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Electrocaloric Effect in Doped Alkali Halides*

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Electric cooling with the polarizable impurities Li^+ and OH^- in KCl and CN^- in RbCl has been measured in the temperature region where the tunnel splitting of the motional ground states of these impurities becomes the limiting factor. In KCl:Li, quantitative agreement with the theoretically expected cooling is demonstrated. The cooling in KCl:OH and RbCl:CN also agrees with the models based on the known tunnel splitting and polarizability. The possibility of using these impurities for practical cooling is discussed.

I. INTRODUCTION

THE electrocaloric effect, the electrical analogue to low-temperature cooling by adiabatic demagnetization, has been used earlier to determine the polarizability of a low-frequency impurity mode observed in KCl containing small concentrations of substitutional Li^+ ions.[1] This impurity mode, assumed to arise from the tunneling motion of the lithium ion between several equivalent potential minima in the potassium vacancy, has since been extensively studied with a number of techniques, see Refs. 2–6, and we refer to these papers for details.

So far, the electrocaloric effect has not been used for practical low-temperature cooling. Its magnetic analogue on the other hand has been the most widely used technique for producing low temperatures for the last 40 yr.[7] The lowest temperature reached by adiabatic demagnetization is determined by the zero-field splitting of the spin states or by the onset of some magnetic interaction between the spins. For electronic spins this limiting temperature is of the order of 0.01°K. Little is known about the details of the cooling in this temperature region.[7]

In KCl:Li, where the zero-field splitting of the motional ground state is 10^{-4} eV, which corresponds to 1.2°K, the limiting influence of this splitting on the cooling should become noticeable around 1°K, i.e., in a temperature range easily accessible to investigation. The earlier measurements had been performed above 1.4°K only[1] and had, therefore, not shown this influence.

In this paper, we report on the electric cooling in KCl:Li and KCl:OH above 0.3°K and in RbCl:CN above 0.07°K. These measurements demonstrate the limitations of the electric cooling resulting from the finite zero-field splitting of the ground state, and can also serve as a model for the magnetic cooling in the simplest case, where spin-spin interactions can be ignored. Furthermore, the data provide a sensitive test for the model of the tunneling states of atomic and molecular impurities in solids. The possible use of the electrocaloric effect for producing low temperatures will also be discussed.

II. EXPERIMENTAL PROCEDURE

The experimental procedure has been described earlier[1] and is similar to that of measuring specific heat by the transient technique.[6,8] Measurements down to 0.3°K were performed in a He^3 cryostat.[9] Below 0.3°K, a cryostat with magnetic cooling[8] was used. For measurements above 1°K, the sample was suspended by nylon strings, below 1°K it was mounted on graphite posts[9] (0.9 mm diam) which reduced vibrational heating. The electric field leads were used to achieve a sample to bath thermal time constant varying between 30 and 100 sec over the entire temperature range, as described by Harrison.[8] The time constant for applying and removing the electric field was 1 sec, i.e., short compared to the thermal one, but long compared to the dipole-lattice relaxation time, which is less than a microsecond in the temperature range studied. The heating and cooling caused by applying and removing the electric field were always found to be reversible to better than 10% except were noted in the text.

III. EXPERIMENTAL RESULTS

A. KCl Containing Lithium Ions

Figures 1, 2, and 3 show some of the data obtained on KCl:Li. At low fields the cooling ΔT, upon depolarization, is proportional to the square of the applied electric field E, and at high temperatures ΔT varies as T^{-4}, as

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[1] G. Lombardo and R. O. Pohl, Phys. Rev. Letters 15, 291 (1965).

[2] A. Lakatos and H. S. Sack, Solid State Commun. 4, 315 (1966).

[3] N. Byer and H. S. Sack, J. Phys. Chem. Solids 29, 677 (1968).

[4] M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. 153, 1009 (1967).

[5] F. C. Baumann, J. P. Harrison, R. O. Pohl, and W. D. Seward, Phys. Rev. 159, 691 (1967).

[6] J. P. Harrison, P. P. Peressini, and R. O. Pohl, Phys. Rev. 171, 1037 (1968).

[7] See, for instance, C. G. B. Garrett, *Magnetic Cooling* (Harvard University Press, Cambridge, Mass., 1954); F. E. Hoare, L. C. Jackson, and N. Kurti, *Experimental Cryophysics* (Butterworths Scientific Publications Ltd., London, 1961), pp. 165–210; F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill Book Co., New York, 1965), Chaps. 6 and 11.

