Study of an Impurity Mode Using Specific-Heat Measurements*

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The low-frequency impurity mode in KCl:Li first observed through thermal-conductivity measurements by Baumann has been studied by measuring the specific heat between 0.06 and 2.0°K for lithium concentrations from 2×10^{17} to 8×10^{18}cm^{-3}. The specific-heat anomaly is of the Schottky type. In crystals doped with Li^{6}Cl, the anomaly peaks at a temperature 40% higher than in crystals doped with Li^{7}Cl. This large isotope effect proves the correctness of the model proposed by Lombardo and Pohl according to which this mode is caused by the tunneling of the substitutional Li$^+$ ion between several equivalent off-center equilibrium sites. The influence of a static electric field on the specific-heat anomaly has also been studied. It can be explained through a polarization of the tunneling states. The analysis of our data is based on the calculations by Gomez, Bowen, and Krumhansl, and by Devonshire. We conclude that the zero-field tunnel splitting is 10^{-4} eV (0.82 cm^{-1}), that the potential minima between which the ion can tunnel are displaced by 1.2 Å in the <111> directions from the center of the potassium vacancy, and that the effective positive charge e^* of the lithium ion is 0.5 of the electronic charge, with an error of $\pm10\%$. At high concentrations the anomaly broadens. This is interpreted through a concentration-dependent stress broadening of the tunneling states. The data provide no evidence for a dipole-dipole interaction of a ferroelectric type. Contrary to the prediction by Quigley and Das, no tunneling states have been observed through specific-heat measurements in KBr:Li. Hence, it is concluded that the reason for the occurrence of a central instability of impurity ions is still not fully understood.

I. INTRODUCTION

IT has been shown by Narayanamurti *et al.*[1] that certain molecular defects in alkali halide host lattices can undergo rapid reorientation at temperatures as low as 1°K, and that this motion can be described as a tunneling of the molecule between equivalent equilibrium orientations in the lattice. For CN$^-$ and NO$_2^-$ in the potassium halides, the tunnel splitting Δ is of the order of 10^{-4} eV, i.e., of the order of 1 wave number (cm^{-1}).[2] The tunneling process is the same as the so-called inversion of isolated molecules, which was predicted by Hund[3] and observed by Clayton and Williams[4] in gaseous ammonia (NH$_3$). One important feature of the tunneling states in solids is that they are strongly coupled to the phonons, i.e., they cause strong phonon resonance scattering which can be observed in thermal-conductivity measurements. They are, therefore, useful for the study of phonon-defect interactions.[5]

Furthermore, these tunneling states are highly polarizable, i.e., the molecules which carry a permanent electric dipole can be lined up in an electric field, which was observed through a rapid rise of the dielectric constant at low temperatures in crystals containing CN$^-$, NO$_2^-$, and OH$^-$ ions.[6,7] This phenomenon has been utilized to produce low-temperature cooling through adiabatic depolarization.[8]

In the course of a systematic study of the thermal conductivity of mixed alkali halides, undertaken in an attempt to explore the phonon scattering by monatomic impurities, strong phonon resonance scattering similar to that found earlier with molecular impurities and with a resonance frequency $\omega_0=2.26\times10^{11}$ rad sec^{-1} (1.2 cm^{-1}) was found by Baumann *et al.* in KCl containing small concentrations of Li$^+$ ions.[9] The ionic conductivity of such crystals showed no increase over that of undoped KCl, which indicated that the Li$^+$ ions occupied regular potassium sites.[10] Sack and Moriarty[6] observed a low-temperature polarizability in this material very similar to the Langevin-Debye polarizability found in crystals containing molecular impurities, which indicated that the small Li$^+$ could be displaced inside the potassium cavity by an electric field. Lombardo

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[1] V. Narayanamurti, Phys. Rev. Letters 13, 693 (1964); W. D. Seward and V. Narayanamurti, Phys. Rev. 148, 463 (1966); V. Narayanamurti, W. D. Seward, and R. O. Pohl, *ibid.* 148, 481 (1966).

[2] 1 cm^{-1} in the wave-number measure corresponds to an angular frequency of 1.88×10^{11} rad sec^{-1} and an energy of 1.24×10^{-4} eV. Quantities measured in wave numbers are designated with a tilde in this paper.

[3] F. Hund, Z. Physik 43, 805 (1927). See also Footnote 27 in Ref. 9.

[4] C. E. Clayton and N. H. Williams, Phys. Rev. 45, 234 (1934).

[5] For a recent comparison of the scattering strength of the tunneling states known to date, see J. P. Harrison, P. P. Peressini, and R. O. Pohl, Phys. Rev. 167, 856 (1968); and R. O. Pohl, in *International Conference on Localized Excitations*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 434.

[6] H. S. Sack and M. C. Moriarty, Solid State Commun. 3, 93 (1965).

[7] W. Känzig, H. R. Hart, and S. Roberts, Phys. Rev. Letters 13, 543 (1964).

[8] U. Kuhn and F. Luety, Solid State Commun. 3, 31 (1965); I. W. Shepherd and G. Feher, Phys. Rev. Letters 15, 194 (1965); and I. W. Shepherd, J. Phys. Chem. Solids 28, 2027 (1967).

[9] F. C. Baumann, J. P. Harrison, R. O. Pohl, and W. D. Seward, Phys. Rev. 159, 691 (1967). A preliminary report was given by F. C. Baumann, Bull. Am. Phys. Soc. 9, 644 (1964).

[10] A crystal containing 150 ppm LiCl had the same ionic conductivity between 200 and 300°C as an undoped sample which had an estimated vacancy concentration of 1 ppm. J. M. Peech, this laboratory (private communication). See also G. Lombardo, thesis, Cornell University, 1968 (unpublished).

and Pohl[11] used the electrocaloric effect to study this polarization and found that it could be described in first approximation through the electric-field-induced alignment of a classical electric dipole consisting of the positive lithium ion and the effective negative charge centered in the potassium cavity, with a dipole moment of 2.54 Debye (1 Debye = 3.34×10⁻³⁰ A sec m). Because of the very similar way in which the lithium ions and the tunneling molecules reduced the thermal conductivity, these authors proposed that the potential to which the lithium ion in the potassium cavity was subjected had several equivalent off-center minima between which the ion could tunnel in a quasi-rotational motion, with a frequency approximately equal to ω_0.

Much work has since been done in order to study the properties of this off-center ion and the model that the low-lying energy states of the Li⁺ are caused by tunneling has been generally accepted. From ultrasonic measurements, Byer and Sack[12] have deduced that the equilibrium positions are displaced from the cavity center along the eight $\langle 111 \rangle$ directions. Assuming eight three-dimensional spherical potential wells, Gomez et al.[13] showed that the harmonic-oscillator ground state should split into four equally spaced levels with the degeneracies 1, 3, 3, 1. Lakatos and Sack[14] found in their microwave absorption experiments in KCl:Li that maximum absorption occurred for $\Delta = 10^{-4}$ eV (0.81 cm⁻¹), which energy they equated to the splitting between two neighboring states. Bogardus and Sack[15] also were able to describe the temperature dependence of the impurity induced dielectric constant in KCl:Li with such an energy level scheme and a level spacing of $\Delta = 0.94 \times 10^{-4}$ eV (0.76 cm⁻¹).

