CHAPTER IV

TIN CENTERS IN KCl AND KCl: NaCl CRYSTALS
SECTION 4.I

OPTICAL ABSORPTION STUDIES

4.I.A INTRODUCTION

Alkali halide crystals doped with heavy metal ions having ns² outermost electron configuration, such as Tl⁺, Ga⁺, In⁺, Pb²⁺, Ge²⁺ and Sn²⁺, have held the interest of several theoretical and experimental investigators⁹⁸-₁₂₆. These crystals show the characteristic absorption bands induced by the doping of the heavy metal ions well separated from the fundamental absorption bands of the host materials. Among the impurity ions with s² configuration extensive studies have been carried out on the thallous centers¹⁰¹-¹¹₀.

Hilsch⁹₈ (1927) did pioneering research in the field and established the presence of three absorption bands in the ultraviolet designated as A, B and C bands in the order of increasing photon energy. Hüniger and Rudolph⁹⁹, Andrianov and Kats¹¹¹, Lushchik et al.¹¹²,¹¹³, Zazubovich¹¹⁴ and Fukuda¹¹⁹,¹²¹,¹²² have made detailed studies of the optical absorption spectra of Sn²⁺ and observe these bands. In addition to these bands there is a high energy band called D, very
close to the fundamental absorption which was originally found in KCl:Tl by Yuster and Delbecq\textsuperscript{105}, later in KCl:Tl by Kuwabara and Aoyagi\textsuperscript{107,108}, in KCl: In and KCl:Sn by Fukuda et al\textsuperscript{160} and in several alkali halides with almost all ions in the ns\textsuperscript{2} configuration group by Inohara\textsuperscript{127}. Seitz\textsuperscript{101} in 1938 proposed a detailed theoretical model for these bands for Tl doped crystals. Considering Tl\textsuperscript{+} ions to be substitutional in the host lattice, he estimated how the electronic energy states arising from s\textsuperscript{2} and sp configurations of the free ion are modified by the electric field inside an alkali halide crystal (f.c.c structure) with a cubic O\textsubscript{h} symmetry. The transitions (Fig. 4.1) assigned by him are as follows,

\textbf{A-Band} \hspace{1em} 1S\textsubscript{0} \rightarrow 3P\textsubscript{1} \hspace{1em} \left( \frac{1}{2}A\textsubscript{1g} \rightarrow 3T\textsubscript{1u} \right)

Spin-orbit allowed

\textbf{B-Band} \hspace{1em} 1S\textsubscript{0} \rightarrow 3P\textsubscript{0} \hspace{1em} \text{and} \hspace{1em} 3P\textsubscript{2}

\left( \frac{1}{2}A\textsubscript{1g} \rightarrow 3A\textsubscript{1u} \text{ and } 3E\textsubscript{u} \text{ or } 3T\textsubscript{2u} \right)

Vibration induced

\textbf{C-Band} \hspace{1em} 1S\textsubscript{0} \rightarrow 1P\textsubscript{1} \hspace{1em} \left( \frac{1}{2}A\textsubscript{1g} \rightarrow 1T\textsubscript{1u} \right)

Completely allowed

The D-band is interpreted as an impurity-perturbed exciton.
FIG. 4.1 Schematic energy level diagram of Sn$^{+}$ ion in cubic field.

The numbers in parenthesis denote the electronic degeneracy of the levels.
Since the singlet-triplet transitions are not consistent with the spin-selection rule, the C-band should be the strongest as observed. The dipole transition responsible for the B-band is allowed only by the admixture of phonons.

Sugano\textsuperscript{126} proposed the use of molecular orbitals $a_{1g}$ and $t_{1u}$ which are considered to be spread over the surroundings of activator ion and concluded that the same result can be obtained as by using the $s$ and $p$ atomic orbitals. Fukuda\textsuperscript{119} has performed extensive absorption and emission measurements at room temperature and at liquid nitrogen temperature (LNT) on NaCl, KCl and KBr crystals doped with Sn\textsuperscript{2+}, Pb\textsuperscript{2+}, In\textsuperscript{+} and Tl\textsuperscript{+} and has verified Sugano's theory.

Very recently Vasilchenko et al\textsuperscript{118} and Lushchik and Zazubovich\textsuperscript{117} have proposed a refined energy level diagram for the Sn\textsuperscript{2+} ion in the alkali halide lattice considering a tetragonal $C_{4v}$ symmetry (Fig. 4.2). It is shown that the lower component of the split $1T_{1u}$ state is a nondegenerate $1A_1$ level while the lower component of the $3T_{1u}$ state is a doubly degenerate $3E$ level. According to their studies the B-absorption band also has a doublet structure. This nature is reported and referred to by Fukuda in his paper\textsuperscript{122} as unpublished work for In\textsuperscript{+} and Sn\textsuperscript{2+} in some alkali halides. The Latest report of Sastry et al\textsuperscript{128} also show a doublet splitting of the B-band for Pb\textsuperscript{2+} in NaCl.
FIG. 4.2  Energy level diagram for a free Sn$^{++}$ ion and for a Sn$^{++}$ ion in weak crystal fields having cubic $O_h$ and tetragonal $C_{4v}$ symmetries. The arrows show the transitions that are resolved along specific axes.
The energy level diagram given in Fig. 4.2 does not take into account the interaction of the center with the crystal lattice vibrations and consequently it does not describe all the properties of Sn$^{2+}$ centers, in particular the triplet splitting of the C-band which to a large extent is associated with the dynamic Jahn-Teller effect. This energy level diagram gives the number and order of the split components of the excited $^3P_1$, $^3P_2$ and $^1P_1$ states of the Sn$^{2+}$ ion in a crystal field having tetragonal $C_{4v}$ symmetry and interprets unambiguously the observed absorption bands as the electronic transitions,

$$^1A_1 ightarrow ^3E \quad (A_1 \text{ - band })$$

$$^1A_1 ightarrow ^3A_1 \quad (A_2 \text{ - band })$$

$$^1A_1 ightarrow ^3E \quad (B_1 \text{ - band })$$

$$^1A_1 ightarrow ^3B_1 ^3B_2 \quad (B_2 \text{ - band })$$

$$^1A_1 ightarrow ^1A_1 \quad (C_1 \text{ - band })$$

$$^1A_1 ightarrow ^1E \quad (C_2 \text{ - band })$$

The results of the optical absorption spectra of the Sn-doped crystals are discussed in this section. Different changes in these spectra are produced when the crystals contain...
F-centers depending on the method of producing the F-centers i.e. by X-ray irradiation or incorporation of excess alkali metal. These results are interpreted in terms of plausible photochemical and other reactions.

