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The Reorientation of Cd^{2+}-Vacancy and Pb^{2+}-Vacancy Complexes in KCl[*]

R. E. CHANEY[†] AND W. J. FREDERICKS

Chemistry Department, Oregon State University, Corvallis, Oregon 97331

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The relaxation of Pb^{2+}-vacancy and Cd^{2+}-vacancy dipoles in purified KCl crystals was studied using a double crystal dc polarization method which self-corrects relaxation effects due to spurious causes. In the radius range from Cd^{2+} to Ba^{2+} these results and most others support Dreyfus' model. The reciprocal relaxation times for each impurity are given by

$$\tau_{Cd}^{-1} = 2.06 \times 10^{12} \quad \exp(-0.64 \pm 0.01\ \text{eV})/kT);$$

$$\tau_{Pb}^{-1} = 1.19 \times 10^{13} \quad \exp(-0.69 \pm 0.01\ \text{eV})/kT).$$

It is also shown that the presence of H_2O or its products greatly perturb the relaxation times observed.

Introduction

Relaxation phenomena resulting from the reorientation of the dipoles which arise from the impurity–vacancy complexes formed when divalent impurities are incorporated substitutionally in an alkali halide lattice have been extensively studied. We will not attempt to review this copious literature, but will restrict our references to those most pertinent to this work. A recent review by Barr and Lidiard (1) covers this area extensively. When both dielectric and anelastic modes have been evaluated, all jump frequencies occurring in the relaxation processes can be assigned if data on the equilibrium dipole population is available (*2*).

In this paper we report the results of dielectric relaxation measurements on purified host crystals of KCl containing Pb^{2+} and Cd^{2+}. The effect of the OH^- added to these divalent guest systems on the relaxation time τ was also investigated. All measurements were made by a dc double-crystal polarization method developed to minimize spurious effects due to electrode capacitance, uncontrolled impurities, and better to isolate relaxation effects due to guest ions.

Experimental

Currently, three methods are used to investigate dielectric relaxation phenomena in ionic solids. Dielectric loss measurements have been made by several workers (*3–6*). Dreyfus (*7*) developed a dc polarization technique. More recently the Ionic Thermocurrent (ITC) method has been developed by Bucci and other workers (*8–10*). In such measurements it is difficult to estimate or detect the effects of spurious capacitance arising from impurities, electrodes, variations in technique, and sample preparation. In an attempt to minimize these effects we developed a technique which measures the difference in dc polarization currents between a pure reference crystal and a doped crystal. This technique will be referred to as the Double Crystal Method (DCM). Dreyfus (*7*) has described in detail the properties of divalent cation–vacancy dipoles in an electric field. Here we need only be concerned with the results of the development.

The time-dependent current density, $j(t)$, due to n types of dipoles in a sample is given by

$$j(t) = j_\infty + \sum_n j_n \exp(\tau_n/-t), \tag{1}$$

where t is time, τ_n is the time constant for the process, j_n is the initial discharge current density, and j_∞ is the current density at $t = \infty$. The total concentration of dipoles (N_n) orientable by the field (E) is given by

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[†] Present address: Department of Chemistry, The University of Western Ontario, London 72, Canada.

$$N_n = 3k[j_0 T\tau/E]/2a^2 e^2, \qquad (2)$$

where k is Boltzmann's constant, j_0 is the discharge current density at zero time, $\sqrt{2}a^2 e^2$ is the dipole moment, and T the temperature.

To investigate the effects of guest radius on polarization, Dreyfus took the solutions of Lidiard (*11*) for the polarization equations for an ac field and adapted them to the dc field case. This treatment was limited to include vacancy jumps at no greater distance than the next nearest-neighbor (nnn) position. He concluded that while the description involved complex combinations of the various possible jump frequencies, two limiting cases could be considered.

In Case I the polarization current should be resolvable into two distinct processes, one associated with the nearest-neighbor (nn), and the other with nnn relaxation. The nnn relaxation is very rapid and increases in magnitude as the radius of the guest decreases. He found this to be the case in NaCl for guest ion radius smaller than that of manganese (0.78 Å).

In the region between these two limiting cases lies a transition where the nnn contribution increases but separation is not possible. In KCl this transition should occur in the guest-radius range of 1.0–1.1 Å or about 0.2–0.3 Å smaller than the potassium ion. In this work we have chosen Pb^{2+} and Cd^{2+} as the substitutional ions. These guests have ionic radii which should give insight into the applicability of the Dreyfus theory in KCl. Dreyfus assumed the radii of the guest ions were proportional to their radii in the respective halides, and any consistent set of radii should show the proposed functional variation.

