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Effect of Ionizing Radiation of Impurity-Vacancy Dipoles in Lead-Doped NaCl and KCl[†]

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The radiolytic behavior of NaCl : Pb and KCl : Pb upon exposure to 1.5-MeV electrons at various temperatures has been investigated by means of optical absorption and ionic thermocurrent (ITC) methods. Irradiation decreases the Pb^{2+} *A* band at 272 nm and introduces two narrow bands at 207(210) and 253 nm in NaCl (KCl). Since the new bands decrease in amplitude when holes are released by warming the crystals into the range where they become mobile, and increase in amplitude at the expense of the *A* band when electrons are released by *F*-band excitation, we conclude that they are associated with Pb states of lower positive charge, i.e., Pb^0 and/or Pb^+. Irradiation also decreases the height of the Pb^{2+}-cation-vacancy ITC relaxation peak near 227 °K and introduces small ITC peaks at lower temperature, which are not produced by similar irradiation doses in pure KCl. One of these, at 175 °K in NaCl and near 200 °K in KCl, anneals at 300 °K but is enhanced by *F*-band bleaching at lower temperatures. It is proposed that this new ITC peak is associated with the relaxation of a pseudodipole composed of a cation vacancy bound by elastic forces to a Pb^+ ion.

I. INTRODUCTION

The presence of Pb^{2+} impurities is known to have dramatic effects on the rate of defect production in alkali halides by ionizing radiation. The efficiency of this ion as an electron trap is well known,[1] and more recently its ability to trap holes has become recognized.[2] Above the hole-motion temperature (200 °K for KCl), aside from a small enhancement of the early-stage *F*-center production, Pb^{2+} drastically suppresses the rate of *F*-center creation[3] and this suppression of defect formation is greater the lower the intensity of ionizing radiation[4] (rate of energy deposition). This effect has been interpreted in two ways: (a) Pb^{2+} acts as an electron-hole recombination center and thereby short-circuits recombination in the lattice proper[3]; the result is the elimination of the energy release accompanying radiationless exciton recombination which is currently held responsible for creation of Frenkel-type defects.[5] (b) Capture of electrons by Pb^{2+} shifts the dynamical equilibrium between free electrons and mobile holes toward a high hole density with the result that anion vacancies produced by the irradiation remain empty a greater fraction of the time.[6] Since empty anion vacancies are thought to be much more mobile than occupied ones[7] (*F* centers), the former are able to migrate to and annihilate halogen interstitials. Recent studies by Sonder[8] on pure NaCl suggest that both of the mechanisms operate to suppress coloration.

A quite different effect appears to operate below the hole-motion temperature where, at least in the case of KCl, Sonder and Sibley[9] have observed an enhancement in the *F*-center creation rate for electron bombardment at 80 °K. This behavior has been explained in terms of the trapping and stabilization of interstitials at the impurity in such a way as to inhibit the back reaction, i.e., interstitial-vacancy recombination. Since the enhancement persists to *F*-center concentrations in excess of that of the Pb^{2+}, it was concluded that each impurity ion must stabilize more than a single interstitial. A similar but somewhat weaker effect was observed for Ca^{2+}-doped KCl as well.

We report here a further study of the influence of Pb^{2+} on radiolysis of both NaCl and KCl with specific attention to that fraction of the impurity bound in complexes. For this purpose we used the ionic thermocurrent (ITC) method[10] to assay the Pb^{2+}-cation-vacancy concentration before irradiation and after irradiation and various anneals and optical bleaches. In essence, the ITC method consists of polarizing the dipole-containing crystal at a temperature where the dipoles are free to move, freezing in the polarization by cooling the specimen with the field applied, removing the field, and recording the displacement current as the dipoles reorient during warming at a constant rate of temperature increase. The area under the first-order peak is proportional to the dipole density, whereas the shape and position of the peak yields the activation energy and frequency factor of the reorienting relaxation. By comparing the change in density of these dipolar complexes with changes in the optical spectra, several things can be inferred concerning the way in which the incorporation of Pb^{2+} in the lattice affects its role in the radiolytic process. In addition irradiation introduces new ITC peaks which indicate that new dipoles, presumably involving Pb in some state of ionization, are created by irradiation.

II. EXPERIMENTAL PROCEDURE

All measurements and operations were carried out with the specimens mounted in a specially de-

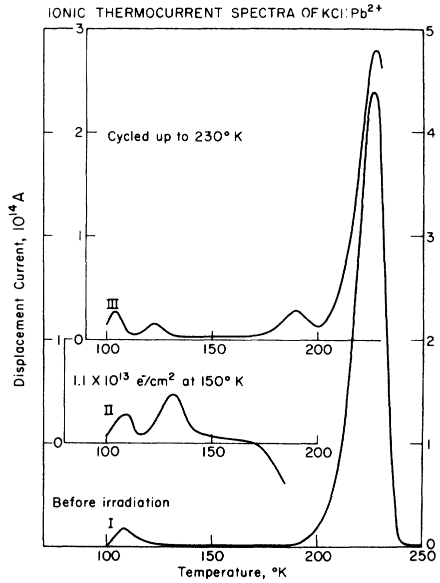

FIG. 1. Ionic thermocurrent spectra for KCl : Pb^{2+}. Curve I: after quenching from 475 °K; curve II: after exposure to 1.1×10^{13} 1.5-MeVe^-/cm^2 at 150 °K; curve III: after thermal cycling up to 230 °K.

