OPTICAL PROPERTIES OF POTASSIUM IODIDE

IN THE FAR-INFRARED

by

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B.Sc., University of Alberta, 1971

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
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of
Physics

We accept this thesis as conforming to the
required standard

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September, 1974
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The University of British Columbia
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Date  October 9, 1974
ABSTRACT

Measurements and calculations of the far-infrared optical properties of K\textsuperscript{39}I at 300, 77, and 12°K are presented. The measurements are mainly those of absorption in crystals of various thicknesses. The calculation assumed cubic anharmonicity only, with nearest-neighbour coupling, and the input lattice-dynamical data were obtained from a shell-model program. These data were generated with a wavevector density of 32000 points per zone, which was sufficient to give 2-3 cm\textsuperscript{-1} resolution. The over-all agreement between experiment and theory, in both the intensity and structure of the spectra, is good. The magnitude of certain calculated features is, however, too large, indicating a need to consider next-nearest-neighbour interactions. Evidence was also found for three-phonon damping, both beyond the two-phonon limit at all temperatures and at \frac{v}{8} by 300°K. From these measurements it was possible to calculate portions of the three-phonon damping spectra, which were found to be reasonable. The higher-phonon effects at 300°K did not seem to be noticeably more pronounced than those found in the much harder LiF, and arguments are presented to understand this. Finally, the isotope-induced one-phonon processes which occur in natural KI were calculated. These are shown to be small away from the resonance frequency \frac{v}{8}, and not to be the major damping mechanism at \frac{v}{8} at low temperatures, in contrast to LiF.
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SECTION I

INTRODUCTION

I.1 General Introduction.

Far infrared radiation incident on an ionic crystal such as KI, interacts with the electronic dipole formed by the KI molecule, resulting in absorption of the radiation. The nature of this absorption may be understood by considering the phonon dispersion in the lattice. Figure I.1 shows the phonon dispersion in the [100] direction for a typical cubic lattice with a polar diatomic basis. The momentum of the phonon at the Brillouin Zone boundary, \( X \), is given by:

\[
\frac{\hbar |\kappa|}{\lambda} = \frac{\hbar}{2r_0}
\]

where \( \lambda \) is the wavelength of the phonon, \( \kappa \) is the wavevector of the phonon, and \( r_0 \) is the lattice spacing as shown in Figure I.2. Since \( r_0 \) equals 3.526\( \text{Å} \) for KI, the momentum of the phonon at the zone boundary is approximately \( \frac{\hbar}{2} \times 10^8 \text{ cm}^{-1} \), whereas the far infrared radiation has a momentum given by equation (I.1) of approximately \( \hbar \times 10^2 \text{ cm}^{-1} \).

Thus, compared with the momentum of the phonons, the incident radiation has effectively zero momentum. Therefore, if we consider the interaction of the incident radiation with an undamped lattice (and neglecting other than the first order electronic dipole moment) it may be seen that in order for momentum to be conserved, the interaction can occur only at the zone center \( \kappa = 0 \). Also, since the incident radiation is transverse in nature, only the transverse optic (TO) phonon may be excited. Therefore, in an undamped lattice with only a first order electronic dipole moment one would find resonant absorption only at the TO (\( \kappa = 0 \)) wavenumber,
Figure I.1 Schematic Representation of the Phonon Dispersion in the $\langle 100 \rangle$ direction of a Cubic Lattice with a Polar Diatomic Basis.
Figure I.2 A portion of the KI lattice (three faces shown)
\[ \bar{v}_i = \frac{1}{\lambda_i} = \frac{\nu}{c} \]  

Absorption at wavenumbers other than that of the resonant TO mode may come about directly through second or higher order terms in the electronic dipole moment, or through coupling of phonon modes through third or higher anharmonic terms in the potential energy. In the case of ionic crystals the off-resonance absorption is thought to occur mainly through the anharmonic mechanism, since the observed absorption is found to be much higher than in homopolar crystals such as diamond and silicon, where absorption is due to the second-order dipole moment only. In this work, therefore, we restrict ourselves to the case of a damped lattice with first-order dipole moment only.

In such a lattice it is possible for the TO mode to be excited by off-resonance radiation and then decay to two phonons, due to the coupling of ionic motions in the lattice. This is known as a two-phonon process. The initial and final states of the system must conserve energy and momentum; thus the two phonons involved in the process must have total energy equal to the energy of the incident radiation, and zero total momentum. This may be accomplished in two ways. First, two phonons may be created of equal, but opposite, momentum and total energy given by:

\[ E_{\text{tot}} = c \hbar \left( \bar{v}_1 + \bar{v}_2 \right) = c \hbar \bar{v}_{\text{rad}} \]  

This is known as a two-phonon summation process.

* Wave number, \( \bar{\nu} \) (cm\(^{-1}\)), is used as an energy unit instead of the more correct unit of frequency, \( \nu \) (Terahertz), since it is more convenient when working with the far-infrared spectrometer.
Secondly, the interaction may result in the annihilation of an already existing phonon of momentum $\hbar k$ and wavenumber $\bar{\nu}_i$, and the creation of another phonon of momentum $\hbar k'$ and wavenumber $\bar{\nu}_x$. In this case in order to conserve energy $\bar{\nu}_x - \bar{\nu}_i = \bar{\nu}_{\text{rad}}$, and these are known as two-phonon difference processes.

The intensity of the absorption of the incident radiation of wavenumber $\bar{\nu}$ by two-phonon processes depends basically on three quantities; the number of phonon pairs satisfying the energy and momentum requirements, the strength of the coupling of each phonon pair to the TO mode, and the probability of creating or annihilating the phonons involved.

It is clear that there is an upper limit to the wavenumber at which the two-phonon process may occur. This limit occurs at

$$\bar{\nu}_{\text{lim}} = \bar{\nu}_{\text{max}} + \bar{\nu}_{\text{max}}$$

where $\bar{\nu}_{\text{max}}$ and $\bar{\nu}_{\text{max}}$ are the wavenumbers of the two highest energy phonons that can combine through a summation process. This wavenumber, $\bar{\nu}_{\text{lim}}$, is referred to as the two-phonon limit.

It is interesting to examine the behavior of these two types of processes at low temperatures where the thermal vibrations of the lattice become small. In this case the total number of phonons existing in the lattice is given by:

$$N_{\text{tot}} = \sum_{\bar{k},j} n(\bar{k},j)$$

where $\bar{k}$ again represents the wavevector of the phonon and $j$ represents one of the polarization branches of the dispersion curves. Thus the pair $(\bar{k},j)$ represents a particular point on the dispersion curves. The term
\( n(k',j) \) represents the number of phonons in the state \((k,j)\), which is given by the Bose-Einstein distribution:

\[
n(k',j) = \left[ e^{\frac{\hbar \nu(k',j)}{k_B T}} - 1 \right]^{-1}
\]  \hspace{1cm} (I.5)

where \( \nu(k',j) \) is the wavenumber of the state \((k',j)\), \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. If the temperature, \( T \), is very small \( N_{\text{tot}} \) will also be very small and will approach zero as \( T \) approaches zero.

Since the occurrence of a difference process requires the presence of an already existing phonon, the number of such processes will become vanishingly small as \( T \) approaches zero. Summation processes, on the other hand, do not require any existing phonons and will, therefore, not vanish for small \( T \). Thus, the two-phonon (and higher) damping at low temperatures is almost exclusively due to summation processes.

The absorption processes described thus far occur if the crystal is composed of two well defined atoms. However, the presence of impurities in the lattice destroys the lattice periodicity and relaxes the condition of momentum conservation by the lattice phonons in an absorption process. This results in a one-phonon band absorption as well as possible local modes and in-band resonances. If one of the ions in the host lattice is replaced by a chemical impurity the potential experienced by this atom is significantly different from that of the ion it replaces. It then requires a complex force model to calculate the one-phonon absorption due to these impurities.

Isotopic impurities, however, act as weakly perturbing mass
defects which if present in sufficient quantities produce a one-phonon band absorption around the TO resonance, the intensity of the absorption depending on the phonon density-of-states of the isotope ion. This process must be considered for the KI lattice since natural KI contains 6.88% $^{41}$K isotope along with the predominant $^{39}$K isotope.

I.2 Motivation for the Thesis

This work represents part of a continuing study of the lattice absorption of alkali-halides being carried out by Eldridge (see Bibliography). Previous studies of the far-infrared optical properties of CsI (Eldridge and Beairsto 17) and LiF (Eldridge 13), as well as an investigation of the isotope-induced absorption of LiF (Eldridge 1) have been carried out, assuming only cubic anharmonicity. The agreement of calculated optical properties with various experimental data was, in general, good. Also it was found that consideration of a few criteria, proposed by Eldridge, for the strong coupling of phonon pairs, allowed one to predict fairly well which phonons with high symmetry wavevector points or branches would combine to produce peaks in the damping spectrum. The results of these investigations brought out several interesting points which suggested similar investigations in KI.

First, in both CsI and LiF it was found that by 300$^\circ$K there was evidence of three-phonon and higher damping, both at high wavenumbers beyond the two-phonon limit, and beneath the main TO resonance. The strength of the three-phonon processes at 300$^\circ$K depends on the crystal "hardness"; a hard crystal being one with high characteristic frequencies, such as LiF whose TO wavenumber at 300$^\circ$K is 305 cm$^{-1}$. "Soft" crystals, such as
CsI whose 300°K TO wavenumber is 62 cm$^{-1}$, will show more evidence of three-phonon damping at 300°K than hard crystals. It was thought, therefore, that KI, being a soft alkali-halide with a TO wavenumber of 109 cm$^{-1}$, would also show considerable evidence of higher order damping at 300°K.

Also in both CsI and LiF it was found that the TO resonance damping was due to two-phonon "difference" processes only (or three-phonon difference processes involving the destruction of at least one phonon). Thus, as the temperature is lowered the damping at the TO resonance becomes very small. Since the width of the TO resonance peak is proportional to, and the height of the peak inversely proportional to, the damping at $\bar{\nu}_0$, this results in an extremely sharp resonant absorption. The sharpness of the absorption in natural LiF was limited by the isotope-induced-one-phonon process, which accounted for a large fraction of the damping at $\bar{\nu}_0$ up to 300°K.

In KI, however, the presence of a large band gap between the acoustic and optic branches of the phonon dispersion curves suggested that relaxation of the TO resonance by two-acoustic-phonon-summation processes should be able to occur at $\bar{\nu}_0$. In this case no really sharp resonance should occur at low temperatures in KI and it was of interest to see if this was indeed the case.

Thirdly, in the previous work consideration was given to interactions involving other-than-next-nearest-neighbours. However, the method used to include these interactions was thought to overaccentuate the calculated spectral features, and it was felt that this work with KI could support this conclusion.
It should be noted, however, that previous calculations of the far infrared optical properties of KI at 300°K have been performed, and measurements of the absorption spectrum made, by Berg and Bell\textsuperscript{2}. Their calculations, however, were performed assuming interactions involving only nearest neighbours, and agreement between their experimental data and theoretical results was obtained by fitting the theoretical results to the experimental absorption maximum. Their results, therefore, showed no evidence of three-phonon and higher processes at $\omega_0$. They performed no low temperature measurements due to the difficulty of doing so with their asymmetric Michelson interferometer technique.

I.3 Outline of the Thesis.

Prior to the writing of this thesis a paper was written for publication containing the results and conclusions of this work. It was felt that rewriting these sections would be of little value and, therefore, this paper has been included in the thesis, following a more complete description of the experimental techniques and theory involved.

Section II describes the experimental techniques involved in the work.

Section III describes the theory and calculations which were performed.

Section IV presents the paper published in 1973 by Eldridge and Kembry describing in detail the results and conclusions of the work.
II.1 The Apparatus

The experiments were performed with a Beckman RIIC FS-720 Fourier Spectrophotometer with a step drive and Golay detector. The far infrared radiation was produced by a quartz-envelope mercury-arc lamp.