In applying Dreyfus' (*7*) dc polarization technique in the DCM two crystals are charged or discharged so that the currents meet in opposition at a junction, the resulting current should be the difference of the two currents in accordance with Kirchhoff's rule as illustrated in Fig. 1. If Z_1 and Z_2 are the resultant impedances, of the respective branches, then the current of each branch (i_i) will be:

$$i_i = (V_i/Z_i)\exp(-t/\tau_i) + i_{i\infty} \qquad (3)$$

for charging, and:

$$i_i = -(V_i/Z_i)\exp(-t/\tau_i) \qquad (4)$$

for discharging, where V_i is the potential across the sample, t is the time and τ_i is the time constant for the branch. The current through the measuring device is a linear combination of the currents in the other branches.

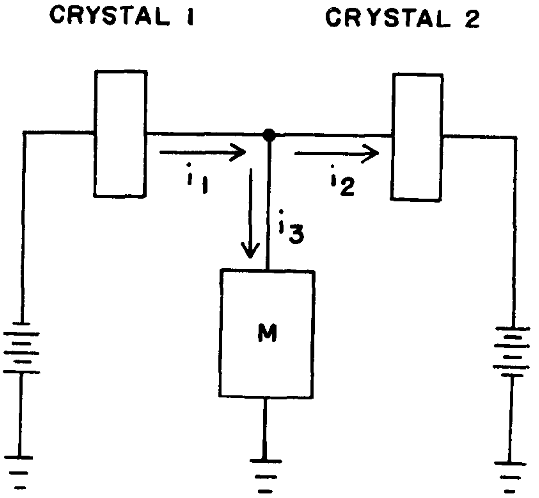

FIG. 1. Schematic diagram of double-crystal method.

If the circuit is arranged so that the potential is applied by a single power supply whose output terminals are maintained at a set voltage difference (V), Eqs. (3) and (4) become

$$i_m = (V/2)\{[\exp(-t/\tau_1)/Z_1] - [\exp(-t/\tau_2)/Z_2]\} + i_{1\infty} - i_{2\infty}, \qquad (5)$$

and

$$i_m = (V/2)\{[\exp(-t/\tau_1)/Z_1] - [\exp(-t/\tau_2)/Z_2]\}, \qquad (6)$$

for charging and discharging, respectively. If each sample contributes a time-dependent current which has a more involved form such as:

$$i_{\text{total}} = i_{\text{dipole}} + i_{\text{lattice}} + i_{\text{electrodes}}$$

then using the DCM, the identical contributions of the two crystals will add and subtract an equal amount to the measured current and thus isolate the time-dependent current contribution produced by differences in the crystals themselves.

Figure 2 shows an exploded view of the double-crystal cell. All metal parts, except the spring, were made of copper and gold plated. Pump-out channels were provided to allow evacuation of the cell after assembly. The cylindrical extension at the top of sample holder A was clamped to a copper block which formed the bottom of the inner wall of a stainless steel dewar. It was electrically insulated from the dewar by a thin teflon disk. The outer wall of the dewar joined to the aluminum cell case with a double o-ring seal. The electrometer lead, two high-voltage leads, the guard circuit, and the thermocouples were brought through the top of the cell case with

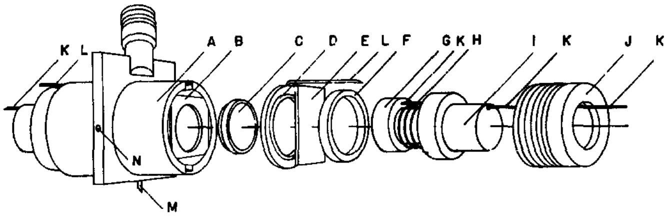

FIG. 2. Exploded view of electrode assembly: (A) sample holder with inside threads; (B) Teflon electrode support; (C) electrode with Teflon collar; (D) guard ring with Teflon support; (E) sample; (F) Teflon washer; (G) electrode; (H) steel spring; (I) Teflon plug; (J) cap; (K) high voltage leads; (L) guard leads; (M) electrometer lead; and (N) thermocouple well.

low-capacity high-voltage glass–metal feedthroughs. The lower half of the cell case was removable to permit loading the sample holder. All parts of the case and dewar were electrically bonded to provide shielding of the cell.

A Keithley Model 241 power supply was used to charge the crystal. A Keithley Model 610A electrometer connected in the fast time response mode was used to measure charging and discharging currents. The output of the 610A was recorded on a Houston Instruments Model HR-98 X-Y,t recorder. The response time of the electrometer–recorder combination was not more than 0.5 sec for full-scale deflection.

The power supply was connected across the high voltage leads (K, in Fig. 2) in parallel with a symmetrical voltage divider to the circuit ground through a low-capacity switch. The switch connected both sides of the supply and 0.33 sec later connected the electrometer to the electrometer lead from the cell to the circuit ground. This delay avoided overloading the electrometer due to switching transients. The guard circuit was connected to the circuit ground through an impedance network comparable to that of the 610A. All cabling except the guard circuits was Transradio No. C33-T low capacitance coaxial cable.

The massive gold-plated copper cell minimized thermal gradients. The temperature of the samples was measured with calibrated copper–constantan thermocouples and was known to within ±0.5°C.

