also observed an emission band about 0.45 eV wide at 1.68 eV in TlCl crystals that had "lost chlorine". It is probably the same as the peak at higher energy in Fig. 1 for TlCl.) In KCl the ground-state Cl_2^- centers cause an absorption band at 3.40 eV and another band, 60 times weaker, at 1.65 eV.[40] The Cl_2^- centers are stable below about 110°K and can be produced by ionizing radiation below this temperature.[40] Christy and Dimock[1] x rayed TlCl at about 100°K and found no absorption bands. Assuming stable Cl_2^- might have been produced, the strong Cl_2^- absorption might have been hidden under the fundamental absorption edge,

and the weak transition too weak to see. An attempt to produce Cl_2^- centers by ionizing radiation in pure and doped TlCl at liquid-helium temperature would be worthwhile.

Thermal Conductivity in Mixed Alkali Halides: KCl:Li and KBr:Li†

F. C. BAUMANN,* J. P. HARRISON, R. O. POHL, AND W. D. SEWARD‡

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

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Phonon resonances have been observed in both KCl:Li and KBr:Li through measurements of the low-temperature thermal conductivity between 0.05 and 100°K. Their frequencies are 1.2 and 63 cm^{-1} in KCl, and 3.2 and 39 cm^{-1} in KBr. Static electric fields are used to change the low-frequency resonances and to help in their identification. The 1.2-cm^{-1} resonance in KCl is ascribed to the tunneling motion of the Li$^+$, very similar to the tunneling of CN$^-$ observed earlier. The frequency dependence of the relaxation rate associated with this resonance is best described with a Lorentzian resonance denominator of the form $\omega^2/(\omega_0^2-\omega^2)^2$, which varies as ω^2 at low frequencies, in disagreement with existing theories. The 3.2-cm^{-1} resonance in KBr is ascribed to an oscillation involving the motion of the Li$^+$ plus its six nearest-neighbor Br$^-$ ions. It is speculated that this LiBr$_6$ molecule ion has a central instability. The high-frequency resonances are attributed to impurity modes involving the oscillations of the ions surrounding the Li$^+$. The 39-cm^{-1} resonance in KBr does not show an isotope effect. It is not possible to describe the resonant scattering by these high-frequency resonances with the existing theory of elastic scattering. The phonon-defect relaxation rate must contain a temperature dependence. It is believed that inelastic three-quantum processes are important in these two systems.

I. INTRODUCTION

FOREIGN atoms in solid solution change the lattice vibrational spectrum and give rise to resonances. They can manifest themselves through phonon resonant scattering, and this has been observed in thermal conductivity.[1-3] In the course of a systematic investigation of this phenomenon we have observed particularly strong resonant scattering in lithium-doped KCl and KBr. Because of the considerable attention which these systems have received lately, it appears desirable to present here a summary of our results to date, although many of the details connected with these resonances are still unclear.

II. EXPERIMENTAL PROCEDURE

For the measurements of the thermal conductivity with the steady-state method, three cryostats were used. The cryostat for the temperature interval between 1 and 100°K, with He^4 as refrigerant, has been described before[4] and is basically identical to the one originally designed in this laboratory.[5] The temperature range between 0.3 and 2°K was covered with a conventional He^3 cryostat. Its design and also the experimental procedure of measuring thermal conductivity used over the entire temperature range covered in this investi-

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* Present address: Physikalisches Institut, Technische Hochschule, Karlsruhe, Germany.

‡ Present address: Department of Physics, University of Illinois, Urbana, Illinois.

[1] C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).

[2] C. M. Wagner, Phys. Rev. **131**, 1443 (1963).

[3] R. F. Caldwell and M. V. Klein, Phys. Rev. (to be published); J. W. Schwartz and C. T. Walker, Phys. Rev. **155**, 959 (1967); R. O. Pohl, NATO Advanced Study Institute, Cortina d'Ampezzo, Italy, 1966, p. VIII. 1 (unpublished). These papers contain introductions to the field of point-defect scattering in thermal conductivity and list many references.

[4] W. S. Williams, Phys. Rev. **119**, 1021 (1960).
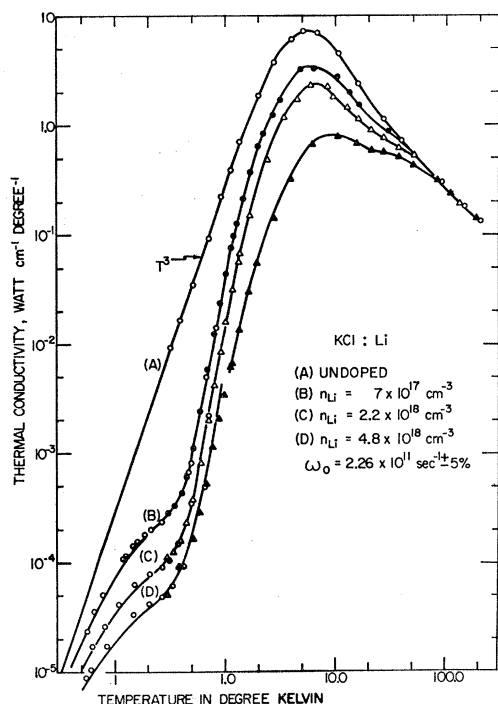
[5] G. A. Slack, Phys. Rev. **105**, 832 (1957).

FIG. 1. Thermal conductivity of KCl containing Li. Sample size $5\times5\times40$ mm³. The solid curve through the pure KCl is a machine fit. In the doped crystals the machine fit (solid curves) extends only up to 1°K.

gation has been published before.[6] Below 0.6°K and down to 0.05°K a cryostat designed and built by one of us (J.P.H.) was used. Its main components were a He⁴ and He³ cryostat and one stage of adiabatic demagnetization using a paramagnetic salt (chrome potassium alum). This cryostat will be described elsewhere.

