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Electric Dipole Interactions Among Polar Defects in Alkali Halides*

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The influence of electric dipole interactions among substitutional polar molecules and atoms in the alkali halides is studied in the systems KCl : Li, KCl : OH, RbCl : OH, NaBr : F, and KCl : CN. A maximum is observed in the dc dielectric constant at a temperature $T_{\max}$ which is shown to be proportional to the average interaction energy. It is also shown that this is not a relaxation effect. A remanent polarization is observed at low temperatures, which is caused by parallel-aligned pairs of dipoles experiencing a reorientation barrier. Specific-heat and thermal-conductivity measurements are also analyzed for the influence of interactions. Owing to the finite zero-field tunnel splitting of the impurity states, there is a threshold concentration, below which interaction effects are vanishingly small. The experimental results are compared to recent theoretical investigations and to results obtained on dilute magnetic alloys. In KCl : OH, the specific heat at high OH^- concentrations N is proportional to $N^{-1/2}T^{3/2}$. An unsuccessful search for direct evidence of polarization waves analogous to spin waves is reported and they are presumed heavily damped. It is conjectured that the above specific-heat result may be due to these modes.

I. INTRODUCTION

Certain atomic and molecular substitutional impurities in alkali halides are known to tunnel among equivalent potential wells within the lattice vacancy they occupy. The tunneling states associated with this motion are well understood.[1] Some of these ions have large electric dipole moments. These ions resemble a dilute gas of polar molecules and therefore allow the study of the dielectric properties of such a gas without the complications of condensation at low temperatures.[2] A particularly attractive question is that of the electric dipole-dipole interaction and the possibility of observing an ordered state.

Electric dipole interactions among such impurities were first reported by Känzig, Hart, and Roberts, who observed a maximum in the ac dielectric constant in KCl : OH at low temperatures.[3] This work led to a number of theoretical investigations of this subject.[4–8]

Analogous magnetic systems, namely, transition-metal impurities in noble metals, have numerous properties resembling the systems studied here.[9,10] Perhaps the most fundamental one is that only local order can exist at moderate concentrations. Anderson has discussed this peculiarity in the magnetic case.[11] Other effects are the appearance of a magnetic remanence that decays in time, a specific heat linear in temperature, and a maximum in the susceptibility occurring at a temperature which is proportional to concentration.

The advantage one finds in the dipolar systems is the basically simple nature of the electric dipole interaction. Consequently, one might hope to observe cooperative phenomena over a wide range of concentration and explain the results in a straightforward manner. It is also possible that a study of dipolar systems will contribute to the understanding of the magnetic alloys.

In this paper we report a detailed study of the dielectric constant of a variety of dipolar impurities and the observation of a hysteresis and remanent polarization, which we explain through electric dipole interactions. These effects are dependent upon temperature, concentration, and time (or frequency). This interaction has also been studied through specific-heat measurements and appears to be noticed in the thermal conductivity. The experimental results will be compared with the published theoretical results and new calculations, presented in Sec. II.

A particularly interesting manifestation of an electrically ordered state would be the existence of the electric analog of spin waves. We shall describe an unsuccessful search for dipolar waves.

These systems had been variously described as ferroelectrics, random ferroelectrics, or as having random local parallel or antiparallel ordering. This investigation finds no evidence for a phase transition and supports the theory of short-range local order.

II. REVIEW AND DISCUSSION OF THEORY

We will give a short summary of the theory of the tunneling defects and existing theories on the effects of interactions. Also, in order to explain our experimental results for the remanent polarization, Sec. IV, we present a theoretical model for this effect.

Two types of substitutional tunneling defects were studied. Molecular ions such as OH^- or CN^- have permanent electric dipole moments and reorient in the crystal by tunneling among a number of equivalent easy directions. Monatomic impurities such as Li^+ in KCl or F^- in NaBr have dipole moments because the ion tunnels among several equivalent off-center positions. However, the properties of both kinds of tunneling systems are quite similar.[1]

We briefly review the well-known properties of the KCl : Li system which is a representative example. The Li^+ ion substitutes for a K^+ ion in the KCl lattice and experiences a crystal field potential having minima in eight off-center $\langle 111 \rangle$ wells. Tunneling among these wells produces a multiplet of eight low-lying energy levels which are split by an energy $\Delta = 0.82\ \text{cm}^{-1}$,[12] proportional to the tunneling probability. The energy-level scheme that results from tunneling between nearest wells was computed by Gomez *et al.*,[13] and is in reasonable agreement with numerous independent experimental results.[1] In a stationary state the expectation value of the dipole-moment operator is zero. Application of a local electric field E_{1oc} destroys the equivalence of the wells, and a dipole moment appears. For small fields, the dipole moment is isotropic and is linear in E_{1oc}; for large fields, the dipole moment saturates as the Li^+ ion is pulled into off-center wells by the electric force. This saturated moment is dependent upon the direction of E_{1oc} and is a maximum when E_{1oc} is along a $\langle 111 \rangle$ direction. We denote the product of the charge and distance along a $\langle 111 \rangle$ direction by μ, the local dipole moment. Maximum polarizability occurs at low fields, dropping off to zero as μE_{1oc} becomes large compared to Δ.

The temperature-dependent polarizability α is computed by taking a thermal average over the polarizabilities of the tunneling levels. There are additional levels sufficiently removed to higher energy as to give a negligible contribution to α over the temperature range we will be considering.[1] The polarizability computed from the Gomez model is

$$\alpha(E_{1oc}, T) = \frac{\partial}{\partial E_{1oc}} \left(\frac{\mu^2 E_{1oc}}{3W} \tanh\left(\frac{W}{kT}\right)\right) , \quad (1)$$

where $W^2 = (\frac{1}{2}\Delta)^2 + \mu^2 E_{1oc}^2$ for E_{1oc} along $\langle 100 \rangle$. For a small applied field,

$$\alpha = \frac{2\mu^2}{3\Delta} \tanh \frac{\Delta}{2kT} . \quad (2)$$

For $kT > \Delta$, α approaches the classical Langevin-Debye expression $\alpha = \mu^2/3kT$.

To combine the polarizability of the pure lattice with that of a concentration N of impurities, we will use the Lorentz local field and the Clausius-Mosotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_m - 1}{\epsilon_m + 2} + \frac{4\pi}{3} N\alpha , \quad (3)$$

where ϵ is the dielectric constant of the doped alkali halide and ϵ_m is that of the pure alkali halide.[7]

The dipole moment is enhanced by the polarizability of the crystal lattice. An external dipole moment, which we denote by p, is derived from the Lorentz local-field calculation:

$$p = \tfrac{1}{3}(\epsilon_m + 2)\mu . \quad (4)$$

The Clausius-Mossotti equation predicts a divergence in ϵ when the right-hand side of Eq. (3) approaches unity. It is clear that for sufficiently low concentrations, no low-temperature divergence in ϵ can occur because α remains bounded. For high concentrations, a Curie-Weiss law is predicted by Eq. (3):

$$\epsilon = \epsilon_m + \frac{(\epsilon_m + 2) T_c}{T - T_c} , \quad (5)$$

with

$$T_c = 4\pi N p^2 / 3(\epsilon_m + 2)k . \quad (6)$$

T_c has been interpreted as a ferroelectric ordering temperature and was compared to the temperature T_{max} at which the maximum occurred in the dielectric constant of KCl : OH.[3]

A number of theoretical models have been published to explain this experiment, specifically, to calculate a value for T_{max}. Brout proposed an analogy with his theory of the Cu : Mn system.[4] This was developed by Klein for modified electric dipole interaction. He showed that at low temperature correlations among the dipoles compete against the Curie-law susceptibility of classical dipoles.[6] Lawless, who used an exact dipole interaction energy, found that the formation of "frozen parallel pairs" contributes an important nonequilibrium effect that would show up in ac measurements.[7] In Sec. IV we make an experimental check on the details of the temperature dependence of the dielectric constant calculated by Lawless.