The crystals used in this investigation were pulled from a melt contained in a semiconductor-grade quartz crucible (General Electric Co.). The salt used for sample preparation was Merck reagent-grade potassium chloride purified by ion exchange (*12*). Pretreatment of the salt prior to crystal growth consisted of vacuum drying in the growth apparatus at 300°C and treatment with HCl and Cl_2 as the salt was raised to the melting point. The crystals were grown under 1/3 atm of HCl. The pure crystals obtained from this process contained about 20 ppb (molar) aliovalent cations as estimated from conductivity measurements and EDTA back-titration (*12*).

The lead-doped crystals were grown under identical conditions except that reagent grade Baker and Adams $PbCl_2$ was added to the purified KCl prior to melting. The cadmium-doped crystals were similarly grown except that reagent grade Baker and Adams $CdCl_2$ was used and the crystals were pulled under a flowing stream of dried argon.

This process in the case of pure crystals, produced crystals which were free of hydroxide, as shown by the absence of detectable absorbance at 204 nm. Unfortunately this test is not reliable for crystals doped with divalent cations. Several investigations (*13*, *14*) have shown that OH^- interacts with divalent cations and the characteristic absorption does not appear unless the concentration of hydroxide exceeds that of the aliovalent metal ion. The crystals were annealed in the growth chamber by heating to 550°C and slowly cooling to room temperature. Samples about 2.5 cm × 2.5 cm × 0.13 cm were cleaved from these single crystals. The doped samples were analyzed for Pb^{2+} and Cd^{2+} content by standard polarographic methods. The samples used for analysis were taken from the boule adjacent to those used for DCM measurements. In order to maximize the number of divalent cation-vacancy dipoles (*15*) each sample was heated to 400°C and quenched in a manner similar to that described by Dryden and Harvey (*16*). Crystals for the study of the effect of OH^- on the relaxation time of Pb^{2+}- and Cd^{2+}-vacancy complexes in KCl were prepared by diffusion of water vapor into the doped sample. The samples were sealed in Vycor tubes under 22 Torr of H_2O; then heated to 400°C for 1.5 hr. The tubes were quenched to liquid nitrogen temperature and opened after they had warmed to room temperature.

The electrode contacts for all DCM samples were made by vacuum evaporating gold onto the crystal, then heating to 400°C for 8 min in vacuum followed by quenching. This treatment produced matched ohmic electrodes and supurious polarization effects were undetectable. The postevaporation heating and quenching is essential to produce ohmic, noncapactive electrodes.

Results

The curves obtained by the DCM obeyed Eq. (1) as predicted. The current varied exponentially with time in the simplest manner for most samples. At low temperatures (less than −50°C) there was no difference between traces taken with 300 V or 0 V applied across the samples. Switching of the electrometer input caused an initial sharp current spike. This spike was usually negative in sign and was short enough in duration to have little effect on the measured current after 10 sec. During the time each series of curves was being run, several curves were run at zero potential. The average of these curves was used to adjust the other curves in that series. This correction varied little between series. As the temperature was slowly raised, the appearance of a slowly decaying current was observed. The shape of these curves changed gradually with successive increases in temperature, then became steeper until the recorded curve was a sharp spike which disappeared as the temperature was continually increased. This behavior was observed for both the $KCl{:}Pb^{2+}$ and $KCl{:}Cd^{2+}$ systems.

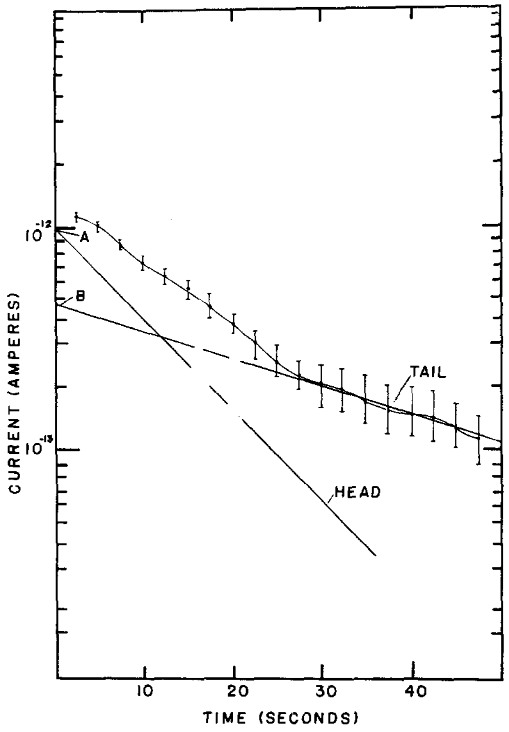

FIG. 3. Typical time-dependent current curve showing the head and tail portions. This curve is from Series 43, No. 60.

Figure 3 shows a typical curve of current versus time on a semilogarithmic plot. Note the linear tail portion and the slightly curved head portion of the curve. By least-squares fitting the points in the tail to an exponential function of the form $i = B\exp(-t/\tau)$, a line can be extrapolated to time zero. The difference between this line and the measured curve is the head portion which can be fitted to a similar function. This method can be used if the curve is of the form of Eq. (6). The constant B is the intercept of the tail portion and A is the head-portion intercept.

