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STUDY OF IMPURITY MODES IN ALKALI HALIDES
THROUGH LOW TEMPERATURE SPECIFIC HEAT AND
THERMAL CONDUCTIVITY MEASUREMENTS

by

Peter Paul Peressini

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68

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TABLE OF CONTENTS

<u>Chapter</u>	<u>Page</u>
I. INTRODUCTION	1
II. SPECIFIC HEAT OF KCl:Li.	6
III. THERMAL CONDUCTIVITY OF KCl:Li	20
IV. SPECIFIC HEAT OF CN IN SEVERAL HOST LATTICES . . .	36
V. CONCLUSION	52
REFERENCES	54

LIST OF TABLES

<u>Table</u>	<u>Page</u>
I. Results of $C = aT^b$ Fits (T in $m^{\circ}K$).	10
II. Details of KCl:OH Samples.	18
III. Results of Computer Fits to KCl:Li Thermal Conductivity Data.	23
IV. Details of CN Samples.	43
V. Distortion and Energy Levels Required to Fit Specific Heat Data for CN in Several Hosts.	48

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. The energy levels for J, the rotational quantum number, equals 0,1,2,3 resulting from the addition of the Devonshire potential to the free molecule Hamiltonian, plotted in units of the rotational constant B as a function of K/B.	2
2. Specific heat anomaly of Li in KCl for several Li concentrations ranging from approximately $2 \times 10^{17} \text{ cm}^{-3}$ to $2 \times 10^{19} \text{ cm}^{-3}$.	7
3. The Schottky specific heat of KCl:Li illustrating the differences between the highest (J) and lowest (A) concentrations measured.	8
4. Relative change in the specific heat of KCl:Li in an applied electric field, $E \parallel \langle 100 \rangle$, as a function of temperature.	12
5. The Schottky specific heat of the highest concentrations of KCl:Li ⁷ ($1.85 \times 10^{19} \text{ cm}^{-3}$) and of KCl:Li ⁶ ($2 \times 10^{19} \text{ cm}^{-3}$, estimated).	14
6. The Schottky specific heat of KCl:OH for a wide range of OH concentrations as given in Table II.	17
7. The thermal conductivity of KCl:Li ⁷ for five concentrations of Li as given in Table III.	21
8. The thermal conductivity of KCl:Li ⁶ for two concentrations of Li ⁶ as given in Table III.	25

9. The relative change of thermal resistivity of KCl:Li, sample I ($20.6 \times 10^{17} \text{ cm}^{-3}$) for an electric field applied parallel to $\langle 100 \rangle$ and perpendicular to the heat flow for two electric fields. 27
10. Same as Fig. 9, but for the electric field parallel to $\langle 111 \rangle$. Sample F ($1.6 \times 10^{17} \text{ cm}^{-3}$). 28
11. The shift in resonant frequency $\omega_0(E)$ in an electric field for fields parallel to the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions showing the stronger electric field dependence for the field in the $\langle 111 \rangle$ direction. 30
12. The behavior of the tunnel levels of KCl:Li in an electric field as given in Reference 14. 31
13. The scattering strength A as a function of the resonance frequency ω_0 . 32
14. The variation of the scattering strength A with ω_0 as ω_0 is varied by changing the electric field (for $\vec{E}$ parallel to $\langle 100 \rangle$ and $\langle 111 \rangle$), the Li concentration and the isotope (Li^6 and Li^7). 34
15. The Schottky specific heat of KCl crystals containing a wide range of CN concentrations. 37
16. The Schottky specific heat of KBr:CN for two CN concentrations. 39
17. The Schottky specific heat of KI:CN showing both the Devonshire and modified Devonshire fits. 40
18. The Schottky specific heat of RbCl:CN for two CN concentrations. 41

<u>Figure</u>	<u>Page</u>
19. Comparison of experimental RbCl:CN specific heat data with theoretical curve based on model of Reference 37.	45
20. The effect of a tetragonal distortion on the Devonshire energy levels after Pompei and Narayanamurti. ³⁸	46
21. The relative change in the thermal resistivity of KCl:CN in an electric field parallel to the $\langle 100 \rangle$ direction.	50
22. Same as Fig. 21 but for KBr:CN.	51

ABSTRACT

Specific heat and thermal conductivity measurements in the temperature range of $.05^{\circ}\text{K}$ to 1°K are used to study the low lying energy levels or tunneling states of certain motional impurities in alkali halides; namely, Li and OH in KCl and CN in KCl, KBr, KI, and RbCl.

It is shown that the specific heat of KCl:Li can be explained in terms of a ground state energy structure of four equally spaced levels characteristic of a potential with minima located along the $\langle 111 \rangle$ directions. The splitting deduced is $.82 \text{ cm}^{-1}$. A forty percent increase in this splitting when Li^6 is substituted for Li^7 , clearly demonstrates that these states arise from a tunneling process. The presence of a similar isotope effect in the thermal conductivity of KCl:Li confirms that the tunnel states are strongly coupled to the phonons. Specific heat and thermal conductivity measurements of KCl:Li in an electric field confirm the polarizability of these levels. Measurements of the phonon scattering strength as the resonant frequency is varied by changing the isotope, concentration, and electric field are consistent with Pohl's observation showing the dependence of the scattering strength on the resonant frequency rather than the nature of the scattering defect.

Specific heat measurements of CN in KCl, KBr, KI, and RbCl are shown to be in disagreement with the predictions of the Devonshire model. However, the introduction by Pompei and

Narayanamurti of a potential representing a tetragonal distortion to the Devonshire potential results in energy levels consistent with the specific heat results. Application of this model to the thermal conductivity measurements of KCl:CN and KBr:CN in an electric field explains previously unexplained data.

The existence of tunnel states in KCl:OH similar to those in KCl:CN is confirmed through extensive specific heat measurements. The splittings are less than half of those for KCl:CN.

Significant deviations from the tunneling model at high concentrations and low temperatures for KCl:Li and KCl:OH, which have similar dipole moments, and the absence of such deviations for KCl:CN, which has a much smaller dipole moment, suggest the possibility of a dipole-dipole interaction in KCl:Li and KCl:OH.