[8] J. P. Harrison, Rev. Sci. Instr. 39, 145 (1968).

[9] W. D. Seward and V. Narayanamurti, Phys. Rev. 148, 463 (1966).

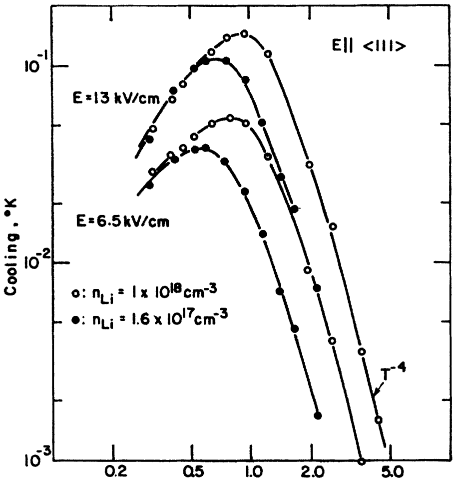

FIG. 1. Experiment. KCl:Li, $E\|\langle 111\rangle$. $\Delta T(T)$ for 13 and 6.5 kV/cm applied field. Open circles: n_{Li} (from cooling) $=1\times10^{18}$ cm^{-3}, same sample as in Figs. 2 and 4. n_{Li} from chemical analysis: 1.2×10^{18} cm^{-3}. Geometry factor $g=$ area of crystal face/area of electrodes $=1.48$. Closed circles: n_{Li} (from cooling) $=1.63\times10^{17}$ cm^{-3}, boule #70425Q, 0.02 mole% LiCl in melt, same boule as sample labelled C in Ref. 6 which had $n_{\mathrm{Li}}=1.62\times10^{17}$ cm^{-3} from chemical analysis, $g=1.13$.

first found by Kuhn and Lüty[10] in KCl:OH. As the initial temperature is lowered, $\Delta T(T)$ (Fig. 1) goes through a maximum and then decreases. The cooling, which is proportional to the lithium concentration in the high-temperature region,[1] becomes independent of concentration at low temperatures, see Fig. 1. Above 1°K, the cooling is isotropic, Fig. 3, i.e., independent of the crystallographic orientation parallel to which **E** is applied. At low temperatures, the cooling is largest for $\mathbf{E}\|\langle 111\rangle$, less for $\mathbf{E}\|\langle 110\rangle$, and least for $\mathbf{E}\|\langle 100\rangle$. Note, however, that the anisotropy becomes quite small for small initial fields.

At high fields ($E>10$ kV/cm) and below 0.5°K the cooling, upon removal of the field, becomes smaller than the heating when the field is applied. At 0.3°K and above 20 kV/cm the crystal actually heats when the field is removed, and the same behavior is found for all concentrations studied. Data taken in this region depend on the previous electrical and thermal history of the sample and have been omitted in Figs. 1–5. The origin of this irreversibility which may be a dipole-dipole interaction, is not understood and is the subject of further study.[11] It shall not concern us in the following.

The high-temperature behavior of the cooling, $\Delta T\propto E^2T^{-4}$, can be explained assuming classical electric dipoles obeying a Langevin-Debye polarizability.[10,1] The decrease in the cooling for lower initial temperatures results from the gradual thermal depopulation of the higher tunneling states. A system whose population is not changed by an applied electric field clearly ceases to cool. In this temperature region, the contribution of the lattice to the total specific heat is negligible.[6] This means that the lithium ions merely cool themselves and hence the cooling of the sample becomes concentration-independent. The anisotropy of the cooling results from

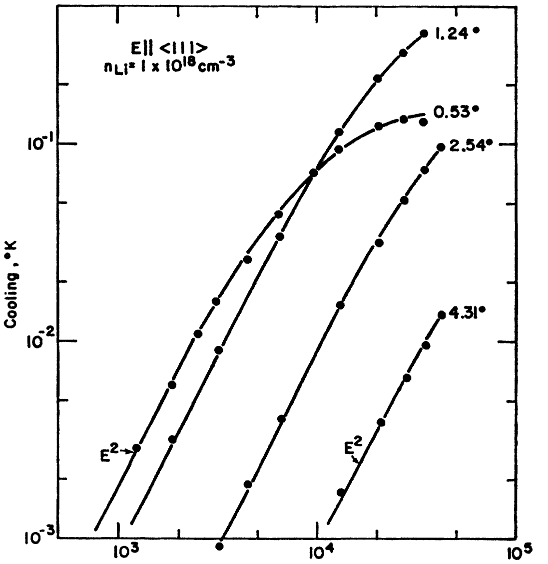

FIG. 2. Experiment. KCl:Li, $E\|\langle 111\rangle$. $\Delta T(E)$ at four temperatures. $n_{\mathrm{Li}}=1\times10^{18}$ cm^{-3}, same piece as in Figs. 1 and 4. Note that $\Delta T(E)\propto E^2$ for small fields, at all temperatures. The apparent dropoff at the highest field at 0.53°K shows the beginning of irreversibility. See text.

