COOLING BY ADIABATIC DEPOLARIZATION OF OH⁻ MOLECULES IN KCl†

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The method universally employed for obtaining temperatures below a few tenths of a degree K makes use of the magnetocaloric effect first demonstrated in 1933.[1,2] This method is based on the change in entropy of an assembly of magnetic dipoles during the adiabatic removal of an externally applied magnetic field. In principle, any system which exhibits an increase in entropy by varying an external parameter may be used for cooling purposes. In this communication we wish to report on the cooling observed from a system of electrical dipoles (OH⁻) embedded in KCl crystals. The entropy change was brought about in two different ways: (1) by removing an external electric field (this we will refer to as the electrocaloric effect); and (2) by removing an external uniaxial stress (henceforth called the piezocaloric effect).

The electrocaloric effect has been recently demonstrated independently by several groups,[3-5] although no coolings below 1°K were reported. In the present experiments the electrocaloric effect was used to reduce the temperature of the KCl crystal from 1.3 to 0.36°K. The piezocaloric effect was first suggested by Känzig,[6] but until now its observation has not been reported.

The OH⁻ centers in[7] KCl were produced by adding KOH to the melt from which the crystals were grown.[8] The OH⁻ concentration was determined from specific-heat measurements discussed in a later section of the paper and from the optical absorption at 204 mμ.[9] For the electrocaloric effect gold electrodes were evaporated on the samples leaving a margin of ~3 mm all around to prevent breakdown. In the piezocaloric effect, weights were applied to the crystal via thin polished-quartz plungers. The temperature was measured with a calibrated $\frac{1}{10}$-W carbon resistor.[10] The same resistor was used to introduce known heat pulses for the specific-heat measurements.

The OH⁻ ions substitute for the Cl⁻ in the KCl lattice. Kuhn and Lüty[11] have shown by optical methods that the OH⁻ dipoles are oriented along the [100] crystalline axes. In the absence of a field the ground state possesses

therefore a sixfold orientational degeneracy. The application of an electric field or uniaxial stress lifts this degeneracy and causes an alignment of the dipoles at low temperatures with a corresponding decrease in entropy. The splitting of the degeneracy for different field directions and its effects on the dipolar specific heat c_D and the entropy S_D are of prime importance in the cooling experiments described here. Fig. 1 shows the splitting of the degeneracy by the applied field and Table I summarizes the pertinent thermodynamic quantities. Another important requirement of these cooling methods is that the reorientation time of the dipoles should be short in comparison to the time it takes to decrease the field. This requirement is easily satisfied for the OH⁻ dipoles in KCl.[12]

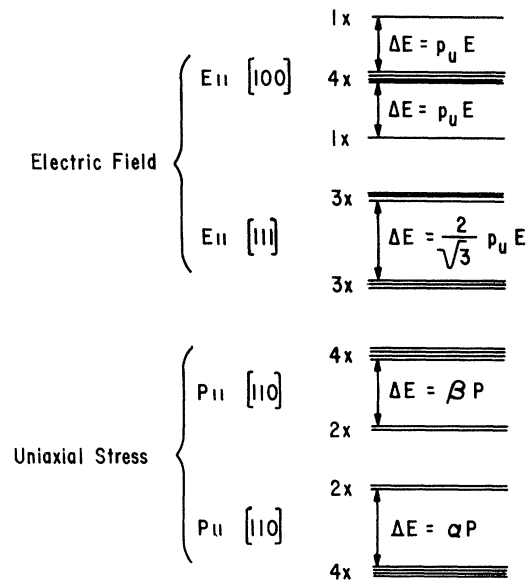In order to determine some of the relevant

