CHAPTER III

IMPERFECTIONS IN ALKALI HALIDES
This chapter gives the survey of the literature on imperfections in alkali halides, with special reference to the imperfections created in alkali halides by irradiating them with different energy radiations. 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 lattice, and these two lattices are interleaved with each other. Any deviation in a crystal from perfect periodic lattice is an imperfection. Real crystals are always imperfect in some respect. The luminescence of crystals is nearly always connected with the presence of imperfections either native or foreign.

(A) **POINT DEFECTS**

On raising its temperature, a crystal departs from the idealized 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 vacancies inside the crystal. In other words, the thermal equilibrium of a crystal at any temperature demands the creation of a
**FIG. VIII**  MODEL OF THE PERFECT ALKALI HALIDE CRYSTAL PERTURBED BY POINT DEFECTS (POINT DEFECTS IN SOLIDS) AS BY CRAWFORD & SLIFKIN
finite number of vacancies in the crystal. The equilibrium number of vacancies will thus be temperature dependent.

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 a negative ion is displaced from its normal site and made interstitial. Vacancies can be formed in crystals of all structures but interstitial atoms or ions require suitable interionic or interatomic voids for their formation. The corresponding point defects in alkali halides are shown in Fig. VIII.

(B) LINE DEFECTS:

Line defects are of two types - (i) edge dislocation and (ii) screw-dislocation. An edge dislocation occurs when a plane of atoms abruptly comes to an end while parallel planes in the crystal continue in normal fashion. For this dislocation Burger's vector $\vec{b}$ is everywhere perpendicular to the dislocation line. A screw dislocation transforms successive atomic planes into the surface of a helix. In this dislocation Burger's vector $\vec{b}$ is everywhere parallel to the dislocation line.

(C) PLANE DEFECTS:

In this case a perfect crystal is deformed in shear by sliding half of it past the other half along the close
Lineage boundary is the boundary between two adjacent perfect regions in the same crystal, which are slightly tilted with respect to each other. The boundary between two crystals in a poly-crystalline solid is called a grain-boundary. The plane separating two incorrectly juxtaposed layers is called a stacking fault.

(D) PRODUCTION OF POINT DEFECTS:

i) High Temperature Quenching:

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 locked inside the crystal. Thus 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.

ii) Plastic Deformation:

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.
Radiation damage studies have contributed significantly in the past to our understanding of defect creation and interaction. In studies of radiation damage, polar crystals are especially useful. These materials, being insulators lend themselves to optical spectroscopy, magnetic resonance, and electro-optical property measurements. Combination of these measurements permit the identification of many defects and thus simplify studies of the interaction of these defects with impurities and among themselves.

When a Polar crystal is subjected to radiation, numerous changes can occur in both the indigenous lattice ions and in the impurities present. The end products of these changes are classified in terms of three categories of defects: (a) electronic defects which involve changes in the valence states (b) ionic defects consisting of displaced lattice ions and (c) gross imperfections like dislocation loops and voids. Each of these types of defects has been observed in Polar crystals.

(a) Electronic Defects:

1) Valence Changes of Impurities in Crystal:

A common product of ionizing radiation is a change of charge state of an impurity in an insulator. The capture
cross-sections of impurities for electrons or holes vary with the type of impurity and the nature of the host lattice, as does the temperature dependence of the stability of the centres.

2) Valence Changes of Lattice Defects:

Imperfections in crystals can also change their nature by trapping electrons or holes. There are reports in the literature of radiation produced changes in the charge states of existing defects in alkali halides. Perhaps the more interesting fact is that free charges can be trapped even in perfect crystals. In the alkali halides characteristic spin resonance spectra and optical absorption bands have been observed due to so called self-trapped holes. It should be emphasised that the self-trapped charges are not lattice defects in the usual sense of involving a vacancy or interstitial, but that the two halide ions (atoms) are displaced from their normal sites so that they have a smaller spacing than the normal negatively charged halide ions. It is to be noted that in order for a self-trapped hole to be produced, the accompanying electron must be trapped at some other defect such as an impurity.

(b) Ionic Defects:

1) Vacancies:

The lattice site of a missing lattice ion or atom is
called a vacancy. Vacancies are probably the best known radiation damage products. Most of the observations of radiation defects in polar compounds have been made on negative ion vacancies. In singly charged compounds, the anion vacancy that contains an electron is known as F-centre \(^{72}\), the centre is uncharged with respect to the perfect lattice. In alkali halides containing impurities, some of the radiation-produced absorption bands with peaks close to that of the F-band have recently been found to be due to F-centres adjacent to alkali impurities. These centres are now generally referred to as \(F_A\)-centres \(^{73}\).

