tion of Ref. 20,

$$T_{ijn}=\{[P^{+}_{nj}+\mu(1+f)]\,e^{P^{+}_{nj}t}-[P^{-}_{nj}+\mu(1+f)]\,e^{P^{-}_{nj}t}\}\times(P^{+}_{nj}-P^{-}_{nj})^{-1}\ ,$$

$$T_{sjn}=\frac{\lambda[P^{+}_{nj}+\mu(1+f)]\,e^{P^{+}_{nj}t}}{(P^{+}_{nj}-P^{-}_{nj})\,(P^{+}_{nj}+\mu)}-\frac{\lambda[P^{-}_{nj}+\mu(1+f)]\,e^{P^{-}_{nj}t}}{(P^{+}_{nj}-P^{-}_{nj})\,(P^{-}_{nj}+\mu)}\ ,$$

where the P_{nj} values are the roots of the equation

$$P^{2}_{nj}+P_{nj}(\lambda+\mu-K_{nj})-\mu K_{nj}=0$$

and

$$K_{nj}=-D[(2n+1)\,\pi/h_j]^2\ ,$$

with the h_j being the lengths of the respective sides.

---

*Work supported by the U. S. Atomic Energy Commission, Contract No. AT-(29-1)-789.

[1] T. S. Elleman, C. H. Fox, and L. D. Mears, J. Nucl. Mater. 30, 89 (1968).

[2] W. A. Stark, Bull. Am. Phys. Soc. 17, 83 (1972).

[3] R. C. Wayne and W. Bauer, Bull. Am. Phys. Soc. 16, 341 (1971).

[4] R. C. Wayne and W. Bauer, Bull. Am. Phys. Soc. 17, 287 (1972).

[5] A. Ong and T. S. Elleman, J. Nucl. Mater. 42, 191 (1972).

[6] F. W. Felix, Proc. Brit. Ceram. Soc. 9, 273 (1967).

[7] S. Kalbitzer, Z. Naturforsch. 17a, 1071 (1962).

[8] H. P. Mundt and A. K. H. Richter, Z. Naturforsch. 20a, 267 (1965).

[9] T. S. Elleman, L. D. Mears, and R. P. Christman, J. Am. Ceram. Soc. 51, 560 (1968).

[10] P. Schmeling, J. Phys. Chem. Solids 28, 1185 (1967).

[11] F. W. Felix, Phys. Status Solidi 27, 529 (1968).

[12] W. Bannasch and P. Schmeling, J. Phys. Chem. Solids 26, 1999 (1965).

[13] P. Schmeling, Phys. Status Solidi 11, 175 (1965).

[14] Hj. Matzke and J. L. Whitton, Can. J. Phys. 44, 995 (1966).

[15] Hj. Matzke and C. Jech, J. Phys. Chem. Solids 31, 753 (1970).

[16] P. P. Pronko and R. Kelly, Appl. Phys. Letters 18, 335 (1971).

[17] A. Sy Ong and T. S. Elleman, J. Nucl. Mater. 42, 191 (1972).

[18] This means of performing permeation experiments was first devised by J. E. Shelby.

[19] Much of the basic analysis can be found in W. Jost, *Diffusion in Solids, Liquids, and Gases* (Academic, New York, 1960), Chap. 1.

[20] A. Sosin and W. Bauer, Phys. Rev. 147, 478 (1966).

[21] W. D. Wilson (private communication).

[22] M. J. Norgett and A. B. Lidiard, Phil. Mag. 18, 1193 (1968).

PHYSICAL REVIEW B VOLUME 6, NUMBER 10 15 NOVEMBER 1972

Dipole Relaxation, Aggregation, and X-Ray Effects in KCl Doped with Eu^{++}, Yb^{++}, or Sm^{++} †

S. Unger and M. M. Perlman

Department of Physics, Collège militaire royal de Saint-Jean, Saint-Jean, Québec, Canada

(Received 26 June 1972)

The behavior of impurity-vacancy (I-V) dipoles has been studied in KCl single crystals doped with Eu^{++}, Yb^{++}, or Sm^{++}, using the ionic-thermocurrents technique. The activation energies and frequency factors for dipole relaxation have been determined. The aggregation of these dipoles in KCl : Eu^{++} follows third-order kinetics in the temperature range 295–323 °K, and their decay rate is comparable to that of KCl : Sr^{++}. The activation energy and frequency factor for the formation of trimers have also been determined. It has proved possible to destroy these rare-earth I-V dipolar systems by irradiation with x rays, and to recover them on subsequent heating or irradiation with a Xe-Hg lamp. This process is postulated to take place through charge conversion of the I-V dipole constituents.

I. INTRODUCTION

In recent years, alkali-halide crystals doped with various doubly valent impurity cations have been studied[1–4] to determine the parameters associated with cation-vacancy motion, when the vacancy is either free, or associated with an impurity in an impurity-vacancy (I-V) dipole.

In the first instance, obtainable at temperatures above 300 °C,[5] the appropriate activation energy and frequency factor are determined from dc ionic-conductivity measurements.[2] At lower temperatures, where significant pairing takes place, the methods of dielectric absorption[6] and ionic thermocurrents (ITC)[7] may be employed to determine the parameters associated with dipole rotation and diffusion. It is the latter technique that has been used here.

In much of the previous work on the aggregation of I-V dipoles, the results have been analyzed taking into account impurity-ion mass and radius.[8] In the present work, we use impurities (Eu^{++}, Yb^{++}, Sm^{++}) whose atomic masses are in the range 150–173, considerably larger than those of most impurities previously studied, but which have comparable radii.

The ITC method is used here to follow three different processes. The shape of the peak is analyzed to find the dipole-relaxation parameters. The area under the peak is proportional to the number of I-V dipoles, and is used to monitor aggregation of the dipoles (under the assumption that a cluster of two or more dipoles has a negligible dipole moment). The I-V complex also loses its significance as a dipole if the impurity should become singly valent, or lose its vacancy compensator. This process is also examined via thermocurrents, using x rays to effect the changes.