I. INTRODUCTION

When certain molecules, such as CN, are dissolved in an alkali halide lattice, they behave essentially as a dilute gas, except for the fact that the molecules cannot perform translational motion. The rotational motion, however, is only slightly affected by the lattice, and in fact, it has been shown that the crystalline potential is felt only on the lowest rotational energy states of the molecule. In this laboratory, the study of rotating molecules in solids has been a continuing topic of interest.¹⁻⁷

Narayanamurti^{2,8} has shown that the crystalline potential in which the CN sits can be described in terms of the lowest order surface harmonic of octahedral symmetry, as first proposed by Devonshire.⁹ It has the form:

$$\tilde{V}(\theta, \phi) = (-\tilde{K}/8)(3 - 30 \cos^2 \theta + 35 \cos^4 \theta + 5 \sin^4 \theta \cos 4\phi) ,$$

where $\tilde{K}$ is a constant describing the barrier height. For $\tilde{K} > 0$, $\tilde{V}$ has minima or potential wells in the six $\langle 100 \rangle$ directions, and maxima in the eight $\langle 111 \rangle$ directions.

When this potential is added to the free molecule Hamiltonian, the energy levels shown in Fig. 1 result. For $K = 0$, the levels are those of a free rotor. For $K > 0$, these lowest rotational levels are modified in such a way that they are more appropriately described as angular oscillations (librations) about the six equivalent $\langle 100 \rangle$ orientations as given by the symmetry of the potential. For finite barrier

Figure 1. The energy levels for J , the rotational quantum number, equals 0, 1, 2, 3 resulting from the addition of the Devonshire potential to the free molecule Hamiltonian; plotted in units of the rotational constant B as a function of K/B .

heights, because of this symmetry, the molecule can tunnel between each of its several equivalent equilibrium orientations, resulting in a tunnel splitting of each of these librational energy levels. The six-fold degenerate lowest librational state is split into a singlet A_{1g} , a triplet T_{1u} , and a doublet E_g ; and it is this lowest librational state which will be of principal concern in the present work.

This situation is analogous 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 the so-called ammonia inversion splitting.¹⁰

For the monatomic impurity system, $KCl:Li$, the picture is remarkably similar. It is generally accepted that Li in KCl does not sit in the center of the potassium ion cavity.^{7,11-17} Rather, it is displaced slightly off-center in any of the eight $\langle 111 \rangle$ directions.¹³ The translation or tunneling of the Li ion between these eight equilibrium positions partially removes the eight-fold degeneracy of the harmonic oscillator ground state. Gomez et al.,¹⁴ assuming a potential consisting of eight three-dimensional spherical wells with minima displaced along the $\langle 111 \rangle$ directions, have shown that the resulting ground state consists of four equally spaced levels with degeneracies 1,3, 3,1, respectively.

The nature of their potential is such that this translation takes place only between adjacent wells; i.e., the barrier in the center of the cavity is too high and the probability for tunneling through it is low. Thus, the Li ion can be thought

to be in quasi-rotation about the center of the cavity, and in fact, it has been shown¹⁶ that the same potential used for rotating molecules can be used here if K is taken to be negative; i.e., the maxima and minima are inverted. As in the case of the CN, a study of this lowest lying tunnel split state will be a primary concern here.

One of the best techniques for observing these low lying energy levels or tunneling states of motional impurities in solids is through the measurement of their contribution to the specific heat. At low temperatures, the specific heat of a pure dielectric crystal, such as KCl, is described by the well known Debye T^3 law, and hence, is very small at temperatures of the order of 1°K . However, when small amounts of these tunneling impurities are added to the crystal, the specific heat will deviate from the pure T^3 line when the temperature is of the order of the tunnel splitting. In the cases under consideration here, the splittings are usually less and sometimes much less than 1°K . Hence, the contribution of these energy levels to the specific heat appears in a temperature region where the background or pure lattice specific heat is quite small.

From the total energy of the impurities:

$$U = N \frac{\sum_i g_i E_i \exp(-E_i/kT)}{\sum_i g_i \exp(-E_i/kT)}$$

where N is the number of impurities, g_i and E_i are the degeneracy and energy of the i^{th} level respectively, T is the

temperature, and k is Boltzmann's constant; one can compute the impurity specific heat:

$$C = \frac{dV}{dT} = \frac{N}{kT^2} \frac{S_0 S_2 - S_1^2}{S_0^2}$$

$$(S_j = \sum_i g_i E_i^j \exp(-E_i/kT))$$

It has also been shown^{2,4,15} that these tunneling states couple very strongly to the phonons, causing a depression in the thermal conductivity when the temperature is of the order of the tunnel splitting. Thus, these systems can be used as model cases for the study of phonon-defect interactions. Although their resolution is limited, thermal conductivity measurements have been an invaluable tool in this laboratory in the early studies of these systems.^{2,4,15} But more recently, it has been the specific heat that has yielded more detailed information on these systems.^{4,16,17} But, this information has further justified some of the interpretation placed on the thermal conductivity data, and in fact, has allowed new results to be deduced from the thermal conductivity data.

As the systems under consideration here are in fact, dilute systems of electric dipoles, the possibility of a cooperative interaction among the dipoles has been suggested.^{18,19} Some experimental evidence of such an interaction has been observed in $KCl:OH$ ^{20,21} and $KCl:Li$.²¹ It is desired to examine these systems closely with the present experiments for such evidence.

II. SPECIFIC HEAT OF KCl:Li

Much of this part of the present thesis has already been published¹⁶ and will not be repeated here. It is assumed that the reader is familiar with that work. The purpose here is to present some additional results that have been recently obtained.

In Fig. 2, a graph showing the Schottky specific heat of KCl:Li for the entire range of concentration (about 3×10^{17} to 2×10^{19} Li/cm³) is shown. Except for the addition of curve J and the omission of the Li⁶ data, this is the same data that was presented in Fig. 9 of Reference 16 and complete information on these samples can be found in Table I of that reference. Curve J represents data on a sample that was prepared from a pure KCl crystal by diffusing the Li⁺ ions in from LiCl powder. The concentration of J as determined from the chemical analysis of a small piece of the sample is 1.85×10^{19} cm⁻³ $\pm$ 10%.

In examining this series of curves there are two characteristics which are quite striking. First is the strong concentration dependence of the shape of the anomaly. This is best illustrated in Fig. 3 where only the curves for the highest (J) and lowest (A) concentrations are shown. Note the broadening of the anomaly compared to the theoretical anomaly, the shift of the peak to higher temperatures, and the fact that the anomaly does not fall off at high temperatures indicating that the total specific heat of the system does not return to that of pure KCl.

Figure 2. Specific heat anomaly of Li in KCl for several Li concentrations ranging from approximately $2 \times 10^{17} \text{ cm}^{-3}$ to $2 \times 10^{19} \text{ cm}^{-3}$. Except for sample J (see text), complete details concerning each sample will be found in Table I of Reference 16.