4.1.8 RESULTS AND DISCUSSION

4.1.8.1 Uncolored Crystals:

The optical absorption spectra of the crystals of KCl:NaCl doped with Sn, grown by the Kyropoulos' method show absorption bands which can be assigned as the characteristic A, B and C bands of Sn\(^{2+}\) ions.\(^{119}\) So far as estimated from the amount of added Stannic Chloride in the ampoules the concentrations of Sn ions seems to be proportional to the integrated absorption coefficients of these bands. Earlier authors\(^{99,113,114,119}\) have found the triplet and the doublet structures of the C and A-bands respectively. In the case of the samples used for the present studies the subbands could not be resolved even at LNT (80 K) in the as grown condition. A broad band around 230 nm (5.387 eV) is related to the C-band though the triplet structure is not clear. The broad shoulder around 285 nm (4.348 eV) corresponds to the A-band. Another shoulder at around 250 nm (4.956 eV) is identified as the B-band. However a thermal treatment such as tempering, quenching or annealing helps in bringing out the bands more clearly. Fig. 4.3 shows the absorption coefficient plotted against photon energy for untreated and treated samples both at room temperature (RT) and LNT (80 K). The peak positions of the
FIG. 4.3 Optical absorption spectra of KCl:Na crystal doped with Sn. (1) depicts the spectrum of an untreated sample and (2) that of a treated one. A, B and C refer the denominations of the bands.
various bands very well agree with those in the literature\textsuperscript{99,113,114,119}. These values are listed in Table 4.1.

**Table 4.1**

Positions of absorption peaks (in eV) of Sn\textsuperscript{2+} in KCl crystals at RT and at LNT. Numbers in parantheses give wavelengths in nm.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Phosphors</th>
<th>Temp.</th>
<th>A (\textsuperscript{nm})</th>
<th>B (\textsuperscript{nm})</th>
<th>C (\textsuperscript{nm})</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>A\textsubscript{1}</td>
<td>A\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>Hüniger et al (1940) KCl:Sn Ref. 99</td>
<td>RT</td>
<td>4.22</td>
<td>4.41</td>
<td>4.88</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zazubovich et al (1963) KCl:Sn Ref. 114</td>
<td>RT</td>
<td>4.23</td>
<td>4.44</td>
<td>4.88</td>
<td>5.12</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fukuda (1964) KCl:Sn Ref. 119</td>
<td>RT</td>
<td>4.23</td>
<td>4.44</td>
<td>4.88</td>
<td>5.12</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>4.29</td>
<td>4.42</td>
<td>4.94</td>
<td>5.20</td>
</tr>
<tr>
<td>Present work KCl:NaCl:Sn</td>
<td>RT</td>
<td>4.23</td>
<td>4.44</td>
<td>4.87</td>
<td>5.11</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>4.29</td>
<td>4.40</td>
<td>4.93</td>
<td>5.19</td>
</tr>
<tr>
<td>Present work KCl:Sn</td>
<td>LNT</td>
<td>4.29</td>
<td>4.41</td>
<td>4.93</td>
<td>5.21</td>
</tr>
</tbody>
</table>

...
On the other hand crystals grown by the vacuum Bridgman technique show very sharp and clear bands in the optical absorption spectrum. The triplet and the doublet natures of the C and A bands respectively are observed clearly. All the bands are very intense and they are well resolved both at RT and LNT (80 K) (Fig. 4.4). The values of the band positions are also given in Table 4.1. The $A_1$ - band at 289 nm (4.286 eV) is clearly brought out at LNT (80 K). As observed by Fukuda$^{119}$, here also the $A_1$ - band shifts towards the higher energy side whereas the $A_2$ - band shifts slightly towards the lower energy side as the temperature falls. The band widths are obviously reduced and the $A_1$ and $A_2$-bands become narrower and higher. The intensity of the B - band is lowered at LNT (80 K) and the position of the band moves towards higher energies as compared to that at RT. The band becomes better resolved at low temperature. The $C_2$ - band slightly shifts towards the higher energy side, the $C_1$ and $C_3$ - bands approaching the $C_2$ - band. The C - band as a whole becomes relatively narrower and higher as the temperature falls, the area under the absorption curves at RT and LNT (80 K) remaining constant. This is consistent with the interpretation of the C-band as arising from dipole-allowed transitions with the transition probability independent of temperature.

Prior to the measurements the crystal was heated to $\sim 675^\circ$C and kept at that temperature for 15 minutes in
FIG. 4.4 Optical absorption spectra of Sn doped KCl crystal. $A$, $B$ and $C$ refer the denominations of the bands.
vacuum before quenching it to 0°C in cold nitrogen atmosphere. The concentration of Sn ions which could be incorporated by this method is about five times higher compared to the crystals grown by the Kyropoulos' method.

A comparison of the Sn$^{2+}$ band positions in KCl and KCl:NaCl shows no significant difference. The D - band occurring at 7.5 eV$^{126}$ is outside the range of the spectro - photometer used and could not be studied during this investigation.

Williams' theory$^{102,103}$ predicts the A, B and C - absorption bands to be Gaussian in shape without structure. To explain the observed structure of the A and C - bands the suggestion of dynamical Jahn-Teller effect has been put forward$^{60,115,117,119,121,124}$. A lowering of the symmetry of the excited impurity center caused by appropriate vibrational modes leads to the splitting in the excited state reflected as fine structure in the absorption bands.

Very recently Lushchik and Zazubovich$^{117}$ have studied these properties in Sn$^{2+}$ and In$^+$ doped alkali halides. They suggest that the splitting of the absorption bonds of the monovalent impurity ( like In$^+$ ) centers is primarily due to the dynamical Jahn – Teller effect, whereas the splitting of these bands in the case of the divalent
impurity (like Sn\textsuperscript{2+}) associated with the charge-compensating cation vacancy is caused not only by the dynamical Jahn-Teller effect but also by the electric field of the charge-compensating vacancy near the impurity. The intensity of B-band is found to be lowered at LNT (80 K) indicating that the transition responsible for this band is vibrationally induced.

Attempts to obtain the tin impurity concentration of the doped crystals by the atomic absorption method and other spectroscopic methods have not been successful.