The radiation passing through the sample was sampled using steps of 10, 20, or 40 microns depending on the wavenumber range of interest. The maximum wavenumber that may be resolved using a given step size, $s$, is given by:

$$ n \frac{\bar{v}_{\text{max}}}{\nu_{\text{max}}} = \frac{10000}{2s} \text{ cm}^{-1} \quad (II.1) $$

where $s$ is given in microns. Thus, the maximum wavenumbers possible with the step sizes mentioned above are 500, 250, and 125 cm$^{-1}$ respectively.

If, however, radiation with wavenumbers greater than $\nu_{\text{max}}$ is present it will be interpreted as radiation with wavenumbers lying in the range 0 to $\nu_{\text{max}}$, causing the spectrum at these lower wavenumbers to appear stronger than it actually is. These contributions due to radiation with wavenumbers greater than the maximum resolvable wavenumber are known as "false energies". In order to avoid this problem radiation with wavenumbers higher than $\nu_{\text{max}}$ were eliminated by using a high-density black-polyethylene lens filter together with Beckman absorption filters. Electrical RC smoothing also acted as a low-pass filter and helped eliminate the higher energies.

The data was punched on paper tape, transferred to magnetic tape and fast-Fourier analysed using an IBM 360/67 computer.

For the low temperature experiments the sample was mounted on a rotatable copper cold-finger, which was in thermal contact with the
coolant reservoir in a metal dewar. The tail-piece to which the samples were mounted was of hexagonal design (Figure II.1) which enabled measurements to be done on two samples without removing the dewar from the system. The dewar was filled with liquid nitrogen or liquid helium and it was possible to pump on the coolant to produce lower temperatures. A copper shield maintained at liquid nitrogen temperature surrounded the cold-finger to reduce liquid helium boil-off and prevent condensation of residual water vapor on the sample.

Using a liquid helium reservoir the temperature of the tail-piece was measured to be $11^\circ K$ using a carbon-resistance thermometer (a previous measurement by Kuwahara (1971) gave $12^\circ K \pm 2^\circ K$). To ensure a good thermal contact between the sample and the tail-piece, the samples were pressure mounted to the tail-piece with silver grease.

II.2 Sample Preparation

A single crystal of natural KI was obtained from Harshaw Chemical Co. This crystal could be cleaved easily to produce the thick samples ($d \approx 3\text{mm}$). To produce the thin samples, however, it was necessary to polish thicker, cleaved pieces; since the sample would bend if cleaved too thinly. The polishing was done on a felt cloth using a fine alumina grit, mixed in ethylene glycol. Since KI dissolves quite rapidly in ethylene glycol the process was largely an etching, but the use of the polishing wheel minimized rounding of the edges and produced a good, uniform sample quickly. The thin samples were made with a slight wedge shape to eliminate interference fringes. The polished samples were then cleaned in acetone and rinsed in trichloro-
Figure II.1 Tail-piece for mounting samples for low temperature experiments.
ethylene and dried. Trichloroethylene was used for the final rinse since it was found to have no noticeable affect on the sample. A great deal of care had to be taken in the cleaning and rinsing of the sample as it was found to bend very easily when wet. Attempts were made to polish very thin samples using a plate with a removable plug, to minimize handling of the sample. It was found, however, that it was very difficult to completely clean the polishing solution from the sample while the plug was in, and removal of the plug while the sample was wet resulted in damage to the sample.

To determine the effects of polishing on the optical properties of the sample, measurements of the absorption and reflectance were performed on cleaved and polished samples. No significant difference was detected.

Using this technique samples were produced ranging in thickness from .01 cm to 1 cm.

II.3 Analysis of Experimental Data

The experimental data, punched on the paper tape in binary code, were then written onto magnetic tape. The double-sided interferogram was then analysed using a fast-Fourier transform routine to give an intensity spectrum of the radiation. Intensity spectra were obtained for the radiation with the sample in the beam, I(ν), and with the sample out of the beam, I₀(ν). These two intensity spectra are related by Airy's formula:

$$I = \frac{I₀ (1-R)² \left(1 + k²/\pi²\right) e^{-\alpha d}}{1 - R² e^{-2\alpha d}}$$  (II.2)
where $\alpha$ is the absorption coefficient, $d$ is the sample thickness, $R$ is the power reflectance, and $k$ and $n$ are the extinction coefficient and index of refraction respectively. The power reflectance was measured and it was found that on the low wavenumber side of the TO resonance $R$ could be approximated by the classical equation:

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (\text{II}.3)$$

and

$$n^2 = \varepsilon_0 + \frac{\varepsilon_0 - \varepsilon_\infty}{1 - \frac{\nu^2}{\nu_0^2}} \quad (\text{II}.4)$$

where $\varepsilon_0$ and $\varepsilon_\infty$ are the low and high frequency dielectric constants. The values of $\varepsilon_0$, $\varepsilon_\infty$ and $\nu_0$ are given in Table II.1. On the high frequency side the measured reflectivity was used. Beyond 140 cm$^{-1}$ this was found to be fairly constant at approximately 5%.

Since the accuracy of the measurement was optimum when $ad = 1$ it was necessary to use a wide range of thicknesses to obtain reliable results over the entire range of $\alpha$. Even using the thinnest sample, however, the signal was so strongly attenuated in the region of the resonance that it was impossible to obtain absorption data from 85 to 145 cm$^{-1}$. Several runs were done at each temperature using different samples and the results were averaged to give the final experimental results and to give an estimate of the experimental error.
### Input Data for the Calculations

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<th>77°K</th>
<th>12°K</th>
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<td>Static dielectric constant</td>
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<td>4.68^c</td>
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<td>High frequency dielectric constant</td>
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<td>2.67^b</td>
<td>2.68^c</td>
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<td>3.501^b</td>
<td>3.492^d</td>
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<td>Compressibility</td>
<td>β (10⁻¹²/barye)</td>
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<td>8.00^b</td>
<td>7.75^d</td>
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<td>Repulsive overlap potential parameters</td>
<td>C(10⁻¹⁰ ergs)</td>
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<td>60.20</td>
<td>71.04</td>
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<td>p(10⁻⁸ cm)</td>
<td>0.3495</td>
<td>0.3369</td>
<td>0.3302</td>
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<td>Third potential derivative</td>
<td>a''''ₙ.T. (r₀)(10¹² erg cm⁻³)</td>
<td>-3.845</td>
<td>-4.234</td>
<td>-4.449</td>
</tr>
<tr>
<td>Coulombic term</td>
<td>e²/r₀^₄</td>
<td>0.576</td>
<td>0.592</td>
<td>0.599</td>
</tr>
<tr>
<td>Repulsive term</td>
<td>Ce⁻r₀/p²/p³ (10¹² erg cm⁻³)</td>
<td>-4.421</td>
<td>-4.826</td>
<td>-5.048</td>
</tr>
<tr>
<td>Second potential derivative</td>
<td>a''ₙ.T. (r₀)/r₀ (10¹² erg cm⁻³)</td>
<td>0.246</td>
<td>0.267</td>
<td>0.278</td>
</tr>
<tr>
<td>First potential derivative</td>
<td>a'ₙ.T. (r₀)/r₀² (10¹² erg cm⁻³)</td>
<td>0.053</td>
<td>0.053</td>
<td>0.055</td>
</tr>
<tr>
<td>Szigeti effective charge</td>
<td>e²/e</td>
<td>0.72</td>
<td>0.72</td>
<td>0.73</td>
</tr>
</tbody>
</table>

^aSee Ref. 2  
^bObtained by interpolation  
^cSee Ref. 7  
^dSee Ref. 8
SECTION III
THEORY

III.1 General Introduction

In this section we will present the theory used, and the calculations performed, in obtaining the theoretical results.

The theory uses the results of calculations by Wallis and Maradudin\(^{18}\) and Cowley\(^{19}\) which use only the first-order dipole moment and include contributions from cubic terms in the potential energy. Solution of the many-body problem for this system shows that the many-body effects may be expressed as a complex phase shift suffered by each of the normal modes. The real part of the phase shift gives the change in energy (wavenumber), and the imaginary part gives the damping of the mode. This damping and wavenumber shift are discussed in Section III.2.

Section III.2.1 discusses the contribution to the damping due to the isotopic impurity.

Section III.3 discusses the calculation of the potential derivatives.

Section III.4 describes the calculation of the phonon eigendata using a shell model calculation.

Section III.5 describes the calculation of the complex phase shift and Section III.6 describes the calculation of the optical properties.
III.2 Damping and Wavenumber Shift of the TO Resonance.

An expression for the complex dielectric constant of a cubic crystal with first-order electronic dipole moment has been obtained by Wallis and Maradudin and Cowley and is given in convenient notation by the expression:

\[ \hat{\varepsilon} = \varepsilon' + i \varepsilon'' = \varepsilon_{\infty} + \frac{e^* (M^+ + M^-)}{\pi \nu_c M^+ M^- \left[ \nu_0^2 + \nu_0^2 + 2 \nu_0^2 [\Delta(0,j0;\nu) - i \Gamma(0,j0;\nu)] \right]} \]  

(III.1)

where \( M^+ \) and \( M^- \) are the masses of the \( K^+ \) and \( I^- \) ions, \( \nu \) is the volume of the unit cell, \( c \) is the velocity of light, and \( \nu_0 \) is the observed wavenumber (\( \text{cm}^{-1} \)) of the TO lattice resonance with wavevector \( \vec{k} \) effectively equal to zero. This expression assumes a crystal with only two atoms per unit cell and, therefore, only one resonance. The terms \( \Delta(0,j0;\nu) \) and \( \Gamma(0,j0;\nu) \) are the wavenumber-dependent wavenumber shift and the damping of the TO resonance respectively. Since we are concerned here only with the TO resonance we will use the abbreviated form \( \Delta(\nu) \) and \( \Gamma(\nu) \) to refer to these quantities. Finally \( e^*_t \) is the macroscopic effective charge associated with the TO mode, given by:

\[ e^*_t = \frac{1}{3} e^* (\varepsilon_{\infty} + 2) \]  

(III.2)

with \( e^* \) equal to the Szigetti effective charge.

If the damping of the TO resonance is assumed to occur through a two-phonon process with a combined wavenumber of \( \nu \) then the damping may be written (Cowley):

\[ \Gamma(\nu) \left( \text{cm}^{-1} \right) = \frac{9}{2 \pi^2 \hbar^2} \sum_{k_j} \sum_{-k_j} \left| \nu^0(0,j0; \vec{k}_j, -\vec{k}_j) \right|^2 S(\nu) \]  

(III.3)
where $V^{(3)}$ is the cubic coupling coefficient which couples the TO
resonance to two other phonons which, in order to satisfy momentum
conservation, must have equal and opposite wavevectors $\mathbf{k}$, and in a
crystal with center-of-inversion symmetry must belong to different
polarization branches $j_1$ and $j_2$. $S(v)$ is the probability of a par-
ticular two-phonon process occurring, and also serves as an energy con-
servation term, as follows.