Figure 3. The Schottky specific heat of KCl:Li illustrating the differences between the highest (J) and lowest (A) concentrations measured. The solid curves are the theoretical specific heats for the chemically determined concentrations, $1.85 \times 10^{19} \text{ cm}^{-3}$ and $2.3 \times 10^{17} \text{ cm}^{-3}$, respectively.

Second is the apparent non-scaling with concentration of the anomaly at high concentrations. This is clearly visible in Fig. 3 where the theoretical anomalies are drawn in for the chemically determined concentrations. But it is most dramatically illustrated by the fact that the low temperature side of the anomaly for the higher concentrations appears to be independent of concentration. For curve G and the higher concentrations, the data below $.3^{\circ}\text{K}$ appear to be a straight line on a log-log plot. Thus an attempt was made to fit these data with a curve of the form aT^b where a and b are constants. Table I shows the results of these fits computed for a temperature of $.15^{\circ}\text{K}$, a temperature chosen because it is in the approximate center of the temperature range of the fitted data. Between curves G and J, the chemical analysis shows a factor of about 10 change in concentration. Examining the computed results, one sees less than a factor of 2 variation in the experimental data. It was unreasonable to make this comparison using the parameter a because of a small variation between curves of b .

In Reference 16, the interesting possibility that this strange behavior at high concentrations is a result of some cooperative effect between the Li ions was discussed. At that time, two reasons spoke against this idea. First, the shape of the anomaly at higher concentrations could be explained using the tunneling model if it was assumed that the levels were broadened. However, though it may be possible to explain the shape of any given curve, it is most difficult to reproduce

TABLE I
Results of $C = aT^b$ Fits (T in m°K)

Curve (Fig. 2)	Boule #	Run #	$a \times 10^5$	b	aT^b at .15°K	Concentration (10^{17} cm^{-3})
G	Q97	27B	2.229	2.660	13.69	18.4
G	Q97	28B ^(a)	2.454	2.640	13.64	18.4
-	60805Q (top)	29B	10.23	2.480	25.50	29
H	70112Q	37A	34.27	2.227	24.05	32.6
-	60805Q (bottom)	29A	2.432	2.729	21.11	34.6
I	70824Q	PP4A	27.92	2.289	26.73	80
J	diffused	PP7B	32.40	2.263	27.23	185

(a) After quenching.

the concentration independence with any reasonable broadening model, except perhaps through some fortuitous cancellation.

The second, and even stronger argument against a cooperative phenomenon, was the fact that the data on the specific heat in an electric field showed no qualitative departure from that predicted by the tunneling model for both a low and a high concentration. It could reasonably be expected that if there was some cooperative phenomena taking place, the electric field data would show a somewhat more dramatic effect. In Fig. 4, the relative change in the Schottky specific heat is plotted vs temperature for several different $\langle 100 \rangle$ electric fields and 3 concentrations. The two lower concentrations are the same data as presented in Reference 16. The higher concentration curve is data on sample J. Even for the highest concentration, where the zero field specific heat is most dramatically different than the lowest concentration, the electric field data is qualitatively unchanged.

However, measurements of the dc dielectric constant by Fiory²¹ in this laboratory have shown evidence for a dipole-dipole interaction in KCl:Li. But, the number of Li ions involved is small and thus their influence on the specific heat may not be large enough to show up above the background of the tunneling ions. This would then make the electric field dependence of the specific heat more understandable. Thus, the low temperature specific heat data may indeed be the result of a cooperative electric phenomenon.

At lower concentrations, it was shown in References 16

Figure 4. Relative change in the specific heat of KCl:Li in an applied electric field, $E \parallel \langle 100 \rangle$, as a function of temperature. The triangles, circles, and squares represent respectively, samples D ($2.3 \times 10^{17} \text{ cm}^{-3}$), E ($3.3 \times 10^{18} \text{ cm}^{-3}$), and J ($1.85 \times 10^{19} \text{ cm}^{-3}$). The differences below $.2^\circ\text{K}$ are believed to be due to experimental error.

and 17 that if Li^6 is substituted for Li^7 , an isotope shift of 40% in the tunnel splitting is obtained; i.e., the Li^6 anomaly is shifted by 40% to higher temperatures. This is interpreted as the most convincing evidence that the Li ions are behaving in a manner as predicted by the tunneling model. It is interesting to investigate this effect for the highest concentration of Li. If a cooperative process were to take place at low temperatures and high concentrations, one would expect it to be independent of the mass and depend only on the dipole moment which is unchanged²² by the isotope. Certainly one should not expect the same isotopic behavior as obtained for the tunneling levels. Figure 5 shows the specific heat for the high concentration Li^7 (J) and a high concentration Li^6 sample (K) that was prepared from a pure KCl crystal and Li^6Cl using a diffusion process as with the Li^7 . The interesting region is the low temperature side of the anomaly where saturation occurs for the Li^7 samples. Between .15 and .3°K, the Li^6 data is shifted to approximately 20% higher temperatures than the Li^7 curve. Below .15°K, the Li^6 data appears to rapidly return to the same saturation line as observed for the Li^7 . While this result is encouraging, one should really have several more concentrations of Li^6 in order to determine if its specific heat approaches a saturation line as does Li^7 . More careful data below .15°K would be useful in determining if the two isotopes do merge into the same curve for all high concentrations.

In Reference 16, it was suggested that the search for a cooperative interaction among impurity ions be carried to

Figure 5. The Schottky specific heat of the highest concentrations of KCl:Li⁷ ($1.85 \times 10^{19} \text{ cm}^{-3}$) and of KCl:Li⁶ ($2 \times 10^{19} \text{ cm}^{-3}$, estimated).

systems with smaller tunnel splittings. In such a system the specific heat of the tunneling levels would hopefully appear in a temperature region below that in which a possible cooperative interaction between classical dipoles might take place. This interaction would then be obscured by neither the tunneling specific heat nor the background specific heat of the pure lattice.

A possible candidate appeared when Harrison found that the specific heat of pure KCl deviated from the pure T^3 line below $.5^\circ\text{K}$.²³ This low temperature deviation was attributed to small concentrations of OH that is present as an impurity in most alkali halide crystals. From this deviation he deduced a tunnel splitting of $2\Delta = .46 \text{ cm}^{-1}$, assuming a $\langle 100 \rangle$ orientation where Δ and 2Δ are the splittings between the A_{1g} and T_{1u} and the T_{1u} and E_g levels respectively. Thus KCl:OH seemed to be a reasonable candidate. An additional advantage of this system is found in the fact that the solubility limit of OH in KCl is about 1 mole %²⁴ or $7 \times 10^{20} \text{ cm}^{-3}$. Thus for concentrations of OH similar to those of Li one is sufficiently far from the solubility limit to eliminate the possibility of any effects (probably in the form of strains) arising from a saturation of the host lattice. This is always a danger with Li in KCl where the solubility limit (approximately 10^{19} cm^{-3}) is near the highest concentration measured.