The usefulness of specific-heat measurements for the study of impurity modes was first pointed out by Kagan and Iosilevskii.[16] This technique has the advantage that it allows one to observe all modes regardless of whether or not they are coupled to electric or stress fields. The first observation of the specific-heat anomaly caused by lithium in KCl was reported by Wielinga et al.[17] We have extended these measurements over a wide range in temperature and lithium concentration and also studied the two lithium isotopes in an attempt to prove that these impurity modes are indeed tunneling states and that the phonon scattering and the dielectric phenomena in the doped crystals are caused by interactions with these modes. Part of this work has been briefly discussed previously.[18]

The central instability of small impurity ions in alkali halide crystals has been the topic of several theoretical investigations.[19] It was found that for lithium in KCl such an instability was indeed possible. Quigley and Das[19] furthermore predicted that the lithium ion should sit off-center in KBr, too, and that the tunnel splitting should be larger than in KCl. We, therefore, also measured the specific heat in KBr:Li in a search for such a mode.

II. EXPERIMENTAL PROCEDURE

The crystals were pulled from the melt under a high-purity argon protective atmosphere to which a small concentration of chlorine gas had been added. The details of the sample preparation have been given before.[9] Information regarding the boules used are given in Table I. Specific heat was measured by the heat pulse technique with the sample ($m \sim 10$–15 g) in partial thermal contact with the heat sink, as described in detail by Harrison.[20] For the study of the effect of heat treatment on the specific heat, samples were both quenched and annealed. For this the crystals were heated to 200°C in vacuum to remove surface contamination, and then heated to 650°C in 0.1 atm of chlorine gas. After 30 min the crystals were cooled to room temperatures at about 75°C per h if they were to be annealed, and at about 1500°C per h if they were to be quenched. After this treatment they were mounted and cooled below 0°C in 5 h. Inspection between crossed polarizers showed strain patterns in the quenched crystals but none in the annealed crystals.

For the study of the influence of electric fields on the specific heat, gold electrodes were evaporated onto the large faces of the samples cleaved to approximately 3×3×0.3 cm³. The gold-film area was kept smaller than the crystal faces in order to minimize the danger of electrical breakdown. The margin around the gold film was of similar size, or smaller, than the thickness of the sample. For the analysis of our data, we assumed that the electric field was uniform throughout the sample. Both heater and thermometer were glued to the grounded electrode using dilute GE 7031 varnish of negligible thermal mass.

III. EXPERIMENTAL RESULTS ON KCl:Li

A. Low Lithium Concentrations

The large increase of the specific heat C_v caused by the low-frequency impurity mode is shown in Fig. 1

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

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

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

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

[15] H. Bogardus and H. S. Sack, Bull. Am. Phys. Soc. 11, 229 (1966). The value of 0.76 cm⁻¹ quoted here was actually given in Ref. 14.

[16] Yu. Kagan and Ya. A. Iosilevskii, Zh. Eksperim. i Teor. Fiz. 42, 259 (1962) [English transl.: Soviet Phys.—JETP 15, 182 (1962)].

[17] R. F. Wielinga, A. R. Miedema, and W. T. Huiskamp, Physica 32, 1568 (1966).

[18] J. P. Harrison, P. P. Peressini, and R. O. Pohl, in International Conference on Localized Excitations, edited by R. F. Wallis, (Plenum Press, Inc., New York, 1968), p. 474.

[19] J. A. D. Matthew, Solid State Commun. 3, 363 (1965); W. D. Wilson, R. D. Hatcher, G. J. Dienes, and R. Smoluchowski Phys. Rev. 161, 888 (1967); R. J. Quigley and T. P. Das, ibid. 164, 1185 (1967).

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

TABLE I. Information about the samples studied in this work. The capital letters in column 4 are used to identify the samples in this paper. The data obtained on boule 60805Q were very similar to those of samples H and are therefore not shown. Lithium concentration n_{Li} as determined by spectrochemical analysis by Dr. R. Skogerboe of the Analytic Facility of the Cornell Materials Science Center.[a] Columns 6–8 are needed in Sec. III C. The relative error is defined as $(\Delta S_{theory} - \Delta S_{expt.})/\Delta S_{theory}$.

Isotope	Mole % in melt	Boule #	Labeling used in present paper	n_{Li} chemical analysis (10^{17} cm^{-3})	Entropy ΔS (erg g^{-1} deg^{-1}) Theory	Expt.	Relative error (%)
Li⁷	0.02	70425Q	C	1.62	23.4	23.2	0
Li⁶	0.02	70201Q	B	2.44	35	24	31
Li⁷	0.02	70111Q	A	2.8	40.3	23.2	42
			D	2.3	33	...	...
Li⁶	0.5	70130Q	F	7.85	116	98.5	17
Li⁷	~0.5	Q97	G	18.4	265	190.5	28
Li⁷	~0.5	60805Q[b]		24.7[c]	355	300	18
				32.7[c]	470	300	36
Li⁷	0.5	70112Q	H	32.6	470	375	20
			E	32.6	470	...	...
Li⁷	~0.5	60805Q[d]		34.6	500	375	25
Li⁷	~1.0	e	M	58.6	840	560[f]	33
Li⁷	1.5	70824Q	I	80[g]			

[a] Reference 9.
[b] Top of boule.
[c] This sample was cleaved into eight equal pieces. Four of them, from diagonally opposite parts of the sample were analysed at one time, and the remaining four pieces were analyzed a year later. The difference in concentration is attributed to the accuracy of the analysis.
[d] Bottom of boule.
[e] Sample prepared and analyzed at Cornell in the same way as all the other samples reported in this work.
[f] Results obtained by Wielinga et al., Ref. 17.
[g] Estimated.

for a sample containing approximately 20 ppm LiCl in solid solution. Below 0.5°K the specific heat of the pure lattice is small in comparison to that of the impurity mode, and the exponential behavior of C_v at the lowest temperatures, demonstrated by the curve drawn through the data points in Fig. 1, indicates that a model of discrete energy levels associated with the impurity mode is indeed correct.