This technique is an extension of the method used by Dreyfus (*7*) and was recently used by Kao et al. (*17*) to separate relaxations which they observed. This method will apply only when the time-dependent current observed is the sum of currents contributed by separate sources which have sufficiently different time constants and pre-exponential factors. For most cases in this work, separation was performed with $\tau_2 > 3\tau_1$ and $0.1 < B/A < 1$. The required ratio of the τ_1 values varies with the conditions of the experiment.

In some cases there remained a slowly decaying relaxation current at the high end of the temperature range used in these experiments. It was small in magnitude and difficult to resolve. It was similar to the "slow" polarization described by Dreyfus (*7*) in NaCl systems which he attributed to impurity–vacancy dipoles with bond length greater than twice the lattice spacing. Kao et al. (*17*) studied short-term relaxations in KCl systems in the temperature range 100–300°C, and concluded that the process observed was due neither to an impurity–vacancy dipole nor a space charge (electrode blocking) mechanism, but instead a mechanism involving the dislocations within the crystals. Since most of the impurity ion content in the samples can be accounted for by nn or nnn impurity–vacancy dipoles, as discussed later, it is probable that the residual relaxations with long time constants which were observed near 260 K are due to centers which are related to the dislocation mechanism described by Kao et al. They were not observed in all series of curves which suggests that some of the samples were well compensated by the pure reference sample, while others were not due to failure of thermal treatment to produce equal dislocation concentrations in both samples.

Equation (7) relates the time constants τ and activation energy (ϵ) for the reorientation process, as follows:

$$\tau^{-1} = A \exp(-\epsilon/kT), \tag{7}$$

where A is the frequency factor, k is Boltzmann's constant and T is the absolute temperature.

Figures 4 and 5 show the results for KCl:Pb^{2+} and KCl:Cd^{2+}, respectively, plotted as ln τ vs $1/T$. The curves are a composite of all series which were run except those in which the samples were exposed to water vapor. In cases where data were taken at the same temperature or within ±0.5 K, they were averaged and are indicated by open circle barred symbols. The solid lines are the best least-squares fit of the data with the averaged points weighted according to the number of points used in the average. The figures include four different series for lead and three for cadmium. Expressed in the form of Eq. (7), these measurements give

$$\tau_{\text{Cd}}^{-1} = 2.06 \times 10^{12} \exp(-0.64 \pm 0.01 \text{ eV}/kT); \tag{8}$$

and

$$\tau_{\text{Pb}}^{-1} = 1.19 \times 10^{13} \exp(-0.69 \pm 0.01 \text{ eV}/kT) \tag{9}$$

The KCl:Cd^{2+} sample which was treated with water vapor gave no observable polarization

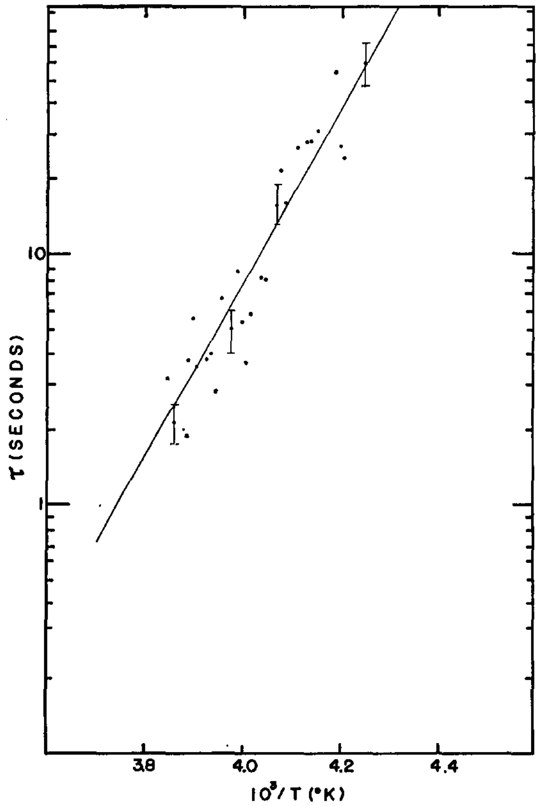

FIG. 4. Results for KCl:Pb^{2+} from DCM measurements. All points have similar error limits. Only a few limits are shown for clarity. The curve shown is given by $\tau = 8.4 \times 10^{-14} \exp(0.69/kT)$.

