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Investigation of Tunneling States Using the Spin-Phonon Interaction. I. Experiment[*]

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Phonons in KCl doped with small amounts of LiCl or KCN are known to be strongly scattered at discrete energies by tunneling states of the impurity ions. The effect of a magnetic field on the low-temperature thermal conductivity of doped KCl containing *R* centers was used to study this resonant scattering of phonons by CN^- and $^6Li^+$ impurity ions. By means of this technique it was possible to resolve the tunneling resonance in KCl:CN^- into two components. The resonant energies were 1.1 and 2.0 cm^{-1}. The resonances in KCl:^{6}Li were found to consist of three components: 1.0, 1.72, and 2.70 cm^{-1}. The effect of an applied electric field in the ⟨100⟩ direction on the tunneling resonances of the Li ion was measured in fields of up to 12 kV/cm. The Devonshire model with potential minima for ⟨100⟩ orientations was applied to CN^- ions in KCl. Good agreement between the predicted and measured tunneling energies was obtained with model parameters which also agree with the results of studies using other techniques. The observed tunneling energies of the ^{6}Li ion were compared with the XY_8 tunneling model of Gomez, and values of the tunneling parameters were deduced from the measured energies. The variations which were observed in the level spacing imply that although tunneling along the cube edge predominates, a significant amount takes place through the center of the unit cell, but that face-diagonal tunneling is negligible within experimental error. Using certain approximations to calculate the tunneling parameters from specific model potentials, agreement could be obtained between the measured energy levels and the levels of the XY_8 tunneling model. Agreement with the observed levels could not be obtained using an elliptical potential well. The measured effects of an electric field on the resonances of the KCl:^{6}Li system are consistent within experimental error with the predictions of the XY_8 tunneling model and with the results of measurements using other techniques.

INTRODUCTION

The work reported here makes use of low-temperature measurements of thermal conductivity to investigate properties of impurity ions in KCl. The standard treatment of the theory of thermal conductivity in insulators can be found in Refs. 1–3. The result is that the thermal conductivity is given by the following expression:

$$K=\frac{V}{6\pi^2}\int_0^{k_{\max}}\tau(k)\,h\omega_{k\lambda}\,\frac{\partial n^0_{k\lambda}}{\partial T}\,v^2_{k\lambda}\,k^2\,dk, \tag{1}$$

where $\omega_{k\lambda}$ is the frequency of photons of wave vector k and polarization λ, $v_{k\lambda}$ is the group velocity, $n^0_{k\lambda}$ is the Bose-Einstein distribution function, $k_{\max}$ is the effective radius of the Brillouin zone, and $\tau(k)$ is a suitably averaged relaxation time.

Information about the interaction of the phonons with defects or impurities in the lattice is contained in the dependence of the relaxation time τ on the wave number k and on temperature T. Equation (1) may be put in a form which is more convenient for judging the effect of τ as a function of k (or ω) and T:

$$K=\frac{k_B^4T^3}{2\pi^2\hbar^3v}\int_0^{\Theta/T}\tau(\omega)\,\frac{x^4e^x}{(e^x-1)^2}\,dx\ , \tag{2}$$

where Θ is the Debye temperature and $x=h\omega/kT$.

The function $x^4e^x/(e^x-1)^2$ has a broad peak with maximum value at $x\approx 4$. Thus, the value of τ at frequencies around $\hbar\omega=4k_BT$ is seen to dominate the integral in Eq. (2). If τ varies slowly with frequency, then Eq. (2) implies that

$$K=\frac{k_B^4T^3}{2\pi^2\hbar^3v}\,\langle\tau\rangle_{x=4}I, \tag{3}$$

where

$$I=\int_0^{\Theta/T}\frac{x^4e^x}{(e^x-1)^2}\,dx\rightarrow\frac{4\pi^4}{15}\quad\text{as}\quad\Theta/T\rightarrow\infty,$$

and where $\langle\tau\rangle_{x=4}$ is the value of τ averaged over the neighborhood of $h\omega=4k_BT$. From Eq. (3) it is seen that as the temperature is changed the thermal conductivity varies as the product $T^3\langle\tau\rangle_{x=4}$ so that the thermal-conductivity measurements as a function of temperature yield information about the frequency and temperature dependence of τ. It is obvious that the resolution of this method is determined by the width of the function $x^4e^x/(e^x-1)^2$ and is on the order of $\Delta(\hbar\omega)=4k_BT$.

The relaxation-time approximation assumes that each of the different scattering mechanisms is characterized by a relaxation time τ_i. The assumption is made also that the scattering rates,

$$\left(\frac{\partial n_{k\lambda}}{\partial t}\right)_{\text{scat}}=\sum_i\frac{n^0_{k\lambda}-n_{k\lambda}}{\tau_i}\,,$$

where $n^0_{k\lambda}$ is the value of $n_{k\lambda}$ at equilibrium, are combined for the different processes by simple addition as if each process acted independently of the others in moving $n_{k\lambda}$ towards its equilibrium value. This approximation amounts to assuming independent scattering probabilities for each process. The validity of combining the individual relaxation times by the equation

$$\tau^{-1}=\sum_i \tau_i^{-1} \tag{4}$$

has been investigated both experimentally and theoretically.[2,4,5] At the temperatures of interest in this work, Eq. (4) appears to be the proper way to combine the effects of different scattering processes.[4,6]

In nearly pure crystals at low temperatures the important phonon scattering processes are of several distinct types. The most important phonon scatterer in long thin specimens at sufficiently low temperatures is the boundary of the sample itself.

One may calculate the thermal conductivity of pure KCl at low temperatures by combining relaxation times due to boundary scattering and point defects using the Casimir[7] expression for the former and a Rayleigh scattering law[4] to account for the latter:

$$\tau_{\text{pure}}^{-1}=v/L+A\omega^4. \tag{5}$$

At higher temperatures phonon-phonon scattering must be accounted for. This process becomes very important[3] at temperatures approaching $\frac{1}{20}$ of Θ, the Debye temperature, but will be ignored here since the temperatures are always below 2 °K, and $\Theta = 230$ °K.