The probability of a particular two-phonon process is determined
from the occupation numbers, $n$, of the two states involved: $k,j_1$ and
$-k,j_2$. According to quantum theory, the probability, $P$, of creation
or annihilation of a phonon is given by (Ziman):

$$
P_{n \rightarrow n+1} \propto \frac{1}{n+1}
$$

$$
P_{n \rightarrow n-1} \propto \frac{1}{n}
$$

where $n$ is given by equation (I,5). Thus the net probability for the
creation of two phonons, $P_{++}$, (summation process) is equal to the prob-
ability of creation of two phonons minus the probability for annihilation
of two phonons:

$$
P_{++} \propto \left[ n(k,j_1) + 1 \right] \left[ n(-k,j_2) + 1 \right] - n(k,j_1) n(-k,j_2)
$$

$$
\quad \propto n(k,j_1) + n(-k,j_2) + 1
$$

and the net probability for creation of one phonon and annihilation of
another, $P_{+-}$, (difference process) is:

$$
P_{+-} \propto \left[ n(k,j_1) + 1 \right] n(-k,j_2) - n(k,j_1) \left[ n(-k,j_2) + 1 \right]
$$

$$
\quad \propto n(k,j_1) - n(-k,j_2)
$$
The temperature dependence of the summation and difference processes at high and low temperature may be found by considering $P_{++}$ and $P_{+-}$ in the case of the high and low temperature limits of equation (I.5) for $n(k,j)$. At high temperatures $n(k,j)$ may be written as:

$$n(k,j) = \left[ 1 + \frac{c \hbar \overline{\nu}(k,j)}{k_B T} + \ldots - 1 \right]^{-1} \quad (III.7)$$

which leads to:

$$n(k,j) \propto T \quad (III.8)$$

so that at high temperatures both summation and difference processes are proportional to $T$. As $T$ approaches zero, however, the probability for a two-phonon difference process becomes vanishingly small, whereas the probability for a summation process remains finite. At very low temperatures, therefore, the difference processes will disappear and the summation processes will remain.

Energy conservation is incorporated into the $S(\nu)$ term by means of a KrDâraer delta, as shown below in the final forms of $S(\nu)$ for summation processes:

$$S(\nu) = \left[ n(k,j) + n(-k,j) + 1 \right] \times \delta \left[ \overline{\nu} - \overline{\nu}(k,j) - \overline{\nu}(-k,j) \right] \quad (III.9)$$

and difference processes:

$$S(\nu) = \left[ n(k,j) - n(-k,j) \right] \times \left\{ \delta \left[ \overline{\nu} + \overline{\nu}(k,j) - \overline{\nu}(-k,j) \right] - \delta \left[ \overline{\nu} - \overline{\nu}(k,j) + \overline{\nu}(-k,j) \right] \right\} \quad (III.10)$$
It may be shown that the coupling of two phonon modes to the TO mode occurs through the third derivative of the potential energy and that the strength of the coupling depends largely on the relative motions of the ions in the two phonon modes involved, and the masses of the ions. The relative motions of the ions in the two phonon modes are given by the eigenvectors of the equations of motion of the ions and may be found using a shell model calculation.

The general expression for the cubic coupling coefficient for a rocksalt structure is given by:

\[
\gamma_{\ell}(\vec{k}_{1},\vec{j}_{1};\vec{k}_{2},\vec{j}_{2};\vec{k}_{3},\vec{j}_{3}) = \frac{1}{q_{0}} \left[ \frac{t_{3}^{3}}{(\pi c N)^{3}} \delta(\vec{k}_{1},\vec{j}_{1}) \delta(\vec{k}_{2},\vec{j}_{2}) \delta(\vec{k}_{3},\vec{j}_{3}) \right] \Delta(\vec{k}_{1}+\vec{k}_{2}+\vec{k}_{3})
\]

\[
x \left\{ \sum_{L_{1}} \sum_{K_{1}} \sum_{\alpha_{1},\alpha_{1}^{'}} \sum_{\alpha_{2},\alpha_{2}^{'}} \Phi_{\alpha_{1},\alpha_{1}^{'},\alpha_{2},\alpha_{2}^{'}}(L_{1},K_{1};L_{1}^{'},K_{1}^{'}) \prod \left[ \frac{m_{\alpha_{1}}^{K}(K_{1},J_{1})}{M_{K}^{K_{1}}} \exp \left( 2\pi i \vec{r}_{e} \cdot \vec{x}(L_{1},K_{1}) \right) - \frac{m_{\alpha_{2}}^{K'}(K_{1}',J_{1}')}{M_{K'}^{K_{1}'}} \right]
\right. 
\]

\[
\left. \times \exp \left( 2\pi i \vec{r}_{e} \cdot \vec{x}(L_{1}^{'},K_{1}') \right) \right] \right\}
\]

where \( N \) is the number of unit cells, \( \vec{x}(L,K) \) the position vector of the \( K \)th type of ion in the \( L \)th unit cell, \( M_{K} \) the mass of the \( K \)th type of ion, and \( \Phi_{\alpha_{1},\alpha_{1}^{'},\alpha_{2},\alpha_{2}^{'}}(LK,L'K') \) the third Cartesian derivative of the potential energy between the two ions at \( LK \) and \( L'K' \) (the first anharmonic term in the potential energy Taylor expansion). \( m_{\alpha_{1}}^{K}(K_{1},J_{1}) \) is the \( \alpha_{1} \)th component of the eigenvector for the \( K \)th type ion when disturbed by the mode \( \vec{k}_{1},j_{1} \). The delta function \( \Delta(\vec{k}_{1}+\vec{k}_{2}+\vec{k}_{3}) \) conserves momentum by being set equal to one when the wavevector sum equals zero or a reciprocal-lattice vector, and by being set equal to zero otherwise. The inclusion of the reciprocal-lattice vectors does not alter the final form of \( \Gamma(\vec{v}) \) and \( \Delta(\vec{v}) \) and therefore, with only the TO resonance \( (\vec{k}_{1} = 0) \) being excited, then
\( \bar{k}_2 = -\bar{k}_3 \) and \( V^{(3)} \) becomes \( V^{(3)}(0,j_j;\bar{k},j_j;\bar{k},j_j) \). Since the crystal has cubic symmetry, \( \Gamma(\bar{\nu}) \) will be independent of the polarization of the incident photon. Assuming it is polarized with its wavevector along the \( x \) direction, \( \alpha_4 \) may be set equal to \( x \) (Johnson and Bell\(^2\)). Converting the effective force constants \( \phi_{\alpha\alpha-\alpha} (\bar{k},\nu) \) to radial derivatives and considering nearest-neighbours only, one arrives at the expression:

\[
V^{(3)}(0,j_j;\bar{k},j_j;\bar{k},j_j) = -\frac{i}{3} \left[ \frac{8N \left( M^* M^* \right)}{\left( M^* M^* \right) \nu_0 \left( 2\pi \nu_c \right)^3} \right]^{1/2} \left[ \nu(\bar{k},j_j) \tilde{\nu}(\bar{k},j_j) \right]^{-1/2} \times \left\{ \phi'''(r_o) \left[ m^+_{\alpha}(k_{ij}) m^-_{\alpha}(k_{ij}) - m^+_{\alpha}(k_{ij}) m^-_{\alpha}(k_{ij}) \right] + \left( \frac{\phi''(r_o)}{r_o^2} - \frac{\phi'(r_o)}{r_o^3} \right) \times \sum_{\alpha=\gamma,j} \left[ m^+_{\alpha}(k_{ij}) m^-_{\alpha}(k_{ij}) - m^+_{\alpha}(k_{ij}) m^-_{\alpha}(k_{ij}) \right] \sin(2\pi r_o k_z) \right. \\
\left. \times \sum_{\delta=\gamma,j} \left[ m^+_{\delta}(k_{ij}) m^-_{\delta}(k_{ij}) - m^+_{\delta}(k_{ij}) m^-_{\delta}(k_{ij}) \right] \sin(2\pi r_o k_z) \right. \\
+ \left( \frac{\phi''(r_o)}{r_o^2} - \frac{\phi'(r_o)}{r_o^3} \right) \sum_{\delta=\gamma,j} \left[ m^+_{\delta}(k_{ij}) m^-_{\delta}(k_{ij}) - m^+_{\delta}(k_{ij}) m^-_{\delta}(k_{ij}) \right] \sin(2\pi r_o k_z) \left\} \right. \\
(III.12) \\

In this expression the third derivative of the potential energy has been given in terms of the first, second and third radial derivatives; \( \phi'(r_o) \), \( \phi''(r_o) \) and \( \phi'''(r_o) \), where \( r_o \) is the nearest-neighbour separation.

The damping, \( \Gamma(\bar{\nu}) \), therefore, depends on the strength of the coupling of the two phonon modes to the TO resonance, and the probability of creation or destruction of the phonons involved.

The wavenumber-dependent wavenumber shift, \( \Delta(\bar{\nu}) \), may be calculated in a manner similar to that described by Johnson and Bell.\(^2\)
and Berg and Bell where $\Delta(\nu)$ is given by an expression similar to equation (III.12). However, in the calculations performed here, it was found convenient to obtain $\Delta(\nu)$ by means of the Kramers-Kronig theorem which relates the real and imaginary parts of the complex phase shift. Using this relationship it may be written (Ziman):

\[
\Delta(\nu) = \frac{2}{\pi} \int_0^\infty \frac{\nu'}{\nu'^2 + \nu^2 + \eta^2} T(\nu) d\nu + \text{const} \quad (\text{III.13})
\]

where $\eta$ is a small number.

The wavenumber dependent shifts caused, for example, by thermal expansion have not been calculated since their effect is compensated by the use of the experimental values of $\nu_0$.

III.2.2 Isotope Induced Damping.

The one-phonon absorption due to an isotopic impurity in an alkali-halide has been obtained by MacDonald, Klein and Martin. However, this expression was derived for regions in the wings of the resonance. A singularity results at $\nu_0$. Eldridge and Howard have used this expression to calculate the effective damping, $\Gamma_{\text{iso}}(\nu)$, of the TO resonance due to the impurity, which is continuous throughout the reststrahlenpeak. This may then be added to the $\Gamma_2$-phonon $(\nu)$, given by equation (III.3), and used in the complex phase shift to calculate the optical properties. As given by Eldridge and Howard:

\[
\Gamma_{\text{iso}}(\nu) = \frac{\pi^2 M^- \langle (\Delta M^+)^2 \rangle}{4 \nu_0 (M^+)^2 (M^++M^-)} \rho^*(\nu) \quad (\text{III.14})
\]

where $\rho^*(\nu)$ is the phonon density of states for the $K^+$ sublattice given
where \( m(k,j) \) is defined as before, and \( \varphi^+(\varphi) \) is normalized such that:

\[
\int_{-\infty}^{\infty} \varphi^+(\varphi) \, d\varphi = 1
\]

### III.3 The Potential Energies

The calculation of the cubic coupling coefficient

\[ V^{(3)}(0, j_0; k_1, j_1; k_2, j_2), \]

(abbreviated to \( V^{(3)} \)) for the pair of phonon modes \( k, j_1 \) and \( k, j_2 \) requires the knowledge of the phonon eigendata and the various derivatives of the potential energy, \( \phi(r) \). These derivatives were determined in the manner employed by Eldridge and Howard in which the effect of other-than-nearest-neighbours was included.

Starting with the general expression for the equilibrium potential due to the attractive coulomb interaction of the entire lattice, and the short range repulsive interaction of nearest-neighbours only, we have:

\[
\phi(r_0) = -\frac{\kappa e^2}{r_0} + \kappa C \frac{e^2}{r_0^3} \rho
\]

where \( \kappa \) is the Madelung constant, and \( C \) and \( \rho \) may be obtained from the temperature-dependent experimental values of the compressibility, \( \beta \), and the lattice constant, \( r_0 \) (nearest neighbour separation).

However, in the evaluation of \( V^{(3)} \) we are interested in the potential energy due to a pair of nearest-neighbours only. In this case we have:

\[
\phi_{NN}(r_0) = -\frac{e^2}{r_0} + \kappa C \frac{e^2}{r_0^3} \rho
\]
which leads to the third derivative,

$$\phi''''_{NN}(r_o) = \frac{6e^2}{r_o^6} - \frac{C_e^{-\alpha/\rho}}{\rho^3}$$  \hspace{1cm} (III.19)

We then assume that the coupling of all neighbours will be of the same form as $V^{(3)}$, but that the coupling will decrease with more distant neighbours due to the decrease in the coulombic interaction. It is also assumed that the repulsive term would decrease sufficiently rapidly that other than nearest-neighbours would not couple to the TO mode through this term and it could, therefore, be left unaltered.