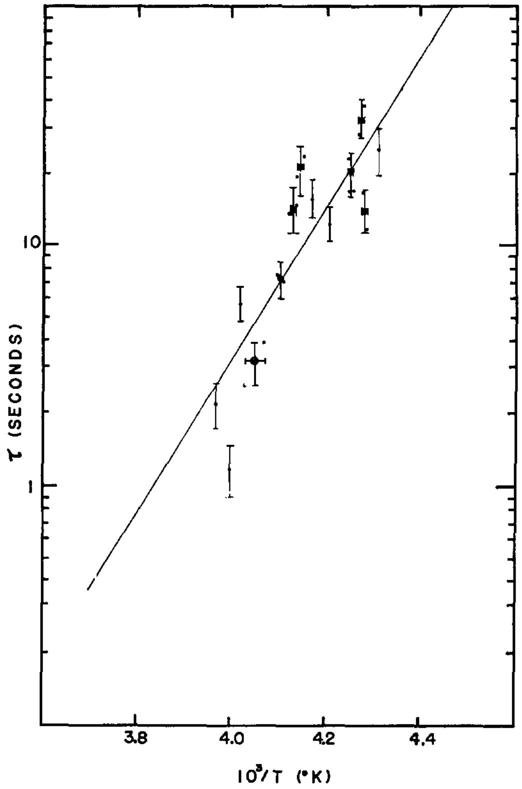

FIG. 5. Results for KCl:Cd^{2+} from DCM measurements. Symbols indicate average of data points which are shown. The curve shown is given by $\tau = 4.85 \times 10^{-13} \exp(0.64/kT)$.

current after treatment. One KCl:Cd^{2+} sample which had been exposed to the atmosphere at room temperature for nearly a year was measured using the DCM. It was vacuum-quenched from 400°C after plating, and measured immediately. It also yielded no measurable polarization current. It was again vacuum-quenched, this time from 450°C after 10 min of heating. (Figure 6 shows the results.) The τ values fall into two groups. Curve B is the best fit of the τ values in the range of 217–227 K obtained from the year-old sample. Curve A is the least-squares fit obtained from the DCM measurements on KCl:Cd^{2+} shown in Fig. 5. The data points near curve A are those obtained from the year-old sample. The parameters for a least-squares fit to these data are given in Table I. These sets of points give a clear indication that two relaxation processes are occurring with a transition between the dominant process under these experimental conditions observed in the region of 225 K.

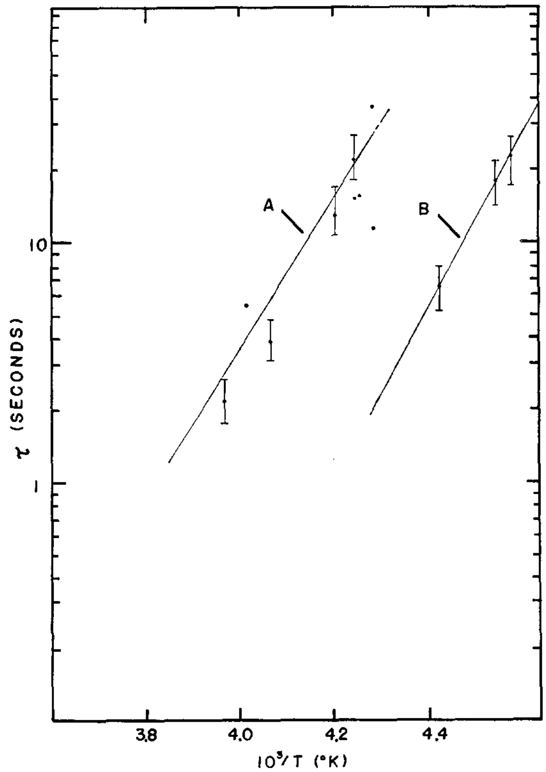

FIG. 6. Results for KCl:Cd^{2+}-(atmospheric H_2O) experiment: (A) the curve is least-squares fit for KCl:Cd^{2+} from Fig. 5; (B) a curve fitted to low-temperature points, is given by $\tau = 1.90 \times 10^{-13}\exp(0.61/kT)$.

TABLE I

WATER-DOPED CRYSTAL DATA FITTED TO $\tau^{-1} = A\exp(-\epsilon/kT)$

System	A (Sec^{-1})	ϵ (eV)	Correlation factor
KCl:Cd^{2+}:OH^-			
Data near (A)	1.1×10^{11}	0.57	0.904
Data near (B)	5.26×10^{12}	0.61	0.999
KCl:Pb^{2+}:OH^-			
Data near (A)[a]	2.88×10^{10}	0.56	0.986
Data near (B)[b]	1.74×10^{6}	0.35	0.995
All data[a]	3.64×10^{8}	0.46	0.998

[a] Highest temperature omitted.

[b] Average values of τ used in calculation.