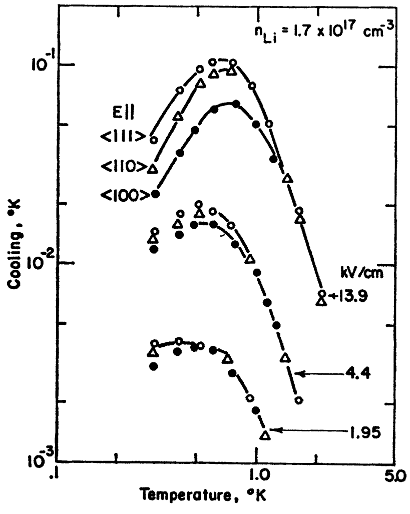

FIG. 3. Experiment. KCl:Li. Anisotropy of the cooling. Average concentration 1.7×10^{17} cm^{-3}. The cooling is largest for $E\|\langle 111\rangle$ and smallest for $E\|\langle 100\rangle$, which is consistent with the assumption that the potential minima point in the [111] directions. Note that the cooling is anisotropic at high field and low temperature only. Open circles: $E\|\langle 111\rangle$, boule #70425Q, see caption Fig. 1. Open triangles: $E\|\langle 110\rangle$, boule #70214Q, 0.02 mole% in melt. $n_{\mathrm{Li}}=1.7\times10^{17}$ cm^{-3}, $g=1.27$. Closed circles $E\|\langle 100\rangle$, boule #70316Q, 0.02 mole% in melt. $n_{\mathrm{Li}}=1.71\times10^{17}$ cm^{-3}, $g=1.18$.

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[10] U. Kuhn and F. Lüty, Solid State Commun. **3**, 31 (1965).

[11] A. T. Fiory (private communication).

the fact that the dipoles point only along certain crystallographic directions. From ultrasonic work,[3] these are known to be the [111] directions. Note, however, that this anisotropy is not observed except at high fields and at low temperatures where the quantum-mechanical nature of the defects is important.

The above discussion shows that the qualitative features of the experimental findings can be understood quite easily. Next, we wish to explore whether our present picture of the tunneling states and their polarization in an electric field will allow a quantitative description of the electrocaloric effect.

The potential to which the lithium ion is subjected in the potassium vacancy has 8 minima along the [111] directions. Because of the overlap of the wave functions describing the particle localized in these wells, the oscillatory states of the ion are split into 4 states of degeneracy 1, 3, 3, and 1. Their splittings are probably equal.[6] If an electric field is applied to the crystal, these energies will change, and the degeneracies will be partially lifted, as has been discussed by Gomez *et al.*[4] (See in particular their Fig. 3.) Analytic expressions for the energies of the tunneling states in an electric field applied along ⟨100⟩ and ⟨111⟩ crystallographic directions have been given by Harrison *et al.*[6] [See their Eqs. (4)–(8) and Fig. 4.] In order to compute the cooling, we must know the entropy $S(E,T)$ of the entire crystal as a function of E and T. From this, the cooling during isentropic depolarization can then be computed with the help of an electronic computer by solving the equation

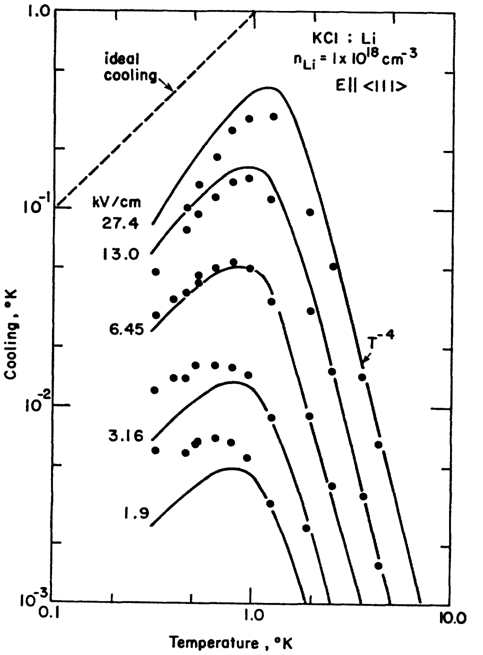

FIG. 4. Comparison of experiment with theory. $E\|\langle 111\rangle$. Closed circles: $n_{\mathrm{Li}}=1\times10^{18}$ cm^{-3} (same sample as in Figs. 1 and 2). Curves: Computed, see text. The dashed line, called ideal cooling, indicates $\Delta T=-T_i$.