Using these assumptions a sum of the coulombic contributions to $\phi''(r_o)$ was performed over shells of neighbours to produce the modified potential derivative, $\phi''''_M(r_o)$, where

$$\phi''''_M(r_o) = \frac{\alpha'e^2}{r_o^6} - \frac{C_e^{-\alpha/\rho}}{\rho^3}$$  \hspace{1cm} (III.20)

where $\alpha' = 3.862$.

This procedure was later found to be incorrect for two reasons. First, according to equation (III.11), coupling can only occur between ions of opposite sign. Thus, the summation of the coulombic term should have been carried out over shells of opposite sign only. Secondly, it has been found by Beairsto and Eldridge\textsuperscript{17} that the short-range-repulsive term does not fall off as quickly as expected, and that next-nearest-neighbours should have been considered in this term.

The expressions for the potential derivatives used in this calculation, then, are given by:

$$\phi'(r_o) = \frac{\alpha'e^2}{6r_o^5} - \frac{C_e^{-\alpha/\rho}}{r_o^2 \rho}$$  \hspace{1cm} (III.21)
The values of these derivatives are given in Table II.1.

Using these values of the potential derivatives and the eigendata supplied by the shell model program the calculation of $V^{(3)}$ becomes relatively straightforward.

### III.4 The Shell Model Calculation

The basic theory of the shell model used in this work is described by Cochran et al.\textsuperscript{22}: This theory assumes that the lattice is made up of ions, each surrounded by a shell representing the outer electron cloud surrounding the ion. This shell is coupled to the ion core by a force constant determined by the mechanical polarizability, $d_{\perp}$, of the ion. In a lattice composed of such units three types of short-range interactions are considered, in addition to the long-range coulombic interaction. These are between neighbouring ions, ions and their surrounding shells, and between neighbouring shells.

These short-range interactions are given in terms of parameters $A$ and $B$, where $A$ and $B$ are defined by Cochran\textsuperscript{22},

\[
\left( \frac{\partial^2 \phi(kk')}{\partial r^2} \right)_|| = \frac{e^2 A(kk')}{2v} ; \quad \left( \frac{\partial^2 \phi(kk')}{\partial r^2} \right)_\perp = \frac{e^2 B(kk')}{2v} \quad (III.24)
\]

where $e$ is the electronic charge, $v$ is the volume of the unit cell,
and $\Phi (K'K)$ is the potential energy at ion K due to ion K'. Interaction between nearest-neighbours then are given by $A(12)$ and $B(12)$, and interactions between next-nearest-neighbours are given by $A(11)$, $B(11)$, $A(22)$, $B(22)$.

In order to reduce the number of independent short-range parameters Cochran et al.\textsuperscript{22} assumed that the short-range forces extend only to next-nearest-neighbours, that the forces are axially symmetric, and that next-nearest-neighbours coupling occurs only through the shells. The parameters then required are: $A_S(12)$, $B_S(12)$, $A_S(11)$, $B_S(11)$, $A_S(22)$, $B_S(22)$, $A_S(12)$, $B_S(12)$, $A_T(12)$, $B_T(12)$, $A_T(21)$, $B_T(21)$, where the subscript S denotes shell-shell interactions, the subscript T denotes ion-shell interactions, and the subscript I denotes ion-ion interactions.

It can be shown, however, that only ten of the above parameters are independent. These ten independent parameters combined with the electrical polarizabilities, $\alpha_i$, the mechanical polarizabilities, $\delta_i$, and the effective charge $Z$, yield a fifteen parameter model.

In order to generate the phonon eigendata the fifteen parameter shell model program of G. Dolling, kindly supplied to us, and modified by R. Howard, was used. This program could also be used as an eleven parameter model, simply by assigning four of the input parameters the value unity.

The values of the input parameters were taken from Dolling et al.\textsuperscript{6}. They found, by fitting to dispersion curves for KI measured at 90 K by inelastic neutron scattering that these curves could be well
described by an eleven parameter model. These parameters are given in Table III.1.

The computer program sets up the appropriate 6x6 dynamical matrix for the two ionic species for any given wavevector \( \vec{k} \). The solution of the secular equation yields six eigenvalues and their corresponding eigenvectors, where the eigenvalues are the frequencies of the phonon modes (in cm\(^{-1}\)) and the eigenvectors describe the polarization of the ionic motions. The program also gives the multiplicity of the eigenvalues, which is the number of nonequal wavevectors \( \vec{k}' \) related by symmetry to the wavevector \( \vec{k} \). To generate the eigendata used in the calculations this procedure was repeated for a grid of wavevectors distributed uniformly throughout the irreducible \( \frac{1}{48} \) of the Brillouin zone. Then by performing the appropriate symmetry operations it is possible to generate eigendata for wavevectors throughout the Brillouin zone.

Eigendata were generated by this method for 915 values of \( \vec{k} \) in the irreducible \( \frac{1}{48} \) of the Brillouin zone, which is equivalent to 32000 wavevector points in the full zone, or 10 evenly spaced wavevectors from the zone center to the \( \langle 100 \rangle \) boundary. This operation took approximately 30 seconds of computer time.

In another mode the program may be used to generate eigendata for wavevectors in a specific direction in the Brillouin zone. A sample of the input data for operation in this mode is shown in Table III.2. Cards 1 through 18 are the input parameters for a fifteen parameter
### TABLE III.1
Shell Model Parameters

<table>
<thead>
<tr>
<th>Parameter ( A_I(12) )</th>
<th>Value ( 13.4 \pm .05 )</th>
<th>Units ( e^2/2v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_I(12) )</td>
<td>-1.0 ± .2</td>
<td>( e^2/2v )</td>
</tr>
<tr>
<td>( A_S(11) )</td>
<td>-0.16 ± .25</td>
<td>( e^2/2v )</td>
</tr>
<tr>
<td>( B_S(11) )</td>
<td>-0.001 ± .06</td>
<td>( e^2/2v )</td>
</tr>
<tr>
<td>( A_S(22) )</td>
<td>-0.29 ± .24</td>
<td>( e^2/2v )</td>
</tr>
<tr>
<td>( B_S(22) )</td>
<td>.05 ± .05</td>
<td>( e^2/2v )</td>
</tr>
<tr>
<td>( Z )</td>
<td>.92 ± .04</td>
<td>( e )</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>2.28 ± .145</td>
<td>( 10^{-24} ; \text{cm}^3 )</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>4.51 ± .4</td>
<td>( 10^{-24} ; \text{cm}^3 )</td>
</tr>
<tr>
<td>( d_1 )</td>
<td>-0.11 ± .04</td>
<td>( e )</td>
</tr>
<tr>
<td>( d_2 )</td>
<td>0.13 ± .05</td>
<td>( e )</td>
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</table>
### TABLE III.2
INPUT DATA FOR THE SHELL MODEL PROGRAM

<table>
<thead>
<tr>
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<th>Data Description</th>
<th>Format</th>
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<tr>
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<td>B(12)</td>
<td>F10.5</td>
</tr>
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<td>-0.01</td>
<td>B(11)</td>
<td>F10.5</td>
</tr>
<tr>
<td>5</td>
<td>-0.29</td>
<td>A(22)</td>
<td>F10.5</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>B(22)</td>
<td>F10.5</td>
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<tr>
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<td>.92</td>
<td>Z</td>
<td>F10.5</td>
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<td>F10.5</td>
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<td>F10.5</td>
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<td>$d_2$</td>
<td>F10.5</td>
</tr>
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</tr>
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<td>number of steps</td>
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<td>21</td>
<td>1 1 1</td>
<td>$k_{\text{initial}}$</td>
<td>$k_{\text{final}}$</td>
</tr>
</tbody>
</table>
shell model. If the program is to be used as an eleven parameter shell model, cards 12, 13, 14, and 15 are set equal to 1.0 as shown. Card 19 specifies if the program is to be used to calculate eigendata for the \( \frac{1}{48} \) part of the Brillouin zone, or if it is to be used to find eigendata for a single direction. In the former case the card specifies the number of wavevectors desired in the [000] direction of the full Brillouin zone, while in the latter case the card carries the value zero, as shown. Cards 20 and 21, not needed of card 19 is not equal to zero, determine the particular wavevectors for which the eigendata are to be calculated. The first three numbers of card 21 are the coordinates of the initial wavevector, \( \vec{k}_{\text{initial}} \), multiplied by a scaling factor, \( F \), (so that \( \vec{k} \) may be represented by integer coordinates). The next three numbers are the coordinates of the final wavevector, \( \vec{k}_{\text{final}} \), multiplied by the same scaling factor. The last number is the scaling factor, \( F \). Card 20 gives the number of steps to be taken in going from \( \vec{k}_{\text{initial}} \) to \( \vec{k}_{\text{final}} \). The last card may be repeated to obtain eigendata for different directions in the Brillouin zone. The output for the input data of Table III.2 would give eigenvectors and eigenvalues for \( \vec{k} = (0.1, 0.1, 0.1) \); \( \vec{k} = (0.2, 0.2, 0.2) \) etc. to \( \vec{k} = (1, 1, 1) \). An example of the formatted output is shown in Table III.3.

It should be noted that this program cannot be used to calculate eigendata for \( \vec{k} = 0 \). Also, the electrical polarizabilities used in this program are polarizabilities per unit volume, so it was necessary to divide the values of \( \alpha \) given by Dolling et al.⁶ by the volume of the unit cell in \( \text{cm}^3 \).
### TABLE III.3

**TYPICAL OUTPUT OF SHELL MODEL PROGRAM**


data:

\[
180^\circ K \quad 90, 90, 90; \quad \text{MULTIPlicity} \quad 4
\]

<table>
<thead>
<tr>
<th>Eigenvalues ((\text{cm}^{-1}))</th>
<th>(m_x^+(k,j))</th>
<th>(m_y^+(k,j))</th>
<th>(m_z^+(k,j))</th>
<th>(m_x^-(k,j))</th>
<th>(m_y^-(k,j))</th>
<th>(m_z^-(k,j))</th>
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</thead>
<tbody>
<tr>
<td>53.91296</td>
<td>0.00000007</td>
<td>0.00000007</td>
<td>-0.00000021</td>
<td>0.38912761</td>
<td>0.42707890</td>
<td>-0.81620497</td>
</tr>
<tr>
<td>53.91310</td>
<td>-0.00000014</td>
<td>-0.00000018</td>
<td>-0.00000010</td>
<td>-0.71780807</td>
<td>0.69589734</td>
<td>0.02191186</td>
</tr>
<tr>
<td>68.81201</td>
<td>-0.00000014</td>
<td>-0.00000018</td>
<td>-0.00000018</td>
<td>-0.57735062</td>
<td>-0.57735062</td>
<td>-0.57735163</td>
</tr>
<tr>
<td>96.25179</td>
<td>0.73000413</td>
<td>-0.68173623</td>
<td>-0.04826769</td>
<td>0.00000045</td>
<td>-0.00000044</td>
<td>0.0</td>
</tr>
<tr>
<td>96.25200</td>
<td>0.36573493</td>
<td>0.44933748</td>
<td>-0.81507176</td>
<td>-0.00000043</td>
<td>0.00000031</td>
<td>0.00000021</td>
</tr>
<tr>
<td>128.15515</td>
<td>0.57735205</td>
<td>0.57735229</td>
<td>0.57735336</td>
<td>-0.00000009</td>
<td>-0.00000020</td>
<td>-0.00000016</td>
</tr>
</tbody>
</table>

**Eigenvectors**
Since the phonon wavenumbers generally decrease as the temperature is increased, it was necessary to make a correction to the wavenumbers for the calculation of the 300°K results. This was done by decreasing the wavenumbers of all modes by 5%, which is approximately the shift seen in the wavenumber of the TO mode as the temperature is increased from 90°K to 300°K.