The entire specific-heat anomaly as a function of temperature is obtained by subtracting the pure crystal specific heat, as shown in Fig. 2. At present, consider

only the data and the temperature scale labeled "Li⁷." The solid curve is a computed Schottky specific-heat anomaly caused by eight partly degenerate states as
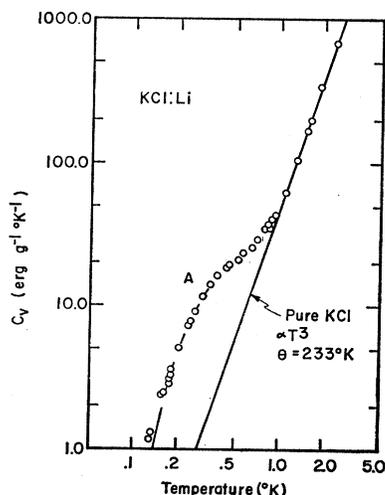
FIG. 1. Specific heat of KCl:Li between 0.14 and 2.5°K. Sample A, $n_{Li} = 2.8 \times 10^{17}$ cm^{-3}. Normal isotopic mixture (92.6% Li⁷, 7.4% Li⁶). The solid line is the specific heat of pure KCl, with $\theta = 233$°K. The curve drawn through the low-temperature points is the calculated low-temperature exponential portion of a Schottky specific-heat anomaly. The full Schottky anomaly is shown in Fig. 2.
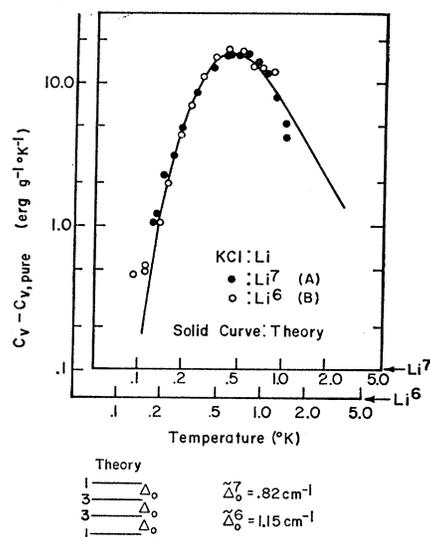
FIG. 2. Excess specific heat caused by the tunneling states of LiCl dissolved in KCl and the influence of the isotopic mass of the lithium ion on it. Closed circles: Li⁷ (Sample A, $n_{Li} = 2.8 \times 10^{17}$ cm^{-3}, actually normal isotopic mixture, 92.6% Li⁷, 7.4% Li⁶); open circles: isotopically pure Li⁶; sample B, $n_{Li} = 2.44 \times 10^{17}$ cm^{-3}. Note that the anomaly for Li⁶ occurs at 40% higher temperatures than that for Li⁷, indicating a 40% larger tunnel splitting for Li⁶. In order to demonstrate this clearly, the temperature scale used for the Li⁶ anomaly (lower scale) was shifted to the left by 40% relative to that used for the Li⁷ anomaly until the two anomalies coincided exactly. Doubly logarithmic plot. The solid curve was computed for a system of four equally spaced levels of spacing Δ_0 with degeneracies 1, 3, 3, and 1, according to the model by Bowen et al., Ref. 25, and $n_{Li} = 1.6 \times 10^{17}$ cm^{-3}. From the best fit to the experimental data, one finds $\tilde{\Delta}_0^7 = 0.82$ cm^{-1}, $\tilde{\Delta}_0^6 = 1.15$ cm$^{-1} = 1.4 \times \tilde{\Delta}_0^7$. Energy measured in wave numbers.

predicted by Gomez et al.[13] Choosing a tunnel splitting Δ_0,

$$\Delta_0 = 10^{-4} \text{ eV}, \quad (\tilde{\Delta}_0 = 0.82 \text{ cm}^{-1}),$$

an excellent fit to the experimental data is achieved (see Fig. 2) which lends strong support to the correctness of the model on which the calculation is based. The Li^+ concentration obtained by adjusting the calculated anomaly vertically until the best fit was obtained is 42% less than the concentration determined by spectrochemical analysis. This is considered satisfactory agreement (see Sec. III C).

Even more direct confirmation of the picture that the Li^+ ion is tunneling between several equivalent positions is derived from a study of the isotope effect of this anomaly. In KCl containing isotopically enriched Li^6 instead of the naturally abundant (92.6%) Li^7, an anomaly of exactly the same shape is found. It occurs, however, at a temperature 40% higher than that caused by Li^7 ions (see Fig. 2 using the temperature scale labeled "Li^6"). In Sec. III C we shall find the same isotopic shift also for a sample of higher lithium concentration (curve F in Fig. 9). Such a shift corresponds to a tunnel splitting $\tilde{\Delta}_0^6 = 1.15$ cm^{-1}. An isotope effect of that magnitude immediately rules out two other explanations of the origin of this impurity mode: A simple harmonic-oscillator model produces an isotope effect of only $(7/6)^{1/2} = 1.08$, i.e., an increase in frequency by 8%, and the model that the Li^+ ion behaves like a quantum mechanical particle-in-a-box, where the K^+ vacancy is assumed to be such a "box," results in an isotope effect of $7/6 = 1.16$, i.e., an upward shift of 16%, still far too small to account for the experimental result of 40%. On the other hand, a tunneling process can explain such a large influence of the mass on the tunnel frequency, as we shall show next. For this, we have to know the harmonic-oscillator, the ground state of which we believe to be split due to the tunneling. Clayman et al.[21] recently reported an infrared active impurity mode at 42 cm^{-1} in KCl:Li^7. It has been shown earlier[18] that with such an oscillator frequency and with the observed tunnel splitting a one-dimensional calculation considering one particle subjected to two harmonic-oscillator potentials, as treated in textbooks on quantum mechanics,[22] yields an increase of the tunnel splitting by 50% if the mass of the particle is decreased by 14%. A study of the isotope effect for the three-dimensional, eight-well harmonic oscillator is presently in progress.[23] A preliminary calculation yielded an increase of the ground-state tunnel splitting of 40%. We want to present here the results of yet

another calculation which is based on the original analogy drawn between the rotational motion of molecular impurities and the translational motion of the Li^+ ion.[11] We assume that the Li^+ ion behaves like a rigid rotor orbiting around the center of the vacancy at the constant distance r_0. Following Narayanamurti,[1] we approximate the potential to which this rigid rotor is subjected by the lowest-order surface harmonic of octahedral symmetry:

$$\tilde{V}(\theta \ \varphi) = (-\tfrac{1}{8}\tilde{K})(3 - 30\cos^2\theta + 35\cos^4\theta + 5\sin^4\theta \cos4\varphi). \quad (1)$$

For $\tilde{K} < 0$, $\tilde{V}(\theta, \varphi)$ has eight minima along

$$\theta = \cos^{-1}(\pm 1/\sqrt{3}), \quad \varphi = \pm\tfrac{1}{4}\pi \text{ or } \pm\tfrac{3}{4}\pi, \quad (2)$$

i.e., the eight $\langle 111 \rangle$ directions in the crystal. Potential maxima occur along the six $\langle 100 \rangle$ directions:

$$\theta = 0, \ \pi, \text{ or } \tfrac{1}{2}\pi; \quad \varphi = 0, \ \pm\tfrac{1}{2}\pi, \text{ or } \pi. \quad (3)$$

Two wells lying in adjacent $\langle 111 \rangle$ directions are separated by a potential barrier of $0.41\tilde{K}$ in the $\langle 110 \rangle$ direction. In the 12 $\langle 110 \rangle$ directions the potential has saddlepoints. We note that this potential, which was first proposed by Devonshire[24] for the treatment of the perturbation of the free rotor states of molecules in crystals, is very similar to the three-dimensional spherical eight-well harmonic-oscillator potential proposed for the Li^+ ion by Bowen et al.[25] in the region where $\tilde{V} \leq \tilde{K}$ as was pointed out by Wilson et al.[19]

In particular, both potentials result in a tunneling motion along the edge of a cube whose corners lie in the eight $\langle 111 \rangle$ directions at a distance r_0. Because of this similarity, the low-energy eigenstates resulting from both potentials should be quite similar, and only the higher states should differ, approaching free rotor and harmonic-oscillator states, respectively. Solutions to the Schroedinger equation for a rigid rotor employing the Devonshire potential have been tabulated,[24,26] and Fig. 3 shows the energies and symmetries of the ground and first excited vibrational (librational) states as a function of the barrier parameter $\tilde{K}$. Here both energy and barrier parameter are measured in units of the rotational constant $\tilde{B} = h/8\pi^2 cI$, where h and c are Planck's constant and the velocity of light, respectively, and $I = r_0^2 m$ is the rotational inertia of the Li^+ ion (mass m) rotating around the cavity center.