For a detailed study of the properties of KCl:OH, the reader is referred to References 24-30 and the references cited therein. A complete description of the low temperature behavior

of the specific heat of KCl:OH as determined in this laboratory as part of this thesis study appears in Reference 6. This work is summarized by the data in Fig. 6 and Table II.

Curves B and C of Fig. 6 agree exactly in shape and temperature with the results of Harrison (curve A), thus proving his assignment of the low temperature deviation in the specific heat of KCl to OH impurities. The existence of tunneling states of OH in KCl similar to those of CN in KCl is confirmed. There has been some discussion³¹ concerning this point in reference to the validity of the assignment of the transitions observed in the paraelectric resonance experiments.^{29,30}

As seen in Table II, over three orders of magnitude both the optically determined OH⁻ concentration and the concentration as determined by the entropy associated with the specific heat anomaly agree to within the experimental accuracy. However, for curves D and E, the anomaly broadens, although the entropy still yields the optically determined concentration. But, as with KCl:Li, the specific heat on the low temperature side of the anomaly appears to saturate.

Dielectric measurements by Kanzig et al.²⁰ and by Fiory²¹ in this laboratory provide evidence for a low temperature dipole-dipole interaction.

Thus, where as the solubility limits, tunnel splittings, and even nature (atomic vs molecular impurity) of KCl:Li and KCl:OH are quite different, the behavior of their specific heat anomalies show some remarkable similarities in their low temperature behavior. Their greatest physical similarity is that

Figure 6. The Schottky specific heat of KCl:OH for a wide range of OH concentrations as given in Table II. The solid curves are computed for the energy levels shown for the optically determined concentrations for samples B and D.

TABLE II
Details of KCl:OH Samples

Run #	Boule #	Curve	$n_{OH}^{(a)}$ (10^{17} cm^{-3})	$\frac{\Delta S}{Erg}$ Gm-Deg	$n_{\Delta S}^{(b)}$ (10^{17} cm^{-3})
31B	SH2	A	.08	2.3	.19
PP12B	612141	B	4.9	54.5	4.3
PP7A	611221	C	12.3	135	11
PP13A	806031W	D	70	695	56
PP9A	606211	E	670	(c)	

(a) The OH^- concentration as determined from the 2050A° U.V. absorption band using the calibration of Klein et al.,³³ 2.4 ppm/cm⁻¹.

(b) The OH^- concentration as determined from $\Delta S = nK \ln 6$.

(c) Not enough high temperature data to determine ΔS .

they both possess a large dipole moment (on the order of 3 Debye in each case).

Perhaps then it would be useful to examine a system with a small dipole moment. Such a system is KCl:CN, which will be described in detail in a later chapter. Its dipole moment has been reported as .3 Debye,³² or a factor of 10 lower than that of Li and OH. Suffice to say here that CN, through measurement of the thermal conductivity,² appears to couple to the phonons in a manner similar to Li¹⁵ in roughly the same temperature region. Its solubility limit in KCl is high (about 5×10^{19} cm⁻³).

Figure 15 in Section IV shows that the specific heat of CN in KCl shows only a broadening effect at the very highest concentration. There is none of the low temperature saturation behavior as observed with Li and OH.

Thus, it is reasonable to conclude, that whatever phenomenon is responsible for the observed behavior of the specific heats of these systems, it is in large part dependent on the dipole moment of the impurity ion. It is important to note that dielectric measurements on OH in KCl^{20,21} and Li in KCl²¹ support this idea.

III. THERMAL CONDUCTIVITY OF KCl:Li

In Reference 15, measurements of the thermal conductivity of KCl:Li were reported. It is the purpose of this thesis to present additional results to expand and further justify some of the conclusions presented there. It is assumed that the reader is familiar with Reference 12. A complete description of the results to be described here appears in Reference 5.

In Fig. 7, the thermal conductivity of KCl:Li is shown for five concentrations of Li. Curves B, C, D, and the pure curve A, are those shown in Reference 15. Curves E and F are recent data. E is a sample grown from the melt as the others. F is a sample prepared from pure KCl through a diffusion technique.

For the most part, only the low temperature depression shall concern us here.

In Reference 15, curves B, C, and D were fitted below 1°K using the Debye model of thermal conductivity with a relaxation time, τ , given by:

$$\tau^{-1} = \tau_b^{-1} + \frac{nA}{\omega_o^2} \frac{(\omega/\omega_o)^2}{[1 - (\omega/\omega_o)^2]^2}$$

where the first term, τ_b , is the boundary scattering relaxation time obtained by fitting the pure crystal. The second term is the relaxation rate of the defects and is a resonant scattering expression of the Lorentzian form; where ω_o is the resonant frequency, n is the Li concentration, and A is a measure of the scattering strength. Briefly, the fits were

Figure 7. The thermal conductivity of $\text{KCl}:\text{Li}^7$ for five concentrations of Li as given in Table III. Curve A is pure KCl. The solid curves below 1°K represent computer fits as described in the text. The solid curves above 1°K are not computed.

obtained by determining ω_0 and A for one sample, fixing these values, and scaling the concentrations to determine the other fits.

A more systematic method of fitting these curves has recently been developed, whereby a least squares technique is used to determine ω_0 and the product, nA, for each curve individually. The results of fitting the data shown in Fig. 7 below 1°K are summarized in Table III and the solid curves in Fig. 7 (below 1°K) illustrate these fits. Note in particular, the excellent scaling with Li concentration of the thermal conductivity for all but the highest concentration as illustrated by Fig. 7 and the constant value of A, to within the error in the determination of the chemical concentration and to within the variation of A with ω_0 . The data for the highest concentration, and also the variation of A with ω_0 will be discussed later.

There is a general increase of ω_0 with concentration from 2.25×10^{11} rad sec⁻¹ to 2.78×10^{11} rad sec⁻¹; the former agreeing with the value of 2.26×10^{11} rad sec⁻¹ quoted in Reference 15. This increase is not surprising in view of the similar shift to higher temperatures of the specific heat anomaly peak with higher concentrations.¹⁶

$\omega_0 = 2.25 \times 10^{11}$ rad sec⁻¹ corresponds to 1.2 cm^{-1} .