III.5 Calculation of the Complex Phase Shift.

As shown in expression (III.3), the calculation of $\Gamma(\nu)$ from $V^{(3)}$ and $S(\nu)$ requires a double summation over all values of $\mathbf{k}$ in the Brillouin zone. As described earlier, the eigendata generated by the shell model represent a total of 32000 wavevector points in the zone. Since it would require an extremely lengthy calculation to evaluate $\Gamma(\nu)$ for all 32000 wavevectors, it was found to be easier, and faster, to calculate a modified coupling term, $|V^{(3)}|_{\text{modified}}^2$, which could be applied to a wavevector in the irreducible part of the Brillouin zone to yield the total damping, $\Gamma(\nu)$, for all symmetry related wavevectors. This modified coupling term was actually an average of $|V^{(3)}|^2$ obtained under rotation and inversion of the coordinates. Due to the high symmetry of $V^{(3)}$ it was necessary to calculate only three values of $|V^{(3)}|^2$; one with $V^{(3)}$ as given by equation III.12, and two others with $x$ replaced by $y$ and $z$ respectively. Using the modified coupling term the total value of $\Gamma(\nu)$ for all modes related by symmetry to the two modes $\mathbf{k},j_1$ and $-\mathbf{k},j_2$ in the irreducible part of the zone is simply $\Gamma(\nu)$ for $\mathbf{k},j_1$ and
\(-k, j\) times the multiplicity of \(\vec{k}\).

It was also found that a 50\% reduction in calculation could be achieved by making the summation in expression III.3 \(\sum_{\vec{k}} \sum_{\vec{k}, j} \cdot \cdot \cdot\)
which is equivalent to \(\sum_{\vec{k}, j} \sum_{\vec{k}} \cdot \cdot \cdot\).

The calculation of \(\Gamma(\vec{v})\) for KI for 32000 wavevector points in the Brillouin zone, using this technique took approximately 30 seconds of computer time.

The wavenumber dependent wavenumber shift, \(\Delta(\vec{v})\), was calculated using expression (III.13) where the integration was taken to some \(\vec{v}_{\text{max}}\) beyond which \(\Gamma(\vec{v})\) is effectively zero (two-phonon limit) and \(\eta\) was taken as \(0.1 \text{cm}^{-1}\). It was not necessary to know the constant in equation (III.13) since \(\Delta(\vec{v})\) was adjusted so that \(\Delta(\vec{v}_0)\) was equal to zero. This was done by subtracting \(\Delta(\vec{v}_0)\) from all values of \(\Delta(\vec{v})\).

III.6 The Optical Properties.

The optical properties examined in this work are the real and imaginary parts of the dielectric constant, the absorption coefficient, the reflectivity and the phase angle, and the refractive index. These quantities may all be derived from the complex dielectric constant through the use of the following macroscopic electromagnetic relations:

\[
\begin{align*}
(a) & \quad \hat{\varepsilon} = \varepsilon' + i\varepsilon'' \\
(b) & \quad \hat{\alpha} = n + ik \\
(c) & \quad \hat{n} = \hat{\varepsilon} \frac{\nu}{c}
\end{align*}
\]
III.6.1 The Real Dielectric Constant.

The real part of the dielectric constant may be derived directly from equation (III.1) and is given by:

\[ \varepsilon'(\nu) = \varepsilon_0 + \frac{e_k^2 (M^* + M^-) \left[ \Delta(\nu) \right]}{\pi \nu c^2 M^* M^- \left\{ \left[ \Delta(\nu) \right]^2 + 4 \Delta^2(\nu) \right\}} \]  

(III.26)

III.6.2 The Imaginary Dielectric Constant.

The imaginary part of the dielectric constant may also be directly obtained from equation (III.1) and is given by:

\[ \varepsilon''(\nu) = \frac{e_k^2 (M^* + M^-) \left\{ \Delta(\nu) \right\}}{\pi \nu c^2 M^* M^- \left\{ \left[ \Delta(\nu) \right]^2 + 4 \Delta^2(\nu) \right\}} \]  

(III.27)

III.6.3 The Absorption Coefficient, \( \alpha \).

The absorption coefficient, \( \alpha \), is most easily calculated by first finding the extinction coefficient, \( k \), and then using the relation:

\[ \alpha = 4\pi k \nu \]  

(III.28)

The extinction coefficient may be found using equations (III.25) to be:

\[ k(\nu) = \frac{1}{2} \left[ |\hat{\varepsilon}(\nu)| - \varepsilon'(\nu) \right] \]  

(III.29)

from which,

\[ \alpha(\nu) = 2\sqrt{2} \pi \nu \left[ |\hat{\varepsilon}(\nu)| - \varepsilon'(\nu) \right]^\frac{1}{2} \]  

(III.30)
III.6.4 The Refractive Index, \( n \).

Using equations (III.25) we find for the refractive index, \( n \),
\[
\hat{n}^2 = \hat{e}
\]
\[
\Rightarrow \quad n^2 - k^2 + 2i\hbar n = \varepsilon' + i\varepsilon''
\] (III.31)
So that:
\[
2nk = \varepsilon''
\] (III.32)
and:
\[
n = \frac{\varepsilon''}{2k}
\] (III.33)

III.6.5 The Reflectivity, \( R \), and The Phase Angle, \( \phi \).

The power reflectivity, \( R \), and the phase angle, \( \phi \), are found from the relation
\[
R = |\hat{r}|^2
\] (III.34)
where \( \hat{r} \), the reflectance amplitude, is given, for normal incidence, by,
\[
\hat{r} = r e^{i\phi} = \frac{n + ik - 1}{n + ik + 1}
\] (III.35)
Writing \( re^{i\phi} \) as \( r(\cos\phi + isin\phi) \) it follows that:
\[
\phi = \arctan \left[ \frac{2k}{n^2 + k^2 - 1} \right]
\] (III.36)
and:
\[
R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}
\] (III.37)
FURTHER MEASUREMENTS AND CALCULATIONS OF THE FAR-INFRINGEMENT ANHARMONIC
OPTICAL PROPERTIES OF KI BETWEEN 12 AND 300°K*

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Department of Physics
The University of British Columbia
Vancouver, British Columbia, Canada

Measurements and calculations of the far-infrared optical properties of KI at 300, 77, and 12°K are presented. The measurements are mainly those of absorption in crystals of various thicknesses. The calculation assumed cubic anharmonicity only, with nearest-neighbor coupling, and the input lattice-dynamical data were obtained from the shell-model program. These data were generated with a wave-vector density of 32,000 points per zone, which was sufficient to give a 2-3 cm⁻¹ resolution. The overall agreement between experiment and theory, in both the intensity and the structure of the spectra, is good. The magnitude of certain calculated features is, however, too large, indicating a need to consider next-nearest-neighbor interactions. Evidence was also found for three-phonon damping, both beyond the two-phonon limit at all temperatures and at \( \bar{v}_0 \) by 300°K. From these measurements it was possible to calculate portions of the three-phonon damping spectra, which were found to be reasonable. The higher-phonon effects at 300°K did not seem noticeably more pronounced than those found in the much harder LiF, and arguments are presented to understand this. Finally, the isotope-induced one-phonon processes which occur in natural KI were calculated. These are shown to be small away from the resonance frequency \( \bar{v}_0 \) and not to be the major damping mechanism at \( \bar{v}_0 \) at low temperatures, in contrast to LiF.
IV.1. INTRODUCTION

Calculations have recently been presented\(^1\) on the far-infrared optical properties of Li\(^7\)F and natural LiF, assuming only cubic anharmonicity. The agreement with various experimental data was, in general, good, and there emerged several interesting points which it was felt could be profitably investigated in the case of a different compound of the same structure. One point was that by 300 °K there was evidence of higher-phonon relaxation, arising from quartic anharmonicity, etc., both at high wave numbers, beyond the two-phonon limit, and underneath the main transverse-optic (TO) resonance at \(\tilde{\nu}_o\) wave number. (The width of the TO resonance peak in the imaginary dielectric constant is proportional to, and the height of the peak inversely proportional to, the damping at \(\tilde{\nu}_o\).) The reason why these higher-order processes were noticeable in the region of \(\tilde{\nu}_o\) was due to two factors. First, the calculations showed that relaxation via the creation of two-phonons ('summation' processes) did not occur at \(\tilde{\nu}_o\) but started at slightly higher wave numbers. Second, the magnitude of the damping by two-phonon 'difference' processes was very small at \(\tilde{\nu}_o\). Above some range of temperatures, proportional to the wave numbers of the phonons involved (through the occupation numbers - see Sec. IV), three-phonon damping will increase more rapidly with temperature than the two-phonon damping. This range of temperatures obviously increases with crystal hardness. In LiF which is one of the hardest alkali halides, 300 °K was sufficient to show the three-phonon damping at \(\tilde{\nu}_o\). It was thought therefore that in KI, one of the softest rocksalt-structure alkali halides, there may be even greater evidence of three-phonon damping at \(\tilde{\nu}_o\) by 300 °K. It should be noted here, however, that Berg and Bell\(^2\) have already measured the optical properties of KI at room temperature by the very accurate method
of asymmetric Fourier spectroscopy. Comparison with the results of their calculation, which also assumed only cubic anharmonicity, did not markedly show any three-phonon effects in the vicinity of \( \nu_0 \), although there was again the expected high-wave-number tail. This result was to be partly expected since they scaled their calculated values by fitting to the \( \nu_0 \) peak height. We will return to this point again.

A second result of the LiF work was that, as already mentioned, the main resonance was found to relax by two-phonon 'difference' processes only (or three-phonon 'difference' processes, involving the destruction of at least one phonon), so that as the temperature is lowered, the resonance in Li\(^7\)F becomes extremely sharp. In natural LiF, containing 7.5% Li\(^6\), the temperature-independent damping by isotope-induced one-phonon processes was found to limit the sharpness of the resonance at low temperatures, and to account for a large fraction of the \( \nu_0 \) damping up to 300 °K. In KI, however, the ionic mass ratio of iodine to potassium is higher than that for fluorine to lithium, and thus the TO-mode wave number \( \nu_0 \) is higher with respect to the zone-boundary acoustic phonons. Consequently it was expected that relaxation by two-acoustic-phonon summation processes would be able to occur at \( \nu_0 \), so that no really sharp resonance should occur at low temperatures in pure KI. (Low-energy acoustic phonons do not couple at all strongly due to their long wavelength and similar nature, which in combination produce very small relative displacements of nearest neighbors: Coupling seems to commence at wave vectors approximately halfway across the Brillouin zone). Natural KI does contain, however, 6.88% K\(^{41}\) with the predominant K\(^{39}\) so that once again isotope-induced one-phonon damping is present. It was not known how great a part this damping would play at \( \nu_0 \) at low temperatures, nor whether it would become evident in absorption measurements below \( \nu_0 \).
where the 'difference' damping at low temperatures is small. If this were the case information could be obtained about the phonon eigenvectors at certain symmetry points, as was done for LiF$^3$.