The crystals were seed-pulled under halogen atmosphere from halogen-treated reagent-grade material.[7] With this technique, molecular impurities such as NO_2^-, CN^-, or OH^-, which are known to be strong phonon scatterers, are completely avoided.[8] This was demonstrated through optical-absorption measurements over the entire spectral range between the exciton and reststrahlen absorption. Within the limit of detection, $K\sim10^{-2}$ cm⁻¹, no absorption by these molecules was

observed. The Li^+ concentrations in solid solution were determined by flame photometry.[9] The highest concentrations used here represent approximately the maximum solubility of Li^+ in these lattices. In previous work on ionic conductivity and the electrocaloric effect[10] and on far-infrared (−IR) absorption[11] it was concluded that the Li^+ ions are randomly distributed and substitute for the K^+ ions. In these investigations the samples were measured within a few weeks after growth without any further heat treatment. It has recently been found, however, that the lithium can rapidly diffuse[12] in KCl and can possibly precipitate even at room temperature. It was therefore necessary to study the thermal conductivity after various heat treatments. The crystals were cleaved along {100} planes and their surfaces were sandblasted. For the study of the influence of electric fields on the thermal conductivity, thin gold electrodes were evaporated on two opposing sides of the crystal, covering approximately 80% of the surfaces between the thermometers. The data shown in Figs. 3 and 5 were corrected for 100% coverage.

III. EXPERIMENTAL RESULTS

In crystals containing lithium the thermal conductivity is greatly reduced, as is shown for KCl in Fig. 1.[13] The phonon scattering is most pronounced around 0.4 and 20°K, indicating two phonon resonant-scattering processes.[14] Neither a rapid quench[15] nor a slow anneal[16] had a noticeable influence on the conductivity measured above 1°K. It was found, however, that the conductivity below 1°K increased by ∼30% over a period of a year during which time the sample was kept at room temperature, although this did not affect the shape of the curve. It appears that under these conditions the Li^+ can diffuse away onto a site where it becomes inactive as a phonon scatterer. It is not surprising that no change was observed above 1°K, because there the relative effect of the Li^+ on the conductivity is smaller. For a better characterization of the scattering processes

[6] W. D. Seward and V. Narayanamurti, Phys. Rev. 148, 463 (1966). W. D. Seward, Ph.D. thesis, Cornell University, Materials Science Center, Report No. 368 (unpublished).

[7] J. M. Peech, D. A. Bower, and R. O. Pohl, J. Appl. Phys. (to be published). The Li-doped samples used in Refs. 10, 11, 23, 28, 32, 33, and 37 were all prepared by the same technique in the crystal growing facility of the Cornell Materials Science Center. The isotopically enriched Li⁶Cl and Li⁶Br was purchased from Oak Ridge National Laboratory. A rough estimate on the basis of spectrochemical analysis, optical absorption, ionic- and thermal-conductivity results in about 10 parts per million unintentional impurities in the crystals, apart from Br^- and Cl^- in KCl and KBr, respectively.

[8] A crystal pulled from the same starting material but under commercial high-purity argon gas showed a strong absorption of unknown origin at ∼9 μ, indicating the presence of a molecular impurity in the sample, which we suspect was introduced with the very hygroscopic lithium salt.

[9] The lithium concentration in the doped samples was determined by Dr. R. Skogerboe in the analytic facility of the Cornell Materials Science Center.

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

[11] A. J. Sievers and S. Takeno, Phys. Rev. 140, A1030 (1965); Phys. Rev. Letters 15, 1020 (1965); I. G. Nolt and A. J. Sievers, Phys. Letters 16, 1103 (1966).

[12] Roland Hanson (private communication).

[13] Preliminary reports of these measurements, covering a smaller temperature range, have been given previously: F. C. Baumann, Bull. Am. Phys. Soc. 9, 644 (1964); A. J. Sievers and R. O. Pohl, in Proceedings of the 4th Conference on Thermal Conductivity, San Francisco, 1964 (unpublished).

[14] R. O. Pohl, Phys. Rev. Letters 8, 481 (1962); V. Narayanamurti, W. D. Seward, and R. O. Pohl, Phys. Rev. 148, 481 (1966).

[15] For this the crystal was heated to 700°C for a few minutes in a Cl₂ atmosphere and quenched by rapidly removing the furnace. The crystal was then mounted in the cryostat and cooled below 0°C in 80 min.

[16] 12 h at 500°C in Cl₂, followed by a cooling at the rate of 40°C/h.

it is desirable to determine its relaxation time. For this we used the Debye model of thermal conductivity[17]:

$$K(T) = \frac{1}{3} \int_0^{\omega_D} \frac{dc}{d\omega} v^2 \tau_{tot} d\omega, \tag{1}$$

where c is the specific heat and v is the velocity of sound of KCl in the Debye approximation. ω_D is the Debye limiting angular frequency,[18] and τ_{tot} is a combined relaxation time determined by

$$\tau_{tot}^{-1} = \sum_i \tau_i^{-1}, \tag{2}$$

where τ_i describes the individual scattering mechanism. This model has been tested in the past[19] and should be particularly valid below 1°K, since in this temperature range the Debye model of specific heat should be a very good approximation. Furthermore, no scattering processes other than the boundary scattering process are active in the pure crystal at these temperatures and this process is quite well understood.[20,21]

A very good description of the experimental data below 1°K was obtained with

$$\tau_{tot}^{-1} = 4.9 \times 10^5 \text{ sec}^{-1} + \frac{nA}{\omega_0^2} \frac{(\omega/\omega_0)^2}{[1 - (\omega/\omega_0)^2]^2}, \tag{3}$$

as shown by the solid lines in Fig. 1. The first term,

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[17] There appears to be considerable confusion about a proper name for this expression. We feel that the important steps in arriving at this formula were made by P. Debye [*Vorträge über die Kinetische Theorie der Materie und der Elektrizität* (B. G. Teubner, Berlin, 1914), p. 46]. He compared the heat flow to a current of particles and introduced the concept of a relaxation time, thus arriving at the famous expression $K = (1/3)cv^2\tau$. The use of a relaxation time tacitly implies that if several scattering processes are active, then Eq. (2) must be used to determine the combined relaxation time. It appears unfair to give anybody special credit for this, except Boltzmann. In connection with conduction phenomena in solids, Eq. (2) was used, for instance, by H. A. Bethe and A. Sommerfeld [in *Handbuch der Physik*, edited by S. Flügge (Julian Springer, Berlin, 1933), 2nd ed., Vol. 24. II, p. 547]. Debye also pointed to the frequency dependence of τ and calculated the first example. He emphasized that a proper theory would have to take this into account. Later, R. Peierls [Ann. Physik **3**, 1098 (1929)] wrote down Eq. (1), using the Debye density of states. For these reasons we believe that the name "Debye model" is the most appropriate one for Eq. (1). The next important step was the correct incorporation of N processes into Eq. (1). This lead to the Callaway model (Ref. 19).