The specific heat results¹⁶ and the microwave measurements¹² indicate a tunnel splitting of $\Delta = .82 \text{ cm}^{-1}$. This apparent discrepancy was explained in Reference 15 as arising from the

TABLE III
Results of Computer Fits to KCl:Li Thermal Conductivity Data

Sample	Isotope	Boule #	Concentration (10 ¹⁷ cm ⁻³)	Applied Electric Field (kV/cm)	Resonance Frequencies		(nA) (10 ³⁰ sec ⁻³)	(nA ₂) (10 ¹² cm ³ sec ⁻³)	(nA) n
					ω_0 (10 ¹¹ rad sec ⁻¹)	ω_2 (F)			
G	Li ⁶	70322 Q	6.7(a)	0	3.27	2.27	1.95	0.284	2.92
H	Li ⁶	(b)	88.5	0	3.61		42.3		4.78
B	Li ⁷	Q 53	7.0	0	2.25		1.66		2.37
C	Li ⁷	Q 13	22.0	0	2.31		5.66		2.58
D	Li ⁷	Q 12	48.0	0	2.51		15.5		3.23
E	Li ⁷	(b)	115.0	0	2.78		26.6		2.31
F	Li ⁷	70425 Q	1.6(c)	0	2.39	1.68	0.321	.0427	2.01
F				3.8 (<111>)	2.41	1.7	0.364	.0485	2.28
F				7.6	2.54	1.81	0.422	.0554	2.64
F				11.4	2.8	1.96	0.47	.0617	2.94
F				15.2	3.08	2.14	0.514	.0664	3.21
I	Li ⁷	Q67A	20.6(d)	0	2.37		5.23		2.54
I				4 (<100>)	2.47		5.39		2.62
I				8	2.59		5.72		2.78
I				16	2.74		6.59		3.2
I				24	2.85		7.14		2.47

- (a) Concentration determined with electrocaloric effect, assuming p_0 (uncorrected) = 6D.
(b) Diffused from pure KCl, boule # 70301Q.
(c) Concentration determined from specific heat anomaly (Ref. 16). The chemical analysis on this boule gave anywhere from 1.6 to $3.0 \times 10^{17} \text{ cm}^{-3}$.
(d) Determined from nA by dividing through the average A_{av} determined from samples B,C,D,R, which is $A_{av} = 2.54 \times 10^{12} \text{ cm}^3 \text{ sec}^{-3}$.
(e) This corresponds to a splitting of $.89 \text{ cm}^{-1}$.
(f) The ω_0 resulting from the two resonance fits.

fact that the relaxation rate for the Li defects is really a composite of several transitions and it is unreasonable to use only one resonant frequency. But, adding more transitions would simply introduce too many additional parameters. However, more will be said about this point later.

This explanation, while it may sound perfectly reasonable, is merely speculation and in fact, leads one to speculate even that the phonons are not coupling to the tunnel states at all. It would not be difficult to postulate a scattering mechanism independent of the tunnel model to explain the results of Reference 15. For this reason, an isotope effect similar to that observed in specific heat^{16,17} was looked for. The reader will recall that when Li^6 was substituted for Li^7 , except for the highest concentration, the specific heat anomaly was unaltered in shape but shifted upwards in temperature by 40%. A shift of such a magnitude was impossible to explain by other than a tunneling model.

Figure 8 shows the thermal conductivity for two concentrations of Li^6 in KCl. Sample G was pulled from the melt. Sample H was diffused from pure KCl using Li^6Cl . Again the solid lines below 1°K are computer fits and the results of these fits are included in Table III. For two similar low concentrations of Li^6 (curve G) and Li^7 (curve B), it is observed that ω_0 for Li^6 is 44% higher than ω_0 for Li^7 . This is in excellent agreement with the specific heat results. Even for the highest concentrations, curves E and H, the shift is 30%. This result is most convincing evidence that the phonons are indeed coupling

Figure 8. The thermal conductivity of KCl:Li⁶ for two concentrations of Li⁶ as given in Table III. The solid curves below 1°K represent computer fits as described in the text. The solid curves above 1°K are not computed.

to the tunneling levels and that this coupling is responsible for the low temperature depression observed in the thermal conductivity.

Before the observation of this isotope effect in the thermal conductivity, it was hoped that experiments on the effect of an electric field on the thermal conductivity of KCl:Li^{15} would yield the above conclusions in addition to information on the scattering strengths of the various transitions and the nature of the phonon coupling to the tunneling states. Unfortunately, this proved to be too optimistic at this time due to the large number of possible transitions and the unknown field dependences of the matrix elements. It will have to await heat pulse measurements where better resolution is available and one can distinguish between the transverse and longitudinal phonons.³⁴ Never the less, some interesting conclusions can be drawn from the data.

Figure 9 shows the relative change in thermal resistivity, $\Delta R/R$, for an electric field applied in the $\langle 100 \rangle$ direction where $\Delta R/R = (R(E) - R(0))/R(0)$. Here R is the reciprocal of the thermal conductivity and E and 0 indicate these values in an electric field and in zero field respectively. The results for an electric field in the $\langle 111 \rangle$ direction on sample F are shown in Fig. 10. The solid curves were obtained by fitting the thermal conductivity for each field individually and computing $\Delta R/R$ from the fits. These fits are different than those in Reference 15 in that they allow for a variation of A with field. More will be said on this point later. One can see

Figure 9. The relative change of thermal resistivity of KCl:Li, sample I ($20.6 \times 10^{17} \text{ cm}^{-3}$) for an electric field applied parallel to $\langle 100 \rangle$ and perpendicular to the heat flow for two electric fields. The solid curves were computed from the least squares fits to the experimental thermal conductivity curves (see text).

Figure 10. Same as Fig. 9, but for the electric field parallel to <111>. Sample F ($1.6 \times 10^{17}/\text{cm}^3$).

that the quality of the fits is quite good. The results of these fits are summarized in Table III.

It is interesting to plot the shift in resonant frequency, $\omega_0(E) - \omega_0(0)$, as a function of electric field for each of these field directions. This is done in Fig. 11. It is easily seen that the variation with electric field is much stronger for the electric field in the $\langle 111 \rangle$ direction than in the $\langle 100 \rangle$ direction. This is understandable if one looks at the polarizability of the tunnel levels as pictured in Fig. 12. In a $\langle 111 \rangle$ field the resonant frequencies for all possible transitions increase in a field, whereas for the $\langle 100 \rangle$ field several of the possible transition resonant frequencies remain unchanged. Since ω_0 represents an average of the resonant frequency of all the transitions it is clear why the $\langle 111 \rangle$ field produces the greatest variation. This result is in agreement with the fact that the potential minima in which the Li ions sit are in the $\langle 111 \rangle$ directions.