A. Dipole Relaxation and Aggregation

Previous studies on I-V dipole relaxation in alkali halides[5,7–9] have generally yielded reorientation energies between 0.6 and 0.7 eV. The relaxation of the I-V dipole is postulated to take place by cation-vacancy jumps from one nearest-neighbor (nn) site to another, via a next-nearest-neighbor (nnn) site.[5] This process involves no motion of the impurity, and hence the activation energy is independent of the impurity. The latter holds true for the impurities used in this work. An oversize or greatly undersize impurity should have an effect. The other mode of dipole relaxation, namely, vacancy-impurity exchange, generally has a higher activation energy than rotation by vacancy jumps. An exception to this rule has been found by Bucci[8] for Be^{++} ions in KCl or NaCl. Since this ion has a particularly small radius (0.35 Å), it easily assumes an off-center position in the lattice, close to the cation vacancy, and the probability for direct exchange is greater than that for vacancy jumps around the impurity ion.

The aggregation of I-V dipoles in alkali halides has previously been observed to follow third-order kinetics.[1,3,10] Cook and Dryden,[1] using dielectric-absorption measurements, initially observed a third-order decay of the dipole concentration in $KCl:Sr^{++}$, followed by a plateau indicating very little decay, and then a region of further aggregation. Their interpretation was that trimer formation takes place first, until equilibrium is reached between dipoles and trimers (plateau region). This is followed by the formation of higher aggregates.

Since a random encounter of three dipoles to form a trimer is expected to be less probable than the encounter of two dipoles (dimer formation), Crawford[11] has treated the possibility that an initial dimerization stage may be masked by the dimers being in a loosely bound state in quasiequilibrium with the free dipoles. This leads to the result that the activation energy for aggregation is less than that for diffusion by an amount equal to the dimer binding energy. Diffusion measurements have in fact given consistently higher energies than aggregation studies (see Ref. 11). Further support for this thesis is provided by aggregation studies in crystals with low impurity content[10] (< 20 ppm), where dimer-dipole equilibrium would not be reached as quickly, and hence a second-order process might be visible. Experimentally, one finds that the aggregation deviates from third order, although it is not strictly second order[12] either. Capelletti and de Benedetti[3] have also measured an initial second-order decay in $NaCl:Sr^{++}$, where aggregation is slow.

B. Effects of Irradiation on I-V Dipoles

Various workers have studied the effects of irradiation on both constituents of I-V dipoles in alkali halides, namely, the doubly valent ion and the cation vacancy. Fong *et al.*[13] have observed the charge conversion of Sm^{++} to Sm^{+} in $KCl:Sm^{++}$ upon γ irradiation at room temperature. The disappearance of the Sm^{++} absorption bands was directly correlated to the appearance of absorption bands associated with Sm^{+} ions. The Sm^{++} bands were recovered by annealing at 150 °C. This charge conversion process has also been observed in $KCl:Eu^{++}$ x irradiated at 300 °K,[14] and in CaF_2 doped with various rare earths,[15] where the ions are converted from 3+ to 2+ valency.

Crawford and Nelson[16] have considered the effects of x irradiation (at 195 °K) on isolated cation vacancies in alkali halides doped with doubly valent cations. In order to explain the increased rate of formation of *F* centers in these crystals, as compared to the rate in undoped crystals, they proposed that cation vacancies, which are in the majority in doped crystals, must be converted to anion vacancies, according to the following scheme. Upon irradiation, a halide neighbor of a cation vacancy captures a hole to become a neutral atom. This atom then relaxes into the cation-vacancy position to form a Cl_2^- molecule ion and an anion vacancy, which moves away. The Cl_2^- center is unstable above − 40 °C in KCl and decomposes into a Cl_2° molecule and a free electron above this temperature. These processes were monitored in $KCl:Ca^{++}$ by measuring the optical-absorption bands of Cl_2^- and Cl_2°.

Varley[17] has proposed an alternative model for the production of stable *F* centers. Anion vacancies are created by multiple-ionization events causing the ejection of halogen ions interstitially with the subsequent trapping of the displaced ions in cation vacancies.

Ikeya *et al.*[18] find that isolated cation vacancies

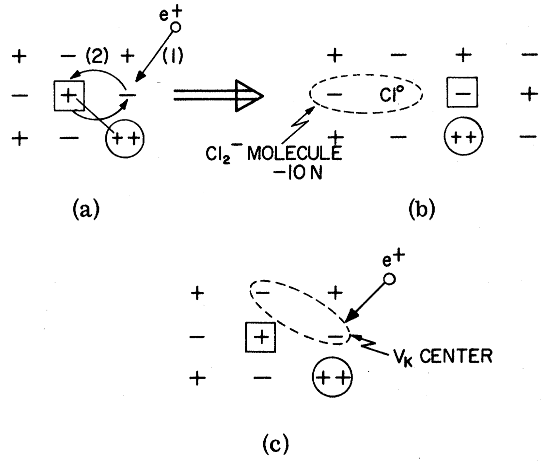

FIG. 1. Hole capture by Cl^- ion. (a), (b) Cl^- ion captures hole (1), and neutralized Cl° relaxes into vacancy (2), to form anion vacancy and Cl_2^- lying in (100) direction; anion vacancy moves off (not shown). (c) V_k center formation in (110) direction by hole capture.

are the source of the F centers, and state that both Crawford's and Varley's models of the mechanism are possible.

Beltrami *et al.*[19] have proposed that since most cation vacancies are bound in I-V dipoles at room temperature, the majority of F centers should be created from converted bound cation vacancies [Figs. 1(a) and 1(b)]. Using ionic thermocurrents in KCl : Sr^{++}, they observed a decrease in the I-V dipole density (upon x irradiation at room temperature) almost equal to the density of F centers produced.