FIG. 1. Energy-level diagram for dipoles in a cubic crystal under the application of an electric field E and uniaxial stress P. The equilibrium orientations of the dipoles are in the [100] directions. Here p_u = dipole moment uncorrected for local fields and α and β are the stress coefficients which were determined experimentally (for our case $\alpha = \sqrt{2}\beta$). The thermodynamic quantities determined from this level diagram summarized in Table I.
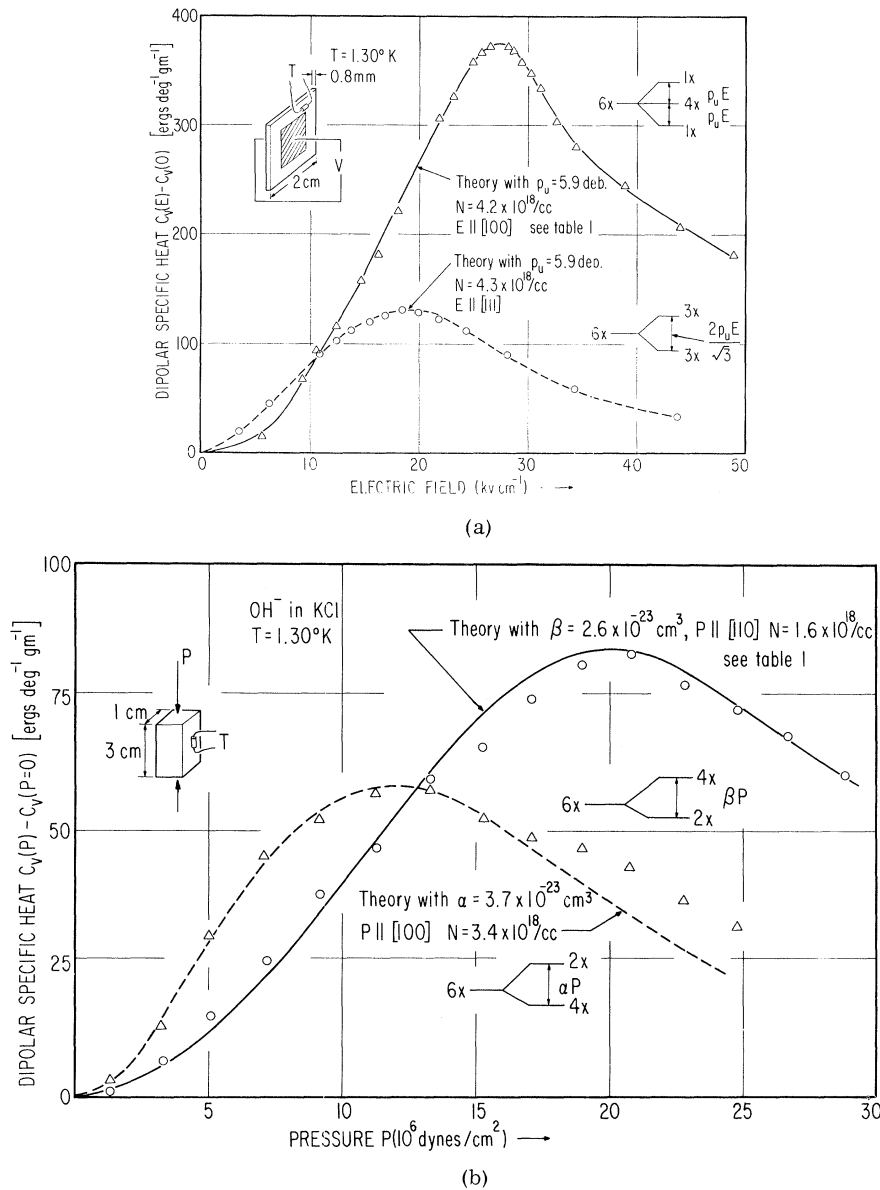
(a)

(b)

FIG. 2. Specific heats of OH^- dipoles in KCl versus applied electric field (a) and uniaxial stress (b). The theoretical fit was obtained with the aid of the relations from Table I. From these data the number of dipoles which are free to reorient themselves, the orientation and magnitude of the dipoles (uncorrected for local fields), as well as the stress coefficients α and β were obtained. The specific heat of these crystals at 1.3°K and zero applied field is approximately 200 erg deg^{-1} g^{-1}. (See Fig. 4 for exact values.)