2) Vacancy Aggregates:

In many cases it is possible to produce groups of vacancies by prolonged radiation. Some of the definitions that are often used in connection with aggregates of vacancies are the following. A "vacancy pair" is composed of nearest neighbour anion and cation vacancies. A "divacancy" consists of two nearest neighbour anion vacancies or two nearest neighbour cation vacancies. The term vacancy aggregate can in general refer to anions and/or cations and can include groups of from two to many.

3) Interstitials:

When a lattice atom or ion is displaced from its normal site, it either returns to a normal site (annihilates)
travels to a surface (a grain-boundry or dislocations) or returns to a position that is not a normal lattice site. Such a position is referred to as an "interstitial" site. Frenkel defect is a double defect consisting of vacancy and interstitial. The only interstitial species produced in Polar compounds by radiation that has been carefully studied is not located at a normal interstitial site, but is an interstitial halide ion that has bonded itself to a lattice halide ion and shares that ion's lattice site. This molecular-ion defect occurs in irradiated alkali halides and is called the H-centre. This is to be contrasted to the \((X_2^-)\) hole trap in the perfect lattice, where the two anions have two lattice sites. Itoh and his collaborators have made a strong effort to put the concept of interstitial aggregates on a better experimental foundation, and found that some of the uv-absorption bands observed in irradiated alkali halides are probably due to interstitial aggregates.

(c) Dislocation or Voids:

The evidence for the production of dislocation loops and voids by irradiation is not very strong but the observation of the growth of large macroscopic defects in alkali halides during electron irradiation at high temperature in an electron microscope suggests that radiation produced defects may aggregate in these crystals to form voids or dislocation loops.
(F) RADIATION DAMAGE PROCESSES:

There are in general three generic classes of radiation damage processes. We define these processes as:

1. Electronic Processes
2. Elastic Collisions and
3. Radiolysis.

1. Electronic Processes:

This class includes all processes in which an electronic state is changed or charge is moved about by the absorption of radiant energy, but in which no ionic or atomic defects are formed. The initial step in the production of these defects is the absorption of energy from the radiation field which occurs somewhat differently for various types of radiation. When energy is absorbed in a crystal it appears in the form of electrons in a normally empty conduction band and holes in the normally occupied valence bands, or in the form of excitons at lattice ions, impurity ions or defects in the crystal. In electronic processes, excitation is the first step and must be followed by processes that lead to observable electronic states. This involves separation of the electrons and holes and trapping of the separated charges at impurities, defects or in the perfect lattice. Motion of electron or hole must occur following electronic excitation. Normally the crystal as a whole must remain neutral, hence for every electron trapping centre there must be a corresponding hole centre.
formed. The penetration depth of a particle in a crystal is very important in radiation damage. Difference between heavy particles, electrons and gamma rays having kinetic energies of the order of 1 MeV is the fact that penetration is least in alpha particles whereas maximum in gamma-rays.

(2) Elastic Collisions:

Elastic collisions are those in which atoms or ions are displaced due to momentum and energy transfer from irradiating particles. In order to create defects through elastic collisions, it is necessary for the incident particle to impart sufficient energy to a lattice atom or ion to displace it through the press of its neighbours into an interstitial site.

(3) Radiolysis:

Radiolysis processes are those in which ionic or atomic defects are produced by a series of reactions beginning with an electronic excitation. In radiolysis defect production there must at least be three steps: (a) an electronic excitation resulting at least momentarily in the creation of a polarized or charged electronic defect in the lattice, (b) the conversion of this energy into kinetic energy of a lattice ion in such a way that the ion moves, and (c) the motion and stabilization of the ion,
(G) DEFECT CREATION IN ALKALI HALIDES

The energies of radiation which can excite alkali halides range from uv photons of 10eV to $^{60}$Co gamma rays of 1.25 MeV to high energy photons of 100 MeV. These radiations produce many types of colour centres maintaining simultaneously the charge neutrality of the crystal and do not change the stoichiometry of the crystal.

The investigation of coloration phenomenon with ultraviolet irradiation has been made by many investigators$^{78-80}$. It was believed that ultraviolet light cannot be thought to have sufficient energy to alter the defect pattern of the phosphor during the irradiation. Hence the free unassociated vacancies existing in alkali halides at room temperature were suggested to be responsible for the colour centres. Smakula$^{78}$ first reported the F-centre generation with uv irradiation. Hersh et al$^{81}$ suggested that most of the colour centres that are produced with high energetic radiation like X-rays, gamma-rays, electrons can also be produced with ultraviolet rays.