signed cryostat. The tail section was provided with a set of nondarkening Corning fused-silica (7943) windows which allows measurement of optical absorption over the range 200–1200 nm with a Cary 14-R spectrophotometer. These windows were shuttered until the assembly was positioned in the spectrophotometer to prevent optical bleaching of irradiated specimens. An irradiation port consisting of a 10-mil aluminum window was located normal to the optical-window axis and the tail section could be rotated to bring either the port or optical windows opposite the broad specimen faces. Before mounting, the specimen was provided with transparent platinum electrodes by cathodic sputtering. A high-impedance electrode from a Cary model 31 vibrating-reed electrometer was brought into contact with one face of the specimen. The peak-to-peak noise in the current measurement was 5×10^{-16} A. Specimens were bombarded at various controlled temperatures with 1.5-MeV electrons from a Van de Graaff generator (current density ~ 0.2 μA/cm^2).

Specimens of KCl : Pb^{2+} and NaCl : Pb^{2+} were obtained from the Harshaw Chemical Company (HAR) and from the Naval Research Laboratory (NRL). The concentration of dissolved Pb^{2+} ranged from 5 to 20 ppm as determined from the amplitude of the A band and by chemical analysis.

III. EXPERIMENTAL RESULTS

A. KCl:Pb^{2+}

Prior to irradiation, all specimens were quenched after annealing at 475 °K. This temperature was chosen because it was necessary to quench the crystal in the cryostat and 475 °K is the maximum temperature to which it could be safely subjected. Moreover, earlier studies[11] have shown that this treatment places into solution most of the Pb^{2+} impurity for the concentrations used in this work (~ 20 ppm). The ITC spectrum for a KCl : Pb^{2+} specimen is shown in Fig. 1. The dominant feature is a peak at 227 °K; in addition a very small peak occurs at 108 °K. Not visible are the small peaks at 140, 152, and 170 °K observed by Cappelletti and Fieschi[12] in more heavily doped (> 100 ppm) specimens. The area P' under the peak multiplied by the heating rate β (= 0.2 deg/sec in these experiments) and the ratio of thickness to area, t/A, yields the polarization per unit volume of the crystal, P, which is given by the expression

$$P = (\beta t/A)P' = (\mu_d^2 N_d / 3kT_p)E , \qquad (1)$$

where μ_d is the dipole moment, N_d the dipole concentration, T_p the temperature of polarization, and E the polarizing electric field. We used $T_p = 230$ °K and an applied voltage $V = Et = 500$ V. From the symmetry of polarized luminescence,[13] it appears that the next-nearest-neighbor (nnn) Pb^{2+}-vacancy dipole is dominant in KCl, which on the basis of an unrelaxed hard-sphere model yields $\mu_d = 1.05 \times 10^{-28}$ C cm. Using these quantities we obtain a dipole concentration of 9.1×10^{16} cm^{-3} (5.7 ppm) for the specimen of Fig. 1. Since an appreciable concentration of nearest-neighbor (nn) dipoles may yet be present and lattice relaxation may reduce in some degree the nnn moment, this value should be regarded as the lower limit on the dipole concentration.

By assuming that the room-temperature value of the oscillator strength of 0.11 determined by Sibley *et al.*[4] for the Pb^{2+} A band is valid at 80 °K, the total unprecipitated Pb^{2+} concentration can be estimated from the absorption spectrum. The value so obtained, taking the A-band half-width to be 0.10 eV, is 1.95×10^{17} cm^{-3} (12 ppm), a value nearly twice that indicated by polarization measurements. Dryden and Harvey[14] have shown that the shape of the A band in KCl is insensitive to whether the Pb^{2+}-vacancy dipoles are dispersed or are in the form of small aggregates. Therefore, we conclude that approximately one-half of the Pb^{2+} is present in the form of free dipoles and the remainder in the form of small aggregates. Some isolated Pb^{2+} may also be present provided there is compensation by O^{2-}.

Computer fits to ITC peaks, such as that at 227 °K in curve I of Fig. 1, according to the first-order expression for dipole relaxation yield the kinetic parameters $\tau_0 = 7.3 \times 10^{-14}$ sec and $E = 0.660$ eV. The reorientation energy compares favorably with values obtained from ITC measurements by

Brun *et al.*[15] (2×10^{-13} and 0.65 ± 0.01 eV) but is somewhat different from the results of Collins[16] using dielectric loss and a higher doping level ($E\simeq0.69$ eV).