In some cases the impurity scattering law may contain resonances where the cross section becomes very large at discrete frequencies.[4] In particular, the CN^- ion[8] and the Li^+ ion[6] in KCl cause such resonant scattering to occur. Several other insulator: impurity systems also require resonant scattering terms in the relaxation time in order to fit the thermal conductivity.[9]

Because the width of the carrier spectrum is so much larger, in general, than that of the resonance, it is very difficult to interpret measurements of the conductivity as a function of temperature. In fact, even the resonance frequency deduced from such experiments will depend on the function assumed for $\tau^{-1}(\omega)$.[10]

Paramagnetic Impurities and Phonon Spectrometry

Walton[11] has introduced a technique for using a paramagnetic impurity in the lattice to determine the presence of resonant scattering of phonons. The method allows the resolution of resonances with much smaller separations than can be resolved by the methods discussed above.[12]

The technique is simple to understand on a qualitative basis. If a magnetic impurity in the lattice is subjected to a magnetic field, its ground state is split into a number of states whose separation depends on the magnitude of the magnetic field H. For simplicity consider a magnetic impurity of spin $\frac{1}{2}$. There are two states of this impurity with the z component of spin equal to $-\frac{1}{2}$ and $+\frac{1}{2}$, respectively. A magnetic field H in the z direction splits these two states by an energy $\Delta E = g\mu_B H$ where g is the Lande g factor and μ_B is the Bohr magneton. For a free electron $g\approx 2.0$, and for magnetic impurities where the orbital contribution to the magnetic moment is zero the g value is essentially that of the free electron. If a magnetic field in the z direction is applied to the sample containing magnetic impurities of spin $\frac{1}{2}$, then the separation of the $S_z=+\frac{1}{2}$ and $S_z=-\frac{1}{2}$ states is just $\hbar\omega_0$, where ω_0 is the Larmor frequency defined by

$$\hbar\,\omega_0=g\mu_B H. \tag{6}$$

If the interaction of the spins with the lattice is strong enough, the phonons with $\omega\approx\omega_0$ will be absorbed and reemitted by flipping the spins. The effect of this process is to scatter very strongly phonons in a band centered at ω_0.

One may approximate the effect on the thermal conductivity by assuming that phonons in a band of width $\Delta\omega$ at ω_0 simply do not contribute to the thermal-conductivity integral in Eq. (2). This assumption is equivalent to postulating that the effect of the magnetic scattering is given by a relaxation time:

$$\tau_{\text{mag}}(\omega)=\begin{cases}\infty, & \omega<\omega_0-\frac{1}{2}\Delta\omega\\ 0, & \omega_0-\frac{1}{2}\Delta\omega<\omega<\omega_0+\frac{1}{2}\Delta\omega\\ \infty, & \omega_0+\frac{1}{2}\Delta\omega<\omega.\end{cases}$$

The effect of eliminating the phonons in a narrow band $\Delta\omega$ is seen from Eq. (2) to be[11]

$$\Delta K=K(\omega_0)-K(0)=-\frac{k_B^4T^3}{2\pi^2\hbar^3 v}\,\tau(\omega_0)\,\frac{x^4e^x}{(e^x-1)^2}\,\frac{\hbar\Delta\omega}{k_BT}\,, \tag{7}$$

where $x_0=\hbar\omega_0/k_BT$ and $\tau(\omega_0)$ is the relaxation time of the nonmagnetic scattering. Since ω_0 varies directly with magnetic field, we see that by sweeping the magnetic field at a constant temperature we should produce a change in the thermal conductivity which behaves as $\tau(\omega_0)$ multiplied by a function which depends on the distribution of the phonons, and by $\Delta\omega$ which also depends on ω_0.[12] If there are resonant scattering terms in $\tau(\omega)$, the magnitude of ΔK should show more or less sharp decreases at magnetic fields where ω_0 is equal to the resonant frequencies.

The function multiplying $\tau(\omega)$ in Eq. (7) depends on the frequency or energy distribution of phonons and has a maximum at an energy $h\omega$ corresponding to $\hbar\omega_T\approx 4k_BT$. The dips in $-\Delta K$, corresponding to resonances at $\hbar\omega_i$, should therefore be strongest

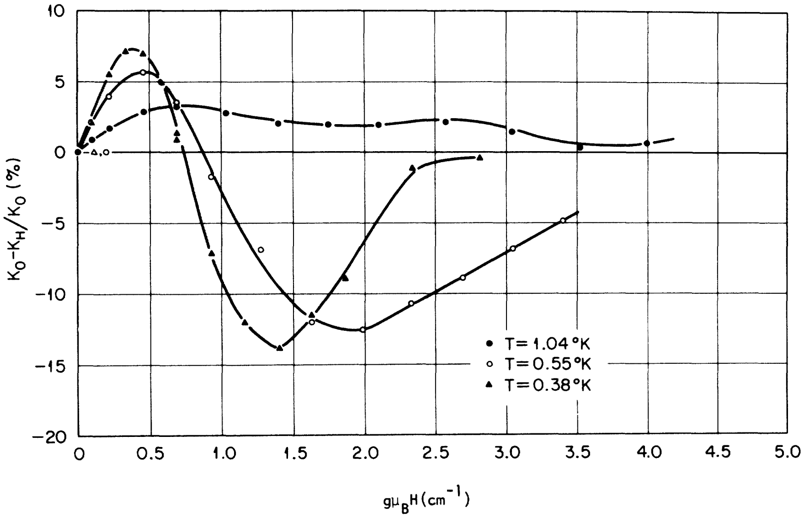

FIG. 1. Effect of a magnetic field on the thermal conductivity of pure KCl. The sample was γ irradiated for 10 h at 77 °K and bleached for 30 min before being mounted.

for temperatures such that $\hbar\omega_T \approx \hbar\omega_i$ and weaker at higher or lower temperatures.

An understanding of the behavior of the effective magnetic scattering width $\Delta\omega$ is crucial to any attempt to retrieve quantitative information about $\tau^{-1}(\omega)$ from the field dependence of ΔK. Unfortunately, if the magnetic impurity is strongly coupled to the lattice, its levels will also be split by static strains. This provides an effective contribution to $\Delta\omega$ which is very difficult to take into account. Nevertheless, even in this case it is still possible to identify individual resonances since $\Delta\omega$ can usually be made smaller than the width of the resonance.