4.I.32 **X-irradiated Crystals:**

The effect of RT X-irradiation on the absorption spectrum of the KCl:Sn crystals grown by the vacuum Bridgman method is plotted in Fig. 4.5. This sample is exposed to X-ray irradiation for successively increasing times of 5, 10, 15, 30, 45, 60 mins, 2, 4, 12 and 20 hrs and the optical absorption spectra are plotted everytime. Curves 1 to 10 represent the spectra of this sample with increasing time of irradiation. It is found that the F-band absorption increases steadily with dose while the A\textsubscript{1}, A\textsubscript{2} and B-bands gradually decrease until they are finally wiped out practically. Moreover the C\textsubscript{1} - band diminishes with increasing irradiation while the absorption in the region of C\textsubscript{2} and C\textsubscript{3} - bands continues to grow in intensity.

...
FIG. 4.5  Optical absorption spectra of Sn doped KCl crystal before and after exposing to X-rays for times as mentioned above.
Here also the crystal was heated to $\sim 675^\circ C$ and kept at that temperature for 15 mins in vacuum before quenching it to $0^\circ C$ in cold nitrogen atmosphere before the studies.

The $A_1$, $A_2$, B, $C_1$, $C_2$ and $C_3$-bands are characteristic absorption bands of Sn$^{2+}$ ions with the electron configuration $5s^2$. Isoelectronic with this ion are Tl$^+$, In$^+$, Pb$^{2+}$, Hg$^0$ etc. The gradual decrease of $A_1$, $A_2$, B and $C_1$-bands under irradiation suggests the conversion of Sn$^{2+}$ ions into a different charge state. The increasing absorption in the region of 229 (5.414) and 223 nm (5.559 eV) can only point to the rise of new absorption bands due to centers growing probably at the expense of the divalent tin centers. V$_2$-band in KCl is located around 230 nm (5.387 eV)$^{46}$. Such high absorption when compared to the F-band as seen in Fig 4.5 cannot be attributed entirely to the presence of V-centers. It is well known that Tl$^+$, Ag$^+$ and Pb$^{2+}$ ions act as very good electron traps in X-irradiated KCl$^{129,130}$. It has also been shown that Tl$^+$, Ag$^+$ and Pb$^{2+}$ ions are good hole traps forming Tl$^{2+}$, Ag$^{2+}$ and Pb$^{3+}$ respectively$^{131-134}$. In a similar manner it can be deduced that Sn$^{2+}$ also may act as a hole trap and becomes Sn$^{3+}$ on irradiation. Schoemaker and Kolopus$^{133}$ have observed three well resolved bands for Pb$^{3+}$ in X or $\gamma$-irradiated KCl crystals and found that they are stable up to $60^\circ C$. According to Butterworth and Harbottle$^{135}$ the RT $\gamma$-irradiation converts a considerable fraction of the Tl$^+$ to a Tl$^{2+}$ species which is stable up to 200-300$^\circ C$. Sn$^{2+}$ being isoelectronic
with Tl$^+$ and Pb$^{2+}$, a similar change of state may well be anticipated. According to Schoemaker and Kolopus$^{133}$ the band positions for Pb$^{3+}$ are 216 (5.74), 303 (4.09) and 465 nm (2.665 eV) with decreasing order of intensity. 216 nm (5.74 eV) band is near the B-band for Pb$^{2+}$. In the present case the irradiation enhances the absorption in the C$_2$ and C$_3$ regions i.e. at 229 (5.414) and 223 nm (5.559 eV). One possible interpretation of the observed changes in the absorption spectrum is as follows: The strong bands occurring at 229 (5.414) and 223 nm (5.559 eV) and a small increase in the absorption around 266 nm (4.65 eV) may be attributed to Sn$^{3+}$ in analogy with the bands for Pb$^{3+}$. However there is no band in the visible region.

On the other hand a more likely possibility seems to be the conversion of Sn$^{2+}$ into the quadrivalent state of the ion, Sn$^{4+}$. A number of points are in favour of this model. It has been observed that Sn can enter the NaCl lattice as Sn$^{2+}$ and Sn$^{4+}$$^{136}$. Murin and Serenga$^{136}$ have recently reviewed Mössbauer studies on a number of Sn doped crystals. Based on the chemical shift and line width observed compared to the corresponding data of SnO$_2$, one emission line has been attributed to Sn$^{4+}$. A poorly resolved quadrupole doublet is ascribed to Sn$^{2+}$. X-ray irradiation decreases the intensity of the Sn$^{2+}$ doublet. Sn doped silver halides exhibit a singlet due to Sn$^{4+}$ both in emission and absorption. Results on
LiCl:Sn and KCl:Sn have also been analysed in terms of the Sn\(^{4+}\) state. In an attempt to choose between the two alternatives (Sn\(^{3+}\) or Sn\(^{4+}\)) an electron spin resonance (ESR) experiment has been carried out (to be described in Section 4.III). Sn\(^{3+}\) is paramagnetic and is expected to show ESR absorption while Sn\(^{4+}\) being diamagnetic would not give any ESR. A search for the presence of Sn\(^{3+}\) under high gain conditions has revealed no resonance signal. This leads to the conclusion that Sn\(^{4+}\) is the stable charged state taken by the impurity after the irradiation. It may be mentioned that the absorption due to V-centers remains submerged in the strong ultraviolet absorption of the Sn centers in the colored crystals. The X-ray irradiation brings about the following reaction,

\[
\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e^-
\]

Optical bleaching with white light at RT restores the impurity to its original charge state (Sn\(^{2+}\)) as evidenced by its characteristic spectrum at RT and LNT (80 K). The Sn\(^{4+}\) ions are converted to Sn\(^{2+}\) again when the electrons are released from the F-centers. According to this model the absorption bands located at 223 (5.559) and 229 nm (5.414 eV) are characteristic of the Sn\(^{4+}\) species.
4.1.3 Additively Colored Crystals:

Crystals from the same ingot of KCl:Sn give interesting results on additive coloration. Instead of an F-band peaking at 556 nm (2.229 eV) a broad band of low intensity at 540 nm (2.295 eV) and a band at 420 nm (2.95 eV) are observed besides three bands around 320 (3.872), 282 (4.393) and 221 nm (5.61 eV) (Curve 'a' of Fig. 4.6). The band located around 540 nm (2.295 eV) is to be considered as the F-band as the apparent position of the broad band is shifted by considerable overlap with bands on the shorter wavelengths. A striking feature is that when the crystal is cooled down to LNT (80 K) all the bands except the F-band are somewhat reduced in intensity. The F-band and the band at 420 nm (2.95 eV) become well resolved. This behaviour is shown by curve 'b' of Fig. 4.6. On exposing the crystal to 540 nm light at LNT (80 K) the F-band could not be bleached for illuminations up to one hour and there is no change in the other bands (curve 'c' of Fig. 4.6). This is understandable as excitation within the F-band at LNT (80 K) does not produce a free electron as the excited state of the F-center is about 0.1 eV below the bottom of the conduction band. It is well known that the efficiency of $F \rightarrow F'$ photoconversion as well as the quantum efficiency for photoconductivity are very low at LNT (80 K). On the other hand illumination at RT with a 100 Watts tungsten filament lamp for 5 hours bleaches out the
FIG. 4.6 Optical absorption spectra of additively colored KCl:Sn crystal (a — RT and b — LNT). c — after bleaching with 540 nm light for 1 hr at LNT, spectrum taken at LNT. d — after bleaching completely with white light at RT, spectrum taken at RT. e — after bleaching completely with white light at RT, spectrum taken at LNT.
F-centers completely. Curve 'd' of Fig. 4.6 represents this spectrum whereas curve designated 'd' of the same figure shows the optical absorption spectrum of the same sample at LNT (80 K) bleached at RT. In this case also the absorption decreases when the crystal is cooled down to LNT (80 K). Except for the F-band and the band at 221 nm (5.61 eV) all the three other bands are of the same intensity as compared to the ones before bleaching at RT (curves 'd' and 'a' of Fig. 4.6). The band at 221 nm (5.61 eV) increases in intensity. At LNT (80 K) all the bands are enhanced after the RT bleaching (curves 'e' and 'b' of Fig. 4.6). Another sample of the additively colored crystal is bleached with 320 nm light at RT and the results are plotted in Fig. 4.7. Curve 'a' is for the unbleached sample and 'b' and 'c' are for the same sample bleached for 30 mins. and 1 hr respectively. After the bleaching the F-band as well as the 420 nm (2.95 eV) band are better resolved and no difference is observed with the increase in bleaching time. The 320 nm (3.872 eV) band instead of diminishing is getting well resolved with the time of bleaching. Thus it is found that the 320 nm (3.872 eV) band centers are stable with respect to 320 nm light. The intensity of the other two bands at 282 (4.393) and 221 nm (5.61 eV) increase considerably with the 320 nm bleaching. In all the cases the absorption at the extreme ultraviolet region continues to rise beyond the last peak. The presence of bands which are out of range for the spectrophotometer used in the present investigation is inferred.
FIG. 4.7 Optical absorption spectra of additively colored KCl:Sn crystal (a). Curve b and c represent the spectra for the same sample after 30 mins. and 1 hr. illumination with 320 nm light at R.T. Note the difference in scale on the ordinate.
Sn appears to introduce a family of new bands in KCl on additive coloration which are not formed by X-irradiation. The 282 (4.393) and the 221 nm (5.61 eV) bands are in the region of the A and C-bands of KCl:Sn$^{2+}$. The associated structure of the A and C-bands is absent so that the 282 (4.393) and 221 nm (5.61 eV) bands may be arising from new type of centers. It may be remarked that the density of F centers ($\sim 10^{16}$ cm$^{-3}$) is much less than that ordinarily produced in additive coloration. If Sn was not present in the lattice a large number of F-centers would have been produced by the capture of excess electrons in the negative ion vacancies during additive coloration. In the present case the intensity of the F-band is very low and it can be assumed that Sn$^{2+}$ is playing an important role while the crystal is being additively treated. So the set of bands can be attributed to a new species formed in the crystal. In normal additive coloration for a pure crystal it may be imagined that incorporation of atoms involves addition of electrons to the crystal and building up new layers of cations and anions with anion vacancies included in the bulk region. The positive ion vacancies present at the elevated temperature are unaffected in this process. From the reduced formation of F-centers in the Sn-doped crystals the following mechanism suggests itself. When the excess alkali atoms are added to the crystal the resulting dissociated electrons may be captured at Sn$^{2+}$ centers which act as electron traps in competition with anion ...
vacancies. The positive ions may be incorporated in the bulk region destroying cation vacancies and without building additional surface layers. It is known\textsuperscript{137,138} that several divalent cations in alkali halides are converted to the monovalent state by electron capture on X-irradiation. On this model we expect to find no dipolar dielectric loss and a lowering of d.c conductivity. Both of these expectations are fulfilled by the results of actual measurements on the additively treated crystals (to be discussed in Chapter V). The dielectric peaks observed before additive coloration disappear after the coloration. The d.c conductivity of a doped crystal decreased subsequent to the additive treatment. An ESR signal (to be discussed in Section 4. III) is observed in the additively colored crystals and it can be attributed to the Sn\textsuperscript{+} center.

Concerning the number of absorption bands which can be attributed to transitions in Sn\textsuperscript{+} ions, we may look for guidance in the literature on similar isoelectronic species such as Tl\textsuperscript{2} and Pb\textsuperscript{+}. Whereas Pb\textsuperscript{+} formed by RT X-ray irradiation\textsuperscript{134} gives only one prominent band at 254 (4.877 eV), Tl\textsuperscript{10} centers formed by \textsuperscript{6} irradiation at 77 K of KCl:Tl crystals show four bands\textsuperscript{29,139} and they are stable at RT. It is also found\textsuperscript{140} that KCl:Pb\textsuperscript{+} show three bands after additive coloration. Similarly one may attempt to attribute the four bands seen here such as 420 (2.95), 320 (3.872), 282 (4.393) and 221 nm (5.61 eV) to Sn\textsuperscript{+} centers in the crystal. However when ...
the intensity ratio among these four bands are calculated it
is seen that these ratios are substantially independent of the
various bleaching treatments given to the samples except for
the 420 nm (2.95 eV) band. The white light used to bleach
the F-centers might have succeeded in bleaching out some of
the centers responsible for this band. The other possibility
is that this band is arising from a different species of
centers such as Sn aggregates. All the bands attributed to
Sn$^+$ ions are reduced in intensity by cooling to LNT (80 K)
suggesting that the transitions are probably of the forbidden
type but allowed by admixture with phonons.

The possible reactions at the additive coloration
temperature may be as follows:

1. $\text{Sn}^{2+} + M + V_c \leftrightarrow \text{Sn}^+ + M^+$
2. $M + V_a \rightarrow M^+ + F$
3. $\text{Sn}^+ + F \rightarrow V_a^+ + \text{Sn}^{2+}$

where $M$ is the alkali metal atom, $M^+$ - the
corresponding ion, $F$ is an F-center and $V_c$ and $V_a$ represent
cation and anion vacancies respectively.