With the librational (harmonic-oscillator) energy as well as the tunnel splitting known for the Li^7 isotope, $\tilde{B}^7$, i.e., r_0, is the free parameter. Using the simple selection rule $\Delta J = \pm 1$, which is correct for free rotor states, we can ascribe the 40-cm^{-1} line to the transitions $T_{1u} \rightarrow E_g$, $T_{2g} \rightarrow T_{2u}$, or $T_{2g} \rightarrow T_{1u}$. Since the first and the second transitions have almost identical energies,

[21] R. P. Clayman, I. G. Nolt, and A. J. Sievers, Phys. Rev. Letters **19**, 111 (1967). More recent experiments indicate that this frequency may be somewhat smaller. [R. D. Kirby (private communication).] In our present calculations we therefore used the approximate value of 40 cm^{-1}.

[22] See, e.g., E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), Chap. 5, Sec. 6.

[23] M. Gomez (private communication).

[24] A. F. Devonshire, Proc. Roy. Soc. (London) **A153**, 601 (1936).

[25] S. P. Bowen, M. Gomez, J. A. Krumhansl, and J. A. D. Matthew, Phys. Rev. Letters **16**, 1105 (1966).

[26] O. Sauer, Z. Physik **194**, 360 (1966).
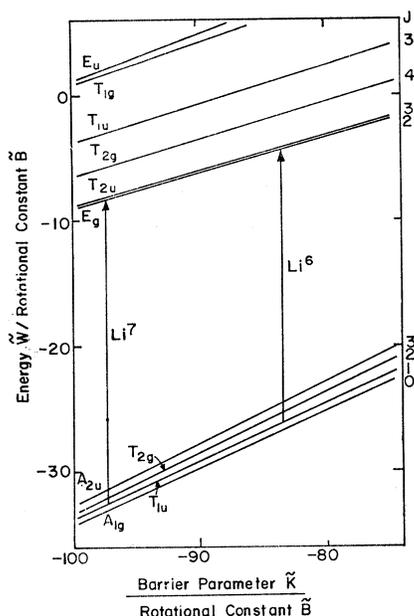
FIG. 3. Devonshire calculation of the perturbed rotational eigenstates, after Sauer, Ref. 26. Energy $\tilde{W}$ and barrier parameter $\tilde{K}$ measured in units of $\tilde{B}$, the rotational constant. Negative $\tilde{K}$ means potential minima in the eight $\langle 111 \rangle$ crystallographic directions. J is the rotational quantum number of the corresponding unperturbed rotor state. The arrows, marked Li^7 and Li^6, are explained in the text.

we assign the 40-cm^{-1} line to these transitions, and ignore the $T_{2g} \rightarrow T_{1u}$ transition for simplicity. We find the correct ratio between the oscillator and the tunneling energy for $\tilde{K}/\tilde{B}^7 = -97.4$ (see arrow) and hence from $\tilde{E}_{osc}^7/\tilde{B}^7 = 24.6$ we determine $\tilde{B}^7 = 1.63$ cm^{-1}, all this for Li^7. From $\tilde{B}^7$ we calculate $r_0 = 1.2$ Å, hence the potential minima are located at the eight corners of a cube whose edges are of length

$$d = 2 \times 1.2 \text{ Å}/\sqrt{3} = 1.4 \text{ Å}.$$

From a study of the interatomic potentials, Wilson et al.[19] computed $r_0 = 1.16$ Å, and Quigley and Das[19] found $r_0 = 0.6$ Å.

For the Li^6 isotope, then, under the assumption that the potential remains unchanged, it follows that $\tilde{B}^6 = 1.9$ cm^{-1}, hence $\tilde{K}/\tilde{B}^6 = -97.4(1.63/1.9) = -83.5$, $\tilde{E}_{osc}^6/\tilde{B}^6 = 21.8$, and $\tilde{E}_{osc}^6 = 41.4$ cm^{-1}. Note that the isotope effect of the oscillator energy thus determined is only 4%. Finally $\tilde{\Delta}_0^6/\tilde{B}^6 = 0.65$, or $\tilde{\Delta}_0^6 = 1.23$ cm^{-1}. This is an increase of 54% over the tunnel splitting for Li,^{7} which agrees very well with our experimental increase of 40%. We also calculate $\tilde{K} = -159$ cm^{-1}, and the energy-barrier height between adjacent $\langle 111 \rangle$ potential minima is $0.41 \times \tilde{K} = 65$ cm^{-1}. All the energies we are concerned with are sufficiently small compared to $|\tilde{K}|$, and this justifies our having applied the Devonshire potential to this problem.

We can summarize our results so far with the statement that the specific-heat measurements have provided

strong evidence for the correctness of the tunneling model. What then is the nature of the low-frequency phonon resonance scattering from which our interest in this defect system originated? This resonance occurs at 1.2 cm^{-1} ($\omega_0 = 2.26 \times 10^{11}$ rad sec^{-1}), and it has recently been found that if the naturally abundant Li^7 is replaced by Li^6, this resonance frequency increases by 40%.[27] This proves the contention that the phonons are reasonantly scattered by the Li tunneling modes. Our model, however, does not contain energy splittings corresponding to 1.2 cm^{-1} (see Fig. 2). On the other hand, 1.2 cm^{-1} corresponds to the average energy of the two triply degenerate tunneling states (at 0.82 and 1.64 cm^{-1}, respectively). We therefore conclude that the phonons can cause transitions between the ground state (which is the only one thermally populated below 1°K) and all the other tunneling states. The resolution of our "phonon spectrometer" is not high enough to resolve the individual transitions. Recently, Walton[28] has been able to refine the resolution of thermal-conductivity experiments, and his work indicates that the phonons indeed can couple the ground state to all three excited tunneling states in KCl:Li.

B. Electric Field Effects

Dielectric[6] and electrocaloric[11] measurements have indicated a polarizability of the tunneling states of the lithium ion. Another way of saying this is that an electric field appeared to change the level splitting of the tunneling states. We have observed this change directly by measuring the specific-heat anomaly in an applied electric field. We begin by analyzing the data obtained in the electric cooling experiments[11] on the basis of the quantum-mechanical tunneling model. Then we shall use these results to predict how the specific-heat anomaly in KCl:Li will vary with applied electric field and finally we compare this with our experimental results.

