

zene-doped matrices would confirm the conclusions of this work, and experiments on solid benzene would locate the band gap where the optical method fails.

It is important to note that the interpretation of the observations reported here in terms of configuration mixing of impurity states and conduction-band states provides support for a recent extension of Frenkel-Davydov exciton theory to include ion-pair exciton states.^{4,11} It appears that even in cases where the tight-binding approximation is a good first-order approximation, the crystal states are not accurately described in terms of having a one-to-one parentage in only free molecule states, but rather that delocalization of the excitation must always be considered.

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³Note that there is a bump in Fig. 1 at about 9.1 eV which may correspond to the 8.61-eV transition in acetylene shifted by about 0.52 eV. It should also be noted that the line shapes of the absorptions at 8.67 and 8.90 eV are not completely symmetric. The origin of this asymmetry in line shape is at present unknown. There may be some configuration mixing of impurity states and host states. In contrast, the spectrum of benzene in argon and krypton shows pronounced anti-resonances, which unambiguously indicate configuration mixing of host and impurity states. It is possible that the very large and sharp dip in absorption at about 9.9 eV for acetylene in krypton might similarly represent one of the higher series members of acetylene interacting with krypton conduction-band states. The behavior of benzene and acetylene as impurities in these solids is then seen to be logically connected by the magnitude and the differences in excitation energies of the Rydberg states of the two compounds relative to the energy gap between the ground state and the conduction band of the host matrix.

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ELECTROCALORIC EFFECT AND A NEW TYPE OF IMPURITY MODE*

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Measurements of the thermal conductivity of mixed alkali-halide crystals¹ indicated the existence of a large number of resonant scattering mechanisms characterized by angular frequencies between 1.9×10^{11} and 1.9×10^{13} rad sec^{-1} (1 and 100 cm^{-1}). They have been attributed to impurity modes.² Some of these modes with energies over 10 cm^{-1} have since been investigated in the far infrared.³ Very little is known about the modes of lower energy.

We have found an electrocaloric effect in KCl doped with LiCl. This cooling upon adiabatic depolarization at low temperatures was first suggested⁴ for paraelectric crystals and observed in SrTiO_3 .⁵ Recently the electrocalor-

ic effect has also been observed in KCl doped with KOH.⁶ It was explained by an alignment of OH^- dipoles. Our experiments concern an alignment of dipoles due to monatomic impurities and are used to study low-frequency impurity modes.

The crystals were grown under chlorine atmosphere from chlorine-treated starting materials by Mr. D. Bower.⁷ The LiCl concentrations were determined by Dr. R. K. Skogerboe.⁷ The electric fields were applied by means of gold electrodes evaporated onto the large faces of samples cleaved to approximately $2 \times 3 \times 0.2$ cm^3 . The gold-film area was kept smaller than the crystal faces in order to minimize the dan-

ger of electrical breakdown. Temperature measurements were made with an Allen-Bradley resistor glued to the sample. The resistance was monitored with an ac bridge dissipating 10^{-9} W. The crystal-to-bath thermal time constant was about 5 minutes at 4°K.

Figures 1 and 2 show the cooling, ΔT , as a function of initial field and temperature. The effect is reversible and proportional to the Li^+ concentration over the range 0.67 to 2.4×10^{18} cm^{-3} . It is observed that in the limit of low-field and high initial temperature, the cooling is proportional to E^2 and T^{-4} . Saturation occurs at the other limits.

Adiabatic removal of an electric field causes a temperature change dT given by

$$dU = C_v dT = PdE, \tag{1}$$

where U is the internal energy, C_v the specific heat, and P the polarization. If we take the specific heat to be that of pure KCl, $C_v = AT^3$, and a polarizability of the Langevin type—brought about by the alignment of electric dipoles of concentration N and dipole moment μ —we find for high temperature and low fields that

$$\Delta T = \frac{N^2}{6kA} E^2 T^{-4}, \tag{2}$$

which is the observed field and temperature dependence. By comparing the data with Eq. (2)

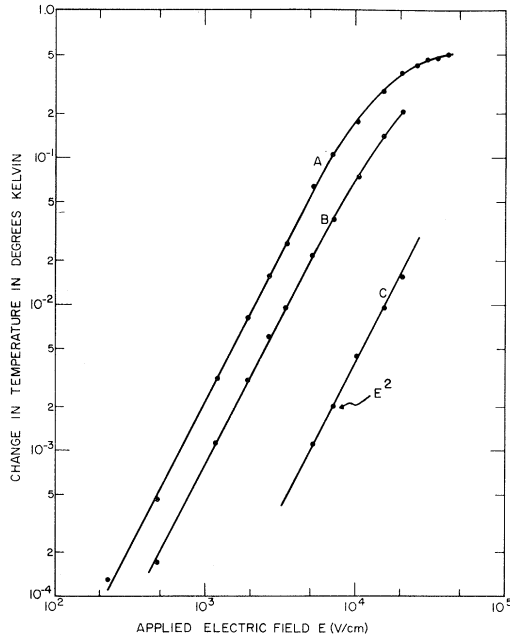


FIG. 1. Electrocaloric effect on KCl:Li. $N_{\text{Li}} = 2.4 \times 10^{18}$ cm^{-3} . Boule Q67, run 19. Field in [100] direction. Curve A: initial temperature 1.37°K; B: 1.95°K; C: 4.26°K.