After exposure to 1.1×10^{13} 1.5-MeV e^-/cm^2 at 150 °K, the ITC spectrum was remeasured (curve II of Fig. 1). In order to keep the specimen below the hole-motion temperature (~ 200 °K), this first run was taken after polarizing at 150 °K. A small but distinct peak at 131 °K appears and the small peak at 107 °K is appreciably enhanced. The bending down of the ITC curve to negative values above 150 °K is apparently caused by some not-well-understood charge-release effect associated with trapped electrons. In other ITC runs, charge-release effects resulted in positive rather than negative currents. If valid ITC data above T_p on an irradiated sample are desired, it is necessary to cycle the specimen thermally up to the highest temperature of interest before polarization to eliminate such charge-release effects. Curve III was obtained after cycling to 230 °K—a temperature in the range where hole mobility is appreciable. It is now evident that the amplitude of the initial 227 °K peak has been markedly decreased. Indeed, since only a portion of the crystal was irradiated, the loss of Pb^{2+}-vacancy dipoles in the affected portion is even greater than indicated by a comparison of curves III and I; in fact ΔN_d amounts to one-half the preirradiated value. Also evident in curve III is an additional peak at ~ 190 °K and a drastic reduction and shift of the 107 and 131 °K peaks. An intervening run in which the specimen was warmed to 190 °K produced hardly any decrease in these two peaks; however, in a separate experiment, annealing for only 5 min at 200 °K caused a pronounced decrease. Therefore, the 107 and the 131 °K peaks seem to be stable to some point in the range 190–200 °K. It should be emphasized that for pure KCl electron bombardments of comparable duration produce no additional ITC peaks in this temperature range.[17]

A second $KCl:Pb^{2+}$ crystal (initial value of N_d $=8.8\times10^{16}$ cm^{-3}) was electron irradiated at 250 °K, i.e., in the range of mobility for both holes and anion vacancies. An exposure of 1.0×10^{13} e^-/cm^2 produced a substantial reduction in N_d (from 8.8×10^{16} to 6.5×10^{16} cm^{-3}) without any evidence of additional peaks in the range down to 100 °K. After a second exposure to a cumulative dose of 3.2×10^{13} e^-/cm^2, small but perceptible peaks at 103 and 125 °K were visible and a third peak centered at 198 °K appeared. The second exposure removed 7×10^{16} cm^{-3} of the dipoles initially present in the irradiated portion of the crystal. Bleaching with light absorbed in the short-wavelength tail of the F band completely eliminates the original dipoles, erases the 103 °K peak, broadens and weakens the 125 °K peak, and enhances the 198 °K peak.

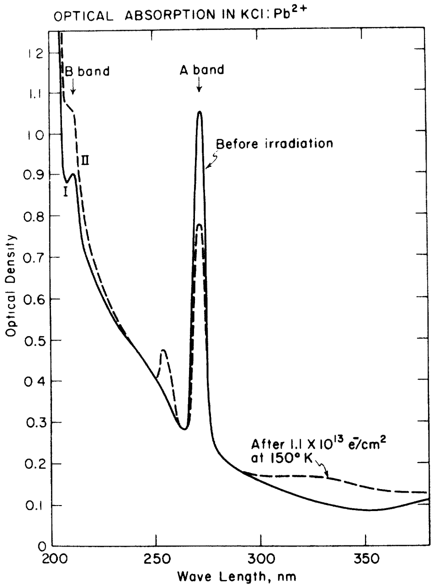

FIG. 2. Absorption spectra of $KCl:Pb^{2+}$ in the near ultraviolet. Curve I: after quenching from 475 °K; curve II: after exposure to 1.1×10^{13} 1.5-MeV e^-/cm^2 at 150 °K. (All spectra measured at 80 °K.)

The effect of electron bombardment at 150 °K on the optical absorption of $KCl:Pb^{2+}$ is shown in Fig. 2, where spectra measured at 80 °K after quenching from 475 °K (curve I) and after exposure to 1×10^{13} electrons/cm^2 (curve II) are compared. Prior to irradiation the A and B bands associated, respectively, with the ${}^1S_0\rightarrow{}^3P_1$ and ${}^1S_0\rightarrow{}^3P_2$ transitions of the Pb^{2+} ion are clearly delineated.[18] After irradiation, the important spectral features are (a) a well-developed F band at 540 nm (not shown), (b) a marked decrease of the A band, and (c) the introduction of sharp bands at 253 and 210 nm. The broad excess absorption between 300 and 400 nm is presumably caused by V_K centers and related hole bands.

Upon warming to 250 °K, complex spectral changes occur. The difference spectrum obtained by subtracting the optical density after warming from values after 150 °K irradiation is shown in Fig. 3. Positive values of the change in the optical density (ΔOD) represent losses in absorption upon warming whereas negative values indicate increases in absorption. Significant changes include (a) a partial restoration of the A band, (b) a partial loss of the 253 and 210-nm bands, (c) the introduction of new narrow band at 250 nm, (d) the introduction of a broad band near 230 nm, and (e) the loss of trapped holes.

The spectral changes resulting from electron bombardment at 250 °K are shown by curve I of Fig. 4. Notable here is the production of the large,

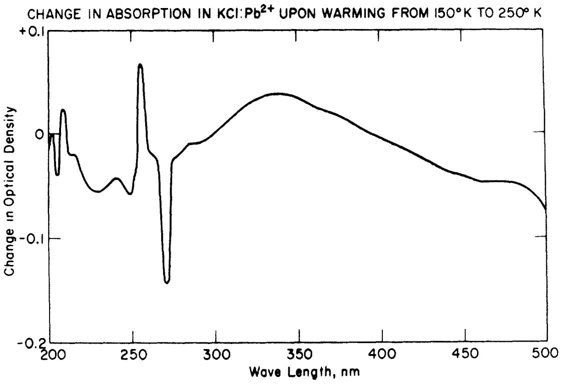

FIG. 3. Change in absorption upon warming specimen of Fig. 2 to 250 °K. +ΔOD's represent decreases in absorption upon warming and − ΔOD's represent increases in absorption. (All spectra measured at 80 °K).

broad 230-nm band and the sharp 210- and 253-nm bands. There is a suggestion of a new band at 280 nm. The sharp suppression of the *A* band also occurs. Curve II of Fig. 4 demonstrates the effect of optical bleaching. To avoid effects associated with defect motion, the crystal was held at 150 °K while the crystal was excited with light in the short-wavelength tail of the *F* band (4350 nm). For curve II positive-ΔOD values represent a decrease and negative values an increase in absorption caused by the bleaching. This operation caused a drastic decrease of the *F*-band amplitude (from an OD value of 4.1 to 0.15). Release of *F*-center electrons into the crystal causes a further decrease in the *A* band and an enhancement of the 210- and 253-nm bands. In addition bands near 465 and 230 nm are reduced in intensity.