The first reaction shows how the reduction of $\text{Sn}^{2+}$
to $\text{Sn}^+$ may proceed. An excess alkali atom ($M$) at the surface
dissociates into an ion ($M^+$) and an electron. The ion ($M^+$)
exchanging with a cation vacancy in the layer immediately beneath the surface and the electron getting trapped at an Sn$^{2+}$ center complete the reaction. It may be pointed out that at the temperature of additive treatment ($\sim 530^\circ C$) the divalent Sn ion and the charge compensating cation vacancy are not expected to be associated. This mechanism does not envisage an increase in the volume. The second reaction describes the formation of the F-centers by the usual mechanism$^1$. The third reaction postulates the formation of Sn$^{2+}$ centers from Sn$^+$ and F-centers.

It cannot be said from the above observations that Sn$^{2+}$ ions are all converted into Sn$^+$ ions. The Sn$^{2+}$ absorption bands are not clearly marked but may be present to some extent underlying the main absorption bands of Sn$^+$. We may hence consider the additively colored crystal to contain a predominant number of Sn$^+$ ions along with a minority of Sn$^{2+}$ and F-centers. The optical bleaching of the F-band can thus be understood in terms of a recombination of the liberated electron at a Sn$^{2+}$ center.

It is interesting to know that Velicescu and Topa$^{141}$ have observed a number of absorption bands in KCl:Sn crystals which are electrolytically colored. The band positions are given in Table 4.2 along with the band positions observed in the present work for X-irradiated and additively colored crystals.
Table 4.2

Absorption band positions (in eV) of Sn centers in KCl. Values in parentheses are the corresponding wavelengths in nm.

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<tr>
<th></th>
<th>5.60</th>
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<th>3.45</th>
<th>2.95</th>
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<td>(252)</td>
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<tr>
<td>Additively</td>
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<td>colored</td>
<td>5.61</td>
<td></td>
<td></td>
<td>4.393</td>
<td>3.872</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td>(Present work)</td>
<td>(221)</td>
<td></td>
<td></td>
<td>(282)</td>
<td>(320)</td>
<td></td>
<td>(420)</td>
</tr>
<tr>
<td>X-irradiated</td>
<td>5.559</td>
<td>5.414</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Present work)</td>
<td>(223)</td>
<td>(229)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

It is clear from the Table that the bands observed in the present work for additively colored and X-irradiated crystals are all produced in the electrolytic coloration besides two additional bands at 252 (4.92) and 359 nm (3.45 eV).
SECTION 4.II

COLOR CENTER FORMATION IN Sn DOPED KCl:NaCl CRYSTALS

4.II.A INTRODUCTION

The mechanism of color center production in alkali halides by ionizing radiations has puzzled physicists for a long time. The growth of F-centers with increasing dose of irradiation is depicted as a growth curve. The growth curves at room temperature (RT) are extremely structure sensitive, there being a wide variation from sample to sample. The growth curve is roughly divided into two stages: an initial fast coloration stage and a later slow growth stage. The first stage tends to a saturation value and the second stage is linear. A number of experimental studies have shown that the fast stage is associated with the process in which some existing anion vacancies in the crystals are populated by electrons. The second hard stage involves creation of vacancies required for the formation of F-centers. This second stage appears to be intrinsic and entails displacements of ions from normal lattice sites during the irradiation. A number of authors have unsuccessfully attempted an
explanation based on an X-ray or γ-ray photon knocking off a lattice ion. The Harsh\textsuperscript{56}, Pooley\textsuperscript{57} mechanism now provides an explanation. The structure sensitivity of the growth curve however seems to be associated with the first stage. At low temperatures (below LNT) the coloration proceeds mainly according to the second stage\textsuperscript{55}. The present work which describes the F-center growth at RT, is primarily concerned with the early stage. In particular the influence of the impurities on the growth parameters is studied. The results of experiments on the effect of Sn doping on the RT F-center growth study are discussed.

4.II.B ANALYSIS OF GROWTH CURVES

A typical curve of F-center concentration versus irradiation time or total dose is schematically shown in Fig. 4.8. This curve is analysed following the method given by Al-varesh Rivas and Levy\textsuperscript{54} : It is postulated that the growth curve is described by the equation,

\[ \mu_F = a_L t + \sum_{i}^{n} A_i \left( 1 - e^{-a_i t} \right) \quad (4.1) \]

The analysis consists of several steps. First, the linear region in stage II is extrapolated to \( t = 0 \). The slope of this linear part is labelled \( a_L \), the rate of the second stage coloration process. The difference \( \mu_3 \) between this extrapolated linear stage and the coloration curve is then

...
FIG. 4.8 (a) Schematic curve of F-center concentration vs. X-irradiation time; (b) schematic representation of the method used to analyze the first-stage coloring into exponential components. The time scales in (a) and (b) are different.
plotted using a semilogarithmic scale, against the irradiation time. This is schematically shown in Fig. 4.8. The intercept of the extrapolation of the curve $\mu_3$ to $t = 0$ gives $a_3$. The constant $a_3$ is deduced from the slope of $\mu_3$. This procedure is repeated using the difference between the extrapolation of $\mu_3$ and the remainder to determine the parameters $a_2$ and $a_2$ which define the curve $\mu_2$ as shown in the figure.

4.II.C RESULTS AND DISCUSSION

The F-center growth curves are measured for various samples: pure KCl:NaCl and four Sn doped samples with different concentrations of Sn. These are given in Fig. 4.9 which shows the variation of the absorption coefficient at the peak of the F-band $\mu_F$, as a function of the corresponding time of irradiation. The studies are made at RT with the X-ray unit operated at 30KV and 15 mA. Care is taken to maintain as closely as possible the same conditions of irradiation at different doses for a given growth curve. All the samples were quenched from $\sim 550^\circ$C to RT before doing the measurements.

Analyses of the present growth curves has led only to two exponential components plus the linear component. The second stage is quite linear over a sufficient range to determine $a_1$ to a few percent accuracy. Also the analysis procedure yields clearly defined regions labelled as $\mu_2$ and $\mu_3$ in Fig. 4.8. The least intense component $\mu_1$ is
not present as it is observed only rarely. Thus neglecting $\mu_1$ the curve of F-center absorption $\mu_F$ versus irradiation time, $t$ may be expressed as,

$$\mu_F = \mu_2 \left( 1 - e^{-a_2 t} \right) + \mu_3 \left( 1 - e^{-a_3 t} \right) + a_L t \quad \ldots (4.2)$$

The first stage coloration is decomposed into two exponential components $\mu_3$ and $\mu_2$. Fig. 4.10 shows the first product of this decomposition, $\mu_3$ plotted for the five cases, while the next faster component $\mu_2$, is plotted in Fig. 4.11. The values of the parameters $a_L$, $a_2$, $a_3$ and $\mu_3$ are placed in Table 4.3.