The magnetic impurity used as a probe in the measurements reported here is a color center, the R center. It is formed on optically bleaching KCl colored by γ irradiation at low temperatures.[12] An R center is formed by the combination of three F centers which are single Cl^- vacancies occupied by electrons. The qualitative approach given above indicates how the R center may be used as a probe to find and measure phonon resonances in KCl. The g value for the R center is approximately 2.0[13] and therefore $\hbar\omega_0$ is 4.7 cm^{-1} at $H = 50$ kOe. The corresponding temperature for which $\hbar\omega_0 = 4k_B T$ is around 1.7 °K. The R center should, therefore, be useful as a probe for the measurement of phonon resonant scattering for energies up to 5 cm^{-1}, and the measurements should be made at temperatures less than 2 °K.

The R center differs from the ideal probe in several respects which must be kept in mind when the measurements are interpreted using Eq. (7). The R center is strongly coupled to the lattice. While this strong coupling is necessary in order to obtain a measurable effect, in addition to broadening the resonance, it leads to a zero-field splitting of the R-center ground state.[13] This zero-field splitting leads to an effective zero shift in the energy scale. The existence of this zero-field splitting is shown by the existence of phonon scattering by the R center at zero magnetic field. The data shown in Fig. 1 illustrate this point. The data were taken with pure KCl under the same conditions as the data on doped specimens which will be presented. The existence of zero-field scattering is shown by the fact that the thermal conductivity can be improved by the application of a magnetic field to the sample. The cause of the upturn in the curves at high fields (decrease of the conductivity), which begins at lower fields as the temperature decreases, is not understood. Since the existence and position of resonances in phonon scattering must be judged by comparing the data on doped samples with the data on pure KCl, this sharp upturn in the curves can interfere with the measurement of resonances occurring at energies near the upturn. This will be apparent when the results of the measurements are presented.

Because of the complexity of the field dependence of the R-center energy levels, no quantitative attempt will be made to take them into account. We will be content to use the R center simply as a probe which yields the resonant frequencies of the nonmagnetic defects present in the crystal.

Previous Experiments

It has been observed[4,6,8] that several host:impurity systems exhibit resonant scattering of phonons by the temperature dependence of their thermal conductivity. Among these systems resonances were observed at energies of 1–2 cm^{-1} for CN^- in the potassium halides and in RbCl,[8] and for Li^+ in KCl and KBr.[4,8]

The observation of specific-heat anomalies has indicated low-lying energy level structures with splittings agreeing with the resonant scattering energies in the system KCl : CN$^-$,[8] in KCl : OH$^-$,[14] and in KCl : Li$^+$.[15] Measurements of dielectric properties[16–22] of these three systems have shown that at low temperatures the impurity ions have dipole moments oriented in discrete directions. In some cases the low-lying level structure has been detected by these measurements[19,20,22,23] and for KCl : OH$^-$ the low-lying transitions have been measured in paraelectric resonance experiments.[24–27]

Studies of the cooling produced on removing an electric field from samples of KCl : Li$^+$ and KCl : OH$^-$ [28–30] have indicated that the Li$^+$ dipole moments are aligned in the ⟨111⟩ directions and the OH$^-$ dipoles are along ⟨100⟩ directions in the crystal (see Fig. 2). The effects of the low-lying level structure on the cooling produced in these systems have been observed,[31] with results in agreement with the level spacings observed by other means. The experiments all indicate that in the system KCl : CN$^-$ there are one or more levels at an energy of approximately 1.6 cm^{-1} (2.0×10^{-4} eV or 2.2 °K) above the ground state.[8] The levels of Li ions of isotopic mass 7 are grouped around an energy of 1.2 cm^{-1}, and an energy of 1.8 cm^{-1} is found for the isotope of mass 6.[6,15,32] However, these results should be viewed with caution.[10] The resonant absorption energy of OH$^-$ in KCl is much lower, appearing in the neighborhood of 0.5 cm^{-1}.

Measurements on the system KCl : ^{7}Li have been made by Walton[12] using the paramagnetic *R* center as a probe. These measurements have resolved the resonance in this system into three components nearly equally spaced, located at 0.7, 1.4, and 2.2 cm^{-1}.

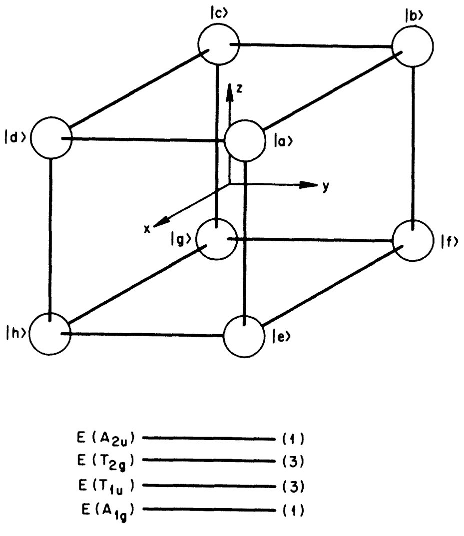

FIG. 2. XY_8 tunneling model. The energy levels are shown with their irreducible representations and degeneracies.

The work reported here began with the growth of good crystals of KCl doped with small amounts of KCN. The thermal conductivities of these samples in which magnetic color centers had been produced were then measured as a function of magnetic field up to 40–50 kG. The purpose of these measurements was to resolve the individual levels of the resonance in the scattering of phonons which has been observed[8] at 1.6 cm^{-1}. The measurements were carried out in a ^{3}He cryostat[33] at temperatures between 0.3 and 1.5 °K.

The second phase of these experiments was to make measurements on the system KCl : ^{6}Li in order to extend the measurements of Walton[12,34] to the isotope of mass 6. These samples were also measured in an electric field in order to observe the effect of an electric field on the individual phonon resonances.

An attempt was made to observe the individual resonances which make up the previously unresolved resonance in KCl : OH$^-$[22] at 0.5 cm^{-1}. These resonances were not observed in the samples available for study.