The electric field dependence of the tunneling states has been studied by Gomez et al.[13] and the results of their calculations are presented in Fig. 3 of their paper. For our purpose we need analytic expressions describing the field dependence of the energies $W_i(E)$ of these eight states. We can obtain them from Fig. 3 of Ref. 13 using the following simple arguments: At high fields, the wave functions of the Li ion can be written as linear combinations of wave functions localized in those potential wells which are equivalent in the presence of the field. Hence, the energy of each state will change as these equivalent potential wells are raised or lowered in the applied electric field, and consequently, the Stark effect will be of first order. Quantitatively this means that the energy W_i varies as $(p_0 E \cos\theta_i)$, where $p_0 = e^* r_0$ (e^* is the effective charge of the Li$^+$ ion and r_0 is the spatial separation of the potential wells from the

[27] P. P. Peressini (to be published).
[28] D. Walton, Phys. Rev. Letters **19**, 305 (1967).

center of the potassium cavity), and θ_i is the angle between the electric field E and the cube diagonals pointing to the equivalent wells. For small fields, however, the Stark effect will be of second order, i.e., W_i will vary as $(p_0 E \cos\theta_i)^2$. Both the high- and the low-field behavior of W_i can be expressed with a single interpolation formula of the form $(a^2 + (p_0 E \cos\theta_i)^2)^{1/2}$, where the constant a^2 takes the finite zero-field splitting into account. Thus, we arrive at the following expressions:

For $E\|\langle 111\rangle$

$$W_{1,8} = \mp[(\tfrac{3}{2}\Delta_0)^2 + p_0^2 E^2]^{1/2}, \quad (\cos^2\theta = 1), \quad (4)$$

and

$$W_{2-4;\,5-7} = \mp[(\tfrac{1}{2}\Delta_0)^2 + \tfrac{1}{9}p_0^2 E^2]^{1/2}, \quad (\cos^2\theta = \tfrac{1}{9}), \quad (5)$$

and for $E\|\langle 100\rangle$

$$W_1 = -\Delta_0 - [(\tfrac{1}{2}\Delta_0)^2 + \tfrac{1}{3}p_0^2 E^2]^{1/2}, \quad W_8 = -W_1, \quad (6)$$

$$W_{2,3} = -[(\tfrac{1}{2}\Delta_0)^2 + \tfrac{1}{3}p_0^2 E^2]^{1/2}, \quad W_{6,7} = -W_{2,3}, \quad (7)$$

and

$$W_4 = -\Delta_0 + [(\tfrac{1}{2}\Delta_0)^2 + \tfrac{1}{3}p_0^2 E^2]^{1/2}, \quad W_5 = -W_4. \quad (8)$$

The energies W_i from Eqs. (4) through (8), measured in wave numbers, have been plotted in Fig. 4 for the zero-field splitting Δ_0 derived in the previous section and for a particular value of p_0, whose choice will become clear later. Figure 4 is similar to Fig. 3 of Gomez *et al.*[13] Note in particular, that for fields applied perpendicular to the cube face the tunneling between the four corners of this face remains unaffected by E, and consequently each of the two quadruplets continue to be tunnel split by the amount Δ_0 even at the highest fields.

Thus, we have seen that the Stark effect of the

(a) $E\|\langle 111\rangle$ (b) $E\|\langle 100\rangle$
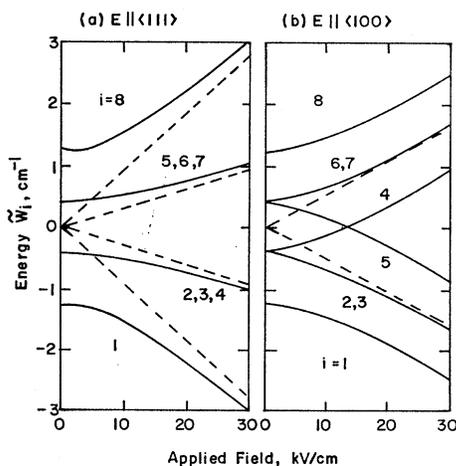
FIG. 4. (a,b) Change of the energies of the tunneling states (in wave numbers) in an applied electric field, using the uncorrected dipole moment $p_0 = 5.5$ D, after Ref. 11. With the Lorentz local field correction, $E_{loc} = \tfrac{1}{3}(\epsilon/\epsilon_0 + 2)E_{appl}$, where $\epsilon/\epsilon_0 = 4.5$ (Ref. 6), this value corresponds to the corrected dipole moment 2.54 D. The numbers on the curves refer to the indices in Eqs. (4)–(8).

tunneling states is determined entirely by the zero-field splitting Δ_0 and the classical dipole moment p_0 ($p_0 = e^* r_0$, with r_0 in $\langle 111\rangle$). From this derivation it appears, however, that in the electrocaloric work the classical limit should be observed in the limit of high fields only where the Stark effect is of first order. Furthermore, one may ask how the tunnel splitting persisting even at the highest fields for $E\|\langle 100\rangle$ influences the results. The experimental data in Ref. 11, however, obtained for $E\|\langle 100\rangle$, could be explained with the polarization of a classical electric dipole at the very lowest fields as well. In order to show that this dipole moment is indeed the moment p_0 used here, we consider the specific entropy S during adiabatic depolarization:

$$T\,dS = 0 = T\frac{\partial S_t}{\partial T}\bigg|_E dT + T\frac{\partial S_t}{\partial E}\bigg|_T dE + AT^3 dT \quad (9)$$

in the usual notation. S_t is the entropy (per volume) of the tunnel states, the last term is the entropy of the host lattice in the Debye approximation. The specific internal energy U_t (per volume) of the tunneling states for the field $E\|\langle 100\rangle$ can be reduced to the following simple form:

$$U_t = n_{Li}\{W_1 - W_2 \tanh(W_2/kT) \\ - \Delta_0 \tanh(\Delta_0/2kT)\}. \quad (10)$$

In the temperature range where $kT > |W_2|$, U_t can be considerably simplified, and one obtains

$$S_t = \frac{U_t}{T} + \int \frac{U_t}{T^2}dT = n_{Li}k \ln 8 - \frac{n_{Li}}{2kT^2} \\ \times (3(\tfrac{1}{2}\Delta_0)^2 + \tfrac{1}{3}p_0^2 E^2) \quad (11)$$

and

$$T\,dS = -\frac{n_{Li}}{3kT}p_0^2 E\,dE + \frac{n_{Li}}{kT^2} \\ \times \{3(\tfrac{1}{2}\Delta_0)^2 + \tfrac{1}{3}p_0^2 E^2\}dT + AT^3 dT = 0. \quad (12)$$

