colouration of the crystal, are the well-known colour centres.

Of the large number of optical absorption bands which have been studied, none appears over the entire range from room temperature to liquid helium temperature so prominently as the F band. The F band thus occupies a key position with respect to colour centre phenomena at all temperatures. The F absorption band in KCl has the peak at 540 mμ (vide Table I) at room temperature, and the centre responsible for this band consists of an electron trapped at a negative ion vacancy. When energy is absorbed in the F band of the crystal, the principal electronic transition raises the electron from 1s ground state to the 2p excited level which is situated few tenths of an electron volt below the conduction band.

Careful measurements have revealed a small hump at the short wavelength side of the F band and three additional, well-resolved but very weak absorption bands at wavelengths still shorter than that of the hump. The hump is called the K band and is best resolved in chlorides and less-resolved in bromides and iodides. The three weak bands on the high energy side of the K band are termed L_1, L_2, and L_3 bands. Lüty suggests that the F and K bands are due to transitions of the F centre to higher bound excited states, resulting in very

TABLE I

Major characteristics of the prominent absorption bands arising from trapped-electron and trapped-hole centres in KCl.

Fundamental absorption edge ... 167 mμ

Centre	Wavelength of the absorption peak mμ	Favourable temperature for formation °K	Maximum temperature for thermal bleaching °K
L_4	190	93	
L_3	251	93	
L_2	288	93	
L_1	344	93	
K	457	93	
F	556	93	
F'	750	170	200
R_1	658	300	320
R_2	727	300	320
M	825	300	400
	177	90	150
	166	90	
V_1	356	77	173
V_k	365	77	133(KCl) 208(KCl:Tl)
V_2	230	300	
V_3	212	300	
V_4	254	90	216
H	345 (30°K)	5	57

... contd.

Centre	Wavelength of the absorption peak $m\mu$	Favourable temperature for formation ^{o}K	Maximum temperature for thermal bleaching ^{o}K
'OH'	204		
U_2	216 (from OH)		100
Z_1	590	300	383
Z_2	610	180 or 353	383 without U 523 with U
Z_3	500	183	

little photoconductivity at low temperatures[15]. The L bands, he suggests, are due to transitions of the F centre electrons to free or unbound states, which give photoconductivity even at the lowest temperatures. Klick and Kabler[16] present a model for L bands as being combinations of the usual F band transitions, which transfer the F centre electron to a neighbouring alkali ion, and the raising of the resulting alkali atom to various excited states. The characteristics of these bands are given in Table I.

Illumination of a KCl crystal containing F centres with light in the F band at 173°K causes a decrease in the F band height and a broad band on long wavelength side appears. This is the F' band. The thermal activation energy at the above temperature is of the order of 0.02 eV. Hence at temperature around 170°K, the electron trapped at the F centre, when excited to the higher level, instead of being thrown into the conduction band, is retrapped by another F centre to form the F' centre. F' centre is stable only at low temperatures, and it decomposes on warming to 200°K, regenerating F centres. The $F \rightarrow F'$ conversion is effective only above 143°K.

Production of F band in alkali halides simultaneously creates another band on the low energy tail of the exciton band, and this is termed the β band. Partial bleaching of the F band at low temperature produces a band on the lower energy side of the β band, called the α band. The parallel occurrence, bleaching, and regeneration of the F and β bands, and the quantitative relationship between these bands suggest that the β centre is directly connected with the F centre. Anion vacancies in isolated sites can be considered to be responsible for α centres . The thermal destruction of the centre at low temperature — 150°K in the case of α centres in KCl — can be caused by the diffusion of isolated vacancies so as to form vacancy pairs. Since plastic deformation is believed to generate vacancies, one might expect to observe α band after deforming a crystal at low temperatures ($\approx$ 100°K). The α and β absorption bands are considered to be due to excitonic transitions on the ions neighbouring a negative ion vacancy and F centres respectively. In other words, the α centre is an exciton trapped at a negative ion vacancy and the β centre is an exciton trapped at an F centre.

While illumination of a crystal containing F centres at low temperatures generate F' centres and α centres, the bleaching of F centres, if performed at room temperature, yields a family of optical absorption bands appearing on the long wavelength side of the F band. These are designated as the R_1, R_2, M, and N bands. One of the characteristic features of this photochemical reaction is that the product centres are created simultaneously, and that the process is accompanied by an ionic motion. This reaction is in contrast to the $F \rightleftharpoons F'$ transformation which is characterized by the pure electronic process in a crystalline field. Based on the fact that these absorption bands appear to be the products of F centre coagulation, created at the expense of the F band, Seitz[14] made tentative proposals for the models of these centres. The kinetics of coagulation of F centres helped Seitz to suggest that the R_1 centre was an electron trapped at a pair of negative ion vacancies and that the R_2 centre consisted of a pair of F centres. The M centre, according to Seitz, has an L shaped configuration, and may be viewed as an aggregate of an F centre with a neutral pair of positive and negative ion vacancies. Implicit in the above models are the asymmetries of the M and R centres, and the prediction that the luminescence of these centres should be polarized if the exciting light is polarized.