EXPERIMENTAL

The CN$^-$-doped crystals of KCl were grown by the Kyropoulos method of pulling from the melt in an atmosphere of dry nitrogen.[35] The starting material was ultrapure KCl supplied by the Pure Materials Group at Oak Ridge National Laboratory.[36] After the crystals were grown, scans were made of the absorption spectrum of each crystal by means of a recording infrared spectrophotometer and a Cary model No. 14 spectrophotometer for the visible to ultraviolet regions. On the Cary spectrophotometer absorption bands due to Pb were always seen at 201 and 272 nm, and a band due to OH$^-$ was seen at 204 nm. The concentrations of Pb and OH, as measured by the strength of these absorption bands, were below 0.05-ppm molar for Pb in all but one crystal and were below 0.2-ppm molar for OH$^-$ in all crystals. In the infrared region, no crystal had absorption lines which could not be identified with CN$^-$ or CNO$^+$.

Samples of the crystals were analyzed for CN$^-$ content by wet chemical methods. There were wide variations in the results of analysis from sample to sample out of the same crystal, even in samples from nearly the same location in the crystal. On the basis of the analyses, the crystals contained roughly 0.05 to 0.5-ppm molar of CN$^-$ (10^{15}–10^{16} ions/cc).

The samples of KCl doped with ^{6}Li were obtained from a crystal grown by Schmidt in Ithaca, N. Y. This crystal was also grown by the Kyropoulos method and was doped with LiCl which contained isotopically pure Li of mass 6. There were approximately 3-ppm molar of Li^+ ions (5×10^{16} ions/cc) in this crystal.

In order to produce the desired magnetic defects in the crystal, *F* centers were first produced in the sample by irradiation in a ^{60}Co γ source at liquid-nitrogen temperature. The low temperature minimized the number of unwanted defects produced in the crystal. Just before the sample was mounted in the cryostat it was exposed to room lights in order to bleach the *F* centers and form the *R* centers.

The effect of varying irradiation time is, of course, to change the sensitivity of the technique: doubling the irradiation dose and bleaching for the same length of time increases the effect of the magnetic field on the thermal conductivity by a factor of 2 or 3. The amount of bleaching also affects the size of the magnetic field effect: for the same irradiation, an increase in bleaching time from $\frac{1}{2}$ to 2 h doubled the effect of the magnetic field at $T = 0.46$ °K. As might be expected, there is an optimum bleaching time. It was found that the size of the effect cannot be increased significantly by bleaching beyond the point at which the crystal becomes nearly colorless. Bleaching far beyond this point decreases the effect.

Measurement of Thermal Conductivity

The measurements of thermal conductivity described here were made by the standard steady-state potentiometric method[8]: The sample (typically $3\times0.2\times0.4$ cm) is fastened to an indium-faced step at the bottom of a copper post cooled by a ^3He pot. The direction of heat flow was the $\langle 100\rangle$ direction for the cleaved samples which were used in this study. The samples were mounted so that a magnetic field could be applied parallel to the heat flux. At the lower end of the sample an indium-faced clamp held a manganin wire-wound heater of known resistance. The thermometers were two Speer carbon resistors, held by indium-faced clamps, at two points along the sample. The Speer resistors were thermally connected to the clamps by No. 16-AWG copper wire stalks which held the resistors out of the strongest part of the magnetic field of the superconducting solenoid. The magnetoresistance correction was determined by measuring the difference in resistance as the magnetic field was increased with no heat flowing through the sample.

Changes in the thermal conductivity as small as 0.5% between successive magnetic field values could be measured accurately. However, the low rate at which the field of the superconducting magnet could be changed limited the relative accuracy with which K at widely different fields could be measured to no more than about 2%.

When the effect of an electric field on the thermal conductivity was measured, the electric field was supplied by a high-voltage dc power supply connected to two gold-film electrodes on the sample. The voltage which could be applied was limited by the Kovar seal where the leads entered the cryostat. The maximum voltage which the seal allowed was 2500 V. The electric field within the crystal was in the [010] direction, perpendicular to the clevage faces with the electrodes, and perpendicular to the direction of heat flow and magnetic field in the sample.

The gold electrodes did not completely cover the sample between the thermometer clamps. The thermal conductivity measured in an applied electric field was corrected to allow for the effect of this partial coverage. It was assumed that the electric field was uniform in that portion of the sample covered by the gold film and that the electric field dropped to zero in those portions not covered by the gold electrodes.

RESULTS

KCl : CN^-

The effect of a magnetic field on the thermal conductivity of doped KCl irradiated and bleached is illustrated in Figs. 3 and 4. The plots are of $(K_0 - K_H)/K_0$ in percent against $g\mu_B H$ in cm^{-1}. Here, K_0 is the thermal conductivity at zero field, K_H is the thermal conductivity at a field *H*, *g* is the Landé *g* factor, μ_B is the Bohr magneton, and *H* is the magnetic field. $g\mu_B H$ is therefore the difference in energy between the spin-up and spin-down states of an electron in the field *H*. The experimental conditions and results are collected in Table I. While the magnitude of the effect was sample dependent, the location of the resonances was not, as shown in Table I.

In an ideal experiment the resonant energies would be determined from plots obtained by subtracting the nonresonant "background" from the measured field dependences, leaving only the part due to the resonant scattering by the impurity ion. In the experiments described here the background would have to be determined from the field dependence of the thermal conductivity measured on separate samples not containing the impurity ions. It is not possible to determine the appropriate background with sufficient accuracy from such data taken on two separate crystals, one pure and the other containing the desired impurity, since the coloration and bleaching of the samples is different in the two samples due to the strong influence of sample impurities on color-center formation. A second source of error in determining the background from data taken on separate samples of pure KCl is the large influence on the *R*-center scattering of the internal strains in the crystal. The variation of internal strain from sample to

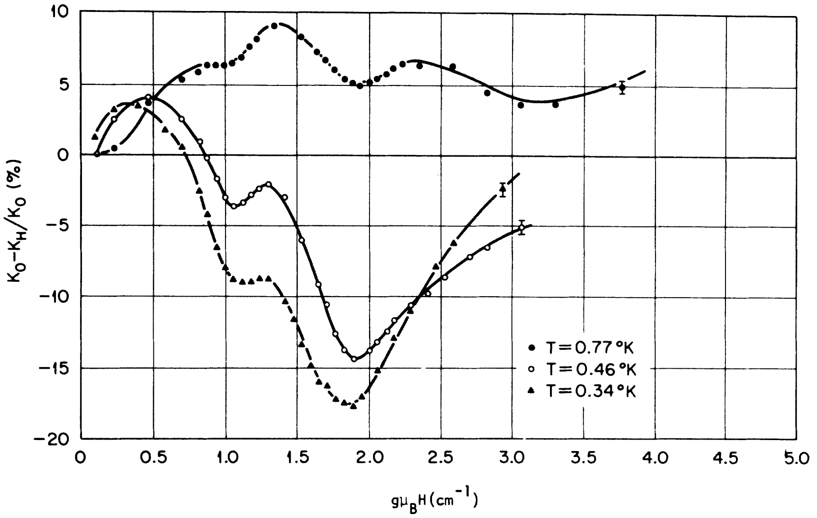

FIG. 3. Effect of a magnetic field on the thermal conductivity of KCl : CN⁻. This sample was irradiated for 9 h and bleached for 0.75 h.