II. THEORY

Those aspects of previous theories used in these experiments are briefly summarized in what follows.

A. Dipole Relaxation and Aggregation

Ionic-thermocurrent dipole peaks have the form obtained by Bucci,[7] assuming monomolecular kinetics:

$$j(T) = [Np^2\alpha\, \epsilon_p / kT_p\, \tau(T)] \exp[- \int_{T_0}^{T} dT'/b\tau(T')], \tag{1}$$

where $j(T)$ is the current density, N is the number of dipoles per unit volume, p is the moment of the I-V dipole, ϵ_p is the polarization field, T_p is the corresponding temperature, α is a geometrical factor depending on the possible dipolar orientations (here $\alpha = \frac{2}{3}$), b is the linear heating rate, and $\tau(T)$ is the relaxation time, where

$$\tau(T) = \tau_0\, e^{E/kT} . \tag{2}$$

The area delimited by the dipole peak is equal to the total charge released on depolarization, and is related to the number of I-V dipoles per unit volume by

$$N = kT_p\, Q/(A\, \alpha p^2\, \epsilon_p) , \tag{3}$$

where Q is the total released charge, A is the electrode area, and all other quantities are as previously defined.

The precipitation of the I-V dipoles into higher aggregates is represented by the rate equation[3]

$$\frac{dn}{dt} = - \nu_0 n^{\beta}\, e^{-E_a/kT} , \tag{4}$$

where n is the molar fraction of I-V dipoles, E_a is the activation energy for the aggregation process, ν_0 is the frequency factor, and β is the order of the kinetics. Integration of Eq. (4) gives

$$(n_0/n)^{\beta-1} = (\beta - 1)\, n_0^{\beta-1}\, \nu_0\, t\, e^{-E_a/kT} + 1 . \tag{5}$$

B. Effects of Irradiation on I-V Dipoles

The destruction of I-V dipoles by irradiation, through charge conversion of the dipole components, may be represented by

$$\frac{dN_1}{dt} = \frac{dN_I}{dt} + \frac{dN_V}{dt} , \tag{6}$$

where N_1, N_I, and N_V are the densities of I-V dipoles, doubly valent ions, and cation vacancies bound in dipoles, respectively, assuming that the linear relation holds if the number of dipoles, both of whose components are converted, is very small. If one also assumes that dipole destruction proceeds mainly through bound vacancy conversion, then $dN_I/dt \ll dN_V/dt$, and

$$\frac{dN_1}{dt} \simeq \frac{dN_V}{dt} = - \frac{N_V}{\tau_V} , \tag{7}$$

where τ_V is a lifetime associated with bound vacancy conversion. The dipole decay should then be a simple exponential.

III. EXPERIMENTAL PROCEDURE

The samples used in this work were grown in our laboratory by the Kyropolous method in a dry nitrogen atmosphere. $EuCl_2$, $YbCl_2$, and $SmCl_2$ obtained from Apache Chemicals were added to KCl in amounts of 0.1 mole% in the melt. Pure KCl was also grown, and its thermocurrent spectrum was run to determine the amount of unwanted divalent impurities in the samples. The only ion detected was Ca^{++}, in 2×10^{-5}-at.% concentration, insufficient to appreciably affect the rare-earth I-V dipoles studied. These were present in densities of about 10^{18}, 3×10^{17}, and 10^{17} cm^{-3}, for Eu^{++}, Yb^{++}, and Sm^{++}, respectively.

An untreated sample was assumed to contain the equilibrium concentration of I-V dipoles at the

TABLE I. Dipole relaxation parameters for KCl:X^{++}.

Ion	Atomic mass	Radius (Å)	T_{MAX} (°K)	E (eV)	τ_0 (10^{-14} sec)
K^+	39	1.33	...	...	...
Eu^{++}	152	1.09	224	0.68 ± 0.01	3.7 ± 1.0
Yb^{++}	173	0.93	215	0.67 ± 0.01	1.1 ± 0.6
Sm^{++}	150	0.96	227	0.70 ± 0.03	2.7 ± 2.5

storage (room) temperature. In order to obtain the maximum number of free dipoles, each sample was annealed in a Cooley furnace for 2 h at 500 °C where the dipole concentration no longer increases with temperature.[20] After quenching to room temperature, the samples were run within $\frac{1}{2}$ h.

Thin samples of about $10 \times 10 \times 1$ mm were prepared for polarization by painting graphite electrodes on both large faces. They were then placed in a horizontal position in a holder, and electric contact was made by means of thin wires; a precaution against stress-induced currents which could arise as the samples were warmed.

The cryostat was evacuated to 10^{-5} Torr and dry nitrogen was then added to 300 Torr to provide an inert atmosphere in the neighborhood of the sample. The gas also eliminated any temperature gradients across the sample.

The crystals were polarized in a static field of about 15 000 V/cm for 5 min at temperatures near the dipole-peak maximum (see Table I). They were then cooled to 120 °K and the field was removed. The sample was heated at a rate of 6 °K/min and the relaxation-current peak of the I-V dipoles[7] was recorded, using a Cary vibrating-reed electrometer and an L & N Speedomax recorder. Peak currents measured ranged from 5×10^{-14} to 10^{-12} A, with the noise level at 5×10^{-16} A. The measurements were reproducible to within 2%.

The low-temperature (22–70 °C) anneals used to study aggregation were carried out in a Freas oven. The samples were also heated in the cryostat up to temperatures of 300 °C during studies of dipole recovery after x irradiation.

X irradiations were made using a Philips generator, capable of supplying 2 kW of power, with a maximum x-ray energy of 60 keV. The crystals were held at 5 cm from the target.

The unfiltered output (200–1400 nm) of an Oriel Corp. 200-W Xe-Hg lamp was used to recover the dipoles.