Up to this point, nothing has been said about the scattering strength A . It is through a study of A for different defects that one hopes to acquire an understanding of impurity mode scattering. There is evidence that the experimentally determined scattering strength depends predominantly on the resonant frequency, ω_0 , and less on the specific defect causing the scattering.³⁵ Results supporting this conclusion are presented in Reference 4, Fig. 4, and that figure is reproduced here as Fig. 13. In addition, the values of A determined here for the low temperature resonances in KCl:Li^7 and KCl:Li^6

Figure 11. The shift in resonant frequency $\omega_o(E)$ in an electric field for fields parallel to the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions showing the stronger electric field dependence for the field in the $\langle 111 \rangle$ direction. The solid curves are not computed.

Figure 12. The behavior of the tunnel levels of KCl:Li in an electric field as given in Reference 14.

Figure 13. The scattering strength A as a function of the resonance frequency ω_0 . This is the same data as presented in Fig. 4 of Reference 4 except for the addition of the KCl:Li^6 data, plotted here as the average of the two samples in Table III.

(Table III) have been entered. For the $\text{KCl}:\text{Li}^7$, Table III shows several values of A, all higher than reported in Reference 15. The reason for this variation is that ω_0 has been allowed to vary in fitting each curve. Also, the uncertainty in the determination of the chemical concentration is the cause of some error in the values of A. The discrepancy with Reference 15 is simply a result of the more systematic and more accurate method of fitting the thermal conductivity curves as described earlier.

Further evidence that A is principally a function of ω_0 only, rather than any other parameter, is provided in Fig. 14 where the variation of A with ω_0 is plotted as ω_0 is varied by changing the concentration (the several Li^7 concentrations), the isotope (Li^6 and Li^7), and the electric field (for both the electric field parallel to $\langle 100 \rangle$ and $\langle 111 \rangle$). In each case, the functional form of the variation of A with ω_0 is essentially unchanged.

Now that a reasonable idea of the frequency dependence of A has been established, it may be possible to make an attempt at including additional transitions in the relaxation rate used in fitting the thermal conductivity curves, without introducing additional parameters. Such fits were tried for some of the data that have been presented here using a relaxation rate that included two transitions, ω_0 and $2\omega_0$, and was of the form:

$$\tau^{-1} = \tau_b^{-1} + \frac{A(\omega/\omega_0)^2}{\omega_0^2(1-(\omega/\omega_0)^2)^2} + \frac{4A(\omega/2\omega_0)^2}{(2\omega_0)^2(1-(\omega/2\omega_0)^2)^2}$$

Figure 14. The variation of the scattering strength A with ω_0 as ω_0 is varied by changing the electric field (for $\vec{E}$ parallel to $\langle 100 \rangle$ and $\langle 111 \rangle$); the Li concentration and the isotope (Li^6 and Li^7). In each case the functional form of the variation of A with ω_0 is basically unchanged. Note that all scales are logarithmic.

where the 4 in the third term arises from the fact that A has been assumed to vary as ω_0^2 . A slight improvement over the single resonance results was obtained. Table III includes the results of the two transition fits. As one would expect, the resonant frequency now obtained agrees more closely with the tunnel splitting derived from the specific heat data.

In the chapter on the specific heat of KCl:Li, there was considerable discussion concerning the possibility of a cooperative interaction among the Li ions at low temperature and high concentration. One would hope to find some support for this hypothesis in the thermal conductivity data. The only evidence that can be offered at the present time comes from a comparison of the scaling of the high (20°K) and low (.3°K) temperature depressions in the thermal conductivity with concentration. One might expect the scaling of each of these depressions to be similar. However, a careful inspection of Fig. 7 shows that this is certainly not the case for the highest concentrations, D and E. The high temperature depression scales as one would expect from the large difference in concentration. But the low temperature depressions are practically identical for the two curves. Hence, it would appear that not all of the Li are participating in the phonon scattering in the temperature range of the low temperature depression. This result is consistent with the behavior of the specific heat of KCl:Li at low temperatures and high concentrations.

IV. SPECIFIC HEAT OF CN IN SEVERAL HOST LATTICES

This section will report results of measuring the Schottky specific heat of the tunnel split librational ground state of CN in various host lattices.

Seward and Narayanamurti measured the specific heat of KCl:CN^2 and found it to be in good agreement with the predictions of the Devonshire model. In Fig. 15, their measurements have been extended to lower temperatures and additional concentrations. The solid curve is the theoretical anomaly for the energy levels shown as predicted by the Devonshire model² for potential minima in the $\langle 100 \rangle$ directions with a barrier parameter $K = 16B$. The agreement is equally good for all but the highest concentration, where the considerable broadening of the anomaly is assumed to be due to strains in the crystal arising as the solubility limit of CN is approached.

Actually, the splittings that best fit the data are smaller by about 20% than those predicted in Reference 2. But it must be recalled that in that reference, the barrier parameter K , and hence the tunnel splittings, were deduced from the librational frequency or $T_{1u}(J = 1)$ to $T_{2g}(J = 2)$ transition, and depended on a knowledge of B , the rotational constant, which was known to only 20%. If B is decreased to make the tunnel splittings agree, the librational frequency is too low. Obviously then, if one examines the Devonshire energy plot (Fig. 1), K must be increased and B decreased until agreement of the tunnel splittings and the librational frequencies is

Figure 15. The Schottky specific heat of KCl crystals containing a wide range of CN concentrations. The solid curves are computed using the Devonshire model with the energy levels shown. The dashed curves are computed using the tetragonally distorted Devonshire levels as given in Fig. 20 and Table V.

found. If one starts fitting the specific heat data for the relative splittings of the tunneling levels predicted for higher values of K , it is quickly seen that the best fit is always obtained for an $A_{1g} - T_{1u}$ splitting of 1.15 cm^{-1} ; i.e., the peak in the specific heat anomaly depends primarily on the lower splitting. Taking the ratio of the librational splitting, $T_{1u} - T_{2g}$, to the $A_{1g} - T_{1u}$ tunnel splitting, one can use the Devonshire energy plot to find K independently of B . This ratio ($12 \text{ cm}^{-1}/1.15 \text{ cm}^{-1} = 10.4$) yields $K = 18B$ and a $T_{1u} - T_{2g}$ splitting of $10.4B$. Hence, $B = 12 \text{ cm}^{-1}/10.4 = 1.15 \text{ cm}^{-1}$. For $K = 18B$ and $B = 1.15 \text{ cm}^{-1}$, the T_{1u} and E_g tunnel levels are predicted at 1.15 and 1.9 cm^{-1} respectively, in excellent agreement with the specific heat results. Thus, combining the specific heat and infrared results, one is able to make a better determination of B and K .