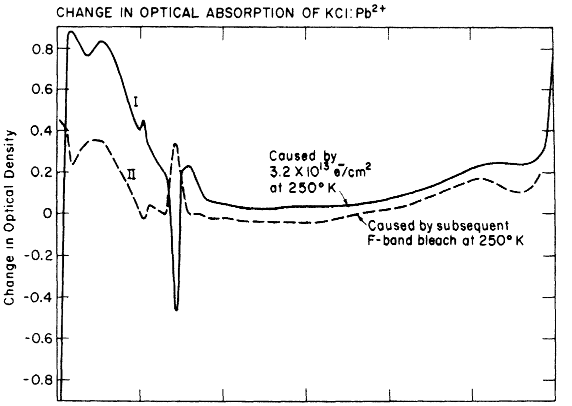

FIG. 4. Effect of 250 °K electron irradiation of KCl : Pb^{2+}. Curve I: change in optical density caused by irradiation with 3.2×10^{13} 1.5-MeV e^-/cm^2 (+ΔOD represents an increase in absorption and − ΔOD a decrease); curve II: change induced by a subsequent *F*-band bleach at 250 °K (+ΔOD represents a decrease in absorption and − ΔOD an increase). (All spectra measured at 80 °K.)

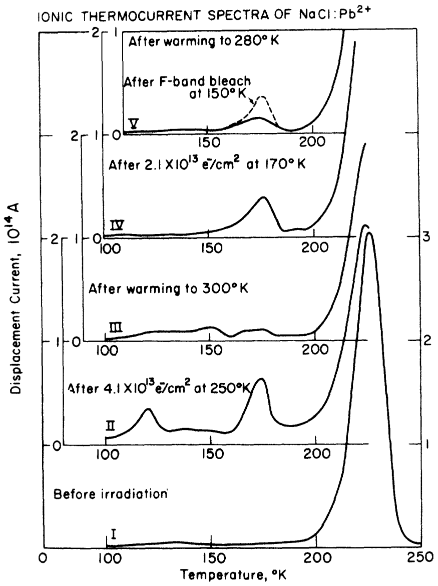

FIG. 5. Ionic thermocurrent spectra for NaCl : Pb^{2+}. Curve I: after quenching from 475 °K; curve II: after exposure to 4.1×10^{13} 1.5-MeV e^-/cm^2 at 250 °K; curve III: after warming to 300 °K; curve IV: after a 475 °K anneal, quench, and re-irradiation (2.1×10^{13} 1.5-MeV e^-/cm^2) at 170 °K; curve V: after warming to 280 °K; the dashed portion was obtained after an *F*-band bleach at 150 °K.

B. NaCl:Pb^{2+}

The dielectric relaxational behavior of NaCl : Pb^{2+} specimens is summarized in Fig. 5. After the initial quench from 475 °K, the only notable feature of the ITC curve (curve I) is a peak at 226 °K. Assuming only unrelaxed nnn dipoles, the area under the peak corresponds to a concentration of 1.29×10^{17} cm^{-3} (5.8 ppm) nnn dipoles. As in the above case of KCl : Pb^{2+}, this should be regarded as a lower limit because of the possibility of an appreciable fraction of nn dipoles. If one assumes that the *A*-band oscillator strength is the same for Pb^{2+} in NaCl as it is in KCl,[4] the *A*-band amplitude corresponds to a Pb^{2+} concentration of 1.32×10^{17} cm^{-3} in good agreement with the dipole concentration. An analysis of the ITC curve yields $\tau_0=2\times10^{-13}$ sec and $E=0.66$ eV for the dipole relaxation process. Curve II results from polarization at 230 °K after exposure to 4.1×10^{13} e^-/cm^2 at 250 °K; in addition to a 75% reduction in the 226 °K-peak amplitude, peaks at 120 and 175 °K appear. Annealing for 5 min at 300 °K largely removes the low-temperature peaks without any appreciable restoration of the 226 °K peak. Curve IV was obtained after a high-temperature anneal, quench, and re-irradiation ($2.1\times10^{13}e^-$/cm^2) at 170 °K. Irradiation at the lower