A Dataline PDP-10 computer aided in performing the calculations.

IV. RESULTS

A. Dipole Relaxation and Aggregation

ITC dipole peaks were obtained for KCl doped with Eu^{++}, Yb^{++}, or Sm^{++}. Figure 2 shows the height of the peak plotted against the applied field for KCl:Sm^{++}. The relation is a linear one, as expected for a true volume polarization.

The ITC curves were analyzed to find E and τ_0 of Eq. (2), using the methods of Bucci,[7] and Cowell and Woods.[21] The results are given in Table I. The larger uncertainties in the results for KCl:Sm^{++} are due to the relative smallness of its peak, and the fact that a slowly varying background current accompanied the dipole curve. Using Eq. (3), the dipole density in KCl:Eu^{++} was calculated to be 1.8×10^{18} cm^{-3}.

The aggregation of I-V dipoles in KCl: Eu^{++} was monitored in the temperature range 22–70 °C. Figure 3 shows the ITC peak after successive anneals at 50 °C. The rates of aggregation at various temperatures are shown in Fig. 4, where $n(t)/n_0$ is plotted against annealing time. The fitting of third-order kinetics to the data of Fig. 4 [see Eq. (5)] is shown in Fig. 5. The fits are good for the decays at 22, 40, and 50 °C. The points obtained at 60 and 70 °C do not fit a second- or third-order plot, and the concavity indicates some higher-order process. A straight line could be drawn using the first three points at these temperatures, implying that the trimer formation stage is over relatively quickly. At very long times one would expect to see the same concavity show up at the lower temperatures.

Using Eq. (5), the Arrhenius plot of Fig. 6 is

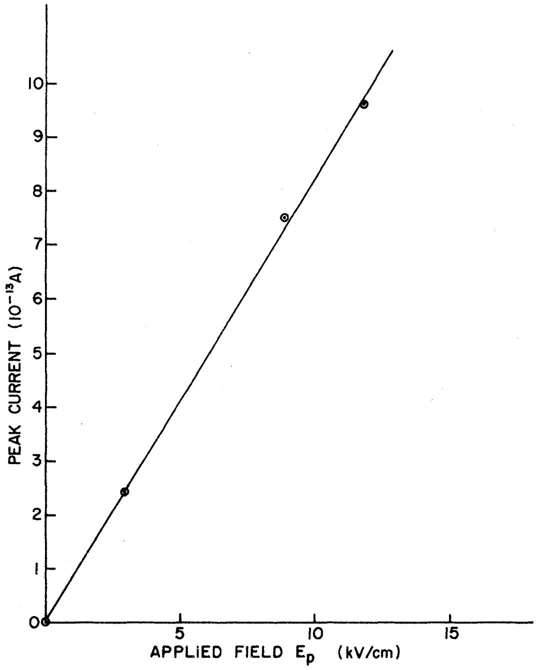

FIG. 2. ITC peak maximum vs applied field E_p for KCl:Sm^{++}.

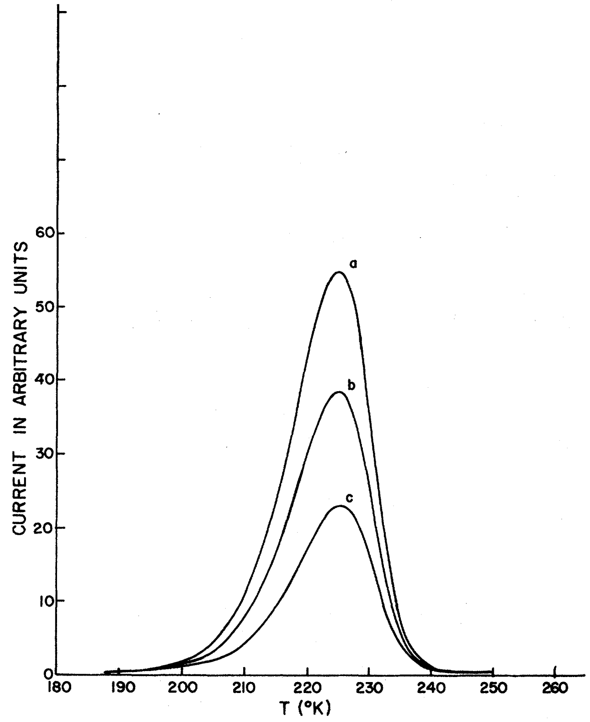

FIG. 3. Precipitation of I-V dipoles in KCl : Eu^{++} at 50 °C: (a) after an anneal for 2 h at 500 °C; (b) after 67 h at 50 °C; (c) after 397 h at 50 °C.

obtained at a time of 50 h. From its slope and intercept, the energy and frequency factors associated with trimer formation are found to be 0.86 ±0.04 eV and 3×10^{15} sec^{-1}, respectively.

B. Effects of Irradiation on I-V Dipoles

The I-V dipole peaks for all three different dopants showed a large decrease in intensity upon irradiation with x rays at room temperature. The results for KCl : Yb^{++} are shown in Fig. 7 for a 2-h dose of 40 kV x rays (3×10^{10} R). Only 10.5% of the original dipole density remains. Under the same conditions the peaks from KCl : Eu^{++} and KCl : Sm^{++} were reduced to 35.4% and 16.4% of the original density, respectively. The dependence of the fraction of dipoles remaining in KCl : Eu^{++} after irradiation, on the x-ray energy, tube current, and irradiation time, is shown in Fig. 8.

The straightline plot of $\log_{10}(N_1/N_0)$ vs t in Fig. 9 is in agreement with Eq. (7).