For KBr:CN and KI:CN , Seward and Narayanamurti² obtained the same barrier parameter ($16B$) as for KCl:CN . Hence, the Schottky specific heat of the CN in these hosts should be identical to that in KCl . For RbCl:CN , they found a larger barrier parameter ($28B$). Thus the tunnel splittings of CN in RbCl should be smaller than in KCl , and the specific heat anomaly should be shifted to lower temperatures.

The specific heats of these systems are presented in Figs. 16, 17, and 18, along with the theoretical anomalies. The observed anomalies are considerably broader than those predicted. In particular, in the case of RbCl:CN , the experimental result shows a two peak structure with one peak occurring

Figure 16. The Schottky specific heat of KBr:CN for two CN concentrations. Both the Devonshire and modified Devonshire fits are shown.

Figure 17. The Schottky specific heat of KI:CN showing both the Devonshire and modified Devonshire fits.

Figure 18. The Schottky specific heat of RbCl:CN for two CN concentrations. Both the Devonshire and modified Devonshire fits are shown.

at approximately the temperature predicted by the Devonshire model, and the other occurring at about .1°K. The perfect scaling with concentration appears to rule out any sort of a concentration dependent broadening mechanism as the cause of this disagreement.

Before discussing these results further, one should note an important point. One of the principal reasons for measuring the Schottky specific heat of a system is to deduce the entropy, and hence, the number of energy levels through the relationship:

$$\Delta S = \int \frac{C}{T} dT = nk \ln(x)$$

where ΔS is the change in entropy, C is the Schottky specific heat, n is the number of impurities, k is Boltzmann's constant, and x is the number of states. The integral is performed from the experimental data graphically. Unfortunately, since $\ln(x)$ is a slowly varying function of x , one needs a reasonably accurate determination of the concentration, n . As pointed out in Reference 4, the chemical analysis has not provided consistent results. Therefore, one cannot obtain an accurate value of the infrared oscillator strength. Thus, at present, one cannot use the values of ΔS obtained to distinguish between $nk \ln(6)$ (<100> defect), and $nk \ln(8)$ or $nk \ln(12)$ (<111> and <110> defects respectively). Most of the experimental results indicate the correctness of the <100> orientation.^{2,4} Table IV summarizes the results of the infrared absorption, and entropy values for the CN samples measured. Also, the concentration determined by assuming $nk \ln(6)$ for the entropy is indicated.

TABLE IV
Details of CN Samples

Host	Run #	Boule	Mole % in Melt	Curve	α_{CN} (cm^{-1})	α_{CNO} (cm^{-1})	$n_{\text{CN}}^{(a)}$ ($10^{17}/\text{cm}^3$)	ΔS $\frac{\text{erg}}{\text{gm-deg}}$	$n_{\Delta S}^{(b)}$ ($10^{17}/\text{cm}^3$)
KCl	PP11B	805025	(c)	A	.015	.099	4.4	57.1	4.6
	33A	610073	.01	B	.045	.24	13.2	140.	11.3
	SH4,SH6 ^(d)	428		C	.175 ^(e)		51.5	740.	60
	44A	610103	.1	D				1080	87.5
	SH1 ^(d)	248	.1	(f)	.42 ^(e)		124	1800	146
	SH3,SH5 ^(d)	388		E	2.		590	(g)	
	PP10A	805035	.5	E	.90	2.1		(g)	
		243	.5						
KBr	PP6B,PP8B	612285	.03					113	12.6
	34A	347	.1		.36	2.18 ^(h) 22.4 ⁽ⁱ⁾	122 ⁽¹⁾	470	52
KI	PP6A,PP8A	705255	.1					518	66
RbCl	32B,33B	516	.007		.03	.09 ^(j) .81 ^(k)	5.4	53	6.0
	34B	475	.07		.18	.30 ^(j) 3.07 ^(k)	32	397	45

- (a) The concentration of CN^- as determined from the infrared absorption constant α_{CN^-} using the latest calibrations,⁴ namely $\sigma_{\text{KCl}} = 2.94 \times 10^{19} \text{ cm}^{-2}$, $\sigma_{\text{KBr}} = 3.4 \times 10^{19} \text{ cm}^{-2}$, $\sigma_{\text{KI}} = 6.7 \times 10^{19} \text{ cm}^{-2}$, and $\sigma_{\text{RbCl}} = 1.84 \times 10^{19} \text{ cm}^{-2}$.
- (b) The concentration of CN^- computed from $\Delta S = nk \ln 6$.
- (c) Grown by taking 1.14 gm of Boule 243 and adding it to 60 gm of pure KCl.
- (d) Runs of Bill Seward.³⁶
- (e) Calculated from Seward's quoted concentration using the value of σ in use at that time, $3.6 \times 10^{19} \text{ cm}^{-2}$.
- (f) Not shown; very close for D.
- (g) Data not available to high enough temperature to perform a good extrapolation to compute ΔS .
- (h) At 2157 cm^{-1} .
- (i) At 2169 cm^{-1} .
- (j) At 2061 cm^{-1} .
- (k) At 2073 cm^{-1} .
- (1) Chemical analysis of this sample gave $6 \times 10^{18} \text{ cm}^{-3}$. This simply demonstrates the difficulties involved in obtaining an accurate determination of the concentration.

The scaling with CN concentration of the specific heat for each host lattice is best illustrated by the relative scaling of ΔS with the infrared absorption constant.

In order to obtain the observed shape of the specific heat curves for KBr, KI, and RbCl, one needs an energy level structure consisting of two manifolds; the first with a typical splitting corresponding to the peak observed at $.1^\circ\text{K}$, and the second split above the first by an energy corresponding to the high temperature specific heat peak or typical Devonshire splitting.

Dreyfus³⁷ has proposed a model to explain his paraelectric resonance results on RbCl:CN. The energy levels he predicts, as shown in Fig. 19, satisfy only the requirements of the lower levels. Hence, the fit one obtains (see Fig. 19) in using this energy level structure, gives only the low temperature peak and does not come close to explaining the data. This again points out the usefulness of specific heat measurements in testing models of these tunneling impurities.