### Table 4.3


<table>
<thead>
<tr>
<th>Concentrations of Na &amp; Sn (mole %)</th>
<th>Sample thickness (cm)</th>
<th>$a_L$ (cm$^{-1}$)</th>
<th>$a_2$ (min$^{-1}$)</th>
<th>$a_3$ (cm$^{-1}$)</th>
<th>$\mu_3$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.0684</td>
<td>0.04101</td>
<td>0.7954</td>
<td>3.24</td>
</tr>
<tr>
<td>0.8</td>
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<td>0.0907</td>
<td>0.02934</td>
<td>0.5339</td>
<td>1.78</td>
</tr>
<tr>
<td>0.8</td>
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<td>0.0945</td>
<td>0.034</td>
<td>0.563</td>
<td>1.09</td>
</tr>
<tr>
<td>3.2</td>
<td>0.4</td>
<td>0.0854</td>
<td>0.02</td>
<td>0.5977</td>
<td>1.19</td>
</tr>
<tr>
<td>6.4</td>
<td>0.8</td>
<td>0.1117</td>
<td>0.013</td>
<td>0.8772</td>
<td>0.43</td>
</tr>
</tbody>
</table>

...
FIG. 4.9  F-center growth curves for doped and undoped KCl:NaCl crystals, x-irradiated at room temperature. a, b, c, d and e correspond to concentrations of Sn as 0, 0.05, 0.2, 0.4 and 0.8 mole % respectively.
FIG. 4.10  The slow exponential component $\mu_3$ of the first stage coloration, plotted on a logarithmic scale. $a, b, c, d$, and $e$ correspond to concentrations of Sn as 0, 0.05, 0.2, 0.4 and 0.8 mole% respectively.
FIG. 4.11 The fast exponential component $\mu_2$ of the first-stage coloration, plotted on a logarithmic scale. a, b, c, d and e correspond to concentrations of Sn as 0, 0.05, 0.2, 0.4 and 0.8 mole% respectively.
As can be seen from Table 4.3 the values of the constant $a_L$ of the second stage coloration are not very dissimilar for the different crystals studied except for the one with the highest concentration of Sn, for which the $a_L$ value is low. On the other hand the parameters $\tilde{a}_2$, i.e. the saturation level of $\mu_2$ and $a_2$, i.e. the slope of the $\mu_2$ component decreases significantly on the addition of Sn. The highly doped sample again behaves differently. The process responsible for the first substage is relatively sensitive to the presence of Sn in the crystal. The saturation levels for the second substage represented by the parameter $\tilde{a}_3$ are invariably more in the doped crystals than in the undoped ones. Its value is about three times that for the undoped one in the lightly doped sample and decreases monotonically with the Sn concentration. The parameter $a_3$, the slope of the $\mu_3$ component, decreases very much in the lightly doped sample. As the concentration of Sn is increased $a_3$ reaches about half the value as that for the undoped one and remains more or less constant. The ratio $\tilde{a}_3/a_2$ is almost equal to 1 in the undoped crystal and between 4 and 10 in the doped ones. It is clear from these results that in the impurity doped crystals the second substage contributes a major portion of the total first-stage F-centers. In the studies of Alvarez Rivas and Levy\textsuperscript{54} on Korth and Harshaw NaCl crystals, the Korth crystals contain a greater amount of trace impurities and show a decreased $a_3$ and an increased $\tilde{a}_3$ when compared with the Harshaw samples. Similar results are obtained...
by Sastry and Srinivasan on Ba, Co and Cd doped KCl crystals. Thus it can be concluded that primarily impurities reduce the rate of coloration or the rate of approach to saturation in the second substage and increase the saturation level for the process responsible for this component. It is interesting to note that the effect of Sn on the growth curves is similar to that of Tl\(^+\), Ca\(^{2+}\), Pb\(^{2+}\) and Cd\(^{2+}\) in KCl 148-150, 138 and Cu\(^+\) in NaCl\(^87\).

It is known that the equilibrium number of F-centers produced depends on the dose rate\(^{151}\). To study this effect growth curves on a fresh set of crystals have been obtained for a higher X-ray dose rate by increasing the tube voltage and current to 40 KV and 20 mA respectively. The F-growth curve analysis proceeds as before and the graphical results of the components \(\mu_\text{F}, \mu_3, \mu_2\) are in Figs. 4.12, 4.13 and 4.14 respectively. The values of the parameters \(a_1, a_2, a_2', a_3\) and \(A_3\) are cited in Table 4.4.

It is clear from Table 4.4 that the \(A_3\) values for the two lightly doped samples are more than that of the undoped crystals and in the case of the heavily doped samples these are smaller. The parameter \(a_3\) increases on the addition of Sn and as the concentration is increased \(a_3\) first falls and then rises. The ratio \(A_3/A_2\) is greater than 1 in all the doped crystals and less than 1 in the undoped one. Thus here again in the Sn
**FIG. 4.12** F Center growth curves for doped and undoped KCl: NaCl crystals, x-irradiated at room temperature. a, b, c, d and e correspond to concentrations of Sn as 0, 0.05, 0.2, 0.4 and 0.8 mole% respectively.
FIG. 4.13 The slow exponential component $\mu_3$ of the first stage coloration, plotted on a logarithmic scale. $a$, $b$, $c$, $d$ and $e$ correspond to concentrations of Sn as 0, 0.05, 0.2, 0.4 and 0.8 mole % respectively.
FIG. 4.14 The fast exponential component $\mu_2$ of the first stage coloration, plotted on a logarithmic scale. $a, b, c, d$ and $e$ correspond to concentrations of Sn as 0, 0.05, 0.2, 0.4 and 0.8 mole% respectively.
doped samples the first-stage coloration is mainly due to the second substage. Álvarez Rivas and Levy\textsuperscript{54} observe that the slope of the linear late stage \( a_L \) is nearly independent of the dose rate. The present results do not admit of this conclusion. The intercept \( A_2 \) increases and the exponential parameter \( a_2 \) decreases with dose rate. Similarly the values of \( A_3 \) have also increased except in the case of the heavily doped one. No systematic relation can be deduced as far as the slopes, i.e. the \( a_3 \)'s are concerned.