[18] P. H. Keesom and N. Pearlman [Phys. Rev. **91**, 1354 (1953)] determined $\Theta_{KCl} = 233 \pm 3$°K. Recently, W. D. Seward and V. Narayanamurti (Ref. 6) found $\Theta_{KCl} = 229 \pm 2$°K. We therefore chose $\Theta_{KCl} = 230$°K. From this follows $\omega_D = 3.0 \times 10^{13}$ sec^{-1}, corresponding to $\tilde{\omega}_D = 160$ cm^{-1}, and, with the number density of atoms $N = 3.22 \times 10^{22}$ cm^{-3} in KCl, a sound velocity $v = 2.45 \times 10^5$ cm/sec.

[19] J. Callaway, Phys. Rev. **113**, 1046 (1959); R. O. Pohl, Z. Physik **176**, 358 (1963); and R. O. Pohl, Ref. 3.

[20] P. D. Thatcher, Phys. Rev. **156**, 975 (1967).

[21] In fact, the only serious shortcoming left in this approach to the determination of the defect-scattering relaxation time is that it ignores the distinction between transverse and longitudinal phonons. It is hoped that such a distinction will be possible using the time-of-flight method with heat pulses and also ultrasonic attenuation. Both measurements are presently underway at Cornell. S. J. Rogers and D. J. Channin (private communication); H. S. Sack (private communication).
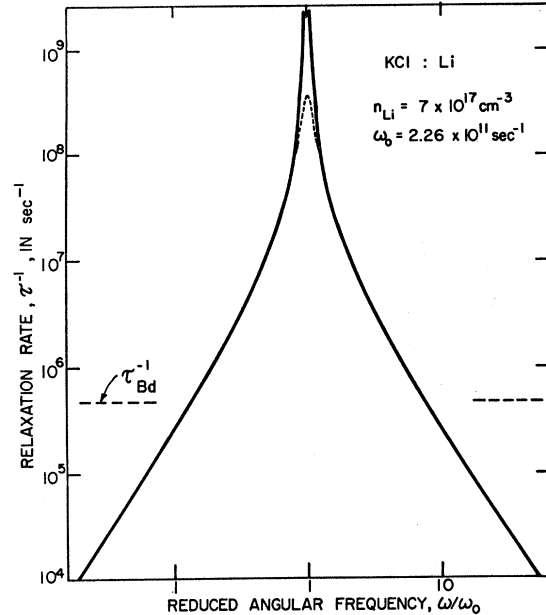

FIG. 2. Resonance relaxation rate of Lorentzian form. The curve shown was used to fit the thermal conductivity of KCl:Li [curve (B) in Fig. 1]. Also indicated is the boundary relaxation rate.

describing the boundary scattering, is very close[22] to that predicted by Casimir's theory;

$$\tau_{Bd,theory}^{-1} = v(1.12d)^{-1} = 4.3 \times 10^5 \text{ sec}^{-1},$$

where d is the width of the sample of square cross section. The additional phonon scattering in the doped samples is described with the second term, a resonant-scattering expression of Lorentzian form. ω_0 is the resonant frequency, n is the lithium concentration,[9] and A is a measure of the scattering strength. The two adjustable parameters ω_0 and A used to fit the three curves (B), (C), and (D) are $\omega_0 = 2.26 \times 10^{11}$ rad sec^{-1}, (1.2 cm^{-1}), and $A = 1.86 \times 10^{12}$ (cm/sec)^3. The two scattering terms from Eq. (3) are plotted in Fig. 2 for the lightest Li doping. This plot demonstrates the breadth of the phonon spectrum which interacts strongly with the defects, and also explains why the thermal conductivity is fairly insensitive to the damping term in the usual Lorentzian resonant denominator;

$$(A/\omega_0^2)(\omega/\omega_0)^2 \{[1 - (\omega/\omega_0)^2]^2 + \Gamma(\omega/\omega_0)^2\}^{-1}.$$

The dashed curve in Fig. 2 was calculated for $\Gamma = 0.07$. For the classical oscillator this Γ means that the energy of the oscillator decreases to 37% in just a little over one period. The influence on the thermal conductivity is unnoticeable, however, because of the narrowness of the band of phonons whose scattering is significantly dependent on Γ. It is for this reason that the damping term was omitted in Eq. (3).

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[22] It has recently been found that the disagreement between experiment and theory for KCl is not caused by residual chemical imperfections; see Ref. 7. See also Ref. 20.
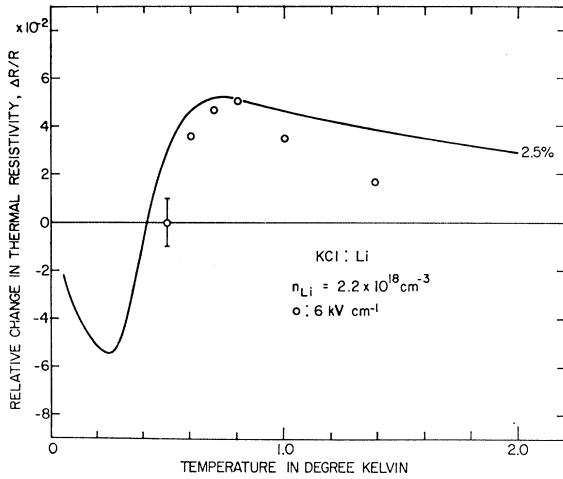
FIG. 3. Preliminary data showing the influence of an applied electric field on the thermal conductivity of KCl:Li. Field applied along ⟨100⟩ perpendicular to the heat flow. Thermal resistivity = (thermal conductivity)$^{-1}$; see Eq. (4).

We have previously associated the resonant frequency with the tunneling motion of the Li$^+$ ion between several equivalent off-center equilibrium positions in the K$^+$ vacancy.[10] Since crystals of KCl:Li show a strong electrical polarizability at low temperatures,[10,23] we expected that the tunneling frequency should be influenced by an applied electric field, resulting in a shift of the "dip" in the conductivity to a
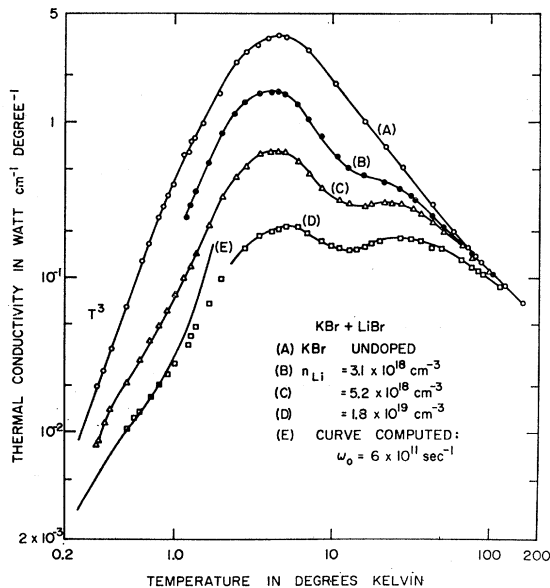

FIG. 4. Thermal conductivity of KBr:Li. The solid lines, with the exception of the T^3 line of the pure KBr below 1°K, and the curve called (E), are not machine fit. Curve (E) was computed using $\omega_0 = 6 \times 10^{11}$ rad sec^{-1}. That it indeed represents the conductivity of crystal (D) was shown with the Stark effect (see Figs. 5–7 and text).