The rate of growth or the efficiency of the production of colour centres and saturation value observed, depend in a complicated fashion on the type of radiation, the dose-rate, the temperature as well as on the particular alkali halide, on purity of the crystal, on the type of impurity introduced
and mechanical state of the samples. The colour centres initially produced by ionizing radiation can be transferred into other centres by appropriate treatment. At room temperature, this may involve ionic motion, as well as the motion of electrons and holes. At low temperature, where ionic motion is inhibited, the transformations are most likely due to ejection and retrapping of the charges.

According to Seitz\textsuperscript{82,83} 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 efficient to cause climb of dislocations, thereby generating vacancies. As per Seitz's estimate, the dislocation has to climb about 1000 atomic distances to account for the production of $10^{18}$ vacancies $\text{cm}^{-3}$. According to Seitz colour centres would then be produced by capturing of electron or hole at appropriate vacancies forming F- or V-Centres.

Varley\textsuperscript{84} 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 Cl$^+$ ion which would now be in a very unstable situation. The electrostatic repulsion from the neighbouring positive ions
will force Cl$^+$ ion into an interstitial position, creating a vacancy thereby. Population of the vacancy by an electron would then transform it into an F-centre. Making the assumption that practically all doubly ionized ions will produce F-centres leads to the right order of magnitude for F-centre production. There seems to be a strong evidence that Varley mechanism operates at low temperature.

The mechanism proposed by Mitchell, Wiegand and Smoluchowaski is a combination of the Varley and Seitz's dislocation jog mechanisms. They proposed that the Varley's mechanism will take place near dislocations, the interstitials joining the dislocation core and causing the latter climb, as in the Seitz's mechanism. It would result in the formation of vacancies only, preferentially located along dislocations.

In general, the overall picture of radiation induced defects in the alkali halides is as follows:

1. Early stage coloration depends strongly on the type of impurity and concentration as well as on the deformation, radiation temperature, intensity and other experimental conditions. Many of the experiments done on alkali halides deal with early stage since it is sensitive to many different parameters.

2. Late stage F-centre coloration is characterized by a saturation concentration that is a function of dose rate and temperature as well as impurity.
F-centre aggregation as indicated by the growth of $F_2$ and $F_3^-$ centres can be caused by ionizing radiation. It has also been demonstrated that radiation can destroy F-aggregate centres and indeed it is because radiation both creates and destroys aggregates, that an equilibrium obtains between F and F-aggregate centres for given radiation conditions.

Most of the early experimental work was done when the samples were irradiated at room temperature and they were not very pure and the dose rate were not very large. But ironically it is this early stage defect production that is least well understood. It has been now shown that the height of the first stage in material moderately doped with a divalent cation increases as the square root of the impurity concentration. The first stage height is also very sensitive to deformation of the sample.

In the following section, we discuss the current state of understanding of the coloration process in alkali halides doped with divalent impurities which is relevant to the present work. There is a growing interest in the role of impurities in these processes.

It has long been recognised that there is a marked enhancement in the rate of formation of F-centres in alkali halides containing certain alkaline earth impurities. Since the divalent impurity enhances the concentration of...
cation vacancies, one would expect the concentration of anion vacancies to be drastically suppressed. Consequently, on this basis decrease rather than an increase in the rate of F-centre production would be expected in crystals doped with divalent cations. It was therefore concluded that the presence of divalent impurity and the accompanying cation vacancies assist in some manner the creation of anion vacancies by the ionizing radiations. In view of this, various theories were put forward to explain the colorability observed in divalent doped alkali halides. Etzel\textsuperscript{103} suggested that the enhancement of the F-band is due to the production of positive ion vacancies by the divalent impurity which by increasing the chances of hole capture, reduces the rate of direct recombination and allows more electrons to be captured by negative ion vacancies already present in the crystal. A clue to more realistic interpretation was however obtained from the electron spin resonance, of Hayes and Nichols\textsuperscript{104} who found a Cl\textsuperscript{-} molecular ion oriented in the \langle\overline{1}00\rangle direction in divalent impurity doped alkali halides which had been X-irradiated at 195\degree K. The centres seen by Hayes and Nichols are unstable above about -40\degree C. The increase in the room temperature colorability of alkali halides doped with divalent cations was explained by Crawford and Nelson\textsuperscript{99} on the basis of the resonance studies of Hayes and Nichols. They suggested that the underlying
process of coloration in alkaline earth impurity doped crystals might be somewhat more complex than the simple population of existing anion vacancies. According to them, the cation vacancies which are introduced with the divalent impurity to maintain charge neutrality, can be converted to anion vacancies by X-irradiation at room temperature in the following manner: A halide ion adjacent to an isolated cation vacancy captures a hole, and that the resulting halogen atom relaxes into the cation vacancy, forming a halogen molecular complex oriented along <100>. The energy released in the capture of the hole is presumed to be sufficient to allow the negative ion vacancy to diffuse away. As an isolated negative ion vacancy, it may trap an electron to form an F-centre. Since \( X_2^- \) molecule-ion is unstable at room temperature, Crawford and Nelson suggested that the \( X_2^- \) molecule-ion loses an electron to form a \( X_2^- \) molecule or perhaps a \( X_3^- \) molecule-ion. This assumption is based on the results of Hersh on the absorption study of the water solutions of the alkal halides and halogens.