Baur and Salzman obtained a T_{max} in their quantum mechanical treatment of interacting pairs.[8]

Mandell has calculated the polarizability of an interacting pair of two-level quantum dipoles, averaged over orientation, and found a maximum in the temperature dependence.[14] Zernick has shown that a phase transition into a ferroelectrically ordered state can also be derived using the Onsager theory of the local field.[5]

The question we hope to resolve in the present study is whether the dipolar systems can display ferroelectricity or are best described as comprising short-range local order. We will see that the latter is the case.

In the present study we have observed a remanent polarization and hysteresis at low temperatures. The origin of this effect can be illustrated by analyzing the properties of an isolated pair of dipoles. Thermally activated reorientation of pairs of interacting dipoles can account for the hysteresis and remanence effects. The pairs occur as local fluctuations in the presumed random placement of the dipoles in the lattice. We initially discuss a simplified model using free rotors, which accounts for qualitative features of the data. This is followed by a comparison with Lawless's calculation of frozen pair formation in KCl : OH.

Consider a pair of electric dipoles in a medium of dielectric constant ϵ_m, $\vec{p}_i$, and $\vec{p}_j$, separated by a distance vector $\vec{r}$. Let $|\vec{p}_i| = |\vec{p}_j| = p$. The interaction energy

$$U_{ij} = \frac{\vec{p}_i \cdot \vec{p}_j}{\epsilon_m r^3} - \frac{3(\vec{p}_i \cdot \vec{r})(\vec{p}_j \cdot \vec{r})}{\epsilon_m r^5} \qquad (7)$$

is a minimum for the two configurations of $\vec{p}_i$ and $\vec{p}_j$ aligned parallel or antiparallel to $\vec{r}$. We would expect that in thermal equilibrium such a pair would jump back and forth over the barrier between these minimum energy configurations. The smallest barrier energy corresponds to an intermediate configuration where $\vec{p}_i$ is antiparallel to $\vec{p}_j$ and perpendicular to $\vec{r}$. From Eq. (7) we compute this barrier height:

$$W = p^2/\epsilon_m r^3 . \qquad (8)$$

The mean time for activation over the barrier is

$$t = \tau_0 e^{W/kT} , \qquad (9)$$

where τ_0 is the ordinary relaxation time of the isolated dipole.[15] We will use the value $\tau_0 = 10^{-8}$ sec,[16,17] but the result is quite insensitive to τ_0.

When a remanence measurement is made, all dipoles are initially aligned in an electric field. Upon removal of the field, most of the dipoles can rapidly depolarize in the time τ_0. But those dipoles having a sufficiently close-by neighbor will take longer to randomize their orientation because the pair must jump over the barrier. Dipoles which are still aligned after a time t are those with a neighbor closer than a particular value of r, given by solving Eqs. (8) and (9):

$$r^3 = p^2/\epsilon_m W = p^2/\epsilon_m kT \ln(t/\tau_0). \qquad (10)$$

Considering that $\vec{r}$ can have any orientation, a remanent dipole contributes an average moment of $\frac{1}{2}p$. If the concentration is sufficiently dilute, and the dipoles are randomly distributed, the probability that a given dipole has a neighbor inside a sphere of radius r is equal to the product $\frac{4}{3}\pi r^3 N$. The remanent polarization is the product of the concentration, $\frac{1}{2}p$, and this probability: The remanent fraction is

$$\frac{P_{\text{rem}}}{Np} = \frac{2\pi}{3} \frac{Np^2}{\epsilon_m kT \ln(t/\tau_0)} . \qquad (11)$$

At $T = 0.2$ K and $t = 60$ sec we obtain a barrier height $W/k = T\ln(t/\tau_0) = 4K$ and a maximum distance $r \sim 25$ Å between Li^+-Li^+ dipole pairs. W turns out to be large compared to both the tunnel splitting of actual defect systems and the temperature, so that the dipole moment induced by the interaction field is indeed saturated and equal to p, as we presumed in Eq. (8). The probability that there is a third dipole 25 Å away is less than 0.01 for our dilute systems. Note that in KCl phonons of energy W have a wavelength about an order of magnitude greater than r.

Since the dipoles do not have translational freedom in the lattice, they are not able to arbitrarily lower their energy by reducing their relative separation. A gas of such dipoles would be unstable toward precipitation at these temperatures. It is possible that the apparent slow coagulation observed in certain defect systems is due to dipolar attraction and their ability to diffuse through the lattice at room temperature or above.[18]

Lawless first used the concept of frozen pairs in his treatment of the dielectric constant of KCl : OH. He computed the thermal average of the moment induced by a given dipole through parallel alignment of neighboring dipoles. Only neighbors interacting with an energy exceeding $2kT$ were considered. The results in Fig. 4 of that paper can be approximated by the expression

$$P(T) = 0.4Np^2/\epsilon_m kT , \qquad (12)$$

where $P(T)$ is the fraction of parallel-frozen dipoles. We have set the external dipole moment used by Lawless equal to p. From our previous discussion of free rotors, we found that the factor $\ln(t/\tau_0) \approx 20$ relates the interaction barrier and kT. Thus, we can probably extrapolate to $t = 60$ sec by dividing Lawless's result by 10. Also, since the OH^- dipoles can align only along $\langle 100 \rangle$ directions, only one-third of them could contribute to the polarization measured along the [100] direction. Thus, the result for the remanent fraction is

$$\frac{P_{\mathrm{rem}}}{Np} = 0.013Np^2/\epsilon_m kT. \qquad (13)$$

A six-orientation calculation predicts a smaller remanence than the free rotor because the barrier height for $\langle 100 \rangle$ dipoles depends upon the angle between $\vec{r}$ and the [100] direction in which P_{rem} is measured. The barrier actually goes to zero when this angle is about 35°. All pairs inside a zone about the [100] direction have a remanent moment equal to p because they point along the [100] instead of along $\vec{r}$ as in the free-rotor case. Those dipoles outside this zone prefer to align themselves perpendicular to [100] and contribute zero moment. We have computed the remanence for such six-orientation dipole pairs. The only difference is to change the coefficient of Eq. (11) from $\frac{2}{3}\pi$ to 0.4. This result comes very close to the prediction derived from Lawless's calculation [Eq. (13)].

In his paper treating the OH^- dipole classically, Klein conjectured that the heat capacity would be linear in T and independent of concentration.[6] Lawless's classical calculation found a small T^{-1} specific heat due to breakup of correlations.[7] We would expect that a correct theory would need to account for the tunnel splitting. However, for high concentrations the local-field splittings dominate the level spacings since Np^2 is larger than Δ. An illustrative calculation was made by Mandell for the specific heat of pairs of strongly interacting dipoles, averaged over the distance between members of the pair.[14] A concentration-independent specific heat which is linear in T was found for $kT < Np^2$, and a T^{-1} dependence at high temperature. The calculated specific heat is also independent of Δ (presumed to be much smaller than Np^2) and depends only upon the strength of the interaction through p^2/ϵ_m. Qualitatively, the magnitude of his calculated specific heat is comparable to the data in the vicinity of 1 K.