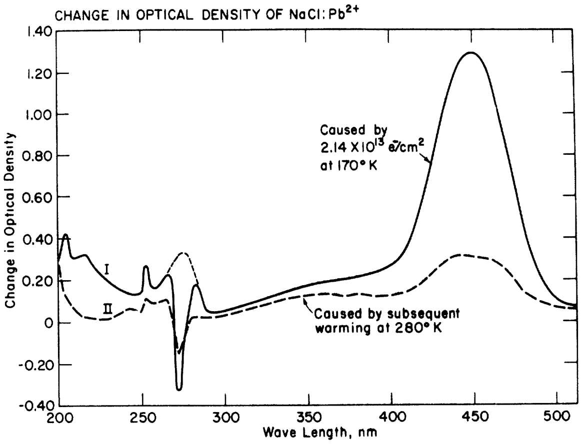

FIG. 6. Change in absorption in NaCl : Pb^{2+} caused by irradiation and subsequent treatment at 170 °K. Curve I: change in optical density caused by exposure to 2.14×10^{13} 1.5-MeV electrons at 170 °K (+ΔOD represents an increase in absorption); curve II: change caused by warming to 280 °K (+ΔOD represents a decrease in absorption). (Spectra measured at 80 °K.)

temperature produced only the 175 °K peak and diminished the 226 °K peak by 50%. Upon warming overnight to 280 °K, curve V was obtained. The partial loss of the 175 °K peak indicates that the responsible defect is not completely unstable at 280 °K. Bleaching with *F*-band light at 150 °K strongly enhances the 175 °K peak and causes a further 15% decrease in the 226 °K-peak intensity. Again annealing at 300 °K virtually removes the 175 °K peak.

The absorption spectrum of a NaCl : Pb^{2+} specimen quenched from 475 °K is almost identical to that for KCl : Pb^{2+}. The main difference is that the three peaks of the *C* band[18] (195, 198, and 203 nm) are somewhat better resolved than for KCl. Changes resulting from electron bombardment (2.14×10^{13} e^-/cm^2) at 170 °K are shown in Fig. 6 by curve I. The familiar decrease in the *A*-band amplitude is clearly evident as is the appearance of the 207- and 253-nm bands (analogous to the 210- and 253-nm bands in KCl). Even though the irradiation temperature is at the edge of the hole-mobility range in NaCl, there appears to be an appreciable concentration of V_K centers. This is perhaps not too surprising since the specimen was quenched to 80 °K immediately after irradiation. The shape of the curve in the vicinity of the *A* band strongly suggests that irradiation introduces a broad band near 275 nm as indicated by the dashed curve. This conclusion is borne out by a comparison of the change in Pb^{2+} concentration N_{Pb} calculated from curve I with the change in dipole density N_d estimated from ITC measurements. Values were 3.7×10^{16} cm^{-3} for ΔN_d versus 3.0×10^{17} cm^{-3} for ΔN_{Pb}, suggesting that ΔOD at 272 nm gives too small a value for the change in *A*-band intensity.

Curve II of Fig. 6 is the difference spectrum obtained upon warming to 280 °K overnight. Again, in contrast to curve I, +ΔOD represents a decrease in absorption. As might be expected, the V_K region thermally bleaches giving rise to a decrease in the concentrations of trapped electrons, i.e., *F* centers, 207-nm centers, and 253-nm centers, with a resultant increase in Pb^{2+} as indicated by an increase in *A*-band amplitude. There is evidence of the creation of a small band at 250 nm analogous to the one observed for a similar treatment in KCl. The behavior of this same specimen upon optical bleaching is also instructive. Figure 7 shows the effect of cooling to 150 °K and exciting with *F*-band light (+ΔOD indicates a decrease in absorption). Release of electrons from the *F* band, which was reduced to 40% of its amplitude by the bleach, increases the concentration of trapped electrons as expected: The *A* band decreases and the 207- and 253-nm bands increase. There is also a reduction of absorption below 240 nm suggesting that a hole band in this region is being destroyed.

Irradiation of NaCl : Pb^{2+} at 250 °K results in a spectrum with several differences. The results are shown by curve I of Fig. 8. Aside from expected changes at 273, 253, and 207 nm, a large broad band at 247 nm dominates the spectrum. Upon warming to 300 °K, there is a modest redistribution of charge resulting in a small increase of the 253-nm band, a larger increase in the *A* band, the appearance of a broad band near 210 nm, and a modest decrease of the broad 247-nm band.

Changes in the values of N_d, $N_{Pb^{2+}}$, and N_F resulting from the various treatments are summarized in Table I. N_d was calculated according to Eq. (1)

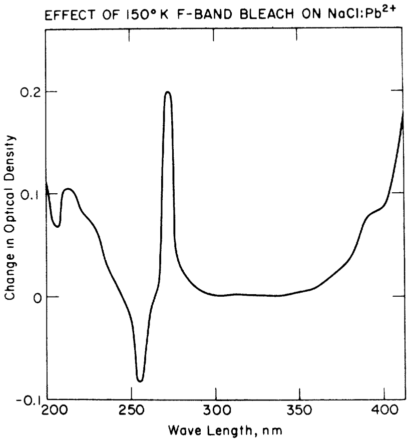

FIG. 7. Effect of *F*-light bleaching at 150 °K on the optical absorption of the specimen of curve II of Fig. 6. (+ΔOD represents a decrease in absorption.) (Spectrum measured at 150 °K.)

with appropriate correction being made for the area of the specimen struck by the electron beam (0.3 cm^2). $N_{\mathrm{Pb}^{2+}}$ and N_F were determined from Smakula's equation, modified for Gaussian shape[19] and the amplitudes of the A and F bands, respectively.