A final point to emerge from the LiF work concerned the size and assignment of the two-phonon peaks or features. By performing a lattice summation of the slowly decreasing electronic term in the third derivative of the lattice potential, consideration was given to the magnitude of the cubic coupling by all neighbors. For similitude, however, the form of the coupling by all neighbors was taken to be the same as that for nearest neighbors. The net result was thought to be an overaccentuation of the calculated spectral features. This work with KI supports this conclusion. With regard to the two-phonon assignments of any features, it was seen that consideration of a few criteria for strong coupling allowed one to predict fairly well which phonons with high-symmetry wave-vector points or branches would combine to produce peaks in the damping spectrum. Investigation of these peaks often showed, however, that large contributions from low-symmetry branches were also present. In the past some careless assignments have been made of these features. The assignments are not inherently of any great importance, but nevertheless are interesting and can be made fairly accurately. Srivastava and Bist$^4$ have recently analyzed the absorption spectra of KI and NaI. Some time ago Renk$^5$ reported some very sharp temperature-dependent absorption peaks in KI below $\nu_0$ at 5 and 6 °K, which he assigned to specific two-phonon difference processes. The measurements and calculations presented here will resolve some of the claims made in these two communications.
IV.2. DAMPING AND FREQUENCY-SHIFT OF THE TO RESONANCE

The final forms used to compute the frequency-dependent damping (inverse lifetime) \( \Gamma (0, j_0; \overline{\nu}) \), and frequency shift \( \Delta (0, j_0; \overline{\nu}) \) of the TO lattice resonant mode, with near-zero wave vector, in rock-salt-structured crystals may be found in Ref. 1. References to the theory underlying these results may also be found there. It may be repeated here that the inclusion of only cubic anharmonicity means that absorption of infrared radiation at any wave number \( \overline{\nu} \) occurs through off-resonance excitation of the TO resonance at \( \overline{\nu}_0 \), which then relaxes to two phonons with equal and opposite wave vector, to give zero final momentum effectively equal to that of the infrared photon, and a combined energy ('summation' or 'difference') of wave number \( \overline{\nu} \).

The form of \( \Gamma (0, j_0; \overline{\nu}) \), which will be abbreviated to \( \Gamma (\overline{\nu}) \), contains the wavevectors, eigenvectors, and eigenvalues of the phonons involved, and the calculation of \( \Gamma (\overline{\nu}) \) requires a summation over a uniform distribution of wavevectors throughout the Brillouin zone. These lattice-dynamical data were obtained from a shell-model program, using the input parameters of Dolling et al., which they found by fitting to frequency dispersion curves measured at 90 °K by inelastic neutron scattering. Model III was employed, and the data were generated with a wave-vector density of 32,000 points/zone (915 points in the irreducible \( \frac{1}{48} \) element of the zone). As a first-order approximation to the temperature-dependent frequency-shifts of the phonons, an over-all 5% frequency reduction, approximately that observed in the TO mode, was applied to produce the 300 °K data. The form of the first, second and third radial derivatives of the nearest-neighbor potential were again taken as in Ref. 1 where consideration was given to the interaction of all neighbors through the slowly decreasing electronic term. A summation over
50 'shells' of nearest neighbors yielded a constant $\alpha''$ equal to 3.862 ± 0.002, which modifies the magnitude of the Coulombic terms. These derivatives appear in the cubic-coupling coefficient which in turn is part of $\Gamma(\nu)$, and their respective magnitudes may be seen in Table IV. Together with all other input data used in the calculations.

Figure 1 shows the 300 °K calculated $\Gamma(\nu)$ spectrum, with the difference and summation processes drawn separately, together with the calculation of Berg and Bell, in which the two processes have been combined. In the present calculation with 915 independent wave-vector points, the spectrum was smoothed by convolution with a nine-point least-squares-fitting function, giving a resolution of 2 or 3 cm$^{-1}$. No hand smoothing has been performed. This resolution explains in part the differences between the two calculations (e.g. the heights and widths of the 142- and 153-cm$^{-1}$ peaks), since the Berg-Bell calculation was performed with only 48 independent wave vectors. Other dissimilarities occur due to the different values of potential derivatives used in the calculations. A fairly important result of this will be seen in the subsection of this section.

Figure 2 shows the 300 and 12 °K frequency shifts $\Delta'(\nu)$ calculated from $\Gamma'(\nu)$ as described in Ref. 1 and adjusted to equal zero at the observed resonance frequency $\nu_0$.

Figure 3 shows the 12 °K $\Gamma(\nu)$ spectra for the sum and difference processes (note the scale change at 120 cm$^{-1}$) together with the damping of the TO mode due to isotope-induced one-phonon processes, $\Gamma_{iso}(\nu)$, calculated as described in Ref. 1. The peak near $\nu_0$ in $\Gamma_{iso}(\nu)$ is due to the TO modes across the zone, and the disappearance at 95 cm$^{-1}$, follows from the presence of a band gap which extends to $69$ cm$^{-1}$. Below this are the small amplitudes of the light $K^+$ ions in the acoustic modes, together with the
<table>
<thead>
<tr>
<th>Input Data for the Calculations</th>
<th>( \bar{v}_0 ) (cm(^{-1}))</th>
<th>300°K</th>
<th>77°K</th>
<th>12°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.O. resonance wavenumber</td>
<td>( \bar{v}_0 )</td>
<td>101(^{a})</td>
<td>107.5(^{b})</td>
<td>109.5(^{c})</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>( \epsilon_0 )</td>
<td>5.09(^{c})</td>
<td>4.78(^{b})</td>
<td>4.68(^{c})</td>
</tr>
<tr>
<td>High frequency dielectric constant</td>
<td>( \epsilon_m )</td>
<td>2.65(^{c})</td>
<td>2.67(^{b})</td>
<td>2.68(^{c})</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>( r_0 ) (10(^{-8}) cm)</td>
<td>3.526(^{d})</td>
<td>3.501(^{b})</td>
<td>3.492(^{d})</td>
</tr>
<tr>
<td>Compressibility</td>
<td>( \beta ) (10(^{-12})/barye)</td>
<td>8.54(^{d})</td>
<td>8.00(^{b})</td>
<td>7.75(^{d})</td>
</tr>
<tr>
<td>Repulsive overlap potential parameters</td>
<td>( C ) (10(^{-10}) ergs)</td>
<td>45.45</td>
<td>60.20</td>
<td>71.04</td>
</tr>
<tr>
<td></td>
<td>( \rho ) (10(^{-8}) cm)</td>
<td>0.3495</td>
<td>0.3369</td>
<td>0.3302</td>
</tr>
<tr>
<td>Third potential derivative</td>
<td>( \phi^{N.T.} (r_0) / r_0 ) (10(^{12}) erg cm(^{-3}))</td>
<td>-3.845</td>
<td>-4.234</td>
<td>-4.449</td>
</tr>
<tr>
<td>Coulombic term</td>
<td>( a \epsilon^2 / r_0 ) (10(^{12}) erg cm(^{-3}))</td>
<td>0.576</td>
<td>0.592</td>
<td>0.599</td>
</tr>
<tr>
<td>Repulsive term</td>
<td>( C e^{-r_0 / \rho} ) (10(^{12}) erg cm(^{-3}))</td>
<td>-4.421</td>
<td>-4.826</td>
<td>-5.048</td>
</tr>
<tr>
<td>Second potential derivative</td>
<td>( \phi^{N.T.} (r_0) / r_0 ) (10(^{12}) erg cm(^{-3}))</td>
<td>0.246</td>
<td>0.267</td>
<td>0.278</td>
</tr>
<tr>
<td>First potential derivative</td>
<td>( \phi^{N.T.} (r_0) / r_0 ) (10(^{12}) erg cm(^{-3}))</td>
<td>0.053</td>
<td>0.053</td>
<td>0.055</td>
</tr>
<tr>
<td>Szigeti effective charge</td>
<td>( e^a / e )</td>
<td>0.72</td>
<td>0.72</td>
<td>0.73</td>
</tr>
</tbody>
</table>

\(^{a}\)See Ref. 2 \(^{b}\)Obtained by interpolation \(^{c}\)See Ref. 7 \(^{d}\)See Ref. 8
Present calculation of the two-phonon damping of the TO resonance of $\text{K}^{39}\text{I}$ at 300°K, with both processes shown separately (solid lines) and the features labeled; together with the calculation of Ref. 2 with both processes combined (dashed line).
Calculated frequency-dependent frequency shift of the TO resonance of K$_{39}$I resulting from two-phonon damping, at 300 and 12°K. $\bar{\nu}_0$ is the observed resonance wave number.
Calculated two-phonon damping of the TO resonance of $K^{39}\text{I}$ at $12^o\text{K}$ via difference and summation processes, drawn separately together with the isotope-induced one-phonon damping of the resonance in natural KI. The left-hand scale refers to all curves up to $120 \text{ cm}^{-1}$. 
large wave-number separation from $\bar{\nu}_o$, the small concentration of the isotopes and the small mass defect all combine to make $\Gamma_{iso}(\bar{\nu})$ very small. (Note that in LiF$^3$ and NaCl,$^{11}$ where larger effects were observed, not only were there no bands gaps, but the mass defect was large in the first case, and the concentration large in the second). Consequently it appears that little information may be obtained from the isotope-induced absorption away from $\bar{\nu}_o$, but that at $\bar{\nu}_o$ at low temperatures these damping processes will be of approximately equal strength with the two-phonon summation processes.

It is also of interest to compare the various values of resonance damping $\Gamma(0, \nu; \bar{\nu}_o)$ calculated or measured by other authors. Table IV.2 lists some of these, and it may be seen that while there is general agreement at room temperature, the one low-temperature experimental value of Jones et al. is far larger than the calculated values. Since the measurements by Jones et al. were performed on thin films, could this indicate surface-mode relaxation? (Their room-temperature value is also high).

Two-Phonon Assignments

Criteria for the strong coupling of two phonons have been given.$^{13}$ On the basis of these, Table IV.3 lists of pairs of high-symmetry phonons which may be expected to produce features in the $\Gamma(\bar{\nu})$ spectrum if the dispersion slopes are matched (parallel for difference, opposite for summation). The approximate reduced-wave-vector position $h$ is given where the slope matching is optimum. Fig. IV.4 shows the dispersion curves resulting from the shell-model calculation, for KI at 90 °K. The $E_g$ curves and those from L through W to X were not measured by neutron scattering. The feature numbers in Fig. IV.1nâ‘County TABLE IV.3 refer to the $0^\circ \text{K}$ spectrum with its 5% frequency reduction, whereas the wave numbers in Table IV.3 were taken from
<table>
<thead>
<tr>
<th>Source</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jones et al.</td>
<td>3.48 (R.T.)</td>
<td>3.025 (4.2°K)</td>
</tr>
<tr>
<td>Dolling et al.</td>
<td>2.06 (300°K)</td>
<td>0.183 (5°K)</td>
</tr>
<tr>
<td>(theo.)</td>
<td></td>
<td>(isotopically pure)</td>
</tr>
<tr>
<td>Berg and Bell</td>
<td>~2.4 (R.T.)</td>
<td></td>
</tr>
<tr>
<td>(expt.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present results</td>
<td>~1.4 (300°K)</td>
<td>0.16 (12°K)</td>
</tr>
<tr>
<td>(theo.)</td>
<td>(~0.6 Diff + ~0.8 Sum)</td>
<td>(~0.08 Sum + ~0.08 Isotope)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
</tr>
</tbody>
</table>