A question related to this work is whether an interacting dipolar system can support collective excitations such as polarization waves. The permanent dipole system was theoretically studied by Lobo *et al.* who have calculated a longitudinal "dipolar plasmon" frequency which is proportional to Np^2/I, where I is the moment of inertia of the dipole.[19] For our dilute dipolar systems, this frequency lies in the 10^{10}–10^{11}-Hz range. The dipolar plasmon was predicted for both ordered and disordered collections of permanent dipoles. The crystals studied in this paper show no evidence for the long-range order of ferroelectricity and would therefore be a good example of the disordered collection of dipoles.

III. EXPERIMENTAL PROCEDURE

A. Specimen Preparation

Crystals used in this study were prepared by the Materials Science Center Cyrstal Growing Facility at Cornell. The highest-concentration KCl : Li crystal was prepared by Narayanamurti who diffused Li^+ into a pure-KCl crystal according to the technique developed by Hanson.[18] The KCl : OH and RbCl : OH starting materials were made by doping the alkali halide with an aqueous solution of KOH or RbOH specially prepared to avoid the $CO_3^=$ impurity, which is known to induce precipitation of the OH^-.[20] High-purity ampoules of K or Rb metal were broken in an argon atmosphere and slowly reacted with distilled water that had previously been boiled to drive off dissolved gases. A portion of the resulting hydroxide solution was then transferred to the growing crucible, containing the host alkali halide, and the excess water was drawn off into a liquid-nitrogen-cooled trap. Crystals were grown by the Kyropoulos technique.

For high-concentration KCl : OH crystals, the amount of dopant was 10% KOH, which meant considerably more water was added. We found it more convenient to remove the excess water in a separate vacuum cold-trapping step prior to transferring the dried KCl-KOH mixture to a platinum growing crucible. Suitable crystals containing 2% OH^- were obtained by the Bridgman growing technique. The OH^- concentration was measured by scanning the ultraviolet absorption band on a Cary 14 spectrophotometer, as described by Klein *et al.*[20]

The measurements of the dielectric constant were used to determine the impurity concentration for KCl : Li and KCl : OH specimens since the dipole moments of these systems are known.[1,3,21] The concentration was obtained from the high-temperature asymptotic limit:

$$\epsilon \simeq \epsilon_m + 4\pi Np^2/3kT . \qquad (14)$$

For RbCl : OH the concentration was derived from the uv absorption.[20] For NaBr : F the concentration was accurately determined by chemical analysis.

Doped alkali halide specimens for dielectric measurements were cut from single crystals and then carefully sanded to form thin (100)-faced wafers approximately 0.03 cm thick. Gold electrodes were evaporated onto each face, leaving a 1-mm margin around the perimeter to inhibit high-voltage arcing around the edges. The specimens were quenched from 500 °C to room temperature in about 10 min in a quartz tube filled with argon. Nichrome wires were attached to the electrodes with silver epoxy. To minimize precipitation of the Li^+ impurities in the KCl : Li specimens, they were immediately mounted and cooled to liquid-nitrogen temperature.[22] This took an additional hour.

B. Dielectric-Constant Measurement

Figure 1 is a schematic of the apparatus used

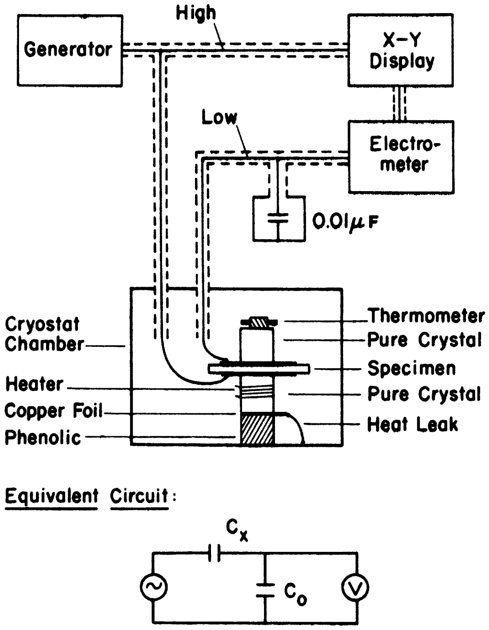

FIG. 1. Schematic diagram of the apparatus used to measure dc and low-frequency dielectric constants, hysteresis, and remanent polarization. The cryostat chamber is thermally anchored to an adiabatic demagnetization cryostat, not shown (see Ref. 23). The equivalent electrical circuit is also shown.

to measure the dielectric constant from 0.01 to 100 Hz, the hysteresis and the remanent polarization. The specimen capacitor was mounted between two pure single crystals, 1 cm on a side, onto which either a Speer carbon thermometer was glued (top) or constantan heater was wound (bottom) as shown. The two faces of the specimen were moistened with parafin oil to ensure good thermal contact. The copper wire heat leak was soldered to a 1-cm-square piece of copper foil greased between the lower KCl block and a phenolic spacer. We used an adiabatic demagnetization cryostat which was designed and built by Harrison, modified to include the shielded cables needed for these measurements.[23] Ordinary RG-1741U coaxial cable was used in the helium bath above the vacuum can. Stycast epoxy feedthroughs were installed in the top of the cryostat chamber. The remaining distance between the feedthroughs and the sample chamber was spanned by a special low-conductivity cable which was thermally anchored at each of the low-temperature stations: the He^4 pot, the He^3 pot, and the salt pill. This cable consisted of a piece of Teflon spaghetti, threaded with a constantan wire, filled with grease, and wrapped with Pb-Sn foil.

When a capacitance measurement was made, a voltage V_{high}, typically 5 V, was applied to the "high" terminal and a voltage V_{low} was read by the electrometer. Since the capacity of the specimen C_x was much less than the 0.01-μF fixed capacitor shunting the "low" cable, the unknown capacity was computed from the following formula:

$$C_x = \frac{V_{\text{low}}}{V_{\text{high}}} C_{\text{low}} , \quad C_x \ll C_{\text{low}} \tag{15}$$

where C_{low} is the sum of the electrometer input capacity, the low cable capacity, and the 0.01-μF shunt. The dielectric constant was then derived from the parallel-plate expression

$$\epsilon = dC_x/\epsilon_0 A , \tag{16}$$

where d is the thickness of the specimen, A the area of the electrodes, and ϵ_0 the permittivity of free space. The correction to C_x due to stray capacitances was much smaller than the other systematic errors. Most of the error was in the measurement of A and d and contributes about 1%.

For dc dielectric-constant measurements, the generator consisted of a 5.4-V mercury battery, a double throw switch, and an $RC = 0.01$-sec filter. The switch was cycled on and off to generate a 1-min period square-wave applied signal. A measurement of V_{low} at the end of the "on" part of the cycle was used to calculate the dc dielectric constant.[24]

A similar apparatus was used for the low-frequency dielectric-constant measurements. The monitor was an X-Y recorder or an oscilloscope. To increase the sensitivity to small changes in capacity, a fixed measured signal divided from and in phase with the generator output was subtracted from the low signal in a differential amplifier. The resulting X-Y displays were ellipses from which real and imaginary parts of ϵ were derived.

Over the range 100 Hz to 100 kHz, a General Radio bridge was used. However, hysteresis heating prevented using this frequency range at very low temperatures. The instrument was useful above about 0.1 K, but that depended upon the bridge amplitude and frequency and the impurity concentration in the specimen.