[23] H. S. Sack and M. C. Moriarty, Solid State Commun. **3**, 93 (1965); H. Borgardus and H. S. Sack, Bull. Am. Phys. Soc. **11**, 229 (1966), and to be published.
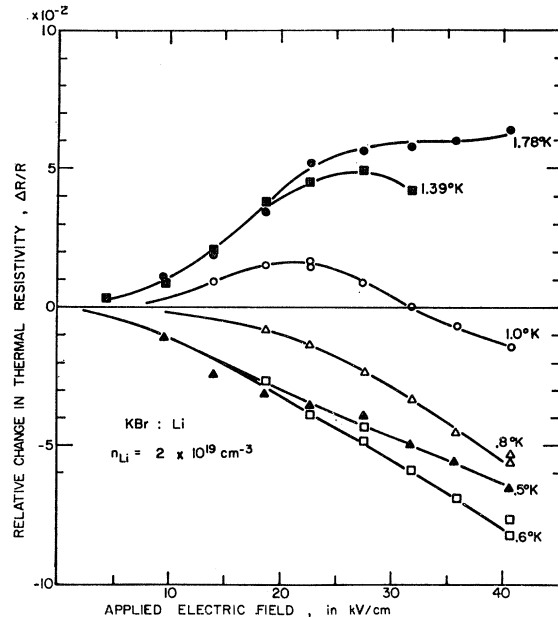
FIG. 5. Influence of an electric field on the thermal conductivity of KBr:Li. Field applied along ⟨100⟩ perpendicular to the heat flow. Curves not machine fitted.

different temperature. Such an effect was indeed observed. Figure 3 shows these data. Here

$$\Delta R/R = [R(E) - R(0)]/R(0), \qquad (4)$$

where $R(E)$ is the reciprocal of the conductivity in an applied field E. Above 0.5°K, the quantity $\Delta R/R$ increases, as would be expected if ω_0 were increased by the electric field. The solid curve in Fig. 3 is the computed $\Delta R/R$ using Eqs. (1) and (3) and resonant frequencies ω_0 and $\omega_E = 1.025\omega_0$.

The computed curve describes the experimental data quite well, giving further support to the picture of the resonant-scattering process [Eq. (3)] and moreover indicates its connection with the polarizability of the Li$^+$ system.

In KBr, too, the lithium causes two depressions in the conductivity curve, one around 1°K, the other around 13°K; see Fig. 4. The low-temperature dip, however, is much less pronounced and one must ask whether this is caused by an overlap with the high-temperature resonant scattering or whether the low-temperature scattering has a more complex cross section than in KCl. The distinction is possible with the help of an electric field applied perpendicular to the heat flow; see Fig. 5. Below 1°K, the field causes a decrease of the resistivity; above 1°K initially an increase, then for large fields a decrease. For a quantitative comparison with the change in the resistivity expected for a shifted resonance, we plot the data as a function of temperature with the field E as parameter; see Fig. 6. Figure 7 shows the change in resistivity computed with Eq. (4) for a resonant frequency shifted by roughly 2, 3, and 4%, respectively. The

field-free conductivity was approximated below 2°K using a Lorentzian scattering cross section as shown in Fig. 4 for curve (D). The relative change in thermal resistivity is very similar indeed to the calculated effect. Hence we conclude that the low-temperature resonant scattering in KBr:Li can also be described with a simple Lorentzian cross section, although it is much weaker than in KCl:Li. The constants are: $\omega_0 = 6 \times 10^{11}$ rad sec^{-1}, (3.2 cm^{-1}) and $A = 1 \times 10^{11}$ (cm/sec)^3.

The high-temperature scattering has practically equal strength in both host lattices. The dip is better resolved in KBr and hence we looked there for an isotope effect by replacing the naturally predominant Li^7 with Li^6. An isotope effect has been detected in KBr in far-infrared absorption.[11] The lighter Li^6 ion absorbs at a frequency about 10% higher than the Li^7. A shift of that magnitude should be detectable in thermal conductivity, too. The theoretically expected change is shown in Fig. 8 as the solid line; see the caption for details. The experimental data, obtained on two samples of almost identical lithium concentration, show (within the experimental accuracy) no isotope effect.

For a detailed discussion of the phonon scattering a determination of the relaxation rate is very important. This was attempted using the model for elastic phonon scattering by a resonant mode. The relaxation rate obtained in a number of different theoretical investigations (see Ref. 3) is always of the same basic form;

$$\tau^{-1} = A\omega^4 / [(\omega_0^2 - \omega^2) + \Gamma\omega^6].$$ (5)

The resonant frequency ω_0 characterizes the frequency range in which the response of the lattice will be a maximum. In neither KCl nor KBr was it possible to describe the high-temperature dip in the conductivity curve with such an expression for a very simple reason. Regardless of the choice of the adjustable parameters or even of the power laws, a purely frequency-dependent scattering term can never produce a conductivity
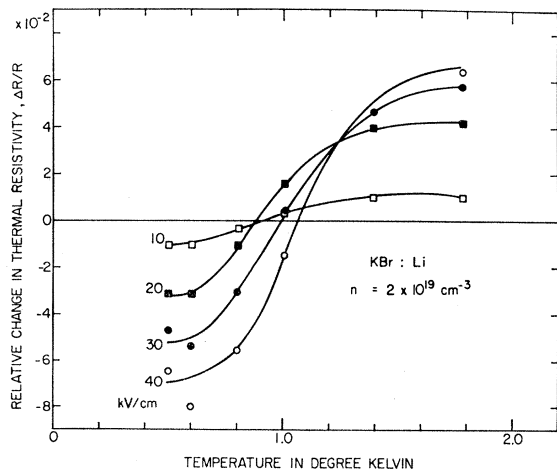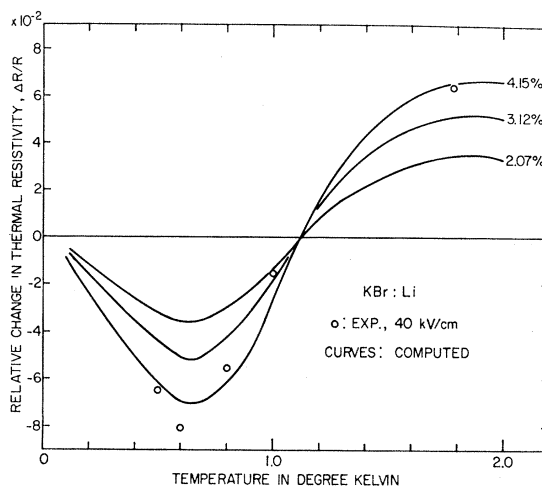