*See Ref. 11, See Ref. 6, See Ref. 2.*
<table>
<thead>
<tr>
<th>Symmetries of combining phonons</th>
<th>Difference</th>
<th>Summation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumbers at, and positions of, (h), maximum expected contribution</td>
<td>Corresponding infrared wavenumber (cm⁻¹) and feature assignment, (n), if appropriate</td>
</tr>
<tr>
<td>$\Delta_1 \Delta_1$</td>
<td>111-66 (0.6)</td>
<td>45 (small)</td>
</tr>
<tr>
<td>$\Delta_5 \Delta_5$</td>
<td>109-28 (0.7)</td>
<td>$81(6)$ at 300°K overall max at 12°K</td>
</tr>
<tr>
<td>$\Gamma_1 \Gamma_1$</td>
<td>116-65 (0.7)</td>
<td>51 (small)</td>
</tr>
<tr>
<td>$\Gamma_4 \Gamma_4$</td>
<td>96-54 (0.5)</td>
<td>42 (3)</td>
</tr>
<tr>
<td>$\Gamma_1 (LO) \Gamma_4 (TO)$</td>
<td>120-96 (0.5)</td>
<td>24 (very small)</td>
</tr>
<tr>
<td>$\Gamma_1 (LO) \Gamma_4 (TA)$</td>
<td>116-53 (0.6)</td>
<td>63</td>
</tr>
<tr>
<td>$\Gamma_1 (LA) \Gamma_4 (TO)$</td>
<td>96-66 (0.5)</td>
<td>30 (2)</td>
</tr>
<tr>
<td>$\Gamma_1 (LA) \Gamma_4 (TA)$</td>
<td>66-54 (0.5)</td>
<td>12 (1)</td>
</tr>
<tr>
<td>$L_1' \Gamma_1$</td>
<td>128-69</td>
<td>59</td>
</tr>
<tr>
<td>$L_1' \Gamma_3$</td>
<td>128-54</td>
<td>74</td>
</tr>
<tr>
<td>$L_3' \Gamma_1$</td>
<td>96-69</td>
<td>27</td>
</tr>
<tr>
<td>$L_3' \Gamma_3$</td>
<td>96-54</td>
<td>42 (3)</td>
</tr>
<tr>
<td>$W_1 W_2$</td>
<td>104-58</td>
<td>46 (3)</td>
</tr>
<tr>
<td>($L_3' \to W_2')+(L_1' \to W_1'$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma = Q$ and $W$</td>
<td></td>
<td>4 and 5</td>
</tr>
</tbody>
</table>
the 90 °K data of Fig. IV.4. Some of the strong low-symmetry combinations are also listed in Table IV.3 but it was not felt worthwhile to list them all. Of importance also is the energy of destroyed phonon in the difference processes, as is obvious by 12 °K, where the maximum around 80 cm⁻¹ corresponds to the Δ₅ Δ₅ combination (combinations at X are forbidden), since the Δ₅ acoustic mode is the least energetic of all.

Of further interest are the phonon pairs which determine the limits of the two kinds of process. Of importance in this respect is the low coupling obtained between acoustic modes. Not only is there very little coupling between small wave-vector acoustic phonons, as already mentioned, so that combinations do not become significant until half-way to the zone boundary, but even after this no great coupling is obtained. Δ₃Δ₅ combine only through a term involving the first and second radial derivatives [φ' (rₒ) and φ'' (r₀)]; see Eq. (6) in Ref. 1] which is typically only 10% of the third derivative φ''' (rₒ) through which major combinations occur. Likewise Σ₃ combines with any other mode in this manner only. Both Σ₃Σ₄ (acoustic) combine through φ'''' (rₒ) but only weakly, since the former are forbidden at the zone boundary due to the motion of one ion only, and the latter is small by virtue of the polarization directions involved in the modes. These produce the same kind of relative displacement along a Cartesian direction where the nearest neighbors are located [see Eq. (6) in Ref. 1]. Consequently the lowest difference combinations in LiF were with optic modes (Σ₄Σ₄ and L'₃L₃), whereas in KI they are the very weak Σ₄Σ₁ acoustic. Similarly in LiF the first summation pairs were the transverse-optic modes near vₒ with low-energy acoustic modes [just far enough away from the origin for the sine-modulation term in Γ(ν) to take effect]. These were then necessarily above vₒ.
Frequency dispersion curves of KI along major symmetry directions, generated by the shell model, for KI at 95°K. The shell model was fitted to neutron measurements, which did not include \( \Sigma_4 \) modes or those from L through W to X.
Similar combinations are seen as features marked 8 in Fig. IV.1. In KI, however, where the TO mode is so high, the first summation pairs are the weak acoustic ones with wave vectors approximately halfway across the zone. Thus it may be seen that the magnitudes of $\phi''(r_0)$ and $\phi'(r_0)$ determine to a great extent the summation damping at $\nu_0$ in KI, and the difference in $\Gamma(\nu_0)$ between the calculated value here and that due to Berg and Bell lies in the different values used for these derivatives.

The high-wave-number limit of the difference processes is simply the highest-energy longitudinal-optic mode near the zone origin, with a low-energy acoustic mode, the intensity decreasing rapidly as the origin is approached. Theoretically the highest summation combination can come from two optic modes, $\Sigma_1\Sigma_4$, for instance, but these are found to be very weak just as were the acoustic combinations, so that the 'effective' limit as in LiF may be taken as $L_1L_1'$.

### IV.13 OPTICAL PROPERTIES

The optical properties will be calculated for isotopically pure K$^{39}$I only, since it has been seen in Fig. IV.3 that the isotopesinduced one-phonon damping has a small effect away from $\nu_0$ where the present measurements were performed. It can easily be included in the calculation if in the future low-temperature measurements are performed in the region of $\nu_0$ on natural KI. The resonance peak at 12 °K should be approximately only half as sharp in natural KI as in the isotopically pure material.

#### A. Dielectric Constants

Figure IV.5 shows the real and imaginary dielectric constant at 0 °C and 12 °K, calculated as in Ref. 1. Once again the Szigeti effective charge $e^*$ has been calculated by using the measured values of $\epsilon_0$, $\epsilon_\infty$, and $\nu_0$, and including the 'static' frequency shift $\Delta'$ (0) of the TO resonance produced by the
Calculated real dielectric constants of $K^{39}I$ at 300 and 12°K. The predicted frequency of the longitudinal-optic mode with near-zero wave vector, $\bar{\nu}_{LO}$, occurs when $\epsilon'$ passes through zero.
cubic anharmonicity [see Eq. (25) in Ref. 1]. This latter is the only departure from the usual harmonic approximation used to obtain \( e^* \). With \( \Delta' (0) \) equal to -2.7, -0.3, and +0.7 cm\(^{-1}\) at 300, 77, and 12 \(^\circ\)K, respectively, the values of \( e^* \) so obtained differ little from the harmonic values\(^8\) and may be found in Table IV.1.

Another departure from harmonicity occurs in the wave number at which \( e' \) passes through zero. This is then the predicted wave number of the longitudinal-optic mode with near-zero wave vector, \( \nu_{LO} \). In the harmonic approximation, the Lyddane-Sachs-Teller (LST) relationship is obtained.

\[
\frac{\nu_{LO}^2}{\nu_{O}^2} = \frac{e_o}{e_\infty},
\]

which with the experimental values in Table IV predicts \( \nu_{LO} \) to be 145 and 140 cm\(^{-1}\) at 12 and 300 \(^\circ\)K, respectively.

Upon including cubic anharmonicity, Eq. (1) is modified as shown in Ref. 1 to be

\[
\frac{\nu_{LO}}{\nu_{O}} = \frac{e_o}{e_\infty} (1 + \frac{2\Delta' (0)}{\nu_{O}} + \frac{2}{\nu_{O}} [\Delta'' (\nu_{LO}) - \Delta' (0)])
\]

With \( \Delta' (\nu_{LO}) \) equal to -12 cm\(^{-1}\) (300 \(^\circ\)K) and -2.4 cm\(^{-1}\) (12 \(^\circ\)K), and the same values of \( e_o \), \( e_\infty \), and \( \nu_{O} \), Eq. (2) predicts the values of \( \nu_{LO} \) to be 143 cm\(^{-1}\) at 12 \(^\circ\)K and 128 cm\(^{-1}\) at 300 \(^\circ\)K, as shown in Fig. IV.5.

The only value of \( \nu_{LO} \) measured by inelastic neutron diffraction is that at 90 \(^\circ\)K, equal to 142 cm\(^{-1}\). This does not discriminate between the harmonic and anharmonic 12 \(^\circ\)K values of 145 and 143 cm\(^{-1}\), both of which are a little higher as expected.
At 300 °K, the optical measurements of Berg and Bell allow \( \nu_{LO} \) to be deduced. It may be shown that at \( \nu_{LO} \), where \( \epsilon' = 0 \), the refractive index \( n \), equals the extinction coefficient \( k \). This occurs in Berg and Bell's data at approximately 129 cm\(^{-1}\), in far better agreement with the anharmonic value of 128 cm\(^{-1}\) than the LST value of 140 cm\(^{-1}\). Furthermore, the temperature variation of \( \nu_{LO} \) as predicted by Eq. (2) is similar to that observed in the resonant mode \( \nu_{O} \), whereas the temperature variation in the LST predicted values of \( \nu_{LO} \) is very small. This gives confidence then in the calculated frequency shifts of Fig.IV.2

Fig.IV.6 shows the imaginary dielectric constants, again at 12 and 300 °K. The factor-of-20 reduction in \( \epsilon''(\nu) \) in going from 300 to 12 °K is seen most clearly in the \( \epsilon'' \) resonance peak, whereas it is not so obvious in the related constants \( n \) and \( k \) (since \( \epsilon'' = 2nk \)).

B. Absorption Coefficient

The absorption coefficient \( \alpha \) from 0 to 300 cm\(^{-1}\) was calculated from \( \epsilon' \) and \( \epsilon'' \) at 300, 77, and 12 °K and may be seen in Fig.IV.7. Also shown are the present experimental data obtained at the three temperatures, and the room-temperature data of Ref. 2, converted from \( k \) to \( \alpha \). For the sake of clarity the data between 140 and 180 cm\(^{-1}\) has been omitted and may be seen in Fig.IV.8 where 300 and 77 °K curves have been vertically displaced.

C. Experimental

The measurements were performed on an RIIC. FS 720 Fourier spectrometer, with a step drive and Golay detector. The single crystals of natural KI were obtained from Harshaw Chemical Co. and cleaned and polished to the desired thickness \( d \), which varied from 0.01 to 1.0 cm. A slight wedge shape was
Calculated imaginary dielectric constants of $K^{39}\text{I}$ at 300 and 120°K.
Fig. IV.7

Present experimental and calculated values of the absorption coefficient of $K^{39}$I at 300, 77, and 12°K, together with the room-temperature experimental data from Ref. 2. The experimental data obtained between 140 and 180 cm$^{-1}$ have been omitted for clarity.
Present experimental and calculated values of the absorption coefficient of K$_3$I at 300 and 77°K in the range omitted for clarity from Fig. 7. The room-temperature experimental data from Ref. 2 have been included. The data for each temperature have been vertically displaced, with the ordinate axis and scale for the 77°K data on the right.
produced in order to eliminate interference fringes. They were then ultrasonicly cleaned in toluene, rinsed in alcohol, and dried. Transmission measurements of intensity with and without the sample in the beam, \( I \) and \( I_0 \), respectively, are related by

\[
I = \frac{I_0(1-R)^2 (1+k^2/n^2)e^{-\alpha d}}{1-R^2e^{-2\alpha d}}
\]  

(3)

where \( R \) is the power reflectivity and \( \alpha \) the absorption coefficient. Below \( \nu_0 \), it was convenient to correct for \( R \) by using the calculated values, which agreed well with experimental values. Above \( \nu_0 \) the measured reflectivity was used. The maximum effect of the \( (1+k^2/n^2) \) term in Eq. (3) was about 5% in the region of highest absorption above \( \nu_0 \) at 300 °K, and the effect was negligible elsewhere. The average of several runs was taken with the most reliable data obtained in the region of \( \alpha d \) equal to unity. Thus a range of thicknesses was needed. An error bar is shown on the 300 °K data around 80 cm\(^{-1}\) and this was typical, although a larger uncertainty should be associated with the highest absorption in Fig. IV.8 which was at the limit of our signal to noise. The larger bars on the 12 °K data were due to several causes. The first was the low absorption combined with high reflectivity. The second was temperature instability, which has a very marked effect below 90 cm\(^{-1}\) where the absorption is due to difference processes. Finally, a peak at 77 cm\(^{-1}\) due to small amounts of Cl\(^-\) impurity\(^{14}\) in the Harshaw KI was subtracted out from the data, causing some uncertainty in the remainder.