The dc method outlined above provided sensitivity to 0.2% changes in dielectric constant. Accuracy was limited by drift in the electrometer and leakage in the insulation between the low terminal and ground. Care was taken to ensure that all connections and switches were clean and dry. The 0.01-μF capacitor was selected for its low leakage. Although the General Radio bridge is a considerably more sensitive instrument, the data were recorded to a precision of only 0.1%.

C. Remanent Polarization Measurement

Remanent polarization measurements required a continuously variable kilovolt power supply connected between the high terminal of Fig. 1 and the ground. While the power supply was on, the electrometer was shunted by a 1-MΩ resistor built into the instrument. Two methods for polarizing the specimen were tried: (i) isothermal and (ii) field cooling. In the isothermal method, the specimen was charged at the same low temperature at which it was discharged. In the field-cooling method, the specimen was charged at a higher temperature and cooled to a final low temperature (about one-tenth of the higher temperature) in the charged state. The latter method achieved a maximum saturated polarization of the impurities.

The field was then removed by reducing the high voltage to zero. The discharge rate was limited in order to control hysteresis heating of the specimen. Suitable values of the discharge time ranged from 0.1 sec at 0.2 K to 15 sec at 0.05 K. When the field was reduced to zero, the electrometer was unshorted and the low voltage was monitored as a function of elapsed time t. For $t \lesssim 10$ sec, a pen recording of the electrometer output was used. As the polarization of the specimen decreased, the voltage on the electrometer increased.

For $t > 15$ min, instrumentation drift dominated changes in the voltage. We therefore adopted a procedure of continuously monitoring the voltage $V_{\text{low}}(t)$ up to the time t_1 (approximately 15 min), at which time the specimen was quickly heated to as high as 10 K. The remaining polarization quickly dropped to zero, an irreversible pyroelectric effect, and a final electrometer voltage was recorded, $V_{\text{low}}(t_1)$. The remanent polarization $P(t)$ for $t < t_1$ was calculated according to the formula

$$P(t) = [V_{\text{low}}(t_1) - V_{\text{low}}(t)]C_{\text{low}}/A . \tag{17}$$

As indicated, the above procedure is not accurate for times longer than 15 min because the polarization changes are very small at long times. Points at times longer than t_1 were obtained by holding the specimen at zero field and constant temperature to the desired longer time t, whereupon it was heated, depolarized, and the change in V_{low} was recorded. Equation (17) was used to compute a (P, t) data point. Getting points this way at longer times became increasingly time consuming because the specimen had to be polarized anew for each data point.

The heating was done by switching approximately 0.01 J from a capacitor into the heater wound around the lower pure-crystal block. The time constant, controlled by the copper wire heat leak, varied from a few seconds at 10 K to a few minutes at 0.05 K. We were therefore able to heat the specimen using the minimum amount of energy. The saltpill has a larger heat capacity, and was capable of satisfactorily absorbing numerous heat pulses. Hence, the specimen cooled back to the low temperature.

Hysteresis measurements were made by recording V_{low} while continuously varying the applied voltage V_{high} through a cycle. A slow rate of 1 cycle/min was used in order to hold hysteresis heating to a minimum. Equation (17) was used to compute the polarization. The electric field is given by $E = V_{\text{high}}/d$, where d is the thickness of the specimen.

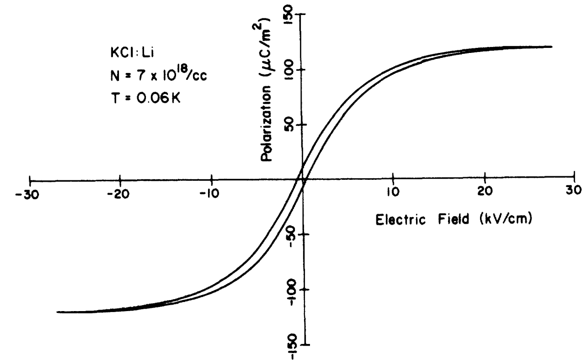

FIG. 2. Low-temperature hysteresis loop of KCl: Li taken at 1 cycle/min at 0.06 K.

IV. EXPERIMENTAL RESULTS

A. Remanent Polarization

Direct evidence that the impurity dipoles can align one another by their mutual interaction is the observation of hysteresis and polarization remanence at low temperatures. The effect becomes appreciable for concentrations exceeding $10^{18}/\text{cm}^3$ (0.01%) and temperatures below 0.3 K. A typical hysteresis curve is shown in Fig. 2. The polarization of pure KCl has been subtracted. The electric field is swept a full cycle in 1 min. Remanence after the field returns to zero is usually less than 10% of the saturated impurity polarization. Since these systems never show the abrupt switching displayed by ferroelectrics, we do not interpret this remanence as a spontaneous polarization. Hysteresis curves such as Fig. 2 also do not show any easily identified coercive switching field. Superposing a small ac field upon a dc bias produces a small hysteresis loop over a wide range of bias fields.

During cycling of the field, either increasing or decreasing it, considerable heat is generated in the specimen. This effect is greatest in the range $|E| \lesssim 1$ kV/cm. At low temperatures, hysteresis heating masks the reversible electrocaloric effect, which has been studied extensively at higher temperatures.[16,25]

Hysteresis measurements for higher temperatures show that the hysteresis loop closes as the temperature is increased and is barely observable above 1 K.

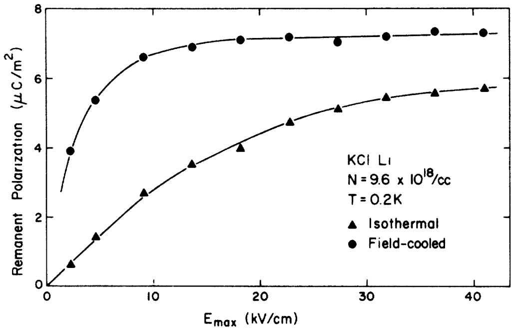

FIG. 3. Remanent polarization vs polarizing field $E_{\max}$ measured 1 min after discharging. For isothermal measurements, the polarizing field was applied for 1 min at 0.2 K. For field-cooled measurements, the polarizing field was applied at approximately 2 K and maintained while the specimen was cooled to 0.2 K.

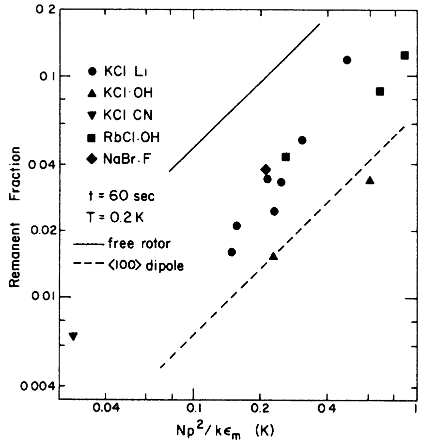

FIG. 5. Fraction of remanent dipoles plotted against $Np^2/k\epsilon_m$. Theoretical estimates for a free rotor and for a six-orientation ⟨100⟩ dipole are also shown.

In Sec. III we outlined our two methods for measuring the remanence. Figure 3 is a plot of the remanent polarization, measured 1 min after the field is removed, as a function of the maximum applied field. For each data point we started the specimen in a virgin unpolarized state. The resulting remanence measured following the two methods of initial polarization are compared in the two curves of Fig. 3. Field cooling produces a saturation in the remanence at large polarizing fields, leading us to conclude that the specimen had been prepared with a saturated initial polarization. Apparently only partial initial polarization can be achieved by the isothermal method. We therefore used the field-cooling method at $E_{\max} \sim 30$ kV/cm to take all the remanence data quoted in the rest of this paper.