sample is sufficient to cause significant uncertainty in the measured background. The determination of resonant energies, therefore, has been made with the assumption that the background can be approximated by a smooth curve drawn through the measured points on each side of the resonances. It can be seen from the field dependences measured for highly purified KCl, shown in Fig. 1, that the apparent position of resonances near 2.0 cm^{-1} should shift to lower fields as the temperature is lowered because of the sharp upturn in the curves for pure KCl which shifts to lower fields as the temperature is decreased. The best values of the resonant energies are taken to be $E_1 = 1.1 \pm 0.05$ cm^{-1} and $E_2 = 2.0 \pm 0.05$ cm^{-1}. The apparent positions of the resonances at E_1 and E_2 are summarized for each run in Table I. The values of E_2 measured at the lowest temperatures have not been considered in arriving at a final value for the resonant energy because of the sharp upturn referred to above. No effect of an electric field was observed on any of the resonances.

It should be noted that there appears to be a third resonance at 3.2 cm^{-1} in Fig. 3. However, it is felt that this is an experimental artifact because its position is sample dependent. Furthermore, if it were real the three transitions would indicate that the CN⁻ is in either XY_8 or XY_{12} (oriented along ⟨111⟩ or ⟨110⟩). But if this were the case, the spacings of the levels can only be accounted for if significant tunneling occurs through the body diagonal, hardly a likely event for the CN⁻.

KCl : ^{6}Li

The results of measurements made on samples of KCl doped with approximately 3 ppm molar (5

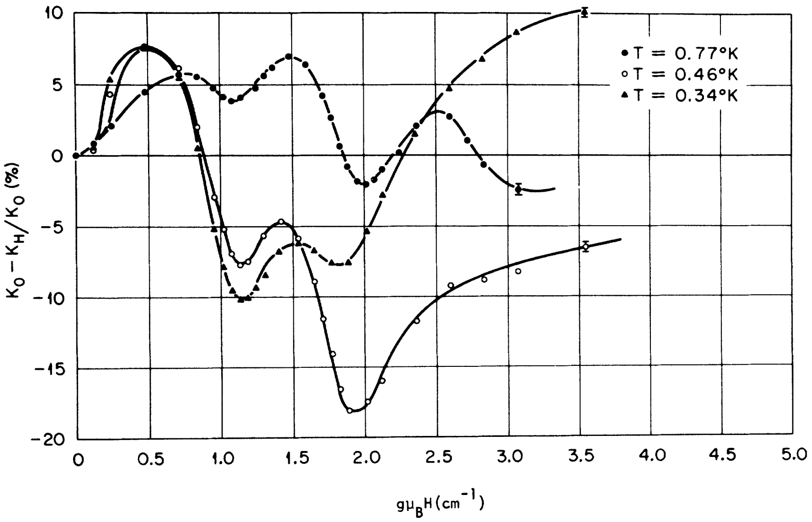

FIG. 4. Effect of a magnetic field on the thermal conductivity of KCl : CN⁻. This sample was irradiated for 10 h and bleached for 2.5 h.

TABLE I. A summary of experimental results on the system KCl : CN⁻. The resonant phonon scattering energies are denoted by E_1 and E_2. The measurements were performed at the indicated temperatures in zero electric field.

Boule	Slice[a]	E_1 (cm^{-1})	E_2 (cm^{-1})	T (°K)	K_0 (mW/cm °K)	$g\mu\beta H_0$[b] (cm^{-1})	T_γ (h)	T_{bleach} (h)
KCl-4	V	0.9	1.9	0.46	6.0	0	5	0.5
KCl-4	I	1.0	1.95	0.77	80.9	0	5	2
KCl-4	I	1.0	2.0	0.46	8.6	0	5	2
KCl-4	I	1.1	2.0	0.77	71.0	0	10	1
KCl-4	I	1.15	2.0	0.46	8.2	0	10	1
KCl-4	I	1.1	2.0	0.77	63.5	0	10	4
KCl-7	I	1.05	2.0	0.77	60.3	0	9.25	2
KCl-7	I	1.1	1.7	0.34	3.4	0	9.25	2
KCl-7	VII	1.1	1.95	0.77	39.3	0	9	0.75
KCl-7	VII	1.1	1.9	0.46	5.0	0	9	0.75
KCl-7	VII	1.1	1.85	0.34	1.6	0	9	0.75
KCl-4	V	1.1	2.0	0.77	38.8	0	10	2.5
KCl-4	V	1.1	1.95	0.46	4.2	0	10	2.5
KCl-4	V	1.1	1.85	0.34	1.3	0	10	2.5
KCl-4	IV	1.1	2.0	0.77	50.7	0	10	1.5
KCl-4	IV	1.1	2.0	0.46	5.3	0	10	1.5
KCl-4	IV	1.1	1.9	0.34	1.1	0	10	1.5
KCl-4	I	1.1	2.0	0.77	55.2	0	10	2.5
KCl-4	I	1.15	1.9	0.46	6.8	0	10	2.5
KCl-4	I	1.15	1.85	0.34	2.7	0	10	2.5

[a] Slice No. increases from top (seed end) to bottom of boule.

[b] H_0 is the field at which K_0 was measured.

$\times 10^{16}$ ions/cc) of lithium ions of isotopic mass 6 are illustrated in Figs. 5–7, where results of measurements with and without an applied electric field are plotted. The data are plotted as percentage change in thermal conductivity against $g\mu_B H$ in cm^{-1}. Table II summarizes the experimental conditions and results.