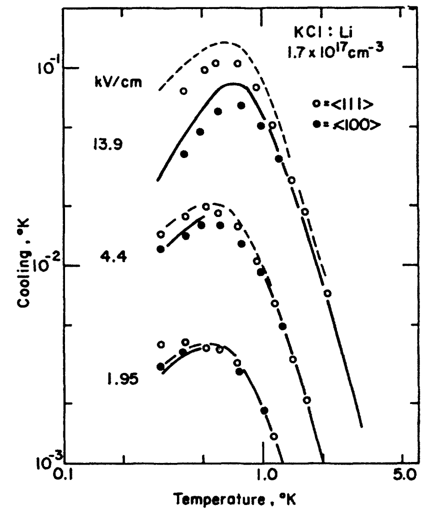

FIG. 5. Comparison of experiment with theory. $n_{\mathrm{Li}}=1.7\times10^{17}$ cm^{-3}. Open circles: $E\|\langle111\rangle$, boule #70425Q, see Fig. 1. Closed circles: $E\|\langle100\rangle$, boule #70316Q, see Fig. 3. Curves computed: dashed for $E\|\langle111\rangle$, solid for $E\|\langle100\rangle$.

$$S(0,T_f)=S(E,T_i)\,, \qquad (1)$$

where T_i and T_f are the initial and final temperatures, respectively. Here, we only give the total entropy $S(E,T)$ for E applied $\|\langle111\rangle$ and $\|\langle100\rangle$.

(i) $E\|\langle111\rangle$:

We call W the energy of the three states next to the highest tunneling state (labelled 5, 6, 7 in Fig. 4 of Ref. 6),

$$W(E)=[(\tfrac{1}{2}\Delta_0)^2+\tfrac{1}{9}p_0{}^2E^2]^{1/2}\,, \qquad (2)$$

where Δ_0 is the zero-field splitting and p_0 is the dipole moment obtained in the high-temperature (classical) limit. The geometry factor g is defined as

$$g=\frac{\text{area of crystal face}}{\text{area of electrode}}\,, \qquad (3)$$

and n_{Li} is the lithium concentration. The entropy of the host is

$$S_{\mathrm{host}}=AT^3/3\,. \qquad (4)$$

The total entropy of the sample can be shown to be[12]

$$S(E,T)=\frac{3n_{\mathrm{Li}}k}{g}\sigma\!\left(\frac{W(E)}{kT}\right)+3\left(1-\frac{1}{g}\right)n_{\mathrm{Li}}k\sigma\!\left(\frac{\Delta_0}{2kT}\right)+AT^3/3\,, \qquad (5)$$

with the abbreviation

$$\sigma(x)=\ln[2\cosh(x)]-x\tanh(x)\,. \qquad (6)$$

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[12] V. L. Taylor, M.S. thesis, Cornell University, Cornell Materials Science Center Report No. 1005, 1968 (unpublished).

(ii) $E\|\langle 100\rangle$:
Here, we call

$$W(E)=[(\tfrac{1}{2}\Delta_0)^2+\tfrac{1}{3}p_0{}^2E^2]^{1/2}, \tag{7}$$

which describes the energy of the two states next to the upper most tunneling state, which move up as E increases (labelled 6 and 7 in Fig. 4 of Ref. 6). Using the same abbreviation as given in Eq. (6), one finds[12] that

$$S(E,T)=\frac{n_{\mathrm{Li}}k}{g}\sigma\left(\frac{W(E)}{kT}\right)+\left(3-\frac{1}{g}\right)n_{\mathrm{Li}}k\sigma\left(\frac{\Delta_0}{2kT}\right)+AT^3/3. \tag{8}$$