Van Doorn and Haven[17] have proposed that the M centre will be of the configuration same as that of R_2 centre suggested by Seitz. This proposal is based on the thermal equilibrium between F and M centres in KCl for various F centre concentrations. The quadratic variation of M centre concentration with that of F centre is consistent with van Doorn's model. Further, this model is in accord with the requirement of inversion symmetry[18], the absence of dielectric loss[19], and inconclusiveness of electron spin resonance of the M centre[20].

The M absorption band maximum for KCl is at 820 mμ. During the room temperature illumination into this absorption band, M centres are partially converted into F centres and partially into R_1, R_2 and N centres. The M centre is highly stable upto 400°K, beyond which it is transformed into an F centre.

The theories for R and N centres have not yet been forthcoming. Van Doorn finds that the F centre luminescence, excited by F band light at low temperatures, loses its efficiency by the presence of M or R centres in the crystal. Further, if the exciting F band light is polarized the resulting emission is also polarized. An explanation put forward by van Doorn envisages higher excited states of M and R centres which lead to absorption bands hidden under the F band. A final pronouncement on these centres has to wait for further investigations on the interaction of electron-trapped centres.

For all the centres that are discussed above, the absorption is due to trapped electrons. Ionizing radiation can as well generate centres due to holes trapped by positive ion vacancies. This group of centres is generally known as V centres. The temperature of irradiation more or less determines the type of V bands that are formed by ionizing radiation.

Irradiating a KCl crystal at room temperature produces the V_3 and the V_2 bands, having the peaks of their absorption bands at 212 and 230 mμ respectively (Table I). The V_3 band dominates over the V_2 in strength. Evidently, these centres are generated along with the F centres. According to Alexander and Schneider[21], F bands can be eliminated completely by the application of an electric field of 2000 volts/cm during irradiation with F light. Field ionization affects only the F centres, and V centres remain unaltered.

Irradiation of alkali halides at liquid nitrogen temperature produces a prominent V_1 band and smaller V_2 and V_3 bands, together with F and F' bands. The V_1 band in KCl becomes thermally unstable at 128°K and it is completely bleached at 173°K and above. The centre has an absorption maximum at 356 mμ.

Warming the crystal after irradiation at liquid nitrogen temperature results in the growth of the V_3 band and decrease of the V_2 band. This phenomenon probably is due to the thermal release of electrons from F' centres or other electron-trapped centres[22].

Lüty[23], Damm and Tompkins[24] have suggested that V_2 and V_3 bands, the only two prominent bands due to holes observed after irradiation at room temperature, are attributable to the presence of impurities in the crystal. Recently Nadeau[25] has observed that these bands do not appear in the crystals when the impurity content of the crystal is reduced considerably.

According to Seitz[14], V_1 centre consists of a positive ion vacancy that has trapped a positive hole, and hence it can be looked upon as an 'antimorph' of the well-established model of the F centre. V_2 and V_3 centres are the counterparts of Seitz's models for R_2 and R_1 centres respectively. Other models[26] for V centres have been proposed by Varley, Nagamiya, Burstein and Oberly. The details of the properties of the above mentioned V centres are at present not so well-understood, as the corresponding ones for F centres, in spite of considerable amount of research on these centres.