The most prominent feature of the measurements made at zero electric field is a resonance at about 1.72 cm^{-1}. At lower temperatures ($T < 0.4$ °K) this resonance appears to shift towards slightly lower fields. For a temperature change of a factor of 3, from 1.04 to 0.33 °K, the resonance shifts no more than 12%, reaching 1.54 cm^{-1} at the lowest. This shift is assumed to be similar to that observed for E_2 in KCl : CN⁻ and similar considerations must be applied to the data analysis in both systems.

The data presented show a relatively weak resonance at 2.70 cm^{-1}. It was not possible to un-

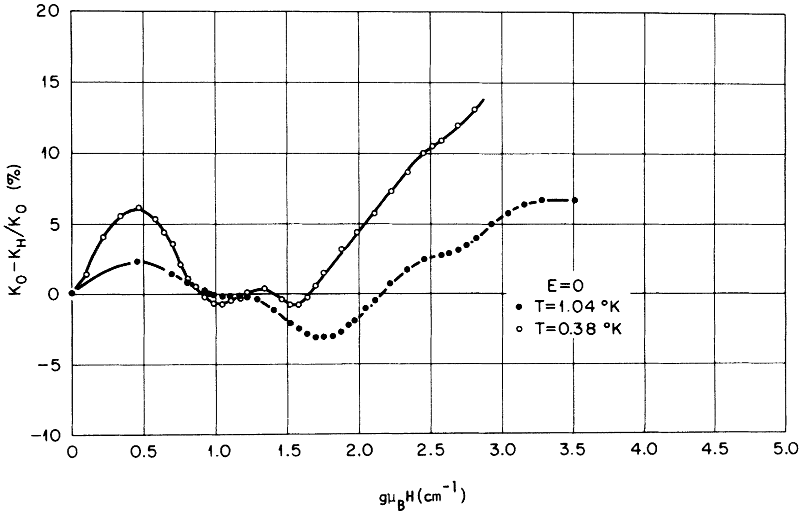

FIG. 5. Effect of a magnetic field on the thermal conductivity of KCl: ^{6}Li. This sample was annealed as described in the text. The irradiation time was 7.8 h and the sample was bleached for 1.5 h.

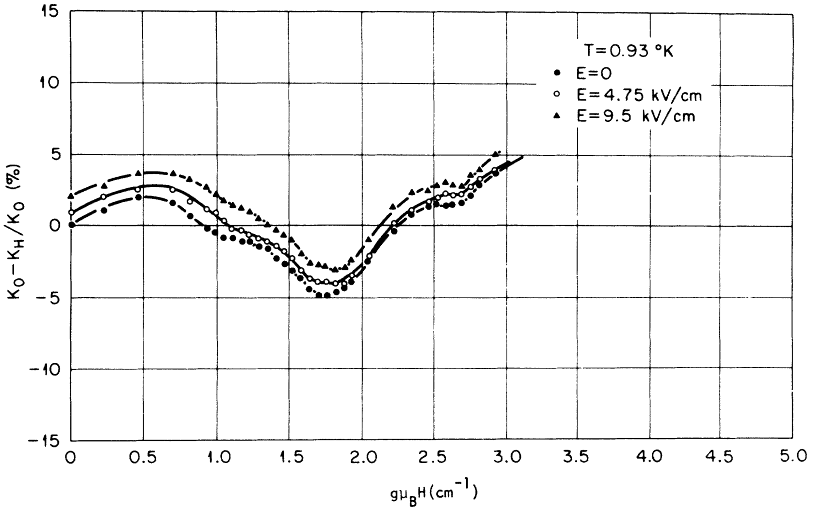

FIG. 6. Effect of a magnetic field on the thermal conductivity of KCl : ^{6}Li. This sample was annealed as described in the text. The irradiation and bleaching times were 9. 5 and 1. 5 h, respectively.

ambiguously resolve this resonance at the lower temperatures. It is clearly present, however, in runs from 0. 93 to 1. 36 °K.

It should be noted that before heat treatment it was possible to detect several very faint resonances near 1. 0 cm^{-1}. Theoretical considerations[37] lead to the expectation of one resonance in this area. The work of Baumann *et al.*[6] has indicated that Li ions in KCl diffuse even at room temperature and that the resonant scattering of phonons is significantly affected over a period of a few months. The KCl : ^{6}Li crystal used in this study was grown several months prior to the experiments and therefore it was hoped that heat treatment of the samples would strengthen the resonant scattering sufficiently so that the resonances around 1 cm^{-1} could be seen more clearly and at more widely differing temperatures. Several freshly cleaved samples were annealed at 700 °C in an argon atmosphere for about 5 min and then quenched by being removed from the furnace. The resonances at 1. 72 and 2. 80 cm^{-1} were not strongly affected by the heat treatment.

The positions of the resonances due to isolated ^{6}Li ions in the KCl lattice are determined from the above to lie at 1. 0 ± 0. 05, 1. 72 ± 0. 05 and 2. 70 ± 0. 05 cm^{-1}

Electric Field Effect KCl : ^{6}Li

In most of the runs made on KCl : ^{6}Li samples, measurements were also made of the effect on the thermal conductivity at each magnetic field of an electric field applied in the [010] direction. The resonance at 2. 7 cm^{-1} can be seen in Fig. 6 to shift either not at all or to slightly higher energy. The magnitude of the shift in this resonance for an ap-

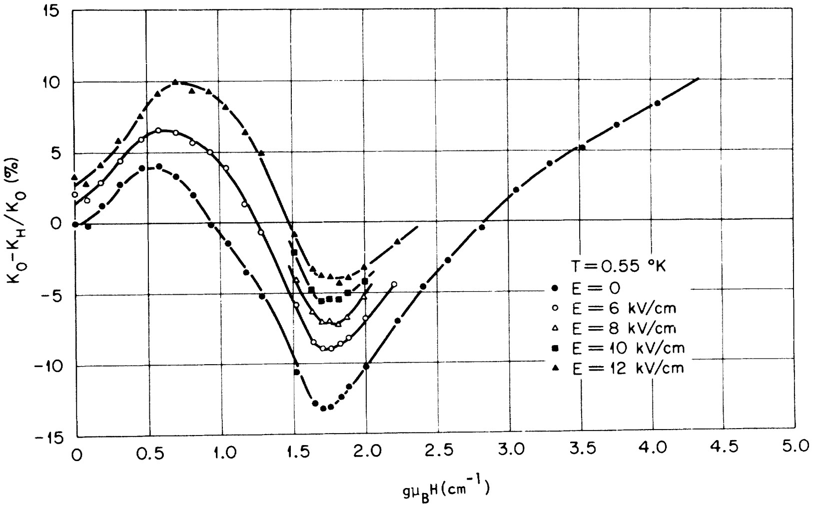

FIG. 7. Effect of a magnetic field on the thermal conductivity of KCl : ^{6}Li. No heat treatment was given this sample. The irradiation time was 8 h.