(iii) In the limit of $E=0$, Eqs. (5) and (8) simplify to

$$S(E=0,\ T)=3n_{\mathrm{Li}}k\sigma(\Delta_0/2kT)+AT^3/3. \tag{9}$$

The smaller the zero-field splitting Δ_0, the lower the temperature at which $\sigma(\Delta_0/2kT)$ rises steeply, i.e., the lower the temperature reached during adiabatic depolarization. For KCl:Li, the parameters in Eqs. (5)–(9) are all known:

$$\Delta_0=1\times10^{-4}\text{ eV }(0.82\text{ cm}^{-1}),\quad(\text{Refs. 2, 6}), \tag{10}$$

$$p_0=2.75\text{ D}\pm5\%.\quad(\text{Refs. 6, 13, 14})\quad(\text{Lorentz local field corrected}). \tag{11}$$

The uncorrected dipole moment

$$p_{0,\mathrm{uncorr.}}=p_{0,\mathrm{corr.}}(\epsilon+2)/3=6.0\text{ D }(\epsilon_{\mathrm{KCl}}=4.5).$$

$$A=86\text{ erg/cm}^3(°\text{K})^4(\Theta_{\mathrm{D}}=230°\text{K},\quad(\text{Ref. 15})\qquad n_{\mathrm{KCl}}=1.6\times10^{22}\text{ cm}^{-3}. \tag{12}$$

n_{Li}, the concentration of Li^+ ions, can be determined spectrochemically, the error, however, is believed to be approximately 20%.[6] Furthermore, we found that aging at room temperature over periods of about 1 yr reduced the apparent concentration of Li^+ ions noticed in electric cooling by as much as 30%, similar to the aging effect noticed in thermal conductivity.[5] Therefore, we have treated n_{Li} as an adjustable parameter. Where we compared this concentration with the concentration determined spectrochemically, agreement to better than 20% was found. See the figure captions.

With $S(E,T)$ and $S(0,T)$ known, Eq. (1) can be solved for $T_f(E,T_i)$. Figures 4 and 5 show the close agreement between theory and experiment. All other experimental observations previously noted in Figs. 1–3 are also reproduced by the simple model of the tunneling states. This lends further confidence in its usefulness. Furthermore, it follows that in the temperature range studied the cooling is indeed limited primarily by the zero-field splitting and not by some other process, for instance, by a dipole-dipole interaction. This conclusion is supported by measurements of the specific heat in an electric field as reported by Harrison *et al.*[6]

Let us briefly compare theory and experiment somewhat more closely: Above $E=15$ kV/cm and below 2°K, the cooling falls somewhat below that predicted as shown in Figs. 4 and 5. Above 0.5°K, this disagreement is larger than can be explained as experimental error or lack of reversibility (10%). We suggest that this represents an indication of a shortcoming of the model, which does not include a relaxation of the ions surrounding the Li^+ ion. Such an effect can conceivably become more pronounced as the lithium gets more highly localized in one well. Below 0.5°K (and above 15 kV/cm), the increasing irreversibility of the electrocaloric effect, referred to earlier, causes an additional discrepancy. The origin of this phenomenon is the topic of another study.[11]

Finally, we note that in samples containing about 1×10^{18} cm^{-3} or more lithium ions, the low-temperature–low-field cooling exceeds the predicted cooling, see Fig. 4. We believe that this results from the broadening of the tunneling levels observed in measurements of the specific heat[6] at these concentrations. This means that some of the ions have smaller splittings, and hence, that they will cool more at lower temperatures.[12] In this concentration range, where the level broadening becomes important, the cooling can be derived from measurements of the field and the temperature dependence of the specific heat, as first measured in Ref. 6. This comparison has been made in Ref. 15, and the electric cooling found in samples with up to about 1×10^{19} Li^+ cm^{-3} has been found to agree with the cooling predicted from $C_v(E,T)$.

B. Influence of Zero-Field Splitting on Cooling

In Sec. IIIA, we have seen that the agreement between experiment and theory is good. It provides strong evidence for the correctness of the tunneling model used and also supports the claim that the cooling is limited essentially by the zero-field splitting predicted by this model.

In order to further prove the latter contention, we studied the electric cooling in KCl containing Li^6 instead of the naturally abundant Li^7, since Li^6 has a tunnel splitting larger by 40% than Li^7, see Ref. 6. The cooling at low temperatures, where there is no concentration dependence, was found to be about 30% less than in a crystal containing ($E\|\langle100\rangle$). The magnitude of this change agrees with the prediction, assuming that p_0 remains unchanged.