FIG. 7. Computed change of relative thermal resistivity assuming that the electric field increases the zero field splitting $\delta(0)$ by 2, 3, and 4%, respectively. The 40-kV/cm data are shown for comparison. The agreement is reasonably good. Note, however, that the computed curves all cross at the same temperature, in contrast to the experimental results. This is an indication that the assumptions of a two-level system and a transition matrix element independent of E are inadequate.

changing as rapidly with temperature as observed experimentally. Even relaxation rates containing cutoff or δ functions produce only slowly varying curves. This is a consequence of the broad spectrum of phonons, important in carrying the heat at any given tempera-
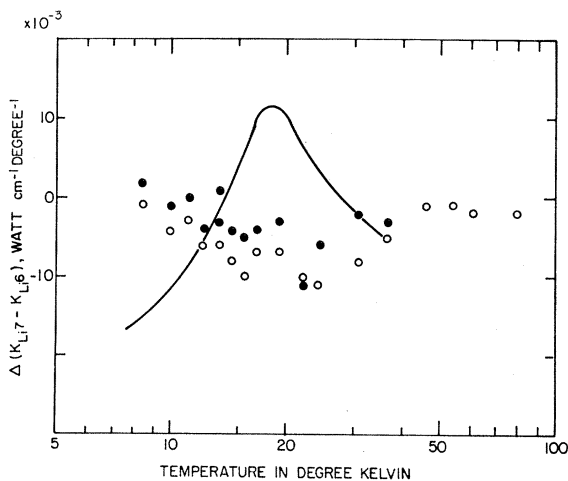

FIG. 6. Some data as in Fig. 5, with applied field as parameter.

FIG. 8. Search for isotope effect of the high-temperature resonance. Under the assumption that the dip in the conductivity in KBr:Li^6 would occur at a temperature 10% higher than in KBr:Li^7, $\Delta(K_{Li^7} - K_{Li^6})$ was determined by shifting curve (D) of Fig. 4 up to higher temperatures by 10%. The difference between this conductivity and the conductivity of the (un-shifted) curve (D) shows a pronounced peak at 20°K (solid curve). The experimental data, taken with two different pairs of thermometers (solid and open circles), are the difference in conductivity between two samples of KBr, one with Li^6, the other with Li^7 [curve (D)]. These data do not show the expected peak. Their scatter is a measure of our experimental accuracy in this temperature region ($\sim 3\%$). The data do not scatter around the zero line: The crystals did not have exactly identical Li concentrations.

ture. The description of the observed rapid variation with temperature requires an additional temperature dependence of the relaxation rate. Such a temperature dependence is found in the theory dealing with inelastic phonon scattering by impurity modes[2] (i.e., scattering by 3-quantum processes), although even this theory results in "dips" in the conductivity of considerable breadth.[1] We therefore conclude that the relaxation rate for the high-frequency resonances is not known. Inelastic scattering is a possible explanation, but the number of freely adjustable parameters reduces the usefulness of this theory. Furthermore, we believe that a modification of the intrinsic phonon-phonon scattering processes due to the point defects, i.e., a breakdown of the relaxation-time approximation, needs careful consideration.

At the present we shall limit our efforts to a determination of the resonant frequency ω_0. On a number of phonon resonances observed at low temperatures, where machine fits to the data using a Lorentzian scattering rate could be made, a simple connection was found between ω_0 and the temperature T_0, which was defined as the temperature at which the tangents drawn to the curve above and below the dip intersect;

$$\hbar\omega_0 = 4.25kT_0. \tag{6}$$

This means, for instance, that $1°K$ corresponds to 3 cm^{-1} in the wave-number measure. The relation (6) was found to be accurate to within 10%. In the system $RbCl:CN$, a thermal conductivity almost identical to that observed on $KCl:Li$ (Fig. 1) was found (see Pohl[3]). The high-temperature resonant scattering could therefore again not be fit with a Lorentzian scattering rate. Yet the origin of this scattering is believed to be the onset of free rotation of the molecule ion in its cavity,[6] and the energy $\hbar\omega_0$ between the vibrational ground state and the barrier height of the Devonshire potential is known from IR spectroscopy. Even for this case, relation (6) was found to hold. We therefore assume that relation (6) can also be used for resonances occurring in the temperature region where phonon-phonon processes are important. Thus we determine the resonance frequencies 1.19×10^{12} rad sec^{-1} (63 cm^{-1}) and 7.35×10^{11} rad sec^{-1} (39 cm^{-1}) for KCl and KBr, respectively. In a paper dealing with other alkali and halogen impurities in the potassium salts[24] a different proportionality factor was chosen, namely, 3.4, which means that $1°K$ corresponds to 2.4 cm^{-1}. This was based on the success which the model of elastic phonon scattering has had in describing resonances caused by heavy impurities. We refer the reader to this paper.[24] In the context of the present paper it is enough to realize that the determination of a resonance frequency ω_0 from a dip in a thermal-conductivity curve is connected with considerable uncertainty, unless the form of the phonon-defect relaxation rate is precisely

known. From our experience we expect this error to be about $\pm 20\%$.

IV. DISCUSSION

The data shown in Figs. 1 and 4 demonstrate beyond any doubt that at least for these cases the phonon scattering by point defects characterized by different mass, volume, and force constant is not of the Rayleigh type, but rather of the resonance type. If this resonance scattering occurs in a temperature region in which anharmonic (U and N) processes are unimportant, the scattering cross section has the particularly simple form of a Lorentz resonance denominator, a form found first in the case of molecular impurities.[14] This raises two questions: What is the simplest description of the resonant states, and what is their scattering mechanism?