IV. DISCUSSION

Before discussing the dipole relaxation, it is advantageous to consider what can be learned about the influence of irradiation and subsequent treatment upon the Pb^{2+} impurity from the optical-absorption behavior. The decrease in the A-band absorption induced by ionizing radiation was first observed in NaCl : Pb^{2+} by Schulman *et al.*[20]; more recently Sibley *et al.*[4] reported a similar effect in KCl : Pb^{2+}. The loss of A-band absorption indicates a change in Pb-charge state by electron or hole capture. The electron-trapping propensity of Pb^{2+} which has played an important role in the investigation of V_K centers is well known.[1] Indeed, as early as 1950, Schulman *et al.*[20] recognized that both Pb^{1+} and Pb^0 might be expected in irradiated crystals. More recently, Schoemaker and Kolopus[2] have demonstrated using EPR methods that, under conditions appropriate for hole migration, Pb^{3+} forms; thus Pb^{2+}, like Ag$^+$, is both a hole and an electron trap. They attribute optical-absorption bands at 216, 303, and 465 nm to this center. From a study of additively colored and irradiated Pb^{2+}-doped alkali halides, Jain *et al.*[21] have attributed broad bands at 250 and 260 nm to the Pb^{1+} in NaCl and KCl, respectively, and a broad band at 240 nm is identified with Pb colloid band. Ben-Dor *et al.*[22] have also studied additively colored NaCl : Pb and KCl : Pb and they observe the sharp 253-nm band which they associate with Pb^{1+} and a band at 325 nm which is attributed to Pb^0. We shall now compare these results with those summarized above.

It is quite clear from the behavior described in Sec. III that the 253-nm band is associated with a reduced-charge state of Pb, i.e., either Pb^{+1} or Pb^0. Not only is this band produced in that range where hole mobility is restricted, it is diminished when self-trapped holes (V_K centers) are released by warming and it is enhanced when the crystal is flooded with electrons by F-band excitation. Simultaneously the A band shows an inverse behavior. Similar remarks apply to the sharp bands at 207 and 210 nm in NaCl and KCl, respectively, which are observed in all spectra after irradiation. We are unable to establish conclusively whether the 253- and 207(210)-nm bands are (a) two transitions of the

TABLE I. Changes in N_d, $N_{\mathrm{Pb}^{2+}}$, and N_F resulting from various treatments.

Specimen	Treatment	N_d (10^{16} cm^{-3})	$N_{\mathrm{Pb}^{2+}}$ (10^{16} cm^{-3})	N_F – (10^{16} cm^{-3})
NCl : Pb NRL-*A*	475 °K quench	8.9	28.8	−1.0
	1.0×10^{13} e^-/cm^2, 250 °K	6.5	16.7	16.6
	3.2×10^{13} e^-/cm^2, 250 °K	~0	13.3	20.2
	Anneal 250 °K, 40 min	1.2	14.5	19.8
	F-bleach 250 °K, 50 min	~0	9.4	0.7
KCl : Pb NRL-*B*	475 °K quench	9.1	19.5	···
	1.1×10^{13} e^-/cm^2, 150 °K	···	12.8	4.5
	Anneal 250 °K, 5 min	4.6	15.9	2.5
	3.2×10^{13} e^-/cm^3, 150 °K	···	8.7	5.8
	Anneal 250 °K, 5 min	1.2	13.5	5.0
NaCl : Pb NRL-*C*	475 °K quench	13.3	14.6	···
	4.2×10^{13} e^-/cm^2, 250 °K	···	3.4	···
	Anneal 250 °K, 5 min	9.7	7.0	···
NaCl : Pb NRL-*D*	475 °K quench	12.9	13.2	···
	1.0×10^{13} e^-/cm^2, 170 °K	···	8.4	5.9
	Anneal 250 °K, 5 min	9.2	10.2	4.4
	2.1×10^{13} e^-/cm^2, 170 °K	···	7.2	7.8
	Anneal 250 °K, 5 min	6.7	10.2	6.1
NaCl : Pb HAR-*A*	475 °K quench	6.1	12.8	···
	2.1×10^{13} e^-/cm^2, 200 °K	···	6.2	15.8
	Anneal 250 °K, 5 min	3.1	7.6	15.7
	4.3×10^{13} e^-/cm^2, 200 °K		4.2	25.1
	Anneal 250 °K, 5 min	0.4	5.7	21.7
	8.4×10^{13} e^-/cm^2, 200 °K		4.3	29.8
	Anneal 250 °K, 5 min	~0	5.7	22.3

same Pb center, (b) associated with Pb ions of the same charge state but located in different crystalline environments, or (c) associated with two distinctly different Pb-charge states. However, we believe that interpretation (c) is the correct one for several reasons: Against (a) is the fact that the amplitudes of these bands induced by the various operations do not appear to occur in any fixed ratio. Secondly, since the positions of these bands are virtually the same in both KCl and NaCl, the transitions are evidently not strongly affected by crystalline environment which would oppose interpretation (b). However, it should be remembered that there are possible environmental changes which may be drastic enough to cause such a shift; one example is the transfer of Pb to an interstitial site. Evidence for both interstitial Mn^{2+} and Mn^0 has been reported[23] for irradiated NaCl : Mn^{2+}. Therefore (b) is not completely excluded. Since the 207(210) band shows a greater amplitude than the 252-nm band at the higher exposures, one is tempted to conclude that the former is associated with Pb^0 whose concentration must grow at the expense of the Pb^+ concentration when most of the Pb^{2+} has been consumed. However, more conclusive evidence is necessary before a definite identification of the responsible defects can be made.