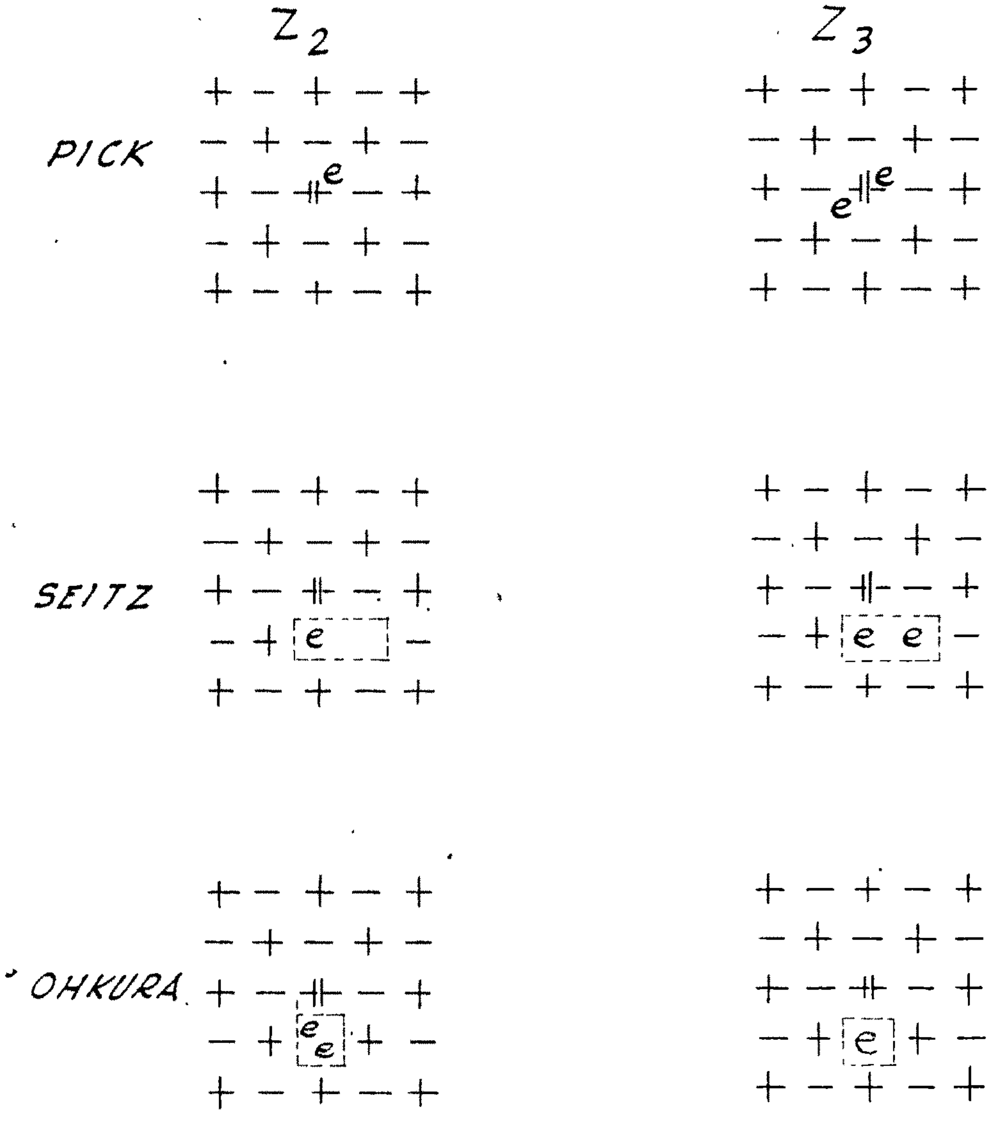
During the irradiation of a pure KCl crystal at liquid nitrogen temperature, it is possible for some of the electrons from the 3p shell of chlorine ions to be ejected. Many such ejected electrons can immediately combine with the holes in the 3p shell; but others will be trapped in other parts of the crystal. The resulting chlorine atom associates with an adjacent negative chlorine ion. To be precise, the electron deficiency is shared by the chlorine atom and the adjacent chlorine ion, so as to form a Cl_2^- molecule-ion. Due to the trapped hole, the distance between the constituents of the halogen molecule-ion is reduced from the normal value of 4.4 A° to 2.16 A°. This may be expected, since the Coulomb repulsion between the Cl^- ions is diminished[27]. It is interesting to note that the efficiency of formation of these centres, known as V_k centres, increases ten-fold in KCl, by the introduction of impurities such as Ag^+, Tl^+ or Pb^{++} into the crystal[28]. As the impurities act as efficient electron traps, probability for annihilation of the hole trapped at the centre is reduced. The absorption band relevant to this centre has the peak at 365 $m\mu$ in KCl, and slight variations are effected by the presence of impurities. Thermal bleaching of the V_k centres occurs in pure KCl at 133°K and in KCl:Tl at 208°K. The difference in the bleaching temperatures are considered to be due to differences in the retrapping and recombination processes. At these temperatures, recombination of electrons and holes at Cl_2^- centres takes place, accompanied by a maximum in the emission[28].