TABLE II. A summary of experimental results on the system KCl : ^{6}Li. E_1, E_2, and E_3 are the energies at which resonant phonon scattering was observed in zero electric field.

Slice[a]	E_1 (cm^{-1})	E_2 (cm^{-1})	E_3 (cm^{-1})	T (°K)	K_0 (mW/cm °K)	$g\mu\beta H_0$ (cm^{-1})	T_γ (h)	T_{bleach} (h)
II[b]	1.00	1.75	2.70	1.04	173.4	0	7.8	1.5
II[b]	1.00	1.54	···	0.38	7.8	0	7.8	1.5
II	···	···	2.70	1.17	233.9	2.12	8	2
II	···	1.72	2.66	1.04	150.8	1.28	8	2
II[b]	1.04	1.72	2.66	0.93	83.2	0	9.5	1.5
II[b]	1.00	···	···	0.56	14.1	0.58	9.5	1.5
II	···	···	2.74	1.36	357.3	2.34	8	2
II	···	1.7	···	0.93	74.3	0	8	···
III	···	1.7	···	0.55	13.02	0	8	···
III	···	1.68	···	0.55	15.5	0	8	1.5
III	···	1.68	···	0.46	8.1	0	5.5	1
III	0.8, 1.1	1.54	···	0.33	3.8	0	4.75	1
III	0.8, 1.05	1.64	···	0.38	5.8	0	8	1
III	0.8, 1.1	1.54	···	0.33	3.8	0	8	2

[a] The samples were cleaved from three sections of the boule, labeled I, II, III starting from the seed end.

[b] These samples were annealed at 700 °C for 5 min and then quenched before irradiation.

plied field of 10 kV/cm is less than 0.05 cm^{-1}. More effect is seen on the resonance at 1.72 cm^{-1} in Figs. 6 and 7. It appears to shift, one component remaining stationary and another moving up about 0.15 cm^{-1} in fields of 10–12 kV/cm. The measurements on this resonance at the lowest temperatures (below 0.5 °K) were not consistent with the higher-temperature data, most likely because of the same effects which lead to a sharp upturn in the pure KCl curves near this energy. The resonance at 1.0 cm^{-1} seen in the data for the heat-treated sample shown in Fig. 6 seems to broaden as an electric field is applied. Its weakening, however, prevents any reliable measurements of its detailed behavior. However, the shape of the $E = 10$-kV/cm curve in Fig. 6 is consistent with a splitting of several tenths of an inverse centimeter with the lower component remaining stationary.

DISCUSSION

KCl : CN$^-$–The Devonshire Model

The measured values of the two resonant phonon scattering energies, 1.1 and 2.0 cm^{-1}, can be compared with the results obtained by Seward and Narayanamurti[8] on the system KCl : CN$^-$. Their measurements, derived from the temperature dependence of the thermal conductivity, yielded resonant phonon scattering at about 1.6 cm^{-1} and around 18 cm^{-1}. The values 1.1 and 2.0 cm^{-1} agree very well with the lower resonance which could not be resolved by using the temperature dependence of the thermal conductivity as a spectrometer.

Electric Field Effect on KCl : CN$^-$

From the tunneling theory of Gomez,[37] the effect of an electric field on the tunneling levels is a function of the ratio of the dipole energy in the electric field, Ep_0, to the tunnel splitting of the levels in zero electric field. The measured dipole moment of the CN$^-$ ion[18] is 0.3 D (1 D = 10^{-18} esu), so that in an electric field of 20 kV/cm the orientational energy of the CN$^-$ ion is only 0.1 cm^{-1}. This energy is much smaller than the tunnel splitting, and therefore a field of this magnitude is not expected to affect the tunneling states significantly, which agrees with our observations.

KCl : ^{6}Li

The temperature dependence of the thermal conductivity has been utilized as a tool for studying the frequency dependence of phonon scattering. These results are in agreement with other studies based on specific heat and dielectric measurements,[15,19,22,23] which show unresolved resonances at 1.3 cm^{-1} in KCl : ^{7}Li and at 1.8 cm^{-1} in KCl : ^{6}Li.

The results presented earlier for the system KCl : ^{6}Li are 1.0, 1.72, and 2.70 cm^{-1} for the positions of the individual resonances. Walton's experiments[12,34] using the same method yielded values for the resonances in the system KCl : ^{7}Li of 0.7, 1.4, and 2.2 cm^{-1}.

If the levels are weighted according to their theoretical degeneracies, shown below, then Walton's results on ^{7}Li give an average value of 1.2 cm^{-1} in good agreement with that obtained by other workers. The present results on ^{6}Li give an average energy of 1.55 cm^{-1} when weighted in the same way. This is about 10% below the results of the other studies mentioned at the beginning of this section. The isotope shift derived from the present results on ^{6}Li and Walton's work on ^{7}Li is 30%. This is less than the 40–50% isotope shift deduced from the measurements of the shifts of the unresolved resonances.

Relative Strength of the Resonances

It is difficult to draw firm conclusions about the relative strengths of the phonon scattering of the tunneling states without knowing more about the effect of a magnetic field on the phonon scattering by the R center in KCl. However, if the strength of the resonances is judged by the magnitude of the dip in the plotted curves, then the $A_{1g} \rightarrow T_{2g}$ transition seems to be the strongest transition. Other methods have given results which imply that all of the transitions scatter phonons proportionally to the degeneracies of the levels involved.[4,15,32] A lower scattering strength is observed for the A_{1g}-T_{1u} transition. In fact it is not clear why this transition appears at all, since it is forbidden by symmetry. Walton's measurements[12,34] on KCl : ^{7}Li also indicate a lower scattering strength for the $A_{1g} \rightarrow T_{1u}$ transition. However, a more thorough understanding of the interaction of phonons with the R center is necessary for deriving valid scattering strengths from the data.