Table 4.4


<table>
<thead>
<tr>
<th>Concentrations of Na &amp; Sn (mole %)</th>
<th>Sample thickness (cm)</th>
<th>( a_L ) (cm(^{-1}))</th>
<th>( a_2 ) (min(^{-1}))</th>
<th>( a_3 ) (cm(^{-1}))</th>
<th>( A_3 ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0</td>
<td>0.071</td>
<td>0.023</td>
<td>0.5957</td>
<td>8.6</td>
</tr>
<tr>
<td>0.8</td>
<td>0.05</td>
<td>0.1075</td>
<td>0.009335</td>
<td>0.376</td>
<td>5.95</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>0.0949</td>
<td>0.05</td>
<td>0.2622</td>
<td>6.65</td>
</tr>
<tr>
<td>3.2</td>
<td>0.4</td>
<td>0.076</td>
<td>0.011</td>
<td>0.2537</td>
<td>4.77</td>
</tr>
<tr>
<td>6.4</td>
<td>0.8</td>
<td>0.0821</td>
<td>0.02767</td>
<td>0.7499</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Attempts have been made by several authors\textsuperscript{46,143,144, 149,152-158} to delineate the role of impurities in the coloration...
process. The fundamental mechanisms responsible for the observed effects of impurities are still far from clear. The proposed suggestions fall broadly in two categories:

(i) the forward F-center generation process may be influenced by the impurities.

(ii) back reactions tending to lower the equilibrium F-center densities may be affected by the impurities.

Divalent cation impurities like Ca\(^{2+}\) are reported to enhance the first stage F-center concentration\(^{154,157,158}\). This is a puzzling result since the impurities enhance the concentration of cation vacancies and suppress the anion vacancies in thermal equilibrium. Probably the equilibrium conditions are not attained at RT. Crawford and Nd\(\text{\textsc{ld}}\)son\(^{158}\) proposed an interesting mechanism whereby cation vacancies are in effect converted to anion vacancies during irradiation. Only isolated cation vacancies are involved in this mechanism. Although there seems to exist some evidence\(^{159}\) that the enhancement in the growth of F-centers depends only on the free vacancy concentration, this does not necessarily constitute proof that this mechanism actually operates in the crystals. Electron trapping impurities like Pb, Ag, Tl and Cd are known to suppress the formation of F-centers especially of the late stage. The Hersh\(^{56}\), Pooley\(^{57}\) mechanism for the primary process of generating F-centers hinges on electron hole recombination...
events. The impurity may act as a competing center for the recombination and reduces the net rate of forward reaction.

The impurities may affect the backward secondary processes in two ways. It is known that the impurities stabilize the interstitial centers produced by irradiation\textsuperscript{152}. Either the impurity ions themselves or the cation vacancies may be responsible for this. The recombination rate between F-centers and interstitials are reduced leading to an enhanced F-center production\textsuperscript{149,152,160,161}. The suppression of the second stage coloration in crystals containing electron trapping impurities may also be explained in terms of increased back reaction rate. The optical absorption studies discussed in Section 4.I.B2 indicate that the impurity is not acting in the role of an electron capture center but the irradiation converts a large fraction of the Sn\textsuperscript{2+} ions to Sn\textsuperscript{4+} ions.

The results of the present work suggest that the F-center growth curves at RT can be described in terms of two saturating substages followed by a linear stage in agreement with the findings of other workers\textsuperscript{54,143}. Alvarez Rivas and Levy\textsuperscript{54} observe that changing the experimental conditions alters one or two of the parameters and the others are unchanged. This suggests that each component in Eq. (4.1) arises out of a separate physical process which is affected in a specific way by any change in the experimental conditions. It has been
observed\textsuperscript{147} that a maximum of three exponential components are required in Eq. (4.1) to describe the experimental growth curves. Of these, the first one $A_1(t)$ is often too small to be observed. The next substage $A_2(1-e^{-a_2t})$ is a fast exponential one, believed to be due to an electronic process\textsuperscript{162,163} involving the trapping of electrons by anion vacancies and competing with a radiation-induced bleaching process. The last, a relatively slow exponential component $A_3(1-e^{-a_3t})$ is attributed to an unspecified process involving the release of vacancies from aggregates or other lattice defects competing with thermally activated vacancy trapping\textsuperscript{163}.

The parameter $a_L$ which represents the rate of generation of F-centers in the linear second stage does not show any regular trend. Alvarez Rivas and Levy\textsuperscript{54} report that the constant $a_L$ is independent of dose rate for NaCl crystals. Similarly Sastry and Srinivasan\textsuperscript{143} observe the same behaviour for pure and Co, Ba and Cd doped KCl crystals. But a suppression of $a_L$ is found for Pb, Mn, Ca and Cd impurities by some investigators\textsuperscript{149,137,164,43}.

Sanchez and Agullo-Lopez\textsuperscript{163} suggest a process consisting of the release of anion vacancies from certain sources with a simultaneous removal of these vacancies by certain traps. According to the present investigation impurities affect this process and it is likely that the
sources and/or traps in question are associated with the impurities present. Recently Alvarez Rivas and Levy\textsuperscript{146} obtain a value of 0.1 eV for the second substage for pure NaCl. Ikeya et al\textsuperscript{157} have also got a value of 0.08 eV for the initial F-center formation in Ca doped NaCl. Taking into account the fact that halogen interstitials are mobile with low activation energies, Farge and co-workers\textsuperscript{160,165} have developed a model for F-center growth in which the mobile interstitials can recombine with F-centers or other traps. Farge\textsuperscript{160} suggests that the presence of divalent impurities introduces a certain number of saturable traps for the interstitials in addition to the nonsaturable ones. His theoretical growth curves show that the approach to the second stage is exponential and the increased numbers of saturable traps result in higher saturation levels for the first stage production. The increase in $A_2$ observed for the lower concentrations for the doped crystals may be accounted for on the above lines. On the other hand the impurity at higher concentrations appears to show a different effect. It is not possible at present to offer an explanation for all the observed results.

The two substages of the initial growth point to the existence of two distinct sources of anion vacancies which may be vacancy pairs or clusters or dislocation jogs. Some of the added impurities are likely to be embedded in these imperfect regions of the crystal, with the corresponding cation vacancies far removed. The divalent cation impurity
can then stabilize a cation vacancy associated with the vacancy aggregates and help release an anion vacancy during the irradiation process. The saturation number of F-centers may conceivably be increased accordingly. On the other hand when the impurity concentration near the vacancy sources increases it may well result in stabilizing both anion and cation vacancies depending upon the configuration of this defect region. It may be mentioned that the thermoluminescence results (Chapter III) also point to the existence of two substages with different local environment. The trap parameters are sensitive to small changes in the environment.