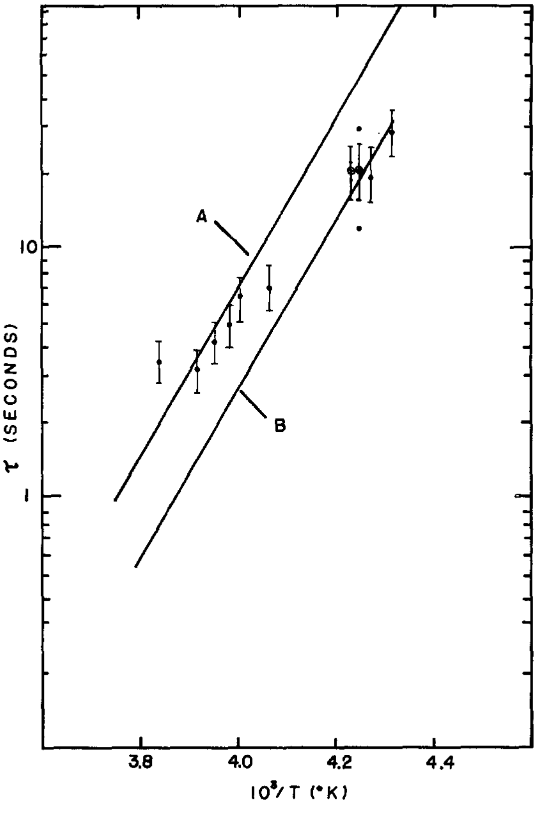

FIG. 7. Results for KCl:Pb^{2+}-H_2O experiment: (A) DCM result from Fig. 4; (B) calculated from data of Brun et al. and Eq. (7). Symbols indicate average of data points shown.

Figure 7 shows the results for the KCl:Pb^{2+} sample which was treated with water vapor. The solid line A is the best fit of the DCM data from Fig. 4. Line B was calculated from Eq. (7) using the value for ϵ and τ_0 reported by Brun et al. (Table II). This data for the KCl:Pb^{2+} into

TABLE II

TABULATION OF DCM AND LITERATURE VALUES OF ACTIVATION ENERGY AND FREQUENCY FACTOR FOR DIPOLE REORIENTATION IN KCl

M^{2+} Ionic Radius (Å)	ϵ (eV)	A (sec^{-1})	Source
Ba^{2+}	0.71 ± .01	3.1×10^{13}	Burn et al. (*9*)
(1.37)	0.70	1.3×10^{12}	Dryden and Meakins (*19*)
	0.70	2.5×10^{13}	Cook and Dryden (*20*)
Sr^{2+}	0.63 ± .01	2.7×10^{12}	Brun et al. (*9*)
(1.15)	0.67	1.3×10^{12}	Dryden and Meakins (*19*)
	0.67	2.5×10^{13}	Cook and Dryden (*20*)
	0.657	9.1×10^{12}	Bucci et al. (*8*)
	0.66		Meakins, "Progress in Dielectrics" [as cited by Suptitz and Teltow, (*21*)]
Ca^{2+}	0.61 ± .01	3.3×10^{12}	Brun et al. (*9*)
(0.99)	0.64	1.3×10^{12}	Dryden and Meakins (*19*)
	0.63	2×10^{13}	Bucci et al. (*8*)
Pb^{2+}	0.65 ± .01	4.8×10^{12}	Brun et al. (*9*)
(1.27)	0.78	1.3×10^{12}	Jain et al. (*18*)
	0.691 ± .01	1.19×10^{13}	This work
Cd^{2+}	0.636 ± .01	2.06×10^{12}	This work
(0.96)			

which H_2O and/or its products were diffused does not resolve into two well-defined relaxation processes as does the data for KCl:Cd^{2+} treated with H_2O. For comparison, the parameters obtained for a least-squares fit to various portions of the data obtained from the H_2O doped crystals are given in Table I.

On the basis of this limited data it is obvious that the presence of H_2O or its products greatly perturb the relaxation of divalent guest–vacancy dipoles in KCl. In the case of cadmium these interactions are easily detected, but good values of relaxation energies cannot be obtained, while in the lead-containing system the error caused by the presence of the second species could remain undetected in simple relaxation measurements.

Discussion

Table II lists values of ϵ and A reported by various investigators for guest ions in KCl. The ϵ values from this work agree quite well with the general trend in energies obtained by most other investigators. However, there is a major difference between the results for KCl:Pb^{2+} shown in Fig. 4 and the two previously reported measurements on this system (*9*, *18*). All three measurements were made by different experimental methods; all of the methods are based on well-understood principles. Thus one would expect the raw data obtained in the various experiments to accurately represent the system measured. The most probable cause of discrepancies must be that we are not all measuring the same system. The results obtained in the DCM measurements lie between those of the ITC and dielectric loss.

The relaxation process in the KCl:Pb^{2+} system was observed in a temperature range about 15 K higher than observed with ITC measurements on KCl:Pb^{2+}. Cappelletti and Fieschi (*10*) reported observing an ITC maximum for KCl:Pb^{2+} at 220 K while studying guest–vacancy dipole aggregation. Brun et al. (*9*) found a peak at 223.5 K using the ITC method. The relationship between T_m and ϵ is given by

$$kT_m^2 = b\epsilon[\tau(T_m)] = b\epsilon\tau_0 \exp(\epsilon/kT_m), \qquad (10)$$

where b is the warming rate, ϵ is the activation energy, $\tau(T_m)$ is the time constant at T_m, and k is the Boltzmann constant. Using the reported values of b(0.1 K/sec), ϵ(0.65 eV), and T_m(223.5 K), $\tau(T_m)$ can be calculated to be 66.2 sec at 223.5 K. This value for τ corresponds to a temperature 15 K lower than the results of the DCM.