The magnitude of the remanence also depends upon impurity concentration, temperature, and the time elapsed since the field is removed. By measuring the remanent polarization, which we will denote by $P_{\rm rem}$, for a number of doped KCl : Li crystals at the same temperature ($T = 0.2$ K) and elapsed time ($t = 60$ sec), we obtain the quadratic concentration dependence shown in Fig. 4. We plot the data against the quantity Np which is the saturated Li$^+$ polarization.[26] Similar results were also obtained for KCl : OH, RbCl : OH, and NaBr : F crystals.

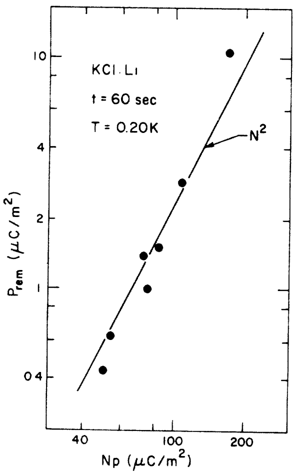

FIG. 4. Remanent polarization of KCl : Li, $P_{\rm rem}$, is plotted against the product of concentration and dipole moment, Np.

The fact that $P_{\rm rem}$ increases quadratically with impurity concentration strongly suggests that dipole pairs are responsible for the remanence. Since $P_{\rm rem}$ is less than 10% of Np, we conclude that fewer than 10% of the dipoles form remanent pairs. This agrees with the model discussed in Sec. II.

In Fig. 5 we compare the six-orientation OH$^-$ result [Eq. (13)], the free-rotor expression [Eq. (11)], and the concentration-dependent remanence data for four systems. The agreement between the data on KCl : OH and Eq. (13) is very good. The free-rotor expression is about a factor of 4 larger than the data average.

We attempted to study the remanence in a KCl : OH crystal containing 2% OH$^-$. Our interest stemmed from the fact that the average distance between OH$^-$ dipoles in that crystal is 15 Å, which is considerably closer than the distance between the remanent pairs in the crystals of lower concentration. The effort was thwarted by an inability to prepare an initially polarized state. Up to the highest fields applied (limited by electrical breakdown), the induced remanence increased with polarizing field, linearly at first, and then quadratically near 30 kV/cm, quite different from the data of Fig. 3.

Temperature and time dependences in KCl : Li

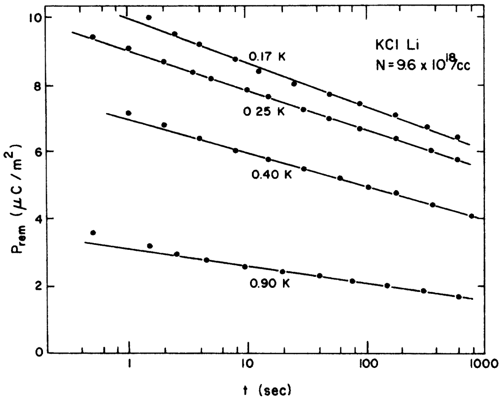

FIG. 6. Remanent polarization of KCl: Li against time (log scale) for several temperatures.

for a particularly high concentration are plotted in Fig. 6. Note the logarithmic time dependence: The polarization decays very rapidly for short times and very slowly for long times. With additional data on another specimen we find that P_{rem} decreases linearly with the logarithm of time to five decades. The data of Fig. 6 are quite linear in log t, whereas Eq. (11) has some positive curvature. Another deviation is that the observed temperature dependence becomes slower than T^{-1} below 0.2 K. Since P_{rem} depends upon $\ln\tau_0$, it is actually quite insensitive to the accuracy to which τ_0 is known. However, if the attempt frequency were dependent upon the zero-point harmonic libration of the interacting pair, then τ_0 would depend upon the barrier height W as well. This would have a small effect upon the magnitude of P_{rem}, but it would tend to make its dependence upon $\ln t$ more linear.

An interesting magnetic analog of parallel-aligned pairs has recently been reported by Tholence and Tournier in Cu: Fe.[10] Nearly magnetic Fe pairs were found to enhance the susceptibility, which has a component that increases as the square of the Fe concentration.

B. Dielectric Constant

The dielectric constant of the doped crystals is enhanced over that of pure alkali halides and shows considerable frequency dependence at low temperatures. A family of isotherms for a high-concentration KCl: Li crystal is plotted in Fig. 7. It is clear from these measurements, as well as the remanence measurements, that relaxation times are present in high-concentration crystals which are many orders of magnitude longer than the measured relaxation time of the isolated defect.[27] Since the dielectric constant changes monotonically over seven orders of magnitude in frequency, we conclude that there is a broad distribution of internal-relaxation times. Note that the loss tangent, plotted for 0.2 K, is practically frequency independent, quite similar to the response of a ferroelectric.

We propose that the data taken at 1 cycle/min are a good approximation to the dc dielectric constant. Our study of the remanence effect indicates that fewer than 10% of the dipoles would not be in equilibrium with the applied field. Temperature dependence of the excess dc dielectric constant for three Li^+ concentrations is shown in Fig. 8(a) on a log-log plot. At high temperatures, the excess dielectric constant approximately scales with concentration and decreases as T^{-1}. Interaction effects are unnoticable in the low-concentration curve. The dielectric constant, obeying the Clausius-Mosotti equation with the calculated Li^+ polarizability [Eqs. (2) and (3)], shows the expected low-temperature saturation. We used $\Delta = 0.82$ cm^{-1} for the tunnel splitting in computing the theoretical curves in Fig. 8(a).

For higher concentrations, there is a maximum in the temperature dependence, which sharpens as the concentration increases. These data do not obey the Clausius-Mosotti equation, which predicts a larger dielectric constant and divergence at a critical temperature. We find similar maxima also in KCl: OH, RbCl: OH, and NaBr: F, but not in KCl: CN. Some of these data are plotted in Figs. 8(b) and 8(c). Känzig *et al.* found a frequency-dependent maximum in the ac dielectric constant of KCl: OH and compared it to the Clausius-Mosotti critical temperature. Observation of a maximum in the dc dielectric constant shows that its occurrence is not primarily a relaxation effect.

The temperature at which the maximum in ϵ occurs, T_{max}, increases linearly with concentration.

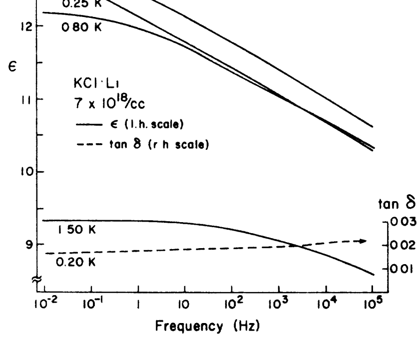

FIG. 7. Dielectric constant (suppressed origin) of KCl: Li plotted against frequency (log scale) for several temperatures. The loss tangent tanδ is plotted for 0.20K. Smoothed curves are drawn to represent four points/decade of frequency.