The recovery of the I-V dipoles upon irradiation with the Xe-Hg lamp at room temperature is shown in Fig. 7 for KCl : Yb^{++}. Twenty percent of the original dipole density is recovered after having been reduced to 10% by the x rays. For KCl : Eu^{++}, the same amount of irradiation recovered 9% of the dipoles. Recovery was also observed for KCl : Sm^{++}. However, the noisy background current introduced by the irradiation made quantitative analysis impossible.

Recovery of I-V dipoles by annealing at temperatures in excess of 150 °C was essentially complete. Since each sample was annealed at 500 °C prior to being irradiated, one cannot expect 100% recovery of peak intensity, owing to the fact that the equilibrium solubility of I-V dipoles is greater at 500 °C than at lower temperatures.

The F-center coloration of the crystals disap-

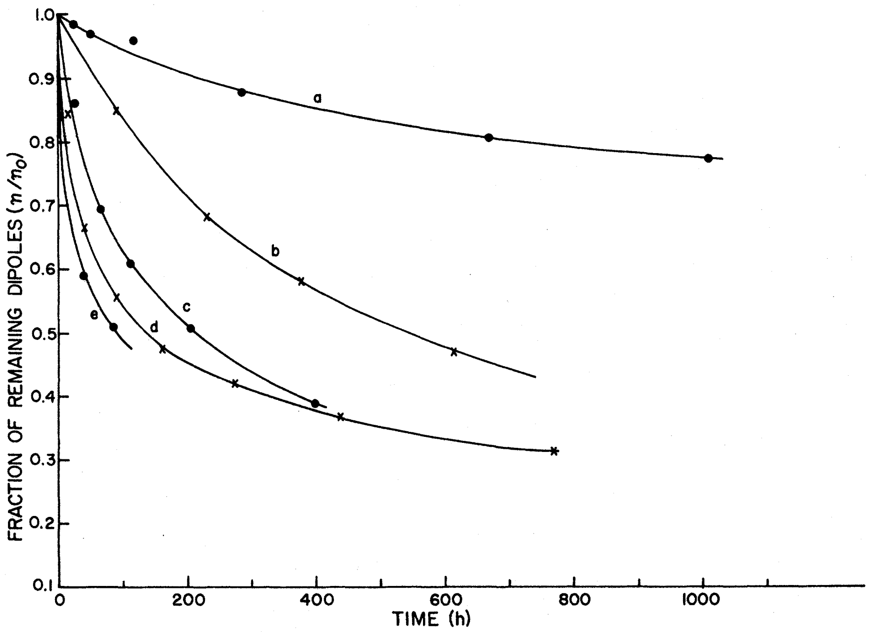

FIG. 4. Precipitation of I-V dipoles in KCl : Eu^{++} at various temperatures: (a) 295 °K; (b) 313 °K; (c) 323 °K; (d) 333 °K; (e) 343 °K. The fraction of dipoles remaining (n/n_0) after successive anneals vs time ($n_0 = 1.1 \times 10^{-4}$ mole fraction).

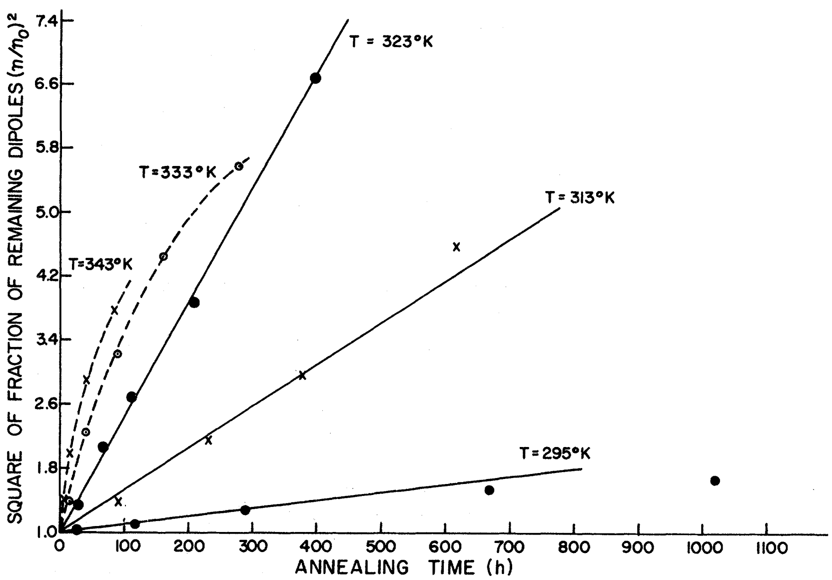

FIG. 5. Fitting of third-order kinetics to the decay of I-V dipoles in KCl : Eu^{++}, at various temperatures.

peared on exposure to the Xe-Hg lamp, or annealing, after x irradiation.

V. DISCUSSION

A. Dipole Relaxation and Aggregation

The dipole-relaxation parameters obtained for the three different impurity dopants were about the same within experimental error. The activation energies found by other workers$^{5,7-9}$ using various doubly valent impurities in KCl and NaCl also agree with those found here. This is consistent with the picture of relaxation taking place by vacancy jumps around the impurity ion. (The measured "rotational" activation energy is that for cation-vacancy-cation exchange in the presence of a doubly valent cation.^{2})

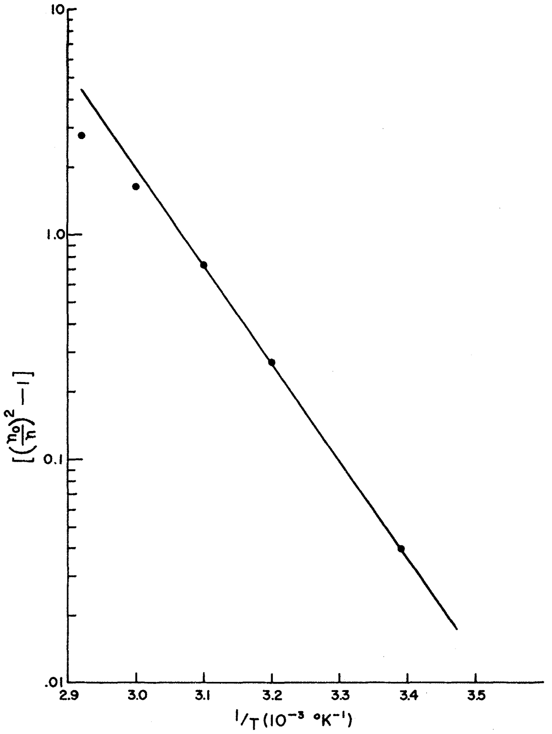

FIG. 6. Arrhenius plot of $(n_0/n)^2-1$ vs $1/T$ to determine E_a and ν_0 for trimer formation in KCl:Eu^{++}.