We begin our discussion with the most striking of the resonances, the lower one in KCl. Its frequency is smaller than one hundredth of the Debye frequency. The phonon scattering scales with the concentration; hence we associate it with individual Li^+ ions in random distribution. How can an individual atom cause a resonance of such a low frequency? One possibility is a modification of the low-frequency modes of the pure crystal, i.e., the defect has to influence modes of long wavelength which requires that binding forces over hundreds of lattice sites be softened moderately, and this is very unlikely to be caused by a single defect. Alternatively, a few binding forces in the immediate vicinity of the defect could be so drastically softened that a new low-frequency mode is created around the defect. The only atom in these crystals for which this could possibly occur is the Li^+ ion itself.[25] But this would require an unreasonable softening of the force constants, as one can easily estimate using a method employed by Sievers and Takeno[11] to calculate the force-constant change required to produce the IR-active low-frequency mode observed by them in $KBr:Li^7$ at $\omega_0 = 3.06 \times 10^{12}$ rad sec^{-1} (16.3 cm^{-1}). Considering nearest-neighbor forces only and using the Debye approximation to evaluate the Green's function of the defect lattice, they obtained for the angular frequency ω_0 of the S-like (A_{2u}) vibrational mode associated with the motion of the impurity

$$(\omega_0/\omega_D)^2 = (1+\mu)/(3\lambda + \lambda\mu - 2\mu). \tag{7}$$

Here $\lambda = (M'/M) - 1$ and $\mu = (K'/K) - 1$, in which M' is the mass of the impurity, K' is the nearest-neighbor force constant, and M and K are the same quantities for the pure lattice, which is assumed to be simple-cubic monatomic. $\omega_D = 12K/M$ is the maximum frequency of the pure lattice (Debye frequency). Solving Eq. (7) for K'/K in the limit of $K'/K \ll M'/M$, we obtain

$$K'/K = 2(M'/M)(\omega_0/\omega_D)^2; \tag{8}$$

[24] F. C. Baumann and R. O. Pohl, Phys. Rev. (to be published).

[25] The possibility of a considerable softening because of the smallness of the Li^+ ion had been suggested to us first by J. A. Krumhansl and C. T. Walker (private communication).

hence, for the low-frequency resonance in KCl:Li, $K'/K = 2 \times 10^{-5}$. Such a softening appears unreasonable because it would imply an extremely delicate balance of forces which would be too easily upset by minute fluctuations and irregularities in the interatomic potential.

If the Li ion is considered as a particle placed in a cubic square-well potential, its energy-level spacings would indeed be of the order of 10^{-4} eV (1 cm^{-1}). But in this case a large number of low-lying states are expected, in contrast to our observations.

On the other hand, low-temperature phonon resonances have also been observed with molecular impurities and have been explained through an excitation of tunneling states by the phonons.[6] This tunnel splitting arises because the molecule (a CN$^-$ ion in the case of Ref. 6) can perform libration around several equivalent orientations in the crystal[26] (the six $\langle 100 \rangle$ directions of the host alkali halide in the case of the CN$^-$). In order to explain the 1.2 cm^{-1} resonance in KCl:Li with a similar tunnel splitting, a central instability of the Li$^+$ ion has been postulated, such that the potential has a maximum at the center of the K$^+$ vacancy, and several equivalent minima in certain crystal directions.[10] This model was confirmed with measurements of the low-temperature dielectric constant[23] and by the observation of an electrocaloric effect.[10] It was found that, using a classical dipole picture, the x coordinates of the equilibrium positions of the Li$^+$ are 0.53 Å away from the cavity center.[10] A schematic one-dimensional model of the potential is shown in Fig. 9(a). The higher states are those of a one-dimensional oscillator, whereas the lower states are split because of tunneling.

We tentatively ascribe the broad absorption band observed by Sievers[27] in the infrared at 40 cm^{-1} to transitions to the first oscillatory state from the tunnel-split ground state.

Byer and Sack have recently studied the propagation velocity of acoustic waves ($f = 3.10^7$ sec^{-1}) as a function of polarization, direction of propagation, and tempera-
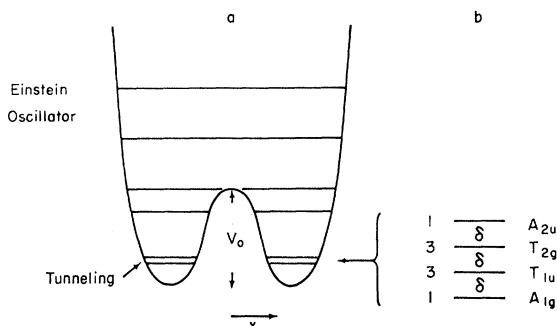

FIG. 9. (a) Schematic one-dimensional potential for an off-center ion. Note that the x coordinate describes a translation, not a rotation. As a result the potential rises high near the cavity wall. The number of tunneling levels will depend on the number of equivalent wells. (b) Tunnel splitting predicted for the oscillatory ground state if the ion finds eight equivalent potential minima in the eight $\langle 111 \rangle$ directions. Degeneracies and symmetries are also indicated. After Refs. 30 and 31. Note that in these calculations an asymmetric relaxation of the nearest neighbors is ignored; see text.

ture from 1.6 to 70°K.[28] They have been able to interpret their results with the model of classical elastic dipoles with $\langle 111 \rangle$ orientations. A quantum-mechanical discussion of this effect and also its concentration dependence is presently in progress,[29] but it is assumed that it will not change the most important conclusion, namely, that the potential minima lie in the eight $\langle 111 \rangle$ orientations.[28] If the potential is approximated through eight equivalent spherical harmonic wells located in the $\langle 111 \rangle$ directions at the corners of a cube, the vibrational ground state can be shown[30,31] to consist of four states of equal separation δ, with degeneracies and symmetries as shown in Fig. 9(b). The tunnel splitting δ has been deduced by Bogardus and Sack from an extension of earlier work[23] on the low-frequency dielectric constant of KCl:Li to lower temperatures to be $\delta = 0.75$ cm^{-1}. This value is in agreement with measurements of the real and imaginary part of the dielectric constant determined in the microwave region by Lakatos and Sack,[32] which these authors interpret with transitions between adjacent states and a tunnel splitting of $\delta = 0.81$ cm^{-1}.

