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OF POTASSIUM IODIDE.

The Ohio State University, Ph.D., 1969
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THE FAR INFRARED OPTICAL CONSTANTS
OF POTASSIUM IODIDE

DISSERTATION

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the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
James Irving Berg, B.Phys.

The Ohio State University
1969

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INTRODUCTION

Potassium Iodide (KI) is an alkali halide crystal of cubic structure, of the NaCl type. Its optical properties are similar to those of the other alkali halides, most of which have been studied experimentally in the infrared.\(^1,\, 2\) These crystals are characterized by a strong absorption spectrum associated with a single frequency of resonance, and peaked very near this frequency. The frequency of resonance is generally known as the eigenfrequency. The eigenfrequency of KI is \(101\text{cm}^{-1}\), where \(100\text{ cm}^{-1}\) corresponds to a wavelength of \(100\, \mu\)\(^*\). Since the far infrared is the region from \(10\text{cm}^{-1}\) to \(1000\text{cm}^{-1}\), approximately, the KI eigenfrequency is in the optimum region for study by techniques designed for far infrared use.

The spectral region covered in the measurements to be described here is limited on the low frequency side by the decrease in power available from a high temperature thermal radiation.


\(^*\)The symbol \(\mu\) denotes microns (1 micron = \(10^{-6}\) m).
source at lower frequencies, and on the high frequency side by the particular method of separating the various spectral components. The instrument used for this purpose is a Michelson interferometer, operating in the asymmetric mode. All spectral information is obtained by taking the Fourier transform of an "interferogram," which is the measured power as a function of an optical path shift in one arm of the instrument due to displacement of a mirror. In the asymmetric mode, a sample, whose optical properties are to be measured, is placed in the other arm of the instrument. Since the mirror must be displaced by distance increments comparable to the shortest wavelength radiation present in the spectrum, and move over distances of hundreds of wavelengths, which must be measured to an accuracy of a fraction of a wavelength, this technique is most reliably used at long wavelengths. Also, the effects of deviation from ideal sample geometry are less marked at long wavelengths.

The quantity which describes the rate of absorption for each frequency component is the extinction coefficient. In mathematical developments it can be incorporated as the imaginary part of a complex number, of which the index of refraction is the real part. This complex number is called the "complex index of refraction," or simply, "complex index." The extinction coefficient and index of refraction as functions of frequency are known as the "optical constants." The optical constants
completely specify the optical properties of a media, in the linear approximation. They are not, however, independent, since if the imaginary part of the complex index is known for all frequencies, the real part can be derived, and vice versa. The index of refraction approaches a constant value in frequency regions far from a resonance region or any absorption region, but undergoes a noticeable change in such a region, if the extinction coefficient becomes comparable to the index of refraction. The asymptotic value reached on the low frequency side of the absorption region is always greater than that on the high frequency side. This behavior is known as "dispersion," and it always accompanies absorption, to some extent. For this reason, the relations connecting the real and imaginary parts of the complex index are known as "dispersion relations."

The dispersion relations also hold between real and imaginary parts of functions of the complex index. A