It is now generally presumed that in one of the processes, associated with the initial rapid room temperature coloration (first stage) of alkali halides, ejected halogen is stabilized in a positive ion vacancy and hence not returning to annihilate the negative ion vacancy by
recombination. Crawford and Nelson\(^99\), Sibley and Russel\(^106\) and Ikeya et al\(^86,107\) all found evidences that isolated cation vacancies are converted to F-centres. However Hayes and Nichols\(^104\) and more recently Fieschi and Co-workers\(^108\) by ITC (ionic thermo conductivity) technique have evidences that bound vacancies participate in the early stage coloration process. Thus it is still not certain whether the site where the conversion of a cation vacancy into molecular halogen ion and an F-centre occurs, is an isolated or a bound cation vacancy.

In the coloration curves (plot of F-centre concentration versus accumulated exposure to ionizing radiations) for room temperature X-irradiated alkali halide crystals, two relatively distinct regions of behaviour have been identified. Each coloration curve could be decomposed into two stages: an early stage in which the coloration is rapid and which saturates after relatively low exposure and late stage which rises much more slowly and shows signs of saturation only for large exposures. Hence it has been concluded that early stage F-centres are produced by a mechanism different from the one governing the late stage. The first stage is associated with rapid filling in of anion vacancies already present in the crystal. As described above, alkaline earth impurities have a strong enhancing effect upon the early stage coloration in which case either free or associated cation vacancies
are converted into anion vacancies. The present understanding of the late stage coloration is given below.

The electron spin resonance study of Kanzig and Woodruff\textsuperscript{66} and the polarized optical absorption investigation of Compton and Klick\textsuperscript{109} conclusively established the structure of the H-centre which is a special configuration of an interstitial halogen atom. The diverse investigations on a variety of alkali halides strongly suggest that low temperature irradiation introduces anion vacancies and interstitial halogen. There is also experimental evidence overwhelmingly in favour of interstitial halogen being introduced in some form along with F-centres during room temperature irradiation\textsuperscript{123-128}. It has been concluded that the production of interstitial halogens does not take place in the process which dominates early stage coloration at room temperature. They are predominantly produced in the late stage coloration. The situation concerning the interstitials formed after room temperature irradiation is not very clear. They have a more complex lattice configuration and the experimental data available suggest that they are stabilized by forming halogen molecules or molecular ions. These molecular complexes may be associated with impurities or other point defects or they may interact with dislocations or dislocation debris. The thermal stability of F-centres and interstitials as
influenced by the irradiation temperature has been discussed by Sibley and Sonder, and it is concluded that only one type of F-centre is involved and that it is the thermal stability of the "anticentre" that determines the dependence of F-centre stability upon formation temperature. Thus available evidence strongly supports the view that Frenkel Pair production is responsible for the late stage coloration of alkali halides in which case either free or associated cation vacancies are converted into anion vacancies.

(H) Z-CENTRES:

The color centres that are characteristic of the divalent impurity are the z-centres. With the proper thermal and optical treatments of the doped alkali halide crystals it is possible to produce color centres that are characteristic of the divalent impurity. Five such color centres have been studied. These are called Z centres and are labelled with subscripts 1 to 5. So far only the alkaline earths have been found to produce these centres. Studies of the optical properties, luminescence, photo-conductivity and paramagnetic resonance of Z centres have provided useful information on the electronic structure of the centres. Although most work has been done with KCl:Sr a few experiments indicate that similar effects occur in KCl:Ca, KCl:Ba, NaCl:Sr, NaCl:Ba etc.