The tunneling states were detected by Wielinga et al.,[33] who measured the specific heat of a KCl sample containing 5.8×10^{18} cm^{-3} lithium ions between 0.18 and 2°K. A reasonable fit to their data could be ob-

[26] The situation is very similar to that of the NH$_3$ gas molecule, where the nitrogen can vibrate on either side of the triangle formed by the hydrogen atoms, resulting in a so-called inversion splitting: The ground state of the vibration (950 cm^{-1}) is tunnel split by 0.8 cm^{-1}. The phenomenon of tunnel splitting was predicted and discussed for various gas molecules, including NH$_3$, by F. Hund [Z. Physik **43**, 805 (1927)] and was first used by D. M. Dennison in a paper by E. F. Barker [Phys. Rev. **33**, 684 (1929)] to explain Barker's near-IR data on NH$_3$. See also D. M. Dennison and J. D. Hardy, Phys. Rev. **39**, 938 (1932); D. M. Dennison and G. F. Uhlenbeck, *ibid.* **41**, 313 (1932). The tunnel splitting in gaseous NH$_3$ was first found in microwave absorption by C. E. Cleeton and N. H. Williams, Phys. Rev. **45**, 234 (1934). For references to more recent work we refer to C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

[27] A. J. Sievers, in Elementary Excitations and their Interactions in Solids, NATO Advanced Study Institute Cortina d'Ampezzo, Italy, 1966 (unpublished); Instituto Documentazione Associaz. Meccanica Italiana, Milano, 1966, p. VI-47 (unpublished).

[28] N. E. Byer and H. S. Sack, Phys. Rev. Letters **17**, 365 (1965).

[29] J. A. Krumhansl (private communication).

[30] J. A. D. Matthew, Solid State Commun. **3**, 365 (1965); S. P. Bowen, M. Gomez, J. A. Krumhansl, and J. A. D. Matthew, Phys. Rev. Letters **16**, 1105 (1966); M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. **153**, 1009 (1967).

[31] M. E. Baur and W. R. Salzman, Phys. Rev. **151**, 710 (1966).

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

[33] R. F. Wielinga, A. R. Miedema, and W. T. Huiskamp, Physica **32**, 1568 (1966); J. P. Harrison and P. Peressini (to be published). A specific-heat anomaly associated with impurity modes was predicted by Yu. Kagan and Ya. Iosilevskii, Zh. Eksperim. i Teor. Fiz. **45**, 819 (1963) [English transl.: Soviet Phys.—JETP **18**, 562 (1964)].

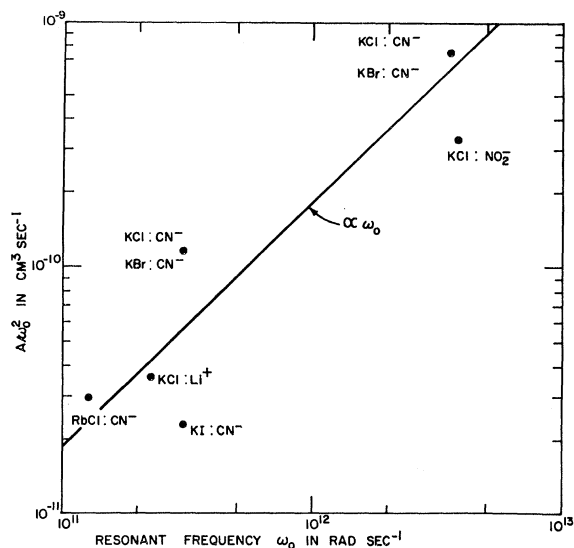FIG. 10. Dependence of the "scattering strength" A [Eq. (3)] on the resonance frequency ω_0. In first approximation A appears to be proportional to $\omega_0{}^3$ for the systems studied. The only exception so far is for KBr:Li; see text. Points are taken from Refs. 6, 14, and 24.

tained by assuming a Schottky specific-heat anomaly consisting of six singly degenerate states split by $\delta = 0.7$ cm^{-1}.

Several authors have attempted to construct a potential surface from these experimental data. The most detailed model was proposed by Dienes et al.,[34] who found that in the KCl lattice in which the nearest-neighbor Cl$^-$ ions were allowed to relax around the Li$^+$, the energy of the lattice had a minimum for the Li$^+$ displaced in the $\langle 111 \rangle$ directions, whereas maxima were found for $\langle 110 \rangle$ displacements. The difference in energy was found to be 56 cm^{-1}. For a motion from $\langle 111 \rangle$ to $\langle \bar{1}\bar{1}1 \rangle$, a barrier height of 2000 cm^{-1} was found. In $\langle 100 \rangle$ the potential is assumed to have a saddlepoint: According to these calculations (and also to the ones discussed in Ref. 30) the ion should avoid the center of the cavity, and its motion should be a quasirotation along the edges of a cube about 1 Å wide whose center coincides with the center of the cavity. The similarity between the motion of the molecular and the monatomic impurities is demonstrated experimentally not only by the shape of the thermal-conductivity curves, but also by a comparison of the so-called scattering strength A from Eq. (3), for both kinds of defects. The scattering strength A for Li in KCl agrees very well with the empirical relation $A\omega_0{}^{-3} = 1.8 \times 10^{-22}$ cm^3 found for the tunneling states and for the states of free rotation of molecular impurities, as demonstrated in Fig. 10.

One might try to associate the high-temperature resonance in KCL:Li at 63 cm^{-1} with the scattering of phonons which excite the Li$^+$ to states near the potential barrier, again in analogy to the phonon scattering by states of free rotation in the case of molecular impurities.[6] This would place the potential barrier between neighboring $\langle 111 \rangle$ wells at $(1/2) \times 40$ cm^{-1} $+ 63$ cm$^{-1} = 83$ cm^{-1}, where the IR-active impurity mode[27] has been used to locate the tunneling states in the well. In view of the crudeness of the models available so far, the agreement with the value obtained from machine computation[34] (40 cm^{-1}) appears reasonable. Finally, we note that this tunneling model can explain the breadth and shape of the IR absorption band.[27] The first-excited state of the Li oscillator state should be split, too, and these splittings should be considerably larger than that of the ground state. Consequently one expects a number of transitions spread over a wide range in energy.[35]