For small fields, the second term on the right-hand side of Eq. (12) approaches the specific heat of the tunneling states at zero field, and, for $n_{Li} = 2.4 \times 10^{18}$ cm^{-3} and $T > 2°$K, it can be ignored in comparison with the pure lattice entropy. Hence we obtain (ΔT is the decrease in temperature)

$$AT^3 \Delta T = \int_E^0 \frac{n_{Li}}{3kT}p_0^2 E\,dE, \quad (13)$$

$$\Delta T = n_{Li}p_0^2 E^2 / 6kAT^4, \quad (14)$$

which is identical to the result derived in Ref. 11 for the classical case. We may, therefore, use the value of p_0 determined from the electrocaloric work to compute W_i, U_t, and from this the specific heat $C_v(T,E)$. In Fig. 4 W_i is plotted as a function of the electric field

applied in both the $\langle 100 \rangle$ and the $\langle 111 \rangle$ directions for this particular dipole moment. Figure 5 shows how the specific-heat anomaly is expected to change with a field applied in these two directions. The experimental relative changes of the specific heat,

$$\Delta C/C = (C_v(E,T) - C_v(0,T))/(C_v(0,T) - C_{v,\text{KCl}}),$$

are shown in Fig. 6. As one might expect from the field-induced level splitting, Fig. 4, $\Delta C/C$ is smaller for $E\|\langle 100 \rangle$ than for $E\|\langle 111 \rangle$. The solid and the dashed curves are the computed changes for the $\langle 111 \rangle$ and $\langle 100 \rangle$ field, respectively, using the known values of Δ_0 and p_0. The good agreement between experiment and theory, obtained without any adjustable parameters, is taken as further evidence for the correctness of the model used to describe these tunneling states. Furthermore, we can easily convince ourselves with a simple qualita-
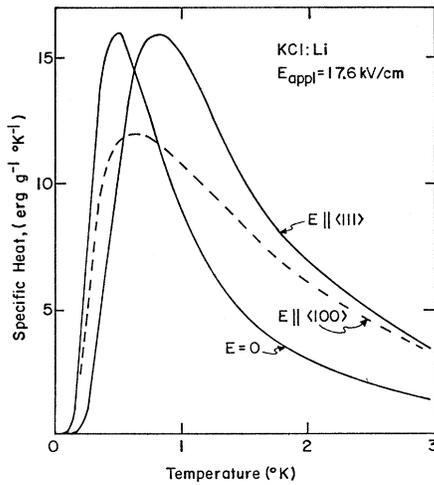
FIG. 5. The computed tunneling specific-heat anomaly under the influence of an applied electric field. $n_{\text{Li}} = 1.6 \times 10^{17}$ cm^{-3}. The applied field of 17.6 kV cm^{-1} corresponds to a Lorentz local field of $E_{\text{loc}} = 38.2$ kV cm^{-1}. Uncorrected dipole moment used was $p_0 = 5.5$ D.

tive argument that these experimental findings are not consistent with the assumption of either six potential minima along the $\langle 100 \rangle$ directions or 12 minima along the $\langle 110 \rangle$ directions: For minima along $\langle 100 \rangle$, $\Delta C/C$ should be larger for $E\|\langle 100 \rangle$ than for $E\|\langle 111 \rangle$, contrary to the experiment, and for minima along $\langle 110 \rangle$ the difference between the two field directions should be much smaller.

Whereas the determination of the dipole moment from the electrocaloric measurements, Eq. (14), required the knowledge of the lithium concentration n_{Li}, $\Delta C/C$ is independent of n_{Li}, depending only on Δ_0 and p_0. It is therefore of interest to determine p_0 directly from $\Delta C/C$. This can be done by attempting to produce a best fit to the data in Fig. 6 by adjusting Δ_0 and p_0. For simplicity, however, we preferred to fit only the points where $\Delta C/C = 0$. With little computa-
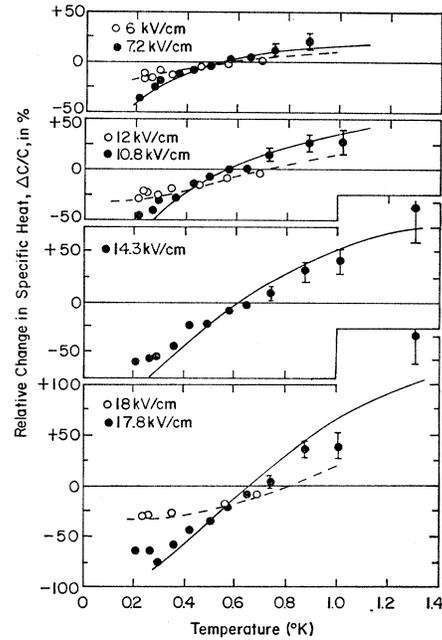
FIG. 6. Relative change of the specific heat $\Delta C/C$ in an applied dc electric field as a function of temperature. Experiment. Closed circles: $E\|\langle 111 \rangle$. Sample C; open circles: $E\|\langle 100 \rangle$, sample D. Solid and broken curves: calculated changes for $E\|\langle 111 \rangle$ and $E\|\langle 100 \rangle$, respectively, using the eight-well potential, a zero-field tunnel splitting of $\tilde{\Delta}_0 = 0.82$ cm^{-1} and p_0 (Lorentz field corrected) $= 2.54$ D.

tional effort, it can be shown how the temperature T_0, at which $\Delta C/C = 0$, depends on Δ_0 and p_0:
for $E\|\langle 111 \rangle$,

$$kT_0 = 0.428\Delta_0 + 2.98 \times 10^{-2}(p_0 E)^2/\Delta_0; \quad (15)$$

for $E\|\langle 100 \rangle$,

$$kT_0 = 0.38\Delta_0 + 0.156 p_0 E. \quad (16)$$

The temperatures T_0 obtained from experiment for $E\|\langle 111 \rangle$, Fig. 6, are plotted in Fig. 7 versus E^2. From the best straight-line fit to the data one obtains from the $\langle 111 \rangle$ data $\tilde{\Delta}_0 = 0.84 \pm 0.03$ cm^{-1} and $p_0 = 2.94$ D. There are not enough data in Fig. 6 for $E\|\langle 100 \rangle$ to perform the same analysis. We did, however, study $\Delta C/C$ for $E\|\langle 100 \rangle$ on a sample of higher concentration (see Fig. 8). In the next chapter it will be shown that the specific-heat anomaly changes its shape somewhat at higher Li concentrations, which makes an analysis based on a simple Schottky anomaly somewhat doubtful. We ignore this difficulty for the moment and plot T_0 versus E (see again Fig. 7). From the best fit to the data (solid line) we obtain for the $\langle 100 \rangle$ data $\tilde{\Delta}_0 = 0.87$ ± 0.05 cm^{-1} and $p_0 = 2.77$ D, or assuming $\tilde{\Delta}_0$ to be known, $\tilde{\Delta}_0 = 0.82$ cm^{-1} (dashed line), we find that $p_0 = 3.1$ D. The tunnel splitting in zero electric field, Δ_0, agrees very well with the value determined in Sec. III A. The dipole moment, however, is 10 to 20% larger than determined in the electrocaloric work. In the next section we shall see that the spectrochemical
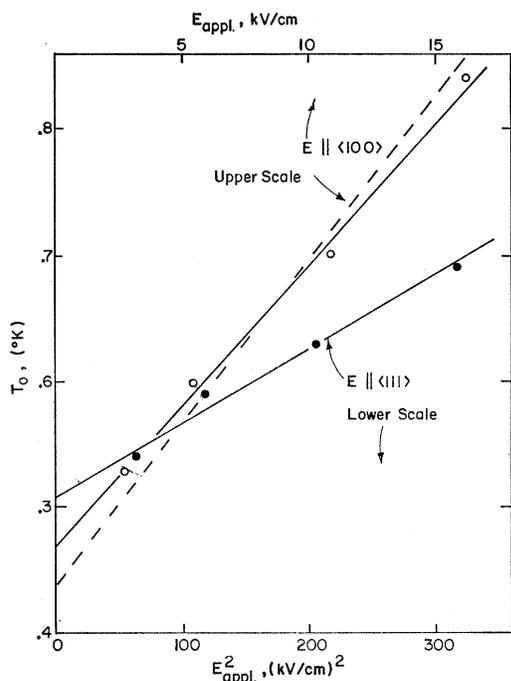
FIG. 7. T_0, the temperature at which the specific heat remains unaltered when the electric field is applied, versus E_{appl}. For $E\|\langle 111\rangle$, T_0 goes as E_{appl}^2, use scale at bottom of figure. For $E\|\langle 100\rangle$, T_0 varies as E_{appl}, use scale at top of figure; the meaning of the solid and the dashed lines is expanded in the text.