parameters of the OH^--KCl system we first measured the specific heat versus electric field E and uniaxial stress P applied along different directions. The experimental results together with the theoretical curves obtained from the relations in Table I are shown in Fig. 2. The good theoretical fit confirms that the dipoles are oriented along the [100] axes. The fit was obtained by adjusting the concentration of the dipoles (N) and the value of the

dipole moment P_u ($p_u = 5.9$ Debye units) uncorrected for the local field.[13] The value of N obtained in this way was always found to be lower (10-50%) then the value obtained from optical-absorption measurements. This is consistent with the assumption that some of the dipoles are "locked" to imperfections,[14] as was also found by Känzig, Hart, and Roberts[3] in their dielectric measurements. From the results shown in Fig. 2(b) one obtains the values

Table I. Summary of relations for noninteracting dipoles with equilibrium orientations in the [100] directions in a cubic crystal. Here $x = \Delta E/kT$; N = number of dipoles/cc; k = Boltzman constant; T = temperature; E = applied electrical field; P = applied unaxial stress; and ΔE is the energy splitting produced by the applied field as defined in Fig. 1.

Field	Field direction	Dipole specific heat c_D/Nk	Maximum value of c_D/Nk erg deg^{-1} cc^{-1}	Value of $\Delta E/kT$ for max c_D x	Dipole entropy S_D/Nk
E	[100]	$x^2(2\cosh x + 1)/(\cosh x + 2)^2$	1.31	2.90	$\ln(1 + 4e^{-x} + e^{-2x}) + 2x(1+2e^{-x})/(1 + 4e^x + e^{2x})$
E	[111]	$x^2 e^x/(1+e^x)^2$	0.44	2.40	$\ln(3 + 3e^{-x}) + x/(1+e^x)$
P	[110]	$2x^2 e^x/(e^x + 2)^2$	0.76	2.65	$\ln(2 + 4e^{-x}) + 4x/(2e^x + 4)$
P	[100]	$2x^2 e^x/(2e^x + 1)^2$	0.24	2.23	$\ln(4 + 2e^{-x}) + 2x/(4e^x + 2)$

for the stress coefficients α and β as defined in Fig. 1 ($\alpha = 3.7 \times 10^{-23}$ cm^3, $\beta = 2.6 \times 10^{-23}$ cm^3).

The results of the cooling experiments are shown in Fig. 3. In the electrocaloric effect [Fig. 3(a)] the electric field was applied in the [100] direction and adiabatically reduced to zero from different initial values. In the piezocaloric experiment [Fig. 3(b)] heating
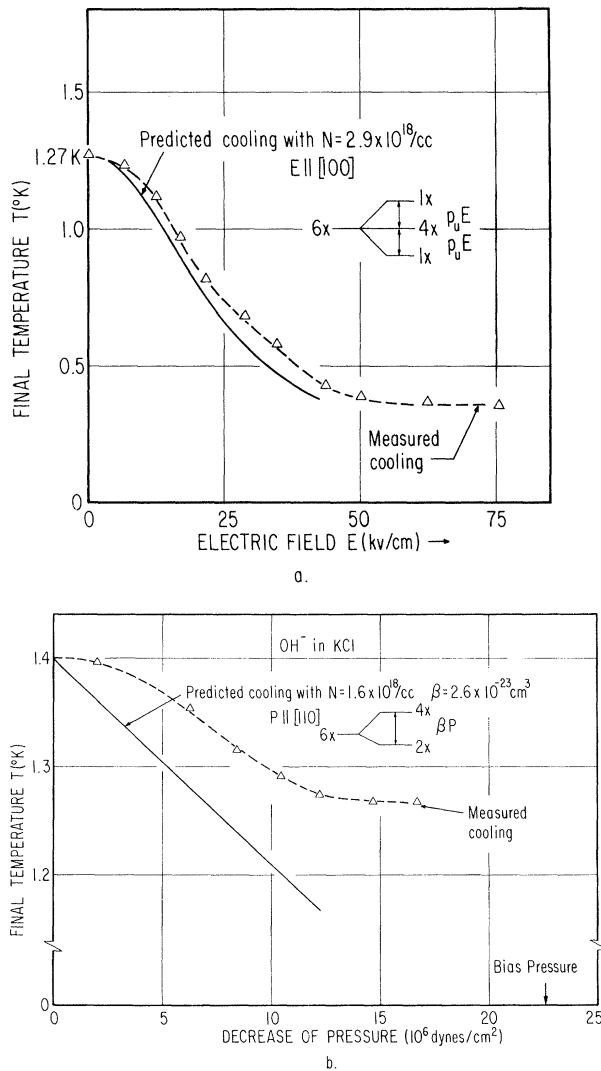