In the following, we shall study two defect systems with tunnel splittings considerably smaller than in

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[13] R. A. Herendeen and R. H. Silsbee obtained this value from measurements of paraelectric resonance (private communication).

[14] In continuing the study of the influence of static electric fields on the thermal conductivity as reported in Ref. 5, P. P. Peressini found $p_0=2.75$ D to give the best agreement with the experiment (private communication). See, also, Ref. 15.

[15] P. P. Peressini, Ph.D. thesis, Cornell University, 1969 (to be published). This thesis also gives a critical comparison of the specific-heat measurements in pure KCl to date.

KCl:Li. The first system in which electric cooling was studied using polarizable defects was KCl:OH.[10,16] The dipole moment ascribed to the OH^- ion is similar to that found in KCl:Li, namely, $p_0 = 4.0$ D $\pm 10\%$ (uncorrected), at least at low concentrations.[17] The potential to which the molecule is subjected in the Cl^- cavity has minima in the six [100] directions.[18] From measurements of paraelectric resonance, the splitting Δ_0 between the lowest and the first excited state has been determined to be $\Delta_0 = 0.5 \times 10^{-4}$ eV,[19] and from specific-heat measurements $\Delta_0 = 0.6° \times 10^{-4}$ eV (0.5 cm^{-1}) has been found.[8,20] The electric cooling observed on KCl:OH for $T_i > 0.3$°K is shown in Fig. 6. The reversibility of the cooling and the beginning of irreversibility at low temperatures and high fields were similar to the findings for KCl:Li. We have not attempted to compute the cooling for this [100] defect (the expressions for the entropy can be found in Ref. 17), but a comparison of the data in Fig. 6 with the data obtained on KCl:Li, e.g., Fig. 1, shows that OH^- cools about twice as much as Li^+ at low temperatures, as is to be expected from the smaller tunnel splitting.

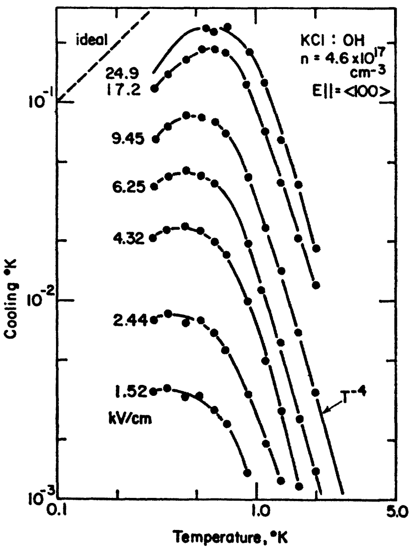

FIG. 6. Experiment. Cooling of KCl:OH, $E \| \langle 100 \rangle$, $g = 1.25$, boule #612141, cleaved from boule on which Peressini measured the specific heat, see Ref. 15, his run #*PP*12*B*. Optical absorption constant at 205 mμ, averaged over the face of the sample: 7.3 cm^{-1}. Using the scaling factor determined by Klein *et al.* [M. V. Klein, S. O. Kennedy, Tan Tk Gie, and Brent Wedding, Mat. Res. Bull. 3, 677 (1968)], namely, 2.4 ppm/cm^{-1}, we obtain $n_{OH} = 2.8 \times 10^{17}$ cm^{-3}. Using this concentration, we obtain $p_0 = 3.8$ D$\pm 5\%$ (uncorrected) from the high-temperature cooling which is very close to the value $p_0 = 4.0$ D accepted so far.