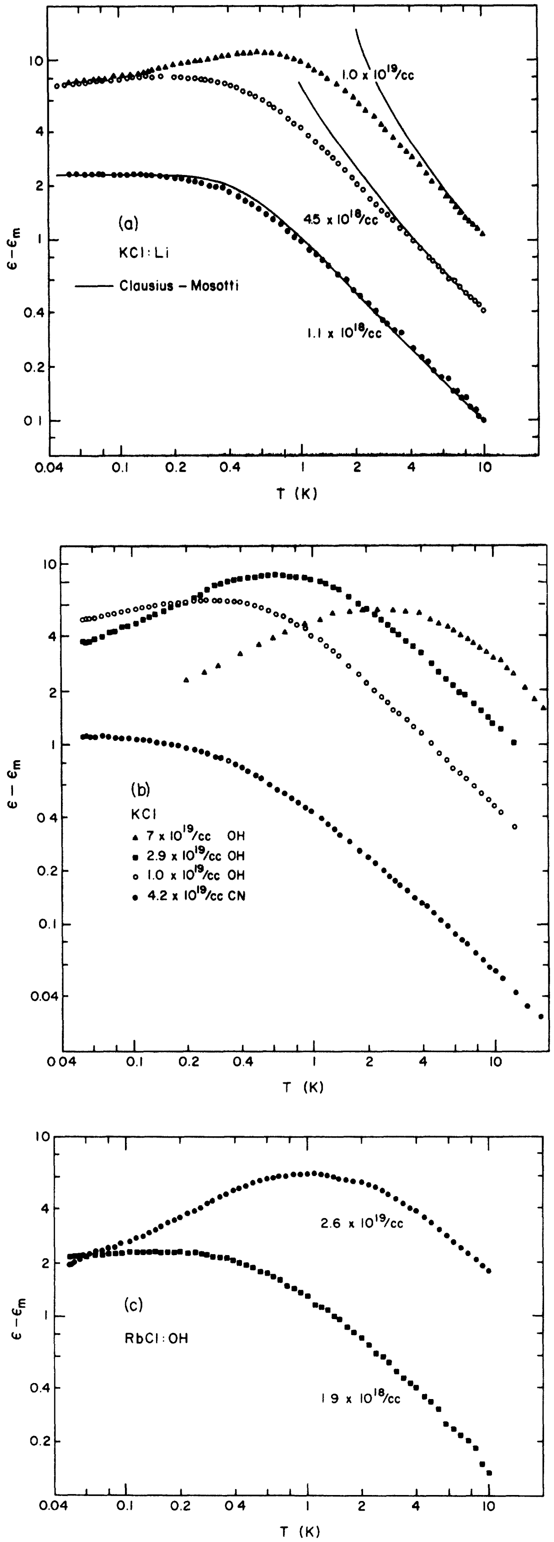

FIG. 8. Excess dc dielectric constant $\epsilon - \epsilon_m$ plotted against temperature for several defect systems. Solid curves of Fig. 8(a) are computed Clausius Mosotti functions, using Eqs. (2) and (3) with $\Delta = 0.82$ cm^{-1}, for the KCl : Li system.

This is summarized in Fig. 9 by combining all of the values of T_{max} for four different systems and plotting them against $Np^2/k\epsilon_m$. This parameter is equal to the electric dipole interaction energy per dipole (in K units) for a pair of dipoles separated by a distance $r=N^{-1/3}$ in the alkali halide lattice, calculated from Eq. (7). Our experimental result is

$$T_{max} = Np^2/k\epsilon_m \, , \qquad (18)$$

which is plotted as the extended line through the data in Fig. 9. This same equation applies to all of the systems, despite their different dipole moments, tunneling frequencies, and relaxation times. Evidently, the electric dipole interaction alone is responsible for T_{max}. The weakness of the electric dipole interaction in the system KCl : CN appears to explain the absence of a maximum there, even though there is a strong elastic interaction between the CN$^-$ ions in this system.[28]

Theoretical results for calculations of T_{max}, mostly for the system KCl : OH, show a linear relation similar to Eq. (18), and are represented by short line segments in Fig. 9. It is interesting to also observe that the theoretical calculations give essentially the same result, to within a factor of 2, demonstrating the insensitivity of T_{max} to the model chosen.

A more detailed test of the theories is to compare them with the magnitude and temperature dependence of the dielectric-constant measurements. We have done this by computing the effective polarizability of the impurity ions in our more concentrated specimens. The Clausius-Mosotti function, Eq. (3), is used to compute values of $N\alpha$ from the dielectric constant.

$N\alpha_{max}$, the magnitude of $N\alpha$ at $T = T_{max}$, is given in Table I for several specimens. We have included for comparison the corresponding theoretical results computed from Fig. 2 of Klein's paper and Fig. 7 of Lawless's paper. We observe that the theories and experiment agree to within a factor of 2.

We now turn to a closer inspection of the temperature dependence of ϵ for $T > T_{max}$. As the concentration is increased, we find that the influence of interactions reduces the effective polarizability of the impurity dipoles. Although the local field tends to enhance the polarizability, correlations among the dipoles keeps the dielectric constant from diverging. For high-concentration specimens, the effective value of α is so much smaller than the noninteracting, or low-concentration, polarizability that we can accurately compute a deviation function from our data. We are considering a temperature region where the noninteracting polarizability is $\mu^2/3kT$, i.e., where it behaves classically. The deviation is nearly T^{-2} and we characterize it by a

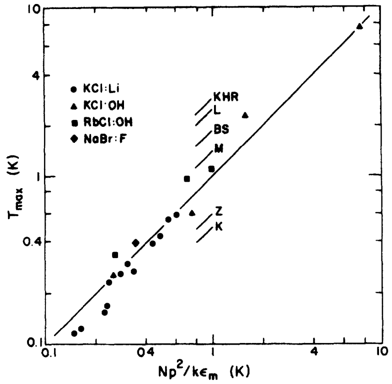

FIG. 9. Temperatures corresponding to the maximum in dc dielectric constant T_{max} against the quantity $Np^2/k\epsilon_m$ for four tunneling defect systems. The curve is a linear fit to the data [Eq. (18)]. The linear dependence predicted by the various theories is shown by short lines. KHR: Eq. (6); Z: Fig. 4 of Ref. 5; K: Eq. (4.9) of Ref. 6; L: Fig. 7 of Ref. 7; BS: Table III of Ref. 8 (some positive curvature is predicted at low concentrations); M: two-level quantum dipoles, averaged over orientation, Ref. 14.

first-order coefficient B, given by

$$N\alpha = (N\mu^2/3kT)(1 - B/T) . \qquad (19)$$

Fits to Eq. (19) are plotted on log-log scales in Fig. 10 for KCl:OH, KCl:Li, RbCl:OH, and KCl:CN, and the fitting constant B is entered in Table I.

The form of Eq. (19) also fits the results of a calculation made by Lawless on KCl:OH.[7] We have made such a fit to Fig. 4 of Ref. 7, which includes the effect of both equilibrium correlations and frozen-pair formation. Taking the external dipole moment used by Lawless, μ_e, to be equal to p, we obtain the result

$$B = 1.0Np^2/k\epsilon_m , \qquad (20)$$

which is denoted by an entry in column 7 of Table I. Our data on KCl:OH yields a value of B about twice as large. Lawless also calculated the case where only equilibrium correlations are taken into account, for which the coefficient of Eq. (20) is reduced to 0.25.

Van Vleck had discussed an expected T^{-3} deviation from Curie's law due to dipole-dipole coupling.[2] The predicted deviation is much larger than the experimental findings and disagrees with the T^{-2} observed temperature dependence.

Baur and Salzman's quantum-mechanical calculation of the effective polarizability of a pair of two-level dipoles does not agree with our data.[8] Their α_{eff} turns out to be larger than the noninteracting polarizability, whereas experimentally, we find that interactions reduce the effective polarizability in all cases. Also, the deviations found in their virial expansion treatment are all too small by over two orders of magnitude and carry the opposite sign. Interacting pair effective polarizabilities evidently cannot accurately describe correlation effects.