FIG. 3. Cooling by adiabatic depolarization of OH$^-$ dipoles in KCl. In (a) the electric field is reduced from an initial value E to zero. In (b) there is a bias pressure of 23×10^6 dyne/cm^2. The pressure is reduced from this bias by the amount indicated on the abscissa. The OH$^-$ concentrations were obtained from dipolar specific-heat measurements (similar to the ones shown in Fig. 2). The discrepancy between predicted and observed cooling in the piezocaloric effect (b) is due to frictional heating effects.

due to frictional effects prevented a complete removal of the pressure. Instead, a biasing pressure of 23×10^6 dyne/cm^2 was applied along the $[100]$ direction and the pressure was adiabatically reduced by different amounts. Even with this precaution substantial heating effects were present. They manifested themselves by an irreversible entropy change when the pressure was alternately increased and decreased.

In order to predict the final temperature for a given change in applied field one needs to know the relation between entropy and temperature of the system. To determine this relationship we have measured the specific heat at zero field by making use of the electrocaloric effect to cool the crystal to 0.45°K. The experimental results for different OH$^-$ concentrations are shown in Fig. 4. The specific heat of the purest sample ($N < 10^{17}$ OH$^-$/cc) exhibits the expected T^3 behavior. In the high-
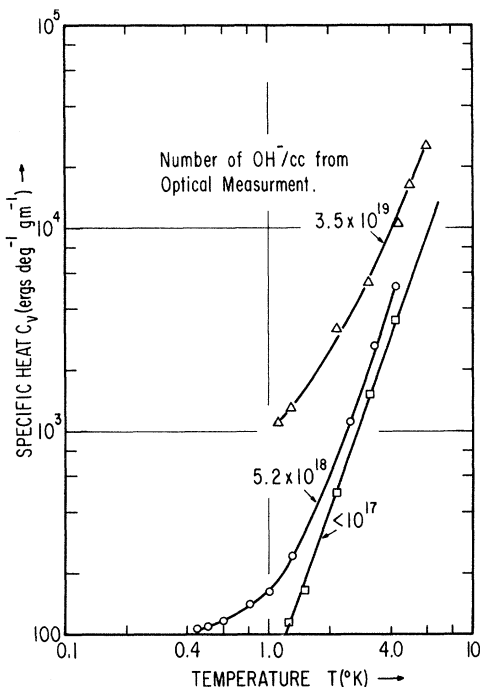

FIG. 4. Specific heat versus temperature of the OH$^-$-KCl system for different OH$^-$ concentrations. Use was made of the electrocaloric effect to cool the samples below 1.3°K. The purest sample (10^{17} OH$^-$/cc) follows the expected T^3 law (with a Debye temperature of 220°K). The deviation from the T^3 relaxation for the higher concentration samples is caused by dipolar interactions. These results were used to check the self-consistency of the observed cooling data (see "predicted cooling" in Fig. 3).

er concentration samples the contribution to the specific heat from dipolar interactions[15] is clearly demonstrated by the deviation from the T^3 law. From these experimental c_v data the entropy versus temperature was obtained, and by knowing the entropy of the dipole system at a given field (see Table I) the final temperature was calculated. For the electrocaloric effect the temperatures predicted in this way agree well with the measured temperatures [see Fig. 3(a)]. In the piezocaloric experiment[16] there is a significant discrepancy between predicted and observed final temperatures. We believe that this discrepancy is due to the frictional heating effects discussed earlier.

In conclusion we would like to point out that the temperatures reached in these experiments represent by no means the limit of the method. Molecules with a smaller dipole moment (CN$^-$ is a likely candidate), a lower starting temperature, and a better crystal geometry should make the attainment of millidegree temperatures feasible. One advantage of these cooling methods is that they are independent of an external magnetic field. This may make it advantageous to use them in conjunction with a nuclear demagnetization stage.