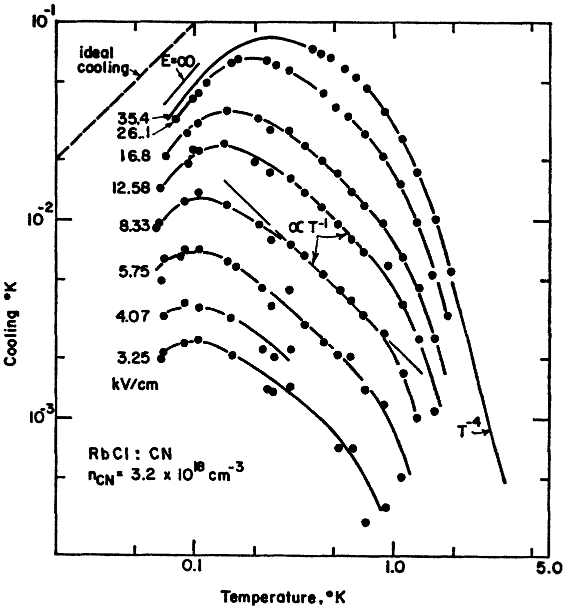

FIG. 7. Experiment. RbCl:CN, boule #475, $g = 1.2$, $\mathbf{E} \| \langle 100 \rangle$, 0.07 mole% RbCN in melt. n_{CN} from infrared absorption (Refs. 9 and 21) $= 3.2 \times 10^{18}$ cm^{-3}, from the entropy $= 4.4 \times 10^{18}$ cm^{-3} (see Ref. 21). With the latter concentration, one determined $p_0 = 0.3$ D (uncorrected) from the high-temperature cooling. Same pieces as sample A in Fig. 5 of Ref. 21. Curve drawn for 35.5 kV/cm below 0.4°K obtained by extrapolating $\Delta T(E)$ to that field. The line labelled $E = \infty$ is an estimated cooling at saturation fields. The dashed line is $\Delta T = -T_i$.

In the upper left-hand corner of Fig. 6, we show a dashed line, called "ideal." It represents the maximum cooling possible, i.e., $\Delta T = -T_i$. By plotting $\Delta T(E)$ at constant T_i, as done for KCl:Li in Fig. 2, and by extrapolating $\Delta T(E)$ toward saturation fields, we find that the lowest temperature that can be reached with KCl:OH will be between 0.1 and 0.2°K.

A specific-heat anomaly caused by a considerably smaller tunnel splitting of a rotational ground state of CN^- ions dissolved in RbCl has recently been observed.[21] The origin of this small splitting, $\Delta_0 = 0.15 \times 10^{-4}$ eV (0.125 cm^{-1}) has been explained by Pompi and Narayanamurti,[22] who also predicted that both the ground and the first excited tunneling state are more polarizable than the higher tunneling states. The electric cooling of this system is shown in Fig. 7, for $T_i > 0.07$°K. It is reversible within the experimental accuracy (10% for $T > 0.1$°K, 20% for $T < 0.1$°K). Considerable cooling is observed at far smaller T_i than in the cases discussed above. At $T_i = 0.08$°K cooling to about 0.5 T_i can be achieved. It appears that the electrocaloric effect is close to becoming a candidate for practical low-temperature cooling. We shall return to this point in Sec. IV.

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[16] I. Shepherd and G. Feher, Phys. Rev. Letters 15, 194 (1965).

[17] I. W. Shepherd, J. Phys. Chem. Solids 28, 2027 (1967).

[18] U. Kuhn and F. Lüty, Solid State Commun. 2, 281 (1964).

[19] W. E. Bron and R. W. Dreyfus, Phys. Rev. 163, 304 (1967); G. Feher, I. Shepherd, and H. B. Shore, Phys. Rev. Letters 16, 500 (1966). There has recently been some discussion as to the validity of the assignments of the transitions observed, see G. Höcherl, D. Blumenstock, and H. C. Wolff, Phys. Letters 24A, 511 (1967); G. Höcherl and H. C. Wolff, *ibid.* 27A, 133 (1968).

[20] The tentative assignment made in Ref. 8 has since been verified by P. P. Peressini, Ref. 15.

[21] J. P. Harrison, P. P. Peressini, and R. O. Pohl, Phys. Rev. 167, 856 (1968).

[22] R. L. Pompi and V. Narayanamurti, Solid State Commun. 6, 645 (1968); see, also, R. L. Pompi, Ph.D. thesis, Cornell University, Cornell Materials Science Center Report No. 942, 1968 (unpublished).

Let us briefly inspect the cooling in RbCl:CN in a semiquantitative manner. At high temperatures ($T > 2°\text{K}$), where the cooling goes to T^{-4}, we can neglect the specific heat of the tunneling states, see Fig. 5 of Ref. 21, and we can analyze the cooling classically as proposed by Kuhn and Lüty.[10] Using $C_{v,\text{RbCl}} = 70.8 \times T^3$ erg (g deg^4)$^{-1}$ from Ref. 21, we determine from the cooling a dipole moment p_0 between 0.3 and 0.35 D (uncorrected). The error in p_0 is determined by the error in n_{CN^-} (Ref. 21 and caption of Fig. 7). At the lowest temperatures studied, we may ignore the higher tunneling states as well as the host specific heat. If we also ignore the partial coverage of the crystal faces by the electrodes, i.e., set $g = 1$, we can derive the dipole moment with the following simple argument.[23] The total entropy of the two-level system is

$$S = \int_0^T n_{\text{CN}} k \left(\frac{\Delta}{kT}\right)^2 e^{-\Delta kT} \frac{dT}{T} \tag{13}$$

$$= n_{\text{CN}} k e^{-\Delta kT} \left(\frac{\Delta}{kT} + 1\right) = S\left(\frac{\Delta}{kT}\right). \tag{14}$$