analysis may have consistently overestimated the concentration of the tunneling lithium ions, resulting in too small a dipole moment determined from the electro-caloric work. We can not, therefore, presently decide whether to prefer the smaller or the larger value of p_0. Hence we quote the following value:

$$p_0 = 2.75 \pm 0.25 \text{ D} \quad \text{(Lorentz-field-corrected)},$$

with a rather large error. We note that this choice does not significantly alter the agreement between the experimental and the calculated values of $\Delta C/C$ (see Fig. 6).

From the displacement of the potential minima from the center of the potassium vacancy, $r_0 = 1.2$ Å as derived in the preceding section, and from the dipole moment $p_0 = 2.75$ D, we determine the effective charge e^* of the lithium ion through the relation $p_0 = r_0 e^*$. We find

$$e^* = 0.5e, \quad (e = +1.6 \times 10^{-19} \text{A sec}).$$

For comparison, Szigeti[29] found for pure alkali halide lattices values of e^* between 0.7 and 0.9e.

Because of the large polarizability of the Li tunneling modes one might expect that at sufficiently low temperatures a transition of a ferroelectric type might occur. Such a transition in a dilute system would be of con-

siderable interest. A theoretical discussion of collective behavior of dipolar impurities has been given by Brout,[30] Zernik[31] and Klein.[32] These authors agree that for dipoles with moments of the order of a few debye and concentrations in the range of 10^{19} cm^{-3} cooperative phenomena should become observable below 1°K. We shall return to this question in the next section.

C. Specific Heat at Higher Concentrations

The specific-heat anomaly increases with increasing lithium concentration (see Fig. 9), and also broadens slightly. Since the highest concentrations studied are close to the solubility limit (ca. 10^{19} cm^{-3}), it was important to search for signs of precipitations. Neither quenching nor annealing the samples were found to alter the anomalies, though. For details, see caption of Fig. 9.

The entropy change associated with an equal probability of population of the eight tunneling states is

$$\Delta S = \int_0^\infty (C_v/T)dT = n_{Li}k \ln 8. \qquad (17)$$

The theoretically expected and the experimentally observed entropy changes are compared in Table I, columns 6–8. They scale over the entire concentration range. This lends further strength to our picture that the anomaly is caused by individual lithium ions. The agreement between theory and experiment is satisfactory since the statistical experimental error of the spectrochemical analysis is about 20% (see, for instance,
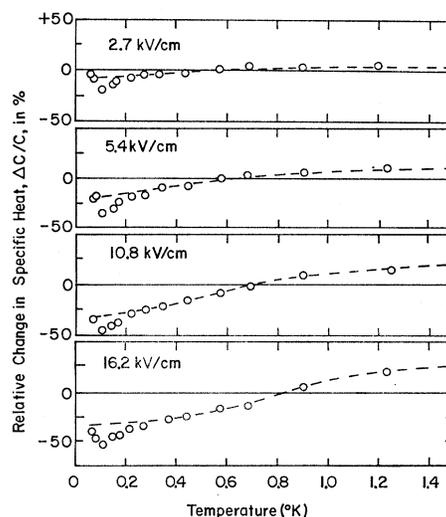
FIG. 8. Relative change of the specific heat $\Delta C/C$ in an applied dc electric field as a function of temperature, with the applied field as parameter. $E\|\langle 100\rangle$, sample E, $n_{Li} = 3.26 \times 10^{18}$ cm^{-3}. Dashed curves not computed.

[29] See, for instance, C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1962), 2nd ed., Chap. 7.

[30] R. Brout, Phys. Rev. Letters **14**, 175 (1965).
[31] W. Zernik, Phys. Rev. **139**, A1010 (1965).
[32] M. W. Klein, Phys. Rev. **141**, 489 (1966).
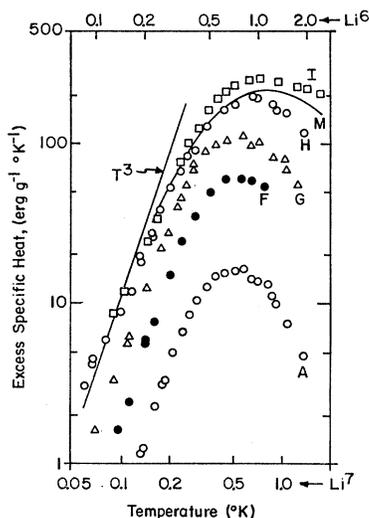
FIG. 9. Specific-heat anomaly for several lithium concentrations: A, $n_{Li}=2.8\times10^{17}$ cm^{-3}; F, $n_{Li}=7.85\times10^{17}$ cm^{-3}; G, $n_{Li}=18.4\times10^{17}$ cm^{-3}; H, $n_{Li}=32.6\times10^{17}$ cm^{-3}; M (solid curve, after Wielinga et al. Ref. 17), $n_{Li}=58.6\times10^{17}$ cm^{-3}; I, $n_{Li}\approx80\times10^{17}$ cm^{-3}. All samples but F doped with normal isotopic lithium composition (92.6% Li^7); temperature scale to be used is at bottom of graph. Sample F doped with Li^6, use temperature scale at top of graph which is shifted to the left by 40% with respect to scale at bottom. See also Sec. III A. Sample A and H were also measured after annealing (see Sec. II), and sample G after quenching. Within the experimental accuracy (5–10%), these heat treatments did not alter the specific-heat measured over the temperature range studied (0.07–1.5°K). The T^3 line corresponds to a specific heat 270 times that of pure KCl. This number emphasizes the profound change of the specific heat caused by as few as 100 ppm of foreign ions (Li$^+$ ions in this case).

footnote c in Table I). We note, however, that the experimental values are, with but one exception, smaller than the theoretical values, on the average by 25%. Let us discuss the possible causes for this systematic deviation.