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[10]We would like to thank Mr. A. Sweedler for the use of his He^3 cryostat used to calibrate the resistors.

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[12]R. W. Dreyfus, V. Bosshard, and W. Känzig [Bull. Am. Phys. Soc. 10, 76 (1965)] have determined the dipolar relaxation time of OH^- in KCL at 1.6°K to be ~10^{-8} sec. We have performed a microwave experiment at 9 Gc/sec and found the relaxation time at this temperature to be at least two orders of magnitude shorter. The technique which we employed is analogous to a paramagnetic resonance experiment. The crystal is placed in the E field of a microwave cavity and an applied dc electric field is continuously varied while the electrical susceptibility is being monitored. Details of this "paraelectric resonance" technique will be published at a later date.

[13]In order to obtain the value of the OH^- dipole moment one has to make corrections due to the dipolar and ionic contributions to the local fields. We are at present trying to separate out these contributions by measuring the position of the c_v peak and the value of the dielectric constant for different OH^- concentrations.

[14]The imperfection which occurs in high concentrations is the CO_3^{--} ion. Its concentration varied in our crystals between 10^{17}/cc to 10^{18}/cc (determined from infrared-absorption measurements[9]).

[15]For a recent discussion of the nature of these interactions, see R. Brout, Phys. Rev. Letters 14, 175 (1965).

[16]We have also observed the piezocaloric effect in the O_2^--KCl system.[6] Because of the difficulties in obtaining high enough O_2^- concentrations, these coolings were significantly lower than obtained from the OH^--KCl system. A possible advantage of the O_2^- centers is their lack of a dipole moment which reduces their interaction energy.

PREFERENTIAL THERMAL REORIENTATION OF V_K CENTERS IN POTASSIUM IODIDE*

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The V_K center, of self-trapped hole, has been identified in several alkali halides as a halogen diatomic molecular ion, X_2^-, whose axis is oriented along a $\langle 100 \rangle$ direction. By bleaching with linearly polarized light in V_K optical-absorption bands, it is possible to achieve a preferential population of V_K centers in one of the $\langle 110 \rangle$ directions.[1] At sufficiently low temperatures oriented V_K centers are stable against reorientation, but at temperatures of order 100°K a thermally excited reorientation occurs. We have measured the thermal activation energy for reorientation of V_K centers in KI, and find that reorientation occurs almost entirely through steps in which the V_K axis changes by 60°; the probability of reorienting through 90° is negligibly small.

Crystals of KI containing ~0.1 mole % TlI or KNO_3 as an electron-trapping impurity were irradiated at 78°K with either 1.7-MeV electrons or x rays from a 40-keV source. Prominent V_K absorption bands were observed at 404 and 800 mμ following irradiation. The crystal was then bleached at 78°K with linearly polarized light at 404 mμ until the induced optical anisotropy reached a maximum value. Optical anisotropy is here defined as $(OD_\perp - OD_\parallel)$, where $OD_\perp$ and $OD_\parallel$ are the optical densities measured with light polarized perpendicular and parallel to the plane of polarization of the bleaching light. The crystal was then quickly warmed (or cooled) to a fixed, controlled temperature, and the anisotropy was measured as a function of time. In all cases it was found that a plot of anisotropy $A(t)$ versus time was accurately described by a single exponential

$$A(t) = A(0) \exp(-Kt), \quad (1)$$

where K is a rate constant characteristic of the temperature. The decay of anisotropy thus obeys first-order kinetics. Isothermal annealing experiments were performed over the range of temperatures from 76 to 88°K, and a value of K was determined at each temperature. Results obtained with $KI(NO_3)$ and with KI(Tl) crystals were found to be the same. Similarly, results obtained with x-rayed crystals were the same as those obtained with crystals irradiated with 1.7-MeV electrons.

Two series of experiments of the above type were performed. In series I the electric vector of the orienting light was parallel to one of the $\langle 110 \rangle$ directions, say the [011] direction of Fig. 1, where the beam is directed into the paper along the x axis. The optical anisotropy was then measured by rotating the polarizer from [011] to [0$\bar{1}$1]. In series II the electric vector of the orienting light was parallel to