There are other centres giving rise to absorption, that are exclusively due to the presence of impurities in the crystal. In fact, the following are often considered as desiderata of a 'pure' crystal:

(a) absence of optical absorption bands, (b) poor F band production after exposure to ionizing radiation, (c) absence of optically excited fluorescence, and (d) low extrinsic ionic conductivity[29].
Absorption bands at 185 mμ in NaCl and at 204 mμ in KCl are found in all synthetic NaCl and KCl crystals grown without the intentional addition of impurities. The impurity responsible for this absorption is suggested to be the hydroxyl ions and the band is termed the "OH" band or the hydroxyl band[29]. It has been established recently[30] that oxygen and moisture together encourage the increase in the "OH" band which is proportional to the length of time the melt is exposed to oxygen and moisture. Specific configuration of the absorbing centre has not yet been established.

The absorption band having a maximum at 216 mμ in KCl is known as the U band. U centre has been studied extensively by Hilsch and Pohl[31], and is considered to be an H^- ion occupying a halogen ion site substitutionally. U centres can be converted into F centres by irradiation with U band light.

Foreign metal ions, atoms or molecules incorporated into alkali halides may form deep-lying trapping centres for electrons or positive holes which are liberated by ionizing radiations. Dielectric loss measurements[32] support the view that at low temperature charge compensation is realized by the more intimate combination of divalent ions such as Sr^{++}, Ca^{++}, and Pb^{++}, with a positive ion vacancy in the nearest (110) or next nearest (200) neighbour positions. A complex formed by KCl:Sr^{++} yields Z centres by capturing electrons. Optical irradiation of impurity-doped crystals containing F centres with F light generates Z_1 centres. If this crystal is then heated to around 380°K the Z_1 centres are destroyed, some of the F centres are re-formed and Z_2 centres appear. According to Pick, Z_1 centre consists of an F centre adjacent to a divalent ion, and Z_2 centre consists of an electron captured by a divalent ion. Seitz identifies his model for Z_1 centre with Pick's model for Z_2, whereas Seitz's



MODELS FOR Z_2 AND Z_3 CENTRES, ACCORDING TO PICK (REF. NO. 33); SEITZ (REF. NO 33) AND OHKURA (REF. NO 35)

FIG. 1.

Z_2 centre model consists of Pick's model for Z_2 plus a vacancy pair[33]. Kojima[34] proposes an interstitial neutral alkaline earth atom for the Z_2 centre. She suggests a singly ionized positive alkaline earth ion, located at an interstitial, as the Z_3 centre. Kojima's model for Z_2 centre is the same as the one suggested by Pick for the Z_3 centre. Z_3 band (500 mμ) is on the shorter wavelength side of the Z_2 band (610 mμ) and has a half-width same as that of the F band. Seitz has proposed that the trapping of an electron by the Z_2 centre converts it into the Z_3 centre. Ohkura[35] has shown experimentally that the Z_3 centre is formed by the loss of an electron by a Z_2 centre. Ohkura's Z_2 centre is an electrically neutral complex consisting of a divalent alkaline earth ion and an F' centre on nearest-neighbour sites. According to Ohkura's model, the Z_3 centre consists of a divalent ion and an F centre, on nearest-neighbour sites. A comparison of the models for Z_2 and Z_3 centres proposed by Pick, Seitz and Ohkura can be drawn from Figure 1.

Since the presence of most of the lattice defects becomes evident in optical or paramagnetic resonance measurements, only after they have trapped electrons or holes, valuable ideas about the nature of the defects present in the crystal can be derived from the mechanism of colouration that operates at the corresponding temperature.

According to Seitz[14], colour centres are formed at dislocation jogs as a consequence of "thermal spikes". The ionizing radiation produces excitons, which on travelling through the crystal meet dislocations, become trapped there and lose their energy in a burst of lattice vibrations. This local heating, which is also known as thermal spikes will be sufficient to cause climb of dislocations, thereby generating vacancies. As per Seitz's estimate[14], the dislocation has to climb about 1000 atomic distances to account for the production of 10^{18} vacancies cm^{-3}.

Varley[36] suggested a mechanism for the formation of F centres, according to which the radiation will directly ionize a halogen ion e.g., transforming a Cl^- ion into a Cl^+ ion. The electrostatic repulsion from the neighbouring positive ions will force Cl^+ ion into an interstitial position, creating a vacancy thereby. There seems to be a strong evidence that the Varley mechanism operates at least at low temperatures[37,38].

The mechanism proposed by Mitchell, Wiegand and Smoluchowski[39] is a combination of the Varley mechanism and the Seitz dislocation - jog mechanism. They propose that the Varley mechanism will take place near dislocations, the interstitials joining the dislocation core and causing the latter to climb, as in the Seitz mechanism. It will result in the formation of vacancies only, preferentially located along dislocations.