Isoentropic depolarization means that

$$\frac{\Delta_E}{T_i} = \frac{\Delta_{E=0}}{T_f} \equiv \frac{\Delta_0}{T_i - \Delta T}; \tag{15}$$

hence, Δ_E can be determined from the experiment. Equation (15) also shows on a simple example how Δ_0 influences the cooling.

In first approximation, let us assume that both levels are polarized equally:

$$\Delta_E = 2[(\tfrac{1}{2}\Delta_0)^2 + p_0^2 E^2]^{1/2}. \tag{16}$$

From this we determine $p_0 = 0.29$ D (uncorrected). This is close to the value determined at high temperatures, indicating the consistency of our model.

We note in passing that the dipole moment of CN$^-$ in the potassium hosts had previously been determined from dielectric measurements to be 0.5 D (uncorrected).[24] Conceivably, the discrepancy between these two values of the dipole moment may be caused by the host lattice.

One pecularity of RbCl:CN is the existence of an extended temperature region in which the cooling goes as T^{-1}, see Fig. 7. Qualitatively, this is easy to understand: In this temperature range, C_v is almost constant,[21] and in the classical picture the polarization goes as T^{-1}. Hence, the cooling also goes as T^{-1}.

IV. SUMMARY AND OUTLOOK

For three different substitutional impurities in alkali halides the cooling has been found to be limited by the zero-field splitting predicted by our tunneling model. In RbCl:CN, with a tunnel splitting of 0.125 cm^{-1}, considerable cooling well below 0.1°K can be achieved.

In order for a substance to be a useful cooler, it must have a substantial specific heat. For this reason, dilute systems are restricted to cooling at very low temperatures where the specific heat of the other components of the cryostat becomes sufficiently small. The specific heat of RbCl:CN is approximately 100 erg (g deg)$^{-1}$ between 0.07 and 1°K, for $n_{\text{CN}^-} = 3 \times 10^{18}$ cm^{-3}. This concentration cannot be considerably increased without causing severe internal stresses and coagulation which tend to immobilize the dipoles. The specific heat of copper is of the same order of magnitude at 1°K and decreases as T below 1°K. Thus, if a host could be found in which the CN$^-$ had a tunnel splitting 10 times smaller than in RbCl, then electric cooling would indeed become a useful technique for cooling from 0.1 or 0.05°K on down, i.e., electric cooling could be used in an additional cooling stage below either a standard paramagnetic refrigeration stage or a small dilution refrigerator. The strong coupling of the tunneling states to the lattice, evidenced in thermal conductivity experiments,[5,21,25] may contribute to the usefulness of such a cooling stage. All presently known tunnel splittings for polarizable defects lie in the range from 1.4 cm^{-1}, for KCl:CN,[9] to 0.125 cm^{-1}, for RbCl:CN.[21] The search for smaller tunnel splittings is continuing.

As one of the possible complications of low-temperature electric cooling we have mentioned an electric dipole-dipole correlation. Our experiments allow us to estimate an upper limit for the temperature at which this phenomenon sets in for CN$^-$. We have seen that the reversibility of the cooling is good in KCl containing Li$^+$ ions in concentrations of order 10^{18} cm^{-3} at temperatures as low as 0.5°K. The Li$^+$ dipole moment p_0 is 6.0 D (uncorrected). Any dipole-dipole interaction is expected to go as p_0^2. The dipole moment of CN$^-$ varies between 0.3 and 0.5 D (uncorrected) in all hosts studied to date, and therefore dipole-dipole interaction is not expected to occur above temperatures of the order of millidegrees. Thus, a small dipole moment may be very important for low-temperature cooling.

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[23] See, for instance, C. Kittel, in *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1962), 2nd ed., Chap. 9.

[24] H. S. Sack and M. C. Moriarty, Solid State Commun. **3**, 93 (1965). The value quoted here is based on the one given in Ref. 16 of Ref. 1, which was Lorentz-local-field corrected ($p_{\text{corr}} = 0.23$ D).

[25] R. O. Pohl, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 434.