Jain et al. (*18*) report a reorientation activation energy 0.09 eV larger than that obtained in this work and 0.13 eV larger than the ITC results.

On comparison of the experimental details between the ITC and DCM studies the major difference was in preparation of the crystals. In this work considerable care was used to eliminate H_2O and its products by pretreatment of the salt and melt with HCl and Cl_2. In both ITC reports cited, the salt used for sample preparation was not treated with HCl or Cl_2: in one (*10*), the crystals were grown under dried N_2, in the other in a controlled atmosphere. In this laboratory (*12*), treatment with HCl was found essential to remove the final traces of H_2O for the preparation of pure KCl. Burton and Dryden (*15*), while studying the aggregation of guest–vacancy dipoles, noted that in $KCl{:}Pb^{2+}$ (without pretreatment) a broader dielectric absorption band was found than expected. This broadening was attributed to the presence of more than one type of dipole. Fritz et al. (*13*) have shown OH^- reacts with Ca^{2+} in KCl, Allen and Fredericks (*14*) have shown that preparation of $KCl{:}Hg^{2+}$ requires careful removal of H_2O to avoid a mixture of impurity species, and Cappelletti and Fieschi (*10*) found that OH^- shifts the ITC peak in $KCl{:}Sr^{2+}$ to lower temperatures. These considerations led to the experiments to determine the effect of water vapor on the polarization properties of the $KCl{:}Pb^{2+}$ and $KCl{:}Cd^{2+}$ systems. Figure 7 does show that unsuspected H_2O or its products can cause a low estimate of the activation energy for dipole reorientation in $KCl{:}Pb^{2+}$. However, the complete disappearance of the polarization current of the $KCl{:}Cd^{2+}$ crystals when exposed to H_2O vapor at 400°C is remarkable. Cappelletti and Fieschi report very similar behavior for $KCl{:}Sr^{2+}$ doped with OH^-. An ITC is observable in such a crystal only after quenching from 597°C, and the major band is shifted to a temperature about 14°C lower than in a clean $KCl{:}Sr^{2+}$ crystal.

Assuming the dipole consists of unit charges located at unperturbed nn lattice sites, the concentration of dipoles oriented by the field can be calculated from Eq. (2). The actual cadmium and lead concentration were measured by polarographic analysis. The ratio of the concentration of polarizable dipoles to the total cadmium concentration gives a degree of association

$$p_{\text{dipole}} = \frac{\text{Concentration of guest–vacancy dipole}}{\text{Total guest ion concentration}},$$

based on the relaxation measurements. In Table III these results are compared with the degree of association p_{diff}, calculated from diffusion data (*22*, *23*) using a simple mass-action law. The Pb^{2+} aggregates into electrically inactive clusters much more slowly than does Cd^{2+}, which is in qualitative agreement with tracer diffusion measurements. However, Pb^{2+} still forms electrically inactive clusters at a rapid rate. When stored 4 days at room temperature the sample containing 55×10^{-6} mf of Pb^{2+} decreased its dipole concentration 42%. The aggregation of divalent cations in alkali halides proceeds by a complex mechanism (*16*, *20*, *24*) and the data reported here are insufficient to contribute to that area. It does show the major differences in dipole concentrations that may occur in crystals doped with various cations which have been annealed and quenched under identical conditions but measured after varying storage periods. Clearly, considerable caution must be used in measurements based on the magnitude of relaxation phenomena in such systems.

Unfortunately the dielectric loss paper does not report sufficient data on preparation, purity, thermal treatment or the characteristics of the

TABLE III

LEAD AND CADMIUM CONCENTRATIONS

Ion	Polarography (mole fraction × 10^6)	Dipoles (DCM) (mole fraction × 10^6)	p_{dipole}	p_{diff}	$p_{\text{dipole}}/p_{\text{diff}}$
Pb^{2+}	55 ± 5	26.7 ± 6	0.48	0.54	0.87
	70 ± 7	35.2 ± 7	0.50	0.58	0.70
Cd^{2+}	59.3 ± 6	8.7 ± 8	0.26	0.63	0.24
	80.1 ± 8	17.8 ± 4	0.22	0.67	0.33

electrodes to allow an estimate of the quality of the crystals used. The annealing temperature, the rate of quenching, and the length of the time elapsed from quenching to measurement (during which the sample was stored at room temperature) affect the magnitude of the polarization signal. As found in this work and by Cappelletti and Fieschi (*10*), the presence of H_2O or OH^- can cause the polarization current to vanish. While this effect could not account for a shift to higher energy of the relaxation it could reduce the magnitude of the expected guest-ion signal to such an extent that impurities inert to H_2O or OH^- present in much lower concentrations could be observed (*25*). It should also be noted that an energy of activation of 0.78 eV is much larger than that reported by any other investigator for any divalent cationic guest in KCl. At present we cannot suggest an explanation of this high value.