The growth of the ultraviolet absorption band around 230 nm (5.387 eV) under X-irradiation (30 KV:15 mA) on the KCl:NaCl:Sn crystals are shown in Fig. 4.15. 'a', 'b', 'c', 'd', and 'e' represent the growth curves for these samples with Sn concentrations corresponding to 0, 0.05, 0.2, 0.4 and 0.8 mole % respectively. For these crystals the optical absorption spectra show only a broad band around 230 nm (5.387 eV) even after irradiation. The A, B and C-bands are not resolved, but the absorption intensity increases around 230 nm (5.387 eV). To draw the growth curves the contribution due to the uncolored sample is always subtracted from the total absorption at this region. The growth curves of these bands can be seen to be similar in their shape and trends to the F-center growth curves.
Fig. 4.15 Growth curves of the 230-nm band for doped and undoped KCl:NaCl crystals, x-irradiated at room temperature. a, b, c, d and e correspond to concentrations of Sn as 0, 0.05, 0.2, 0.4 and 0.8 mole % respectively.
SECTION 4. III

ELECTRON SPIN RESONANCE STUDIES

4.III.A INTRODUCTION

Electron Spin Resonance (ESR) technique has been extensively employed to study paramagnetic centers and to help in verifying the models proposed for a number of color centers. Centers with unpaired electrons are paramagnetic and exhibit characteristic ESR. Measurement of the ESR of such centers usually yields information on the nature of the center, its symmetry and spread of the wave function. Examples are the F-center, excited state of the M-center, \( V_K \) - center besides impurity centers in an appropriately charged state. The \( V_K \) - center which is a halogen molecular ion \( X_2^- \) was in fact isolated by ESR study. Irradiation of an impurity doped crystal may lead to the conversion of the impurity to a paramagnetic charge state, when the impurity traps or loses electrons. Thus simple observation of an ESR signal or the mere lack of it can provide a useful guideline for the interpretation of experimental results. It should be pointed out however that even though
paramagnetic centers are present in the crystal the corresponding resonance absorption may not be observable in some cases. For instance a center may have a large $g$-anisotropy and a random distribution of the orientations of the centers might smear out the signal. Optimum relaxation times are also required for observing the ESR.

When a crystal containing the paramagnetic centers having magnetic moment $g \beta$ is placed in a static magnetic field $H$, power may be resonantly absorbed by the crystal from an applied microwave electromagnetic field (the polarization of the alternating magnetic field being at right angles to the static magnetic field) when the following resonance condition is satisfied,

$$h\nu = g\beta H$$  \hspace{1cm} (4.3)

where $\beta = \text{Bohr magneton}$,
$g = g$-factor of the center,
$\nu = \text{the frequency of the alternating field,}$
and $h = \text{Planck's constant}$.

For a static magnetic field of about 3000 Gauss the frequency of resonance occurs in the microwave region. The experiment in principle consists of placing the crystal in a tuned microwave cavity which is held in a homogeneous
magnetic field and scanning the static field $H$ through the resonance condition. $\mathcal{V}$ is held constant. Resonance absorption is marked by a pronounced dip in the power level. The spectra are usually obtained on a phase sensitive detector system so that the derivative of the absorption is plotted against the magnetic field. When the unpaired spin interacts with one or more nearby nuclei with nonvanishing nuclear spin a hyperfine structure may be observed which often helps in the identification of the center. The results of the ESR experiments to detect the presence of paramagnetic Sn ionic species are described in this Section.

4.III.B RESULTS AND DISCUSSION

The $\text{Sn}^{2+}$ ion with the $5s^2$ configuration is diamagnetic in the $1S_0$ ground state. Another stable valence state of the Sn ion (as in SnO$_2$) is $\text{Sn}^{4+}$ which is also diamagnetic in its $1S_0$ ground state. The monovalent ion $\text{Sn}^+$ has the electron configuration $5s^25p$. The trivalent ion $\text{Sn}^{3+}$ (5s) also has an unpaired spin and both Sn ions of odd valency are expected to be paramagnetic. Experiments on the Sn doped crystals colored by X-irradiation (Section 4.I.B2) strongly suggest that the impurity ion undergoes a transformation in its charge state. An unsuccessful search for the ESR signal at RT and at 100 K ($\sim$ LNT) has shown that the new state of the impurity is more likely to be diamagnetic. The obvious conclusion is that the
\( \text{Sn}^{2+} \) ions are converted to \( \text{Sn}^{4+} \) ions by irradiation.

Crystals colored by the additive method have shown substantial changes in the optical absorption spectra of the ultraviolet region (Section 4.I.B3). A change in the charge state of the impurity ion is indicated. These crystals have shown an isotropic singlet ESR line with \( g \) values 2.015 at RT and 2.018 at 100 K (\( \sim \) LNT). The actual reproduction of the recorder chart is shown in Fig. 4.16. (LNT in the figure refers to 100 K). The width between the derivative peaks being 10 and 2.2 Gauss at RT and at 100 K (\( \sim \) LNT) respectively. The Sn nuclei have preponderant isotopes (\( \sim 84\% \)) with nuclear spin \( I = 0 \), the other isotopes having nonzero nuclear spins of \( 1/2 \) and \( 3/2 \). The singlet line can therefore be assigned to an Sn species and not to any other species with the unpaired electron centered on either the alkali or the halogen ions both of which have nonzero nuclear spins. The suppression of the F-center growth in the additive coloration strongly suggests that the impurity has captured an electron to become \( \text{Sn}^+ \). Moreover the ionic conductivity and dielectric loss measurements discussed in Chapter V lend support to this view. Therefore the ESR signal can be assigned to \( \text{Sn}^+ \). The monovalent \( \text{Sn}^+ \) will not be associated with any vacancy and the 5p electron wavefunctions remain degenerate so that no g-anisotropy may be expected. But the sizeable orbital
FIG. 4.16  Electron spin resonance spectrum of an additively colored Sn doped KCl crystal
contribution would reduce the $g$ factor significantly from the free electron value in the case of an electron excess center and raise it above the free electron value for hole centers. As the Sn$^+$ ion contains an electron outside a closed shell, it is not clear why the $g$ value is larger than the free electron value. The $g$ has been measured accurate to at least two units in the third decimal place.

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