KCl : ^{6}Li *in an Electric Field*

The measured effect of an electric field on the resonances in KCl : ^{6}Li may be compared with the predicted effect based on the XY_8 tunneling model. Gomez[37] has described the effect of an electric field on the tunnel split energy levels of the XY_8 potential when η, in Gomez's notation, is the dominant tunneling parameter. The only effect of a small amount of tunneling through the cubic center is to alter the tunnel splitting. The behavior of each tunneling state in an electric field is not significantly different from the case where η is dominant. Figure 8 is essentially the same as Fig. 3 of the paper by Gomez *et al.* showing the effect of an electric field in the $\langle 100 \rangle$ direction on the energy levels for the XY_8 tunneling model for $\eta \gg \nu$. The axes have been changed: The plot is now in terms of energy of the tunneling states against $E_{\text{loc}}p_{0x}$, where E_{loc} is the local field acting on the Li ion and $P_{0x} = e^* x_0$ (all energies are in cm^{-1} and e^* is the effective charge[38] of the Li ion). The effect of a small tunneling coefficient is also included since the levels are plotted for $\eta = -0.44$ and $\nu = -0.08$ to coincide with the measured levels at zero electric field. The local field at the Li ion is E_{loc}, and the component of the dipole moment of the Li ion in the $\langle 100 \rangle$ direction is P_{0x}. If we assume that the dipole moment of the Li ion in the $\langle 111 \rangle$ direction is 4.0 D as measured by Letzring and Sack,[21] then the energy $E_{\text{loc}}P_{0x}$ in a $\langle 100 \rangle$ electric field is 1.0 cm^{-1} at a field of $E_{\text{loc}} = 25.8$ kV/cm. If the Lorentz factor is 0.09 as found by Letzring and Sack, then the local field is about 35% larger than the applied field. In an applied field of 8 kV/cm in the $\langle 100 \rangle$ direction Peressini *et al.*[32] observed the average resonant energy of ^{7}Li ions in KCl at an energy 0.1 cm^{-1} higher than in the case of zero electric field. With an isotope effect of about 40% a shift of about 0.15 cm^{-1} would be expected in a 9.5 kV/cm $\langle 100 \rangle$ electric field for the ^{6}Li isotope. The observed shifts for the 1.72-cm^{-1} resonance and the 2.70-cm^{-1} resonance are smaller than this shift, but if the 1.0-cm^{-1} resonance does split into a component at 1.0 cm^{-1} and a component at 1.4 cm^{-1} as the data suggest, then the results are compatible with the observed shifts for the ^{7}Li ion reported by Peressini *et al.*

Far-infrared absorption measurements by Kirby, Hughes, and Sievers[39] reveal that the upper component of the first resonant energy has shifted to about 2 cm^{-1} in an applied field of 15.8 kV/cm if

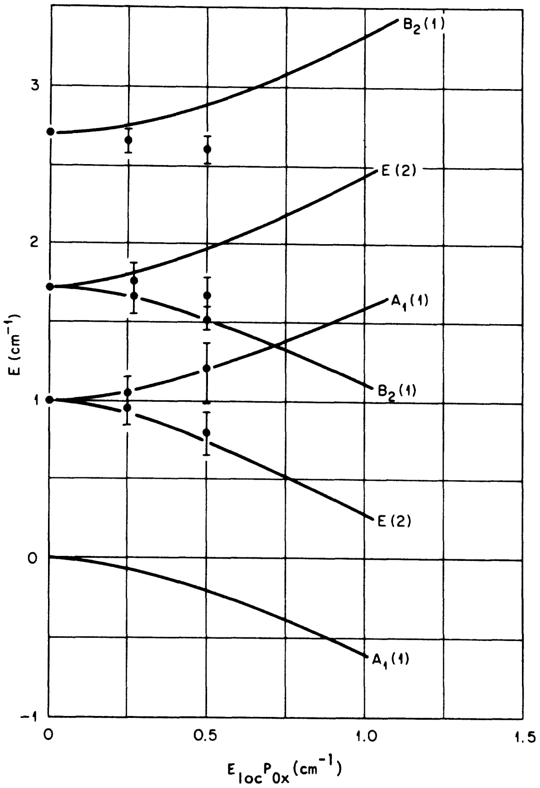

FIG. 8. Effect of an electric field on the phonon resonances in KCl : ^{6}Li. The curves have been calculated using $\eta = -0.44$, and $\nu = -0.08$ at zero electric field. The experimental points are plotted as circles with error bars.

the lack of resolution of the component at 1.4 cm^{-1} is considered. In conclusion it may be stated that it appears that the resonances at 1.72 and 2.70 cm^{-1} are shifted less than expected theoretically and that the effect of the resonance at 1.0 cm^{-1} is in agreement with theory when an electric field is applied in the ⟨100⟩ direction.

CONCLUSIONS

It is concluded from these studies that CN$^-$ impurities in KCl show resonant phonon scattering at discrete energies of 1.1 and 2.0 cm^{-1}. It will be shown, in the following paper, that by assuming that the CN$^-$ ion is in a Devonshire potential which has minima for orientation of the ion in the ⟨100⟩ directionsthese resonants energies may be fitted within the experimental error. The values of the parameters of the Devonshire potential which give a good fit to the resonant energies also give a good fit to the energy levels determined in other studies.[8]

Resonant phonon scattering by isolatea ^{6}Li ions in KCl is observed at energies of 1.0 ± 0.05, 1.72 ± 0.05, and 2.70 ± 0.05 cm^{-1}. The resonances are not evenly spaced and the variations are greater than the experimental errors. From the variation in spacing of the energy levels and with the assumption of an XY_8 tunneling model, it will be shown in the following paper that Li tunneling takes place between diagonally opposite wells through the center of the unit cell. Nevertheless, most of the tunneling is between adjacent potential wells along the edge of the cubic unit cell.

The electric field effects on the resonances of the system KCl : ^{6}Li are consistent with the results of calculations based on the XY_8 tunneling model[37] and with the results of measurements using other techniques.[32,39]

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