Aggregation in KCl : Eu^{++} took place in a shorter time than in the other two crystals, since the form-

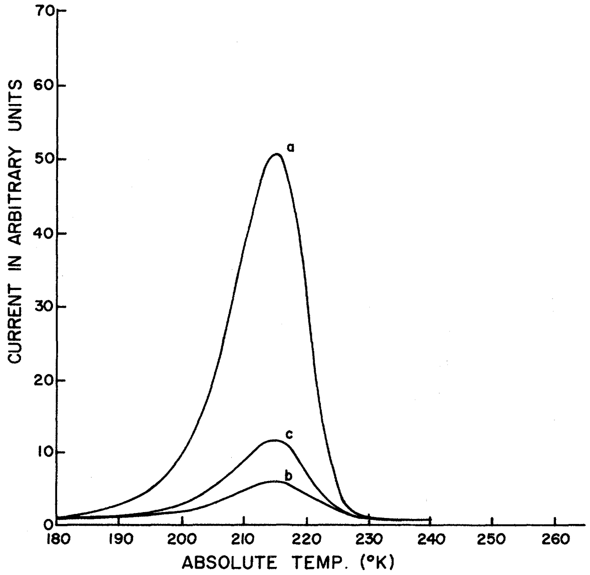

FIG. 7. The I-V dipole thermocurrent peak from KCl:Yb^{++}: (a) after an anneal of 2 h at 500 °C; (b) after an x-ray dose of 3×10^{10} R at 25 °C; (c) after 90 min of irradiation with a Xe-Hg lamp at 160 W and 25 °C.

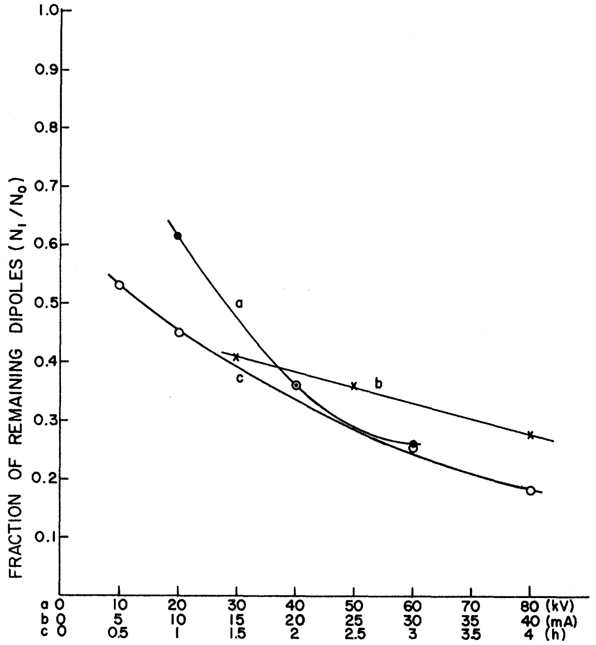

FIG. 8. The fraction of I-V dipoles remaining (N_1/N_0) in KCl : Eu^{++} after various x-ray doses. (a) Voltage dependence at 25 mA for 2 h; (b) current dependence at 40 kV for 2 h; (c) time dependence at 40 kV and 25 mA.

er had the highest impurity concentration, and precipitation rates are strongly proportional to the initial dipole density.[3] The greater solubility of the Eu^{++} ion compared to Yb^{++} or Sm^{++} is consistent with the observation by Merz and Pershan[15] that Eu is the most stable divalent ion of the lanthanide series. Initially, in the temperature range studied, the rate of aggregation increases with temperature (Fig. 4). At longer times, however, the higher temperature decays flatten out sooner than those at lower temperatures. It appears that some of these curves will intersect if carried out further. This intersection was observed by Cook and Dryden[1] in the plateau region mentioned earlier. In our case, there is no sign of an inflexion point beyond the plateau, although the 60 °C measurements were carried out to 800 h, beyond the point where this occurred in KCl : Sr^{++}. It is possible that the slower decay at the higher temperatures is merely due to the fact that the equilibrium dipole density increases with temperature.[20]

The third-order kinetics found here and for other dipoles[1,3,10] do not necessarily prove that trimer formation is the initial aggregation process. As already mentioned, the type of dimer formation discussed by Crawford[11] may be occurring, with dimer-dipole equilibrium being established too quickly for a second-order decay to be detected. It should be interesting to redo the KCl : Eu^{++} aggregation measurements, using much lower impurity concentrations, to see if a second-order decay is observed. A deviation from third order found in NaCl : Pb^{++} [10] was for an impurity content of 20 ppm, whereas our crystals had a concentration of about 115 ppm.

The activation energy for trimer formation in KCl : Eu^{++} found here is larger than that for dipole relaxation. This is expected, since the diffusion of dipoles involves both vacancy jumps and impurity-vacancy exchange, and the latter requires the greater energy.[3] The value of 0.86 eV is in the range found by others [see Ref. (11)] for various impurities.