The broad band at 230 nm in KCl, which appears upon either warming an irradiated specimen into the range of hole mobility (Fig. 3) or irradiation of a specimen in this range (Fig. 4), is probably identical with the V_2 band first studied by Casler *et al.*[24] and is apparently not intimately associated with Pb. This band evidently has a counterpart in NaCl at 225 nm (Fig. 6). *F*-band bleaching destroys this absorption indicating that it is caused by some type of hole center. There are several other broad bands of unknown origin which we shall not discuss here. Some of these may involve Pb together with some configuration of irradiation-produced defects, i. e., either with interstitials or with anion vacancies; the latter seem to become mobile above ~ 200 °K in KCl and ~ 250 °K in NaCl. However, careful study of the way in which these spectra develop will be necessary to identify them. These include bands at 280 nm (Fig. 4) in KCl and at 215 nm (Figs. 6 and 8), 275 nm (dashed curve, Fig. 6) and 248 nm (Fig. 8) in NaCl.

A careful search for the Pb^{3+} bands reported by Schoemaker and Kolopus[2] turned up only the band at 465 nm (Fig. 4) which appears to be due to a trapped-hole band since it is erased by *F*-band bleaching. However, it should be noted that the concentration of Pb^{2+} that they used (~ 0. 3 mole%) was much greater than in our specimens (~ 10^{-3} mole%). Therefore, competition for holes by centers with a higher cross section might well keep the Pb^{3+} concentration below detection limits.

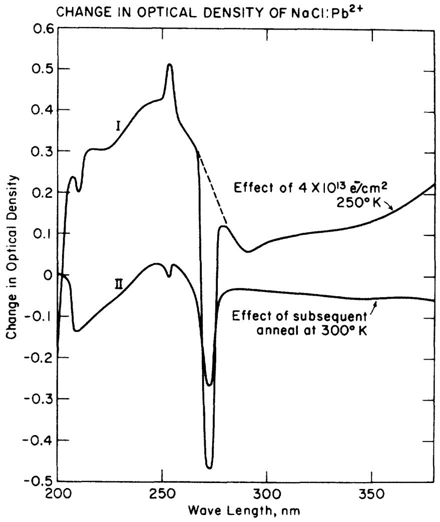

FIG. 8. Change in absorption in NaCl : Pb^{2+} caused by electron irradiation at 250 °K and subsequent treatment. Curve I: change in optical density caused by 4×10^{13} 1.5-MeV e^-/cm^2 (+ΔOD represents an increase in absorption); curve II: change in optical density caused by warming to 300 °K (+ΔOD represents a decrease in absorption). (All spectra measured at 80 °K.)

There is some evidence for a sharp transition involving a trapped hole, namely, the band at 250 nm in both KCl (Fig. 3) and NaCl (Fig. 6) but its origin is uncertain.

So far we have considered these spectral features without comment as to the way in which the Pb ions are incorporated in the lattice. As noted above, prior to each series of operations the specimens were quenched from 475 °K, a treatment designed to put an appreciable fraction of the Pb^{2+} into the form of isolated impurity-vacancy dipoles. Upon irradiation below 200 °K, the concentration of these dipoles decreases as revealed by the area under the ITC peak (Figs. 1 and 5 and Table I). The loss of area under the 227 °K ITC peak may result from either interstitial capture or electron capture by the Pb^{2+}-vacancy complex. The capture of an interstitial may occur by the interstitial halogen actually entering and occupying the vacant cation site; this would produce a complex of the type reported by Hayes and Nichols[25] to exist in alkaline-earth-doped alkali halides after irradiation. Alternatively, one or more halogen interstitals may be trapped in the stress field of the Pb^{2+}-vacancy couple in the form of interstitial entities. Elastic interactions between these and the dipolar complex would interfere with its reorientation. In support of the last possibility is the fact that Sonder and Sibley[9] have found that the degree of enhancement of colorability of KCl : Pb^{2+} crystals upon irradiation at 77 °K is consistent with the capture of several interstitials by each Pb^{2+} dissolved in the lattice. On the other hand, electron capture by the Pb^{2+} would destroy the dipolar nature of the complex (at least to first order) and thus eliminate its contribution to the ITC polarization peak (however, see below). Examination of the results for NaCl(NRL-*D*) in Table I suggest that both causes are responsible. After the first irradiation, 3.7×10^{16} dipoles/cm^3 are lost as compared to a loss—if we can believe our assumption regarding oscillator strength—of 3×10^{16} Pb^{2+}/cm^3. The second irradiation produces an even greater disparity: 7.9×10^{16} dipoles/cm^3 versus 3×10^{16} Pb^{2+}/cm^3. Similar results are obtained for KCl(NRL-*B*). These results indicate that not all dipole loss occurs as a result of electron capture by Pb^{2+} and one must conclude that either a portion or all of the loss can be attributed to interstitial capture by the Pb^{2+}-vacancy complex. Proof that electron capture by Pb^{2+} can eliminate the dipoles under consideration is given by the bleaching experiments: Release of electrons by *F*-band bleaching virtually eliminates the ITC peak at 226 °K.