The error introduced by performing the integral, Eq. (17), between 0.06 and 1.5°K only, can be shown to be less than 10%. The error introduced by decomposing the measured specific heat into two independent sums, $C_{v,\text{total}}=C_{v,\text{tunnel}}+C_{v,\text{KCl}}$, is difficult to estimate. However, $C_{v,\text{KCl}}$ is so small in the important temperature range that we assume this error to be small, too. A third possibility would be an error in the measurement of the tunneling specific heat, which can arise if the repopulation time constant were longer than the heat pulse decay time (sample to bath time constant). For instance, if the A_{1g} and T_{2g} levels (Fig. 3) were strongly coupled together, but isolated from the T_{1u} and A_{2u} levels which in turn are strongly coupled, then the measured specific heat could indeed be expected to be lower than the true equilibrium specific heat by the correct amount (we would be dealing with one 1:3 system and one 3:1 system). This interesting possibility was investigated by virtually isolating the sample thermally, waiting for a day for it to cool to 0.3°K and then applying a pulse of heat. If the above hypothesis

were correct there would have been a partial decay of the temperature rise corresponding to the slow repopulation. No such effect was found. We therefore conclude that either the above hypothesis is incorrect, or that the repopulation time is greater than 45 min, which appears unlikely. Another explanation of the discrepancy would start from the assumption that the form of the eight-well potential could be quite different from that assumed in Eq. (1). Such cases have also been discussed by Gomez et al.[13] This could, for example, cause the ground state to become degenerate. If it were doubly degenerate, as would be the case if the ions could tunnel diagonally across the cube faces only, the theoretical entropy change would be $\Delta S=n_{Li}k\ln4$, i.e., about 30% smaller. Although such a potential can be constructed, it is unlikely that in reality there would not be a finite amount of splitting remaining between the lowest two states. The fact that no indication for this was observed in specific heat to below 0.1°K, in particular when an electric field was applied to the sample, seems to speak against such a possibility. Finally, we consider the possibility that there exists a systematic difference between the spectrochemically observed lithium concentration $n_{Li,\text{chem}}$ and the concentration of lithium ions observed to tunnel. A systematic error in the analysis is unlikely since this method is basically straightforward, it was checked carefully, and it is believed to be accurate to about $\pm10\%$, at least for the higher concentrations. Conceivably, though, a certain fraction of the lithium ions is always frozen into positions where they cannot tunnel. That a difference between $n_{Li,\text{chem}}$ and $n_{Li,\text{tunnel}}$ may indeed exist is also indicated by the following observation: In the electrocaloric work the dipole moment was determined to 2.54 D (Lorentz corrected) using the chemically determined n_{Li}. From the change of specific heat in an applied electric field, which is independent of the lithium concentration, a dipole moment larger by 10–20% was determined in the preceding section. If we assume that the correct dipole moment is 2.54 D +10%, i.e., 2.8 D, we can use the electrocaloric measurements to determine n_{Li}, which is then 20% smaller than the spectrochemically determined concentrations. Since the spectrochemical method has given consistent and reproducible results over the period of years, we then conclude that $n_{Li,\text{chem}}$ is systematically higher than $n_{Li,\text{tunnel}}$ by 20%. The test whether this explanation of the discrepancy between the theoretically and the experimental entropy ΔS is correct requires a more accurate determination of p_0, the dipole moment of the lithium ion. This work is presently in progress at Cornell.[33]

Although the discrepancy between the experimental results and the theoretical predictions of the entropy discussed in the preceding paragraph should not be ignored, we believe that it is not large enough to be

[33] R. A. Herendeen and R. H. Silsbee (private communication).

clearly outside our experimental errors since so much evidence speaks in favor of the 1, 3, 3, 1 level scheme discussed earlier. We have, therefore, chosen not to attach great significance to this discrepancy at the present time.

We now turn to the discussion of the shape of the anomaly at higher concentrations. The anomaly broadens, the exponential low-temperature dependence giving way to a dependence proportional to $T^{2.5}$. Furthermore, the low-temperature part of the anomaly appears to become almost independent of concentration. According to Brout[30] and Klein,[32] such a behavior is to be expected for a dilute system of classical electric dipoles which they demonstrated to freeze into a configuration of random orientation characterized by a local antiferroelectric order. In the case of an Ising model with only two orientations allowed for the dipoles, Brout obtained a specific heat proportional to T and independent of concentration. In extending this work, Klein predicted that a set of classical dipoles with unrestricted orientations would have a specific heat proportional to T^3, and independent of concentration. Although the experimental observation of such an ordering in a dilute dipolar system would be of considerable interest, our feeling at present is that the experimental evidence for its occurrence is not conclusive. Our reason is twofold: The theory was derived for a set of classical dipoles, and not for a set of tunneling states which have a specific heat even without any dipole-dipole interactions. In fact, the observed specific-heat anomaly at high concentrations can be described by the same set of tunneling states, if we merely assume that a random internal stress boradens the levels at higher concentrations. Thus, we were able to describe the anomaly for $n_{Li} = 24.7 \ 10^{17} \ cm^{-3}$, if we assumed that the excited tunneling states were broadened with either a Lorentzian or a Gaussian shape with halfwidths $H \sim 0.5\Delta_0$, corresponding to $H \sim 0.4 \ cm^{-1}$. The existence of an inhomogeneous line broadening of that magnitude in alkali halide crystals has been postulated at several occasions before (see, for instance, Seward and Narayanamurti[1]). The second, and perhaps more convincing, argument against the picture of a cooperative phenomenon and in favor of the model of the stress-broadened tunneling states is provided through the electric field measurements reported in the preceding section for the high lithium concentration. These measurements could be explained with the same polarization of the tunneling states that was successful for the lowest Li concentration. It is difficult to imagine that a cooperative phenomenon should not be more dramatically influenced by an electric field.

To summarize then, the specific-heat anomaly associated with LiCl dissolved in KCl can be explained with the model of a quantum-mechanical tunneling of the lithium ion over the entire range of temperature and concentration studied. The search for a possible cooperative phenomenon involving the electric polarization of the impurity ion will have to be carried to lower temperatures and also possibly to systems with considerably smaller zero-field tunnel splitting. The search for such defects is presently in progress.

IV. SEARCH FOR TUNNELING STATES IN KBr:Li

Our search for a low-lying mode in KBr:Li has been unsuccessful. A sample containing $1 \times 10^{19} \ cm^{-3} \ Li^6Br$, seed pulled under bromine protective atmosphere,[9] was measured between 0.4 and 1.8°K. Its specific heat was $C_v = 65 \ (erg/g \ deg^4)T^3 \pm 5\%$. Within the experimental accuracy, this is identical to the specific heat of pure KBr[34] which in this temperature range is $C_v = 62 \ (erg/g \ deg^4)T^3 \ (\Theta = 174°K)$. It follows that no energy states with frequencies between 0.01 and 10 cm^{-1} can be associated with lithium ions in KBr. The same result was obtained by the Leiden group on a sample containing an estimated $n_{Li} = 5 \times 10^{18} \ cm^{-3}$ of Li^7Br.[35] This demonstrates that the resonance observed in the thermal conductivity[9] in KBr:Li (normal isotopic mixture) at $\omega_0 = 3.2 \ cm^{-1}$ is not caused by the lithium ions, or at least not by the majority of them, a possibility discussed in Ref. 9 (on p. 699). Quigley and Das[19] predicted that Li in KBr should have a tunnel splitting larger than in KCl. In view of our findings, it seems that the conditions causing central instabilities are still not well understood.

ACKNOWLEDGMENTS

[34] W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **242**, 467 (1957).
[35] W. T. Huiskamp (private communication).