After having presented the picture of the tunnel-split ground state, we must ask where precisely the resonant frequency of 1.2 cm^{-1} derived from thermal conductivity fits in. Because of the breadth of the phonon spectrum involved in carrying the heat at any given temperature, it is quite likely that the relaxation rate shown in Fig. 2 is a composite of several transitions, with $\omega_0 = 1.2$ cm^{-1} being only an average. Indeed, one would expect several if not all of the tunnel states to couple to the phonons. It is possible to fit the data of Fig. 1 with a relaxation time which is a composite of a number of Lorentzian expressions with resonance frequencies ranging between δ and 3δ. This procedure is not advisable at present, however, because too many adjustable parameters (the A's) would be involved. We therefore postpone such an analysis until we have gathered more details about the influence of an electric field on the conductivity.[36] But even at this stage, one definite conclusion can be drawn from our data: At the lowest temperatures ($kT \ll \delta$) only the ground state will be populated. Its phonon-scattering cross section is proportional to ω^2 at low frequency ($\hbar\omega < 0.5\delta$); see the computed curves at low temperatures, Fig. 1. In the long-wavelength limit, defects of atomic dimensions must scatter proportionately to ω^4, no matter what the scattering law is at high frequencies.[37] An ω^4 dependence, on the other hand, can definitely not fit the data. This is a very important result which cannot be discussed until more data on the specific-heat anomaly of the tunnel states become available; from these data, information about lifetimes and line shapes are expected. It is therefore premature to attempt any guesses as to the nature of the scattering cross section and the scattering mechanism, and we simply restate the finding

[34] G. J. Dienes, R. D. Hatcher, R. Smoluchowski, and W. Wilson, Phys. Rev. Letters **16**, 25 (1966); R. D. Hatcher and W. Wilson (private communication); Bull. Am. Phys. Soc. **12**, 351 (1967). The earlier calculations for the $\langle 100 \rangle$ directions were found to be unreliable and hence the question whether the potential in $\langle 100 \rangle$ has a saddle point cannot be decided with certainty. [R. D. Hatcher and W. Wilson (private communications)].

[35] This explanation was suggested independently by S. P. Bowen and J. A. Krumhansl (private communication), and by H. Dreizler (private communication).

[36] J. P. Harrison and P. Peressini (private communication).

[37] This was pointed out to us by Dr. W. Ludwig and Dr. C. M. Wagner.

that a relaxation rate of Lorentzian form, as given in Eq. (3), does fit the data.

The thermal conductivity of KBr:Li is similar to that of KCl:Li. Hence the same model for the resonances suggests itself, with a tunnel splitting δ between 2 and 3 cm^{-1} (Fig. 9). The far-IR data of Sievers and Takeno,[11] however, cast doubt on such an interpretation. The absorption band at 16.3 cm^{-1}, which was explained as an oscillation of the Li$^+$ ion in the K$^+$ vacancy, showed no evidence for a fine structure of the ground state of magnitude δ. Less direct evidence against a quasirotational tunneling motion comes from the strength of the low-temperature scattering. The quantity A falls by about a factor 300 below the line found for the other resonant-scattering processes; see Fig. 10. If we want to associate the low-temperature resonance with the same Li$^+$ ions which cause the IR absorption, we have to look for a different model. The most questionable assumption underlying the tunneling model is that the asymmetric position of the impurity itself does not change the symmetry of the nearest-neighbor position.[38] For the bromine ions, which are more polarizable than the chlorine ions, this assumption may be fatal. The Li$^+$ ion may well experience a central instability similar to that in KCl, but the six Br$^-$, because of their high polarizability, rearrange around the Li$^+$ so that this ion still finds itself in an essentially octahedral (nearest) neighborhood. Therefore the stress-induced dichroism observed by Nolt and Sievers[11] can be explained assuming that the Li$^+$ is in a symmetric environment. Yet the lithium ion plus its six nearest neighbors can rearrange with respect to the rest of the lattice, and this motion of the LiBr$_6$ molecule is what is observed as the low-temperature resonance. This resonance can be influenced by an electric field, hence the Stark effect; see Figs. 6 and 7. In the very simplest quantum-mechanical model the level splitting will be $\propto E^2$ for small fields, and $\propto E$ for large fields. We therefore use as the splitting the following expression:

$$\delta(E) = [\delta^2(0) + (2\mu E)^2]^{1/2}. \qquad (9)$$

Reasonable agreement between calculated and observed relative change in thermal resistivity is obtained for $E_{\text{appl}} = 4.0 \times 10^4$ V/cm, if $\delta(E_{\text{appl}})/\delta(0) = 1.0415$ is chosen; see Fig. 7. Using the Lorentz local-field correction, $E_{\text{loc}} = \frac{1}{3}(\epsilon + 2)E_{\text{appl}}$, with $\epsilon = 4.5$, we obtain the dipole moment $\mu = 0.3$ Debye $= 0.06e$ Å, where e is the electronic charge. Such a dipole moment is not in disagreement with the absence of an electrocaloric

effect reported.[39] Because of the large splitting $\delta(0)$, cooling can be expected to occur only at temperature comparable to $\delta(0)/k$, i.e., 4°K and above, and there 0.3 Debye with the concentrations used and the maximum E that can be applied produces negligible cooling ($<10^{-3}$°K). We note in passing that the above calculations will vary slightly, depending on whether a 6, 8, or 12 well potential is used, but this is unimportant for the rough estimate presented here.

Before discussing this model in greater depth, it appears that the question must be settled whether the 3.2 cm^{-1} resonance is indeed caused by the dissolved Li ions, or whether only a fraction of them, or even some impurities which happen to scale with the Li concentration, are its cause. In the second case the weakness of the scatter could then be explained through the small concentration. A determination of the total entropy from specific-heat measurements should give the clue (see, for instance, Ref. 6). We believe, however, that such asymmetric rearrangements of nearest-neighbor ions is something one must seriously consider in any attempt to calculate impurity modes, and not only asymmetric positions of the impurity ion itself.

Finally we consider the high-temperature resonance at 39 cm^{-1}. It cannot be explained as a $\Delta n = 2$ transition of the infrared-active Einstein oscillator, because it does not show an isotope effect. Therefore it must be attributed to an impurity mode involving motions of the neighboring atoms, but we postpone the discussion as to which mode this may be to a forthcoming paper.[24] The similarity between the high-temperature conductivity in KCl:Li and KBr:Li suggests that a similar mode might be excited in KCl:Li too, rather than a jumping of the Li$^+$ over the potential barrier.

ACKNOWLEDGMENTS

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[38] A change in symmetry of the nearest-neighbor ions surrounding a molecular object has been suspected before. See Narayanamurti et al., Ref. 14. See also the recent discussion of this effect by H. B. Shore, Phys. Rev. Letters **17**, 1142 (1966).

[39] G. Lombardo and R. O. Pohl, Bull. Am. Phys. Soc. **11**, 212 (1966).