The results just described were obtained after irradiation below 200 °K where the empty anion vacancies are immobile and where destruction of dipoles by the out-migration of cation vacancies is not expected to occur. Above this temperature, at least in the case of KCl, Guilaini *et al.*[26] have shown that the empty anion vacancy becomes unstable and disappears, presumably by migration to sinks (interstitial halogen stabilized elsewhere in the lattice). This is evidently part of the reason that enhancement of *F*-center production in KCl: Pb^{2+} does not persist to room temperature where a suppression of coloration is observed[4]; mobile anion vacancies can migrate to an annihilate halogen interstitials trapped at an impurity. The results of irradiation at 250 °K (KCl: Pb NRL-*A* and NaCl: Pb NRL-*C*, HAR-*A*) are consistent with this explanation since the change in dipole density is less than the loss of Pb^{2+} in each case.

Next, we take up the matter of the small radiation-induced ITC peaks observed at temperatures well below that of the principal peak. In KCl there appear to be two sets of such peaks, a pair of peaks below 140 °K and one in the range 190–200 °K. The positions of these peaks seem to be somewhat sensitive to the irradiation temperature. Little can be said at present concerning the low-temperature set. However, the peak near 200 °K is enhanced by *F*-band bleaching. The situation is analogous in NaCl except that only a single peak at 120 °K is produced by irradiation at 170 °K, while a better-defined peak of larger amplitude appears at 175 °K. Both of these peaks, like their counterparts in KCl, disappear upon annealing for a short time near room temperature, and the 175 °K peak is enhanced by bleaching as is the 200 °K peak in KCl.

We believe that the intermediate-temperature peaks (175 and 200 °K) are associate with a Pb^{+}-cation-vacancy complex formed when a Pb^{2+}-vacancy dipole captures an electron. Any permanent dipole moment this peak may possess would arise because Pb^{+} is of a different size and polarizability from the Na^{+} it replaces. Such a moment would be quite small. However, this complex can reorient in an electric field and give rise to a displacement current upon relaxation provided the vacancy is bound by some type of interactive force to the impurity. Presumably, the interaction in this instance is elastic and attractive since Pb^{+} is expected to be larger than K^{+} or Na^{+}. In a sense such a center is a pseudodipole whose relaxation rate will be controlled by the activation energy for motion of the vacancy in the elastically distorted environment of the impurity. Its "effective" dipole moment is essentially the same as that of the corresponding Pb^{2+}-vacancy structure since the displacement current arises from displacement of charge an equivalent distance. When the crystal is warmed to room temperature, thermal energy should overcome the weak elastic attractive force permitting the vacancy to escape. However, these pseudodipoles can be readily reformed by cooling the crystal to a suitable temperature and flooding the crystals with electrons. Capture of electrons by Pb^{2+}-vacancy complexes should recreate a quantity of the Pb^{+}-vacancy pseudodipoles. Optical spectra lend support to this interpretation. Immediately after an *F*-band bleach at 150 °K, the 253-nm band in NaCl: Pb is quite broad, whereas annealing for only 5 min at 300 °K produces a substantial narrowing. Such a narrowing might be expected to result from the loss of the perturbing influence of the vacancy on the Pb^{+} ion.

Figures 1 and 5 bring out an inherent limitation in the ITC method associated with annealing of defects during a single cycle. For example, since the relaxation peak of the Pb^{2+}-vacancy dipole lies in the range of hole mobility, it is not possible to assay in a single run the Pb^{2+}-vacancy content without the annealing of an important component of the radiolytic damage. Other defects may also anneal during the cycle which could restore or reduce the dipole concentration as revealed by the 227 °K peak. Thus in analyzing ITC results, the possibility of perturbation of the later peaks by annealing earlier in the cycle must be kept in mind. Cycling to successively higher temperatures only partially solves this problem since the initial effect of irradiation on the 227 °K peak cannot be ascertained.

V. SUMMARY AND CONCLUSIONS

Irradiation of Pb-doped NaCl and KCl with 1.5-MeV electrons decreases both the *A* band and the

Pb^{2+}-cation-vacancy ITC peak and introduces narrow optical bands at 207(210) and 253 nm in NaCl(KCl) as well as additional ITC peaks at lower temperature. The optical bands are evidently associated with Pb^0 and Pb^+ and one of the radiation-induced ITC peaks (175 °K in NaCl and 190 or 200 °K in KCl) seems to arise from the relaxation of a complex composed of a vacancy bound by elastic forces to a Pb^+ ion. We therefore conclude that both isolated Pb^{2+} and Pb^{2+} involved in complexes are able to capture electrons producing Pb^+, or perhaps Pb^0.

Because of electrostatic interactions, one would expect the Pb^0-vacancy complex to be unstable against either dissociation or loss of one electron when sufficient thermal activation is supplied. With regard to Pb^+ vacancies, decomposition of this weakly bound complex is expected to occur at room temperature as indicated above. Because of these processes, one would expect room-temperature irradiation to result in the breakup of Pb^{2+} complexes with isolated Pb^{2+}, Pb^+, and Pb^0 as products. The positive-ion vacancy released in the process would be captured at positively charged sites and one likely candidate is the negative-ion vacancy. Similar considerations would be applicable to crystals colored by irradiation below 200 °K, subsequently warmed to room temperature and bleached in the *F* band. Either operation should lead to the production of an appreciable quantity of cation-anion-vacancy pairs. It would be interesting to search for evidence of this dipolar complex in irradiated Pb^{2+}-doped alkali halides.

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