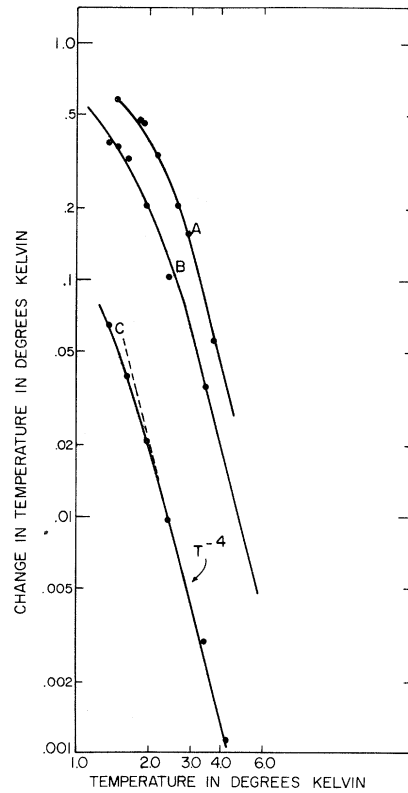


FIG. 2. Electrocaloric effect on KCl:Li, same crystal as in Fig. 1. Curve A: initial field 40.6×10^3 V cm^{-1} ; B: 20.5×10^3 V cm^{-1} ; C: 5.2×10^3 V cm^{-1} .

we determine the constants A and μ , assuming N to be equal to the Li^+ concentration. The value of A agrees with the value for pure KCl within 10%. For μ we find the large value of 2.54 Debye.⁸ For comparison we note that for water $\mu = 1.85$ Debye. The observed saturation is explained by saturation of the dipole polarization and an additional heat capacity due to the defects, $C = C_{\text{KCl}} + C_{\text{Li}}$. This contribution has been determined from our low-temperature low-field data and is in agreement with preliminary specific-heat data.⁹

The ionic conductivity of KCl is unaltered by the addition of LiCl.¹⁰ Thus the Li^+ ion is not mobile or interstitial. From our measurements we conclude that the lithium ion occupies an off-center position ($r_{\text{Li}^+} = 0.68$ Å; $r_{\text{K}^+} = 1.33$ Å).¹¹ The dipolar properties result from the separation of the effective negative charge of the K^+ vacancy and the Li^+ ion. (We recognize that a Langevin polarization is only approximately applicable. But a Brillouin function would serve only to reduce μ by at most a factor of $\sqrt{3}$ to 1.53 D. In preliminary measurements of the dielectric properties of KCl:LiCl, Sack and Moriarty¹² found a dipole moment of about 1

Debye.) Quantum mechanically the off-center position produces a degenerate ground state which is split by the translational tunneling of the ion among its equilibrium positions.¹³ The electric field alters the tunnel splitting, thereby causing a change in level population. These tunneling states are also responsible for the resonant scattering in thermal conductivity at $\omega_0 = 2.3 \times 10^{11}$ rad sec⁻¹ and the specific-heat anomaly discussed earlier.

This model would predict that large ions do not show an electrocaloric effect. We tested this with RbCl ($r_{\text{Rb}^+} = 1.48$ Å) and AgCl ($r_{\text{Ag}^+} = 1.26$ Å) in KCl and found indeed no effect ($|\Delta T| < 10^{-4}$ degree at 1.4°K and $E = 3.5 \times 10^4$ V cm⁻¹) for concentrations of ca. 1%.

Our results imply a strong similarity between the tunneling of the Li⁺ ion and the tunneling motion observed for polyatomic defects. It was therefore interesting to verify the occurrence of an electrocaloric effect for a molecular system of which tunnel splitting and dipole moment are known from different investigations. The best understood system is KCl:CN.¹⁴⁻¹⁶ On such a crystal we indeed found an electrocaloric effect in quantitative agreement with the predictions. We would like to emphasize, however, one important difference: The CN⁻ cools because of orientational alignment, i.e., negligible center-of-mass motion, whereas the Li⁺ cools because of translational alignment, i.e., involving center-of-mass motion. For sufficiently small molecules we expect both a rotational and a translational freedom, and consequently cooling should result from both motions. There is some evidence for both motions in measurements of the dielectric properties of NO₂⁻ in KI.¹² Another example where we expect translational motion to be important is OH⁻ in⁶ KCl ($r_{\text{OH}^-} = 1.33$ Å; $r_{\text{Cl}^-} = 1.85$ Å).

The strong phonon scattering at low frequencies observed in thermal conductivity studies of *F*- and *U*-center-containing crystals is not well understood.¹⁷ In the hopes that this scattering could be explained by a tunneling mode we looked for an electrocaloric effect in such crystals. No cooling was found for *F* centers in KCl ($N = 7 \times 10^{17}$ cm⁻³) and *U* centers in KBr ($N = 2.5 \times 10^{18}$ cm⁻³) indicating the absence of a tunneling splitting.

The electrocaloric effect in KCl:Li has demonstrated the existence of a new impurity mode, one associated with the tunneling of the impurity ion between several equilibrium positions. The relation of these energies to the well-stud-

ied resonant states and localized modes can be thought of in analogy to the rotation-vibration energy-level scheme: a type of fine structure. These translational tunneling modes will exist for ions considerably smaller than the vacancy they fill. Paraelectric cooling—aside from its potential as a refrigerant—is an interesting probe for the quantitative study of these low-energy states.

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