There appears to be no direct relation between the activation energy for trimer formation, and the mass of the impurity. For example, in KCl : Pb^{++}, the heaviest ion used, the activation energy found was 0.74 eV.[10] In fact, the energy for cation-vacancy-cation exchange in pure KCl has been found,[2] by conductivity measurements, to be 0.84 ± 0.05 eV. It is only when the impurity has a considerably smaller radius than the ion it replaces,[8] that one sees a large change in the activation energy, since dipole "rotation" rather than exchange then governs the diffusion process. The

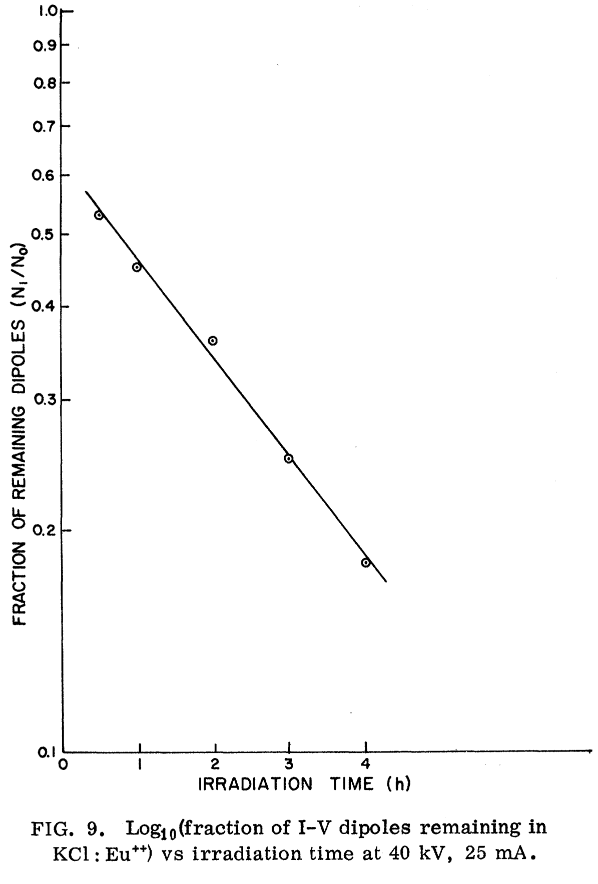

FIG. 9. Log_{10}(fraction of I-V dipoles remaining in KCl : Eu^{++}) vs irradiation time at 40 kV, 25 mA.

case of NaCl : Cd^{++} is an anomalous one, since the radii of Cd^{++} and Na^{++} are the same (0.97 Å). The activation energy measured here was 0.5 eV.[3]

B. Effects of Irradiation on I-V Dipoles

As already mentioned, the I-V dipoles may be destroyed in two ways on x irradiation. The doubly valent cations may capture an electron to become singly valent, or the bound cation vacancy may be converted to an anion vacancy,[16] which then moves away from the neighborhood of the impurity. We propose that both processes are at work here, with vacancy conversion playing the larger role.

Since most vacancies in alkali-halide crystals doped with doubly valent impurity ions are cation vacancies,[16] and these vacancies are mostly bound in I-V dipoles at room temperature,[2] the assumption of Beltrami *et al.*[19] that most F centers are created from converted bound cation vacancies is a reasonable one. Supporting this theory is their measurement of an F-center density of 2.3×10^{17} cm^{-3}, and I-V dipole destruction of 2.8×10^{17} cm^{-3} upon exposure to x rays. The observation by Fong *et al.*[13] (who detected only electron capture by divalent ions and not dipole destruction), that the F band grows about three times as fast as the Sm^{+1} band, is also consistent with this view, and with the proposal that vacancy conversion is more prevalent than divalent ion conversion.

Using the changes in I-V dipole and F-center densities found by Beltrami *et al.*[19] in KCl : Sr^{++}, and neglecting the possibility that both the ion and vacancy of the same dipole may be converted, one finds the amounts of ion and vacancy conversion to be 18% and 82% of the total, respectively. From the observations by Fong *et al.*[13] on the growth of the F and Sm^{+1} bands, the corresponding amounts are 25% and 75%.

Since the irradiations in this work were performed at room temperature, where the Cl_2^- molecule is unstable,[16] one would expect to find the Cl_2° center instead. Optical-absorption measurements are planned with the goal of verifying this, as well as the rate of F-center production. It might also be interesting to irradiate at temperatures below 138 °K, where the V_k center is stable. Perhaps under these circumstances, V_k centers [self-trapped holes lying in the (110) direction] would be formed [Fig. 1(c)], competing with the vacancy conversion process described here, and thus eliminating part of the I-V dipole destruction.

Subjecting an irradiated sample to the Xe-Hg lamp destroys the F centers and releases electrons to recombine with trapped holes at the Cl_2° centers. (Alternatively, the trapped holes themselves may be released.) The univalent rare-earth ions are also ionized and revert to the more stable doubly valent state. Annealing the sample at temperatures above 150 °C initiates the same processes, but is a much more efficient means of recovering the original I-V dipole density. This is because at the elevated temperatures, the anion vacancies obtain the mobility necessary to return to the neighborhood of the impurity ion, and be reconverted to cation vacancies. The greater efficiency of the annealing process compared to the lamp irradiation is further proof that bound-vacancy conversion has occurred. Irradiation should be sufficient to recover all of the I-V dipoles, if reionization of the impurity ions was all that was required.

If the relative efficiencies of recovery by irradiation and annealing are taken as a measure of the relative amounts of ion and vacancy conversion (once again, the possibility of both types of conversions at the same dipole is neglected), it is found that ion conversion accounts for only 11% of the dipole destruction in KCl: Yb^{++}, and 14% in KCl: Eu^{++}. This lends credence to the approximations leading to Eq. (7).

VI. SUMMARY

I-V dipoles have been studied in KCl doped with Eu^{++}, Yb^{++}, or Sm^{++}, using the ITC technique. The dipole relaxation parameters are independent of the impurity used, indicating vacancy jumps around the impurity ion as the relaxation mechanism.