D. Refractive Index and Reflectivity

Fig. IV.9 shows the present calculated values of refractive index together with the 300 °K measured values from Ref. 2. The 300 °K calculated reflectivity and phase angle are shown in Fig. IV.10 together with the
Calculated refractive indices of $K^{39}I$ at 300 and $12^\circ K$, together with the room-temperature experimental data from Ref. 2.
Calculated 300°K reflectivity and phase angle of K$^{39}$I. Together with the present experimental reflectivity, the experimental data from Refs. 2 and 14 are presented.
measurements from Ref. 2, and the reflectivity measured both by ourselves and by Hadni. Both of the power reflectivity measurements are fairly well but fall below the square-of-the-amplitude measurement of Berg and Bell. This latter measurement is probably the more accurate. We were able to see the two small reflectivity features at 145 and 155 cm\(^{-1}\), not so apparent in the other data. The structure over the peak depended on surface preparation and is probably not a good indication of the \(\Gamma(\nu)\) features in that region (see Fig. IV.1).

**IV. DISCUSSION**

**A. Three-Phonon Damping**

The evidence for three-phonon damping around \(\nu_o\) at 300 °K may be seen in Fig. IV.7 (from 80 to 100 cm\(^{-1}\)), in Fig. IV.8 (from 100 to 130 cm\(^{-1}\)), and in Fig. IV.9 (from 100 to 125 cm\(^{-1}\)). The more direct evidence of higher-phonon damping is the present set of absorption measurements above the two-phonon limit (from 200 to 300 cm\(^{-1}\)) at all three temperatures, seen in Fig. IV.7. Assuming this is indeed three-phonon (or higher) damping of the TO resonance, and not due to second-order electric moments, then these measurements of \(\alpha\) may be converted to damping by means of the relation:

\[
\alpha(\text{cm}^{-1}) = \frac{4\nu_o e^2 (\epsilon_\infty + 2)^2 (M^+M^-)\nu(\nu)}{9nvc^2M^*M\left\{\frac{2}{\nu_o^2 - \nu^2 + 2\nu_0 \Delta \Delta(\nu)}\right\}^2 + 4\nu_0^2 \Delta^2(\nu)},
\]

which may be obtained from Eq. (20) in Ref. 1. If \(\Gamma(\nu)\) is removed from the denominator, since its effect will be negligible away from the resonance at \(\nu_o\), and if the calculated value of refractive index \(n\) is used, since this will be fairly accurate beyond 180 cm\(^{-1}\), then Eq. (3) relates \(\Gamma(\nu)\) due to
Portions of the three-phonon (and higher) damping of the TO resonance of K$_{39}$I at 300, 77, and 12°K. The methods of obtaining these curves are explained in the text.
three-phonon (or higher) processes, to the absorption coefficient $\alpha$ measured beyond the two-phonon limit. The values so obtained may be seen in Fig. IV.11, from 180 cm$^{-1}$ onwards.

The 300°K values in Fig. IV.11 between 80 and 130 cm$^{-1}$, which are responsible for the effects mentioned above, were obtained in an approximate fashion by merely subtracting our values of $\Gamma_{\text{2-phonon}} (\nu)$ from those of Berg and Bell (see Fig. 1). This was done because the latter authors obtained fairly good agreement between theory and experiment for $n$ and $k$ in the vicinity of $\nu_0$. Their agreement followed from their peak-height fitting [which determined their value for $\phi''' (r_0)$] and their larger second and first derivatives, which gave greater values of $\Gamma(\nu)$ around $\nu_0$ as explained in Sec. IV.12A

The final resulting 300°K partial curve of Fig. IV.11 appears very reasonable, being fairly smooth, and peaking around 160-170 cm$^{-1}$. This would correspond to the creation of three acoustic phonons from regions near the low-energy critical points (e.g. $L_3$, $\Sigma_4$, or $X_2$), which all have wave numbers around 55 cm$^{-1}$.

It may be noted that, contrary to expectation, the high-wave-number tail and the discrepancy around $\nu_0$ in KI does not appear to be noticeably more pronounced than the similar effects found in the much harder LiF. This may be understood by considering the following approximate relations:

$$\Gamma_{\text{2-phonon}} (\nu) \approx S(\nu)_{\text{2-phonon}} \mu \overline{\nu} \overline{v}_1 \overline{v}_2 \overline{v}_0,$$

$$\Gamma_{\text{3-phonon}} (\nu) \approx S(\nu)_{\text{3-phonon}} \mu \overline{\nu} \overline{v}_1 \overline{v}_2 \overline{v}_3 \overline{v}_0,$$

where $\mu$ is the reduced mass, $\overline{\nu}_1$, $\overline{v}_2$, and $\overline{v}_3$ are the wave numbers of the phonons involved, and $S(\nu)$ are terms involving the occupation numbers.
of the phonons. $S(v)_{2\text{-phonon}}$ was fully defined in Ref. 1, but may be given here for the summation processes,

$$S(v)_{2\text{-phonon-summation}} = [n(\hat{k},j_1) + n(-\hat{k},j_2) + 1]$$

$$x\delta[\nu - \nu(\hat{k},j_1) - \nu(-\hat{k},j_2)],$$

where

$$n(\hat{k},j) = \frac{e^{\hbar \nu(\hat{k},j)}}{k_B T}.$$  \hspace{1cm} (8)

The equivalent three-phonon-summation expression is given by

$$S(v)_{3\text{-phonon-summation}} = [n(\hat{k}_1,j_1)n(\hat{k}_2,j_2)$$

$$+ n(\hat{k}_2,j_2)n(\hat{k}_3,j_3) + n(\hat{k}_1,j_1)n(\hat{k}_3,j_3)$$

$$+ n(\hat{k}_1,j_1) + n(\hat{k}_2,j_2) + n(\hat{k}_3,j_3) + 1]$$

$$x\delta[\nu - \nu(\hat{k}_1,j_1) - \nu(\hat{k}_2,j_2) - \nu(\hat{k}_3,j_3)].$$

and

$$\hat{k}_1 + \hat{k}_2 + \hat{k}_3 = 0.$$ \hspace{1cm} (9)

Equations (5) and (6) do not contain the potential derivatives, which increase rapidly in magnitude with increasing order of derivative, nor any details of the coupling coefficients. The point is that we are concerned with the ratio of $\Gamma_{3\text{-phonon}}(v)/\Gamma_{2\text{-phonon}}(v)$ for different compounds of the same structure, and the variation in the ratio of the factors omitted, from one compound to another, is much smaller than that obtained from the factors present.

The ratio (R for brevity) is then given approximately by

$$R = \frac{\Gamma_{3\text{-phonon}}(v)}{\Gamma_{2\text{-phonon}}(v)} = \frac{S(v)_{3\text{-phonon}}}{S(v)_{2\text{-phonon}}} \mu_{\nu},$$
where $\overline{\nu}$ is some average or characteristic wave number. $R$ obviously depends on temperature and to some extent on the process, but in the high-temperature limit $S(\overline{\nu})_{3\text{-phonon}}$ approximates to $(k_B \overline{T}/\hbar \overline{\nu})^2$, while $S(\overline{\nu})_{2\text{-phonon}}$ approximates to $k_B \overline{T}/\hbar \overline{\nu}$. Thus $R$ becomes proportional to $T/\mu \nu^2$. In the gross approximation of equal central force constants for all alkali halides, $\mu \nu^2$ is constant. Furthermore, the ratio of the damping due to any higher-order process to that due to any other-order process will contain some power of $\mu \nu^2$ and may thus be expected to be the same order of magnitude for all compounds of the same structure at high temperatures. A similar situation exists in the ratio of the peak heights of two-phonon damping to the resonance frequency $\nu_0$ at high temperatures, which may be seen to be approximately equal for KI and LiF. This ratio, however, involves $\mu^{3-5}$, and depends much more on the structure of $\Gamma_{2\text{-phonon}}$.

At very low temperatures it is interesting to observe that for the summation processes, $S(\overline{\nu})$ becomes unity and thus $R$ should be even greater for LiF than for KI ($\frac{\mu_{\text{LiF}}}{\mu_{\text{KI}}} = \frac{1}{6}$ and $\frac{\nu_{\text{LiF}}}{\nu_{\text{KI}}} = 3$). The difference processes, which are the ones responsible for the greater majority of the damping at $\overline{\nu}_0$, are not so straightforward. It may be argued, however, that $R$ will again be approximately constant from one compound to another, since the larger $S(\overline{\nu})_{3\text{-phonon}}$ in the softer compounds will be compensated by the larger $\mu$. $R$ at these low temperatures will of course be very small for the difference processes. Although 300 °K may be considered high for KI but only intermediate for LiF, the general similarity in the 300 °K spectra of KI and LiF may thus be understood.
B. Two-Phonon Damping Structure

It may be seen from Fig. IV.7 that no distinct features exist in the difference spectrum (below $\nu_0$) of KI at any temperatures. The hump around 75 cm$^{-1}$, prominent at 77 °K, merely reflects the over-all maximum in the difference $\Gamma(\nu)$, which then decreases strongly until the summation processes start. The sharp features reported by Renk at 5 and 6 °K must therefore be due to impurities. Almost certainly Cl$^-$ would be responsible for the sharp peak at 77 cm$^{-1}$ (trace amounts in our Harshaw sample gave us a similar peak). It is also known that larger concentrations of Cl$^-$ give rise to band structure around 60 cm$^{-1}$. The temperature variation of the peaks is a little hard to understand, although the two-phonon background is certainly temperature dependent. Nevertheless no sharp peaks can occur in the difference spectrum of any compound at very low temperatures, and in the case of the rocksalt-structured ones, no two-phonon combinations from X, as claimed by Renk, are allowed in any circumstances.

In the summation region, Figs. IV.8 and 9 show two distinct features. The positions of these agree very well with theory at 77 °K (161 and 150 cm$^{-1}$) and seem to agree satisfactorily at 300 °K, with the 5% reduction that was applied (155 and 145 cm$^{-1}$: a slight anharmonic frequency shift is also present). The magnitude of these calculated features, however, together with the 'hump' at wave numbers just above them, appears once again to be too large. The coupling, assumed to be between nearest neighbors only, has over accentuated them, and next-nearest-neighbor interactions are necessary. The features in question have been labeled 9, 10, and 11 both in Fig.IV.1 and in Table IV.3. It may be seen that many strong combinations from nearest-neighbor coupling have by chance contributed to the same peaks. $\Sigma_4\Sigma_4$ and $L_3L_3$ are both
contributing to peak 9. \( \Sigma_1(\text{LA}) \Sigma_4(\text{TO}) \), \( \Gamma_{\text{III}} \), and combinations from the branches labeled A and B in Fig. IV.4. All the way from \( \Gamma \) to \( W \) have produced peak 10. The four strong contributors to the hump 11 may also be seen in Table IV.3. Thus these calculated features seem to be at least twice as strong as they should be, (and possibly even more when the three-phonon damping is included). The reason why the same features calculated by Berg and Bell are not as large is due mainly to the lower resolution obtained from their wave-vector grid.

In view of the comments above and in the subsection of Sec. II, the assignments made by Srivastava and Bist may be seen to be incomplete, and erroneous. Furthermore, from an inspection of the data they obtained, the usefulness of the nujol mull technique in investigating these damping processes appears to be limited.

\textit{Note added in proof.} While working with CsI, Beairsto and Eldridge (to be published in Can. J. Phys.) realized that no cubic coupling can occur through next-nearest-neighbor interactions, since they are ions of the same type. Coupling can occur through further opposite-type-neighbor interactions due to the long-range Coulombic terms and this will reduce the sharpness of the features calculated here. It was also found, however, that the next-nearest neighbors should be included in the repulsive component of the lattice potential energy.

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BIBLIOGRAPHY

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7Note that for the parameters to be compatible with the program as described in Ref. 1, the electrical polarizabilities need to be divided by the volume of the unit cell in cm$^3$ times $10^{24}$.