With the exception of the anomalously high value Jain et al. obtained for Pb^{2+}, the activation energies obtained in these experiments and those reported by others (*8, 9, 19, 21*) for ions with radii (*26*) greater than that of cadmium are plotted in Fig. 8. They apparently fall into two groups: three measurements by Brun et al. (*9*) on Ca^{2+}, Sr^{2+}, and Pb^{2+} which as a group lie well below the second group consisting of all other measurements. Within each group the activation energy increases with increasing radii as Dreyfus (*7*) suggests for systems in which nn → nnn jumps are the predominant relaxation mechanism. The different observations for the KCl:Pb^{2+} system by the ITC (*9*) and DCM techniques are probably due to different methods used in crystal growth and sample preparation.

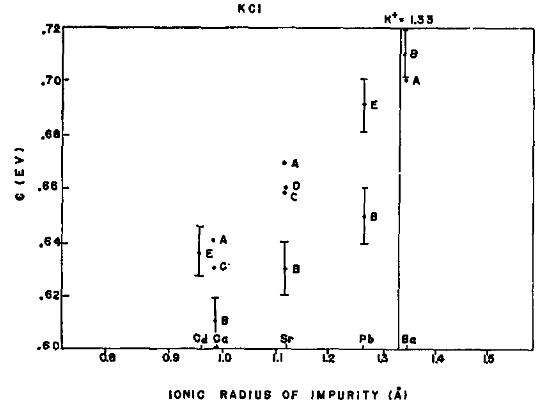

FIG. 8. Relationship between ϵ and impurity radius: (A) Dryden and Meakins (dielectric loss); (B) Brun et al. (ITC); (D) Meakins (dielectric loss); (E) DCM. The three lower points marked B fit a curve given by the equation $\epsilon = 0.142\,r + 0.469$, where ϵ is the energy in eV and r is the ionic radius (26) in Å. The remaining nine points fit the equation $\epsilon = 0.176\,r + 0.464$.

The odd behavior of alkali halides containing divalent cations when aged in the atmosphere or when exposed to H_2O vapor for short times at high temperatures has been observed by several investigators. The decay of the magnitude of the polarization current is usually ascribed to the formation of trimers (*16, 20, 24, 27*) or Suzuki phases (*28*). Dryden and Harvey (*16*) have shown that quenching from 400°C dissociates clusters such as trimers into measurable concentrations of isolated guest–vacancy dipoles. A Suzuki phase for Cd^{2+} ions in KCl has not been identified. However, in NaCl it is stable only to 250–300°C (*29*). A compound of the composition $CdCl_2 \cdot 4KCl$ ($R\bar{3}m$) has been reported by Chandrasekaran and Mohanlal (*30*), but not as a Suzuki phase. However, under quenching conditions which would have produced 25–30% of the cadmium present as Cd^{2+}-vacancy dipoles in a fresh sample, none were detectable in either the sample exposed to H_2O vapor or the sample aged in the atmosphere. On quenching from 450°C polarization currents were measured with characteristics different from those of pure KCl:Cd^{2+}.

The lead-doped crystal behaved similarly. Thus, even in this case, guest clustering or Suzuki phase formation won't explain its behavior. It must be concluded that aging in the atmosphere followed by quenching develops a divalent cation–hydroxide ion complex (*31*).

In the aged-sample experiment the only source of H_2O or OH^- is from that absorbed on its surface. Effusion studies of OH^- in KCl have shown that an atmosphere of Cl_2 or HCl is required to efficiently remove OH^- from the surface (*32*).

To form such complexes OH^- or H_2O must diffuse into the crystal. If the diffusing species is OH^- then at 400°C in 1.5 h OH^- would diffuse only about 0.4 μm into each face of the crystal (*32*). This would have little effect on the bulk of the Cd^{2+} present in the crystal. If this model is correct, the presence of Cd^{2+} or Pb^{2+} must facilitate the diffusion of OH^- in KCl. Such facilitated diffusion has not been reported in these systems. In the KCl:Hg^{2+} system the solubility of Hg^{2+} is markedly increased by the presence of OH^- in the crystal (*14*). Gründig and Rühenbeck

(*33*) have shown H_2O diffuses very rapidly into KCl to which K_2O has been added. If similar diffusion constants apply to $KCl:Cd^{2+}$ then sufficient OH^- or H_2O could be present in the crystals. However the solubility of H_2O in $KCl:Cd^{2+}$ would have to be greater than in $KCl:K_2O$ (*33*). The other possibility for such rapid diffusion would be migration of the H_2O or OH^- along dislocations. However this did not appear to be a factor in the reported studies of OH^- and H_2O diffusion.

The $KCl:Cd^{2+}:OH^-$ system is apparently similar to the $KCl:Hg^{2+}:OH^-$ and $KCl:Sr^{2+}:OH^-$ systems and is being studied further.

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