The aggregation of the dipoles in KCl: Eu^{++} appears to follow third-order kinetics initially in the range 295–323 °K, for the high-concentration (115 ppm) samples used here. Studies of low-concentration samples are planned, to see if a second-order process is being masked. The large mass of the Eu^{++} ion compared to other ions studied does not seem to affect the activation energy for aggregation.

I-V dipoles for all three dopants studied have been destroyed by x irradiation and recovered upon annealing or irradiation with a Xe-Hg lamp. It is postulated that charge conversion of both the impurity ion and the vacancy take place, with vacancy conversion predominating. Optical-absorption measurements are contemplated, with a view to verifying this proposal.

[†] Work supported by the Defence Research Board of Canada.

[1] J. S. Cook and J. S. Dryden, Proc. Phys. Soc. (London) 80, 479 (1962).

[2] R. W. Dreyfus and A. S. Nowick, J. Appl. Phys. Suppl. 33, 473 (1962).

[3] R. Capelletti and E. de Benedetti, Phys. Rev. 165, 981 (1968).

[4] K. C. Kao *et al.*, J. Appl. Phys. 39, 3955 (1968).

[5] R. W. Dreyfus and R. B. Laibowitz, Phys. Rev. 135, A1413 (1964).

[6] J. S. Cook and J. S. Dryden, Australian J. Phys. 13, 260 (1960).

[7] C. Bucci and R. Fieschi, Phys. Rev. 148, 816 (1966).

[8] C. Bucci, Phys. Rev. 164, 1200 (1967).

[9] P. Dansas, J. Phys. Chem. Solids 32, 2699 (1971).

[10] W. C. Collins and J. H. Crawford, Jr., Phys. Rev. 84, 3745 (1971).

[11] J. H. Crawford, Jr., J. Phys. Chem. Solids 31, 399 (1970).

[12] The simultaneous formation of dimers of various geometrical configurations does not necessarily give a second-order decay rate. In general, we are dealing with the formation of several species of dimers or trimers, and the dipole decay equation is more complicated than Eq. (4). See, for example, the chapter on reaction kinetics in *Physical Chemistry* by W. J. Moore (Prentice-Hall, Englewood Cliffs, N. J., 1962), and/or S. L. Naberhius and F. K. Fong, J. Chem. Phys. 56, 1174 (1972).

[13] F. K. Fong, J. A. Cape, and E. Y. Wong, Phys. Rev. 151, 299 (1966).

[14] B. S. Gorobets, A. I. Novozhilov, M. I. Samoilovich, and L. M. Shamovskii, Dokl. Akad. Nauk SSSR 180, 1351 (1968) [Sov. Phys. Doklady 13, 519 (1968)].

[15] J. L. Merz and P. S. Pershan, Phys. Rev. 162, 217 (1967).

[16] J. H. Crawford, Jr. and C. M. Nelson, Phys. Rev. Letters 5, 314 (1960).

[17] J. H. O. Varley, J. Phys. Chem. Solids 23, 985 (1962).

[18] M. Ikeya, N. Itoh, T. Okada, and T. Suita, J. Phys. Soc. Japan 21, 1304 (1966).

[19] M. Beltrami, R. Capelletti, and R. Fieschi, Phys. Letters 10, 279 (1964).

[20] R. Capelletti and R. Fieschi, in *Crystal Lattice Defects* (Gordon and Breach, Belfast, 1969), Vol. 1, p. 69.

[21] T. A. T. Cowell and J. Woods, Brit. J. Appl. Phys. 18, 1045 (1967).

PHYSICAL REVIEW B VOLUME 6, NUMBER 10 15 NOVEMBER 1972

Theory of Surface Polarons[*]

Josef Sak
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 15 May 1972)

We attempt to determine the binding energy and the wave function of the ground state of an electron that is attracted to the surface of an ionic crystal by its image potential and is repelled from the interior of the solid. For ionic crystals, such as LiF, the electrostatic theory is inadequate and the solid must be treated as a dynamical system. For shallow levels, the correction to the electrostatic approximation is small and behaves asymptotically as z^{-3}, where z is the distance from the surface. The mass of a shallow electron is not enhanced. For deep levels the ground-state energy is calculated by a variational procedure in the limits of both weak and strong electron-phonon coupling. For the ground-state energy of an electron trapped on the LiF surface we find the value -0.29 eV. The mass of the deeply bound electron is enhanced.

I. INTRODUCTION

Let us consider an insulator which has a bottom of the conduction band above the vacuum level (Fig. 1). An electron outside the insulator induces positive charges on the surface and is attracted to it by the force whose potential is[1]

$$V_{\mathrm{im}}(z)=\frac{e^2}{4}\,\frac{\epsilon_s-1}{\epsilon_s+1}\,\frac{1}{z}\,, \qquad (1)$$

where ϵ_s is the static dielectric constant and z is the distance of the electron from the surface which is considered to be a plane. For sufficiently low energy the electron cannot penetrate inside the insulator.

Cole and Cohen[2,3] worked out a theory of the surface states which are induced by the potential (1) and applied it to atomic and molecular insulators

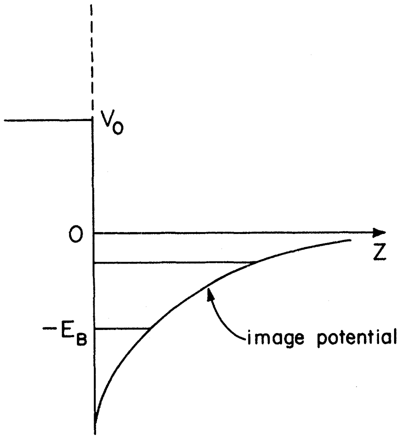

FIG. 1. Image potential of the electron outside an insulator.