Narayanamurti has pointed out that a small tetragonal distortion of the Devonshire potential will cause the T_{1u} level to split in such a manner as to give the required energy level structure. Using the size of this distortion K' as a parameter, Pompi and Narayanamurti³⁸ were able to fit the specific heat results. From the distortions they obtained, they also were able to explain their data on the effect of an electric field on the infrared vibration-libration absorption band of CN in these host lattices. Figure 20 schematically shows the effect

Figure 19. Comparison of experimental RbCl:CN specific heat data with theoretical curve based on model of Reference 37.

Figure 20. The effect of a tetragonal distortion on the Devonshire energy levels after Pompi and Narayanamurti.³⁸

of this distortion on the Devonshire energy levels and Figs. 15, 16, 17, and 18 show the resulting fits to the specific heat data. Table V gives the size of the distortion required to fit the specific heat data and the resulting energy levels.

The energy levels given in Table V are calculated in terms of the rotational constant B . B was determined by shifting the temperature axis of the calculated anomaly until the best fit to the specific heat data was obtained. The values of B obtained are considerably lower than previously thought. The reason for this is certainly due to some error in the value of K as explained earlier for KCl . Here, the error is magnified when the perturbation K' is applied. The correct procedure should be to take the new values of B , use the undistorted Devonshire model and the infrared librator frequency to find K , and apply the tetragonal distortion obtaining new values of K' and B that best fit the specific heat data. This iteration should be repeated several times until the values of B at the beginning and end of a calculation agree. But this would be an extremely lengthy and tedious procedure from which no new physics would be obtained.

One must also remember that the value of B was deduced in Reference 2 from higher temperature data. It is not unreasonable to expect a smaller value at lower temperatures representing the increased drag on the molecule by the surrounding lattice.

In addition to explaining the specific heat results, this proposed model provides a qualitative interpretation of the

TABLE V

Distortion and Energy Levels Required to Fit Specific
Heat Data for CN in Several Hosts

	KCl	KBr	KI	RbCl
K	16B	16B	16B	28B
K'	.04K	.10K	.10K	.03K
A _{1g}	0	0	0	0
A _{2u}	.847B	.477B	.477B	.244B
E _u	1.586B	2.203B	2.203B	1.305B
A _{1g}	2.107B	2.344B	2.344B	1.172B
B _{1g}	2.562B	3.200B	3.200B	1.603B
B(a)	.86 cm ⁻¹	.51 cm ⁻¹	.47 cm ⁻¹	.66 cm ⁻¹

(a) Deduced by shifting temperature axis to obtain best specific
heat fit. See text.

effect of an electric field on the thermal conductivity of two of these systems, KCl:CN and KBr:CN, as first reported by Seward and Narayanamurti² and extended here to lower temperatures. The data are plotted in Figs. 21 and 22. The results are qualitatively different than those found in KCl:Li (see previous chapter), where essentially, the effect of the electric field was to increase the conductivity below the temperature corresponding to the resonant frequency, and to decrease it above. For the CN systems, the thermal conductivity continues to decrease at temperatures well below the temperature of the low temperature resonance; i.e., .6°K.

Figure 20 shows the effect of an electric field on the energy levels arising from the tetragonally distorted Devonshire potential.³⁸ In first approximation, the only effect of the field is to increase the splitting between the $1A_1(1)$ and $2A_1(1)$ levels, thus causing scattering in a temperature range in which there was no scattering previously (below .6°K) and hence a large decrease in the thermal conductivity. The data for KCl:CN and KBr:CN indicate that the level causing the additional scattering in an electric field appears at a lower temperature in KBr:CN than in KCl:CN; i.e., for KCl:CN the scattering does eventually decrease in a field below .2°K, whereas it increases for all temperatures in our range for KBr:CN. This simply means that the size of the tetragonal distortion required for KCl:CN is smaller than for KBr:CN, as confirmed by the specific heat results.

Figure 21. The relative change in the thermal resistivity of KCl:CN in an electric field parallel to the $\langle 100 \rangle$ direction. The solid curves are not computed.

Figure 22. Same as Fig. 21, but for KBr:CN.

V. CONCLUSION

Measurements of the specific heat of KCl:Li can be explained in terms of a ground state energy level structure consisting of four equally spaced levels of degeneracies 1,3,3,1, characteristic of a potential with minima located along the $\langle 111 \rangle$ directions. The splitting deduced is $.82 \text{ cm}^{-1}$. The large increase of the splitting by 40% to 1.15 cm^{-1} when Li^6 is substituted for Li^7 , can be explained only if this splitting arises from a tunneling process. Specific heat measurements in an electric field indicate the polarizability of these tunneling states. These results are consistent with previous experimental and theoretical work.

The presence of a large isotope effect in the thermal conductivity of KCl:Li, similar to that observed in specific heat measurements, confirms that the tunnel states are indeed strongly coupled to the phonons. Measurements of the scattering strength or strength of this coupling as the resonant frequency is varied by changing the isotope, concentration, and electric field, support the previous observations of Pohl that the scattering strength depends primarily on the resonant frequency, and to a lesser degree on the nature of the particular defect.

For CN, however, specific heat measurements in several host lattices are found not to be in agreement with the predictions of the Devonshire model. This fact has led Pompi and Narayanamurti to postulate that introduction of the CN molecule

into the host lattice distorts the cubic symmetry of the surrounding cavity. By adding a term representing this distortion to the Devonshire potential, the Devonshire energy levels are modified in such a way as to give the observed specific heat. That no such similar distortion appears present in KCl:Li , is an indication that the distortion is caused by the molecule itself.

In addition to explaining the specific heat data, application of this model to other experiments; namely, the infrared measurements and the thermal conductivity measurements of KCl:CN and KBr:CN in an electric field, provides an interpretation of previously unexplained results.

The existence of tunneling states in KCl:OH , similar to those in KCl:CN , is confirmed through extensive specific heat measurements. The splittings found are less than half of those for KCl:CN .

For KCl:Li , significant deviations from the tunneling model are found for high concentrations and low temperatures. The possibility that a dipole-dipole interaction, as predicted in several theoretical works, is responsible for this behavior, is supported by the fact that analagous behavior is observed for OH in KCl where the dipole moment is similar, but not for CN in KCl where the dipole moment is much smaller. These results are consistent with dielectric measurements which show evidence of a dipole-dipole interaction in KCl:Li and KCl:OH .

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