Equivalent quantitative information is obtained by plotting $1/N\alpha$ against temperature on linear scales. Over a broad temperature range, above 2 K, the data fits a Curie-Weiss Law:

$$N\alpha = N\mu^2/3k(T+\theta). \qquad (21)$$

We have results for several concentrations of OH^- and find that θ is positive and linear in concentration. Some of the data are listed in Table I, and for KCl:OH the best fit is

$$\theta = +3.2Np^2/k\epsilon_m . \qquad (22)$$

This result suggests agreement with the classical calculations of Lawless[7] and Klein,[6] which show that an antiparallel ordering of neighboring dipoles is favored, analogous to an antiferroelectric ordering, and is responsible for the decrease in dielec-

TABLE I. Experimental and theoretical values of parameters which describe the results for the dc dielectric constant.

	N (10^{18} cm^{-3})	p (Debye)	B (K)	$Np^2/k\epsilon_m$ (K)	θ (K)	$\frac{B}{Np^2/k\epsilon_m}$	$N\alpha_{max}$
Experiment							
KCl: Li	10	5.5	0.56	0.61	1.0	0.92	0.068
KCl: OH	10	3.8		0.16	0.8		0.054
KCl: OH	29	3.8	1.2	0.68	2.6	1.8	0.062
KCl: OH	70	3.8	3.4	1.6	4.6	2.1	0.051
RbCl: OH	26	6.7	1.6	1.0	5.0	1.6	0.052
KCl: CN	42	0.5	0.25	0.028			
Theory (KCl: OH)							
M. W. Klein	25						0.12
W. N. Lawless	25 (average)					1.0	0.061

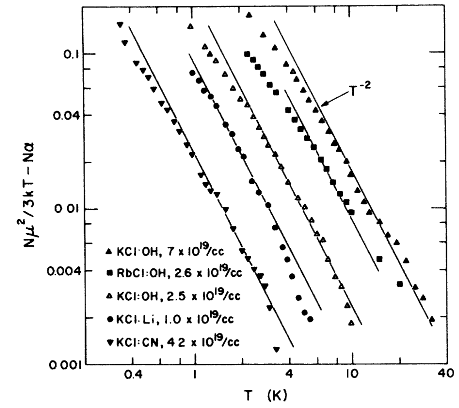

FIG. 10. Difference between Langevin-Debye law and $N\alpha$ computed from dc dielectric constant of five doped crystals plotted against temperature. Solid lines are T^{-2} fits to obtain the parameter B of Eq. (19).

tric constant.

We note here that Lüty had found a concentration-dependent Curie-Weiss temperature dependence of the elasto-optical effect in KBr : OH.[17] Also, Byer and Sack found a Curie-Weiss temperature dependence in ultrasonic compliance experiments on KCl : Li.[22]

Our experiments confirm the theoretical predictions that correlations overcome the Lorentz local-field enhancement effects inherent in Eq. (3). As the temperature is lowered, interactions of a given dipole with its neighbors reduces its effective polarizability. From Eq. (2) we observe that the presence of a random internal electric field produced by the correlations, as discussed by Klein, can reduce the polarizability of a dipole. It is also clear from Eq. (2) that the influence of the internal field is important only if $pE_{1\alpha}$ is comparable to or greater than Δ. Hence, it is understandable that for low concentrations, such that $Np^2 \ll \Delta$, the local field and the influence of interactions is very small, even at low temperatures, where $kT \ll Np^2$.

C. Specific Heat and Collective Excitations

Concentration-dependent effects in the shape of the specific heat of tunneling systems have been reported before.[29] We have made measurements of the specific-heat anomaly for several concentrations of the system RbCl : OH, which illustrates the general effect of interactions.[30] The specific-heat anomaly due to the OH$^-$ impurities, obtained by subtracting the heat capacity of pure RbCl from the measurements, is plotted in Fig. 11. For low concentrations, there is the expected peak characteristic of the tunneling states.[31] For the highest concentration, the temperature dependence is markedly different. Over the temperature range from which we can take data, the specific heat is monotonically increasing with temperature. We are limited in our ability to extend the data to higher temperatures by the large host specific heat, which increases nearly as T^3. Note that there is no indication of an ordering temperature. For a comparison, the corresponding places where the dielectric constant goes through its maximum are marked by the arrows.

In their study of the specific heat of KCl : OH and KCl : Li, Pohl and co-workers had obtained families of curves which are qualitatively the same: The specific heat for high concentrations broadens into an apparent monotonic function of temperature over the same temperature range.[29]

The excess specific heat is almost linear in temperature for the high-concentration specimens. It could be argued that a random internal field, caused by the correlations, produces random Stark-effect splittings of the tunneling states. The net result is a broad density of states. An electric field separates the energy levels, giving enhanced high-temperature specific heat and diminished low-temperature specific heat. In particular, a linear temperature dependence in the specific heat implies a constant density of states in the system.

The deviations observed in the heat capacity at high concentrations are not easily compared to a classical calculation because the specific heat of the tunneling states is much larger than that due to the correlations or ordering. We find no evidence for a T^{-1} term in the specific heat due to breakup of correlations that Lawless calculated for KCl : OH.[7] Since we cannot obtain precise data at high temperatures, because of the large host specific heat, we never observe a decrease in the ex-

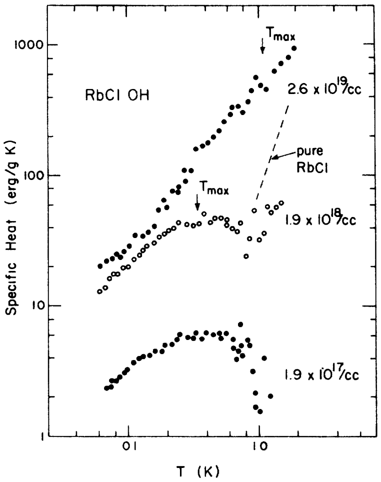

FIG. 11. Excess specific heat of three concentrations of OH$^-$ impurities in RbCl plotted against temperature. The temperature of the maximum in the dc dielectric constant is displayed by the arrows labeled T_{max}. The specific heat of pure RbCl is also shown.

cess specific heat at high temperature.

In the system KCl:OH where we have been able to prepare specimens in which the interaction energy is large compared to the tunnel splitting, we have discovered that the specific heat follows an unusual function at high concentration. Specific-heat data taken on our 2% OH^- crystal and data by Peressini *et al.*[29] are plotted in Fig. 12, showing a $T^{3/2}$ temperature dependence. Since this power law is expected for ferromagnetic spin waves, we have compared the heat capacity at the various OH^- concentrations to the specific heat of a cubic ferromagnet. For the exchange constant we have taken Np^2/ϵ_m. The specific heat is given by[32]

$$C = 0.11 Nk\left(\frac{kT}{2Np^2/\epsilon_m}\right)^{3/2} . \tag{23}$$

Equation (23) for the three OH^- concentrations are shown as solid lines in Fig. 12. The agreement is quite striking, and perhaps fortuitous. Note that the over-all $N^{-1/2}$ concentration dependence appears to be obeyed. The lowest-concentration specific heat shows the high-temperature decrease of the Schottky specific heat of the tunneling states. For the highest concentration, $Np^2/k\epsilon_m = 8$ K, or about ten times the tunnel splitting. Since the specific heat is very insensitive to damping, it is possible that the $N^{-1/2}T^{3/2}$ behavior is due to the collective modes. One could conjecture that these are modes of clusters of OH^- dipoles.

We searched for a propagating polarization disturbance in a KCl crystal containing 2% OH^- ions. The experiment used a pulse technique at 1 K on a crystal 1 cm square by 0.1 cm thick. A pair of 0.1-mm × 1-cm electrodes were painted onto each end of the crystal. 100-V pulses 0.1–1 μsec long were applied to one pair of electrodes, while the pair at the other end was monitored with a high-impedance low-temperature mosfet amplifier.[33] No response was observed. We also determined that this crystal is not piezoelectric at 1 K in a separate experiment which searched for a piezoacoustic resonance. A possible explanation is that these modes are overdamped. Because of the fact that reorientation of a dipole involves mass motion, one could expect that the dipolar modes are strongly coupled to the lattice vibrations. Indeed, in the alkali-halide systems the coupling of the paraelectric defects determined by thermal-conductivity experiments is often quite strong. One should contrast this with magnetic systems where the spin waves are coupled more weakly to the phonons.

In view of the above results, one may try to observe the dipolar mode in the microwave dielectric constant of NaBr:F or RbCl:Ag. We suggest these systems because of the following evidence that the F^- or Ag^+ ion is weakly coupled to the host lattice: From electrocaloric measurements on RbCl:Ag, Kapphan and Lüty measured a relaxation time of 8×10^{-6} sec at 1.4 K.[16] From audio-frequency dielectric-constant measurements, Rollefson measured a relaxation time of 10^{-4} sec for NaBr:F.[34] Neither system shows an observable resonant phonon scattering in the thermal conductivity.[34] OH^- and Li^+ show strong resonances and have relaxation times on the order of 10^{-8} sec.

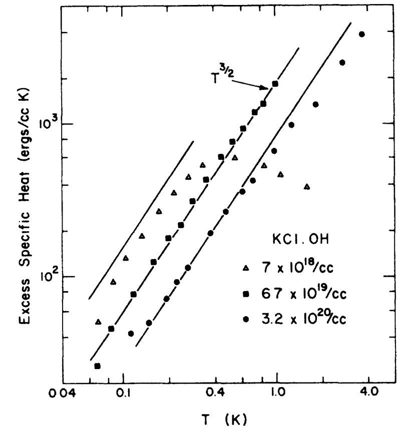

FIG. 12. Excess specific heat of several concentrations of KCl:OH compared to spin-wave specific heat, Eq. (23), denoted by $T^{3/2}$ lines. The two lower curves are data from Ref. 29.

D. Thermal Conductivity

In a study of the thermal conductivity of the system KCl:Li, Pohl and co-workers observed concentration-dependent effects.[35] We will present here an analysis of those data to illustrate the influence of interactions upon the tunneling states. Thermal-conductivity experiments are interpreted as a phonon spectroscopy upon the tunneling levels of the impurity sites due to their resonant scattering of the lattice phonons. Let us denote the thermal conductivity of pure KCl by κ_m, and that of KCl:Li by κ. The following expression for the fraction increase in thermal resistivity per unit of concentration is proportional to the strength of the Li^+-phonon scattering process:

$$(\kappa^{-1} - \kappa_m^{-1})/N\kappa_m^{-1} . \tag{24}$$

We have analyzed Pohl's data this way and plot the above function in Fig. 13. The peak occurs at a temperature where the phonons dominating the heat conduction have energies comparable to some average of the level splittings of the Li^+ defect. As the concentration is increased, the peak appears to shift to a higher temperature. Note that there is remarkably more scattering above the peak and diminished scattering below. A similar set of curves, not shown here, were obtained from the

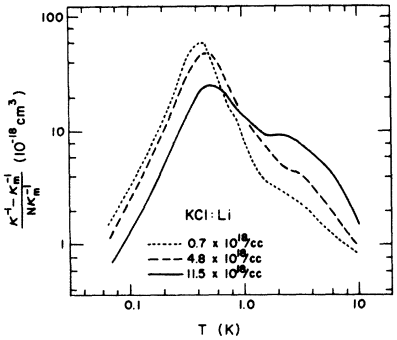

FIG. 13. Fraction increase in thermal resistivity, per unit concentration, of several concentrations of KCl : Li plotted against temperature. The data of Ref. 35 were used in this analysis.

thermal-conductivity measurements on KCl : OH by Rosenbaum.[36]

The above results are consistent with the view that the electric dipole interaction can cause an increase in the splittings between the tunneling states via the Stark effect. These larger splittings scatter more effectively at high temperatures, where they are at resonance with the phonons, and rather less effectively at low temperatures, where they are off resonance. Of course this is a simplified viewpoint, since the relaxation time also depends upon the level spacing, as was observed in Pohl's work. A reduction in the level spacing could be expected to reduce the phonon scattering rate and vice versa.

V. SUMMARY AND CONCLUSIONS

Through measurements of the dielectric constant and specific heat, we have verified that electric dipole interactions among polar substitutional defects in the alkali halides cause significant perturbations for concentrations where $Np^2/\epsilon_m \gtrsim \Delta$, and temperatures $kT \lesssim Np^2/\epsilon_m$. Under these conditions, there is an internal electric field which splits the tunneling energy levels and reduces their polarizability. Classical treatments of the dielectric constant are sufficient to explain the occurrence of T_{max} and the reduced polarizability observed at temperatures above T_{max} for high-impurity concentrations. Classical theories also find that the polarizability is reduced both by the $\vec{p}_i \cdot \vec{p}_j$ type of interaction,[6] as well as the correct tensor electric dipole interaction, Eq. (7).[7]

The maximum in the dielectric constant is shown to be simply proportional to the average electric dipole interaction energy, i.e., we can say more than just T_{max} is linear in N. The deviations from the Curie law agree with the calculation of the onset of two-dipole correlations at temperatures above T_{max}. Classically, this indicates that there is a favored antiparallel ordering on the average, since the dielectric constant is a function of $1/(T+\theta)$ with positive θ.

A model of strongly interacting pairs of nearby dipoles is shown to account for the polarization remanence observed at low temperatures. A distribution of long relaxation times results from the reorientation of dipoles which are parallel aligned with a neighbor. Consequently, the dielectric constant is frequency dependent over many orders of magnitude in frequency. However, at 10^{-2} Hz and at $T \gtrsim T_{max}$, one measures a very good approximation to the static dielectric constant.

A search for collective-polarization waves was unsuccessful, and we expect that they are strongly damped. We suggest that a search for a mode in NaBr : F the microwave region might be more successful, since this system is more weakly coupled to the lattice.

By way of outlook, it would seem that some refinement of the theory of the specific heat and dielectric constant, to include the tunnel splitting, would be desirable. Although a two-dipole model can go quite far in discussing the occurrence of T_{max} and remanent polarization, it cannot account for even simple correlation effects. In view of the fact that the specific heat may be indicating the presence of polarization waves, a careful theoretical treatment seems justified. It would be interesting to find out if the observed $N^{-1/2}T^{3/2}$ dependence of the specific heat can be calculated directly from the influence of interactions upon the tunneling states.

Because of the simple nature of the electric interaction, the dipolar systems might be suitable as models to aid understanding more complicated phenomena in dilute noble-transition-metal alloys. In particular, it would be important to study the time dependence of the magnetic remanence and the frequency dependence of the magnetic susceptibility at low concentrations. The dipolar systems have a disadvantage in that the concentration of dipoles is limited to a few percent. Thus we are unable to observe the onset of long-range ordering in a concentrated system. The absence of long-range order at low concentrations appears to be a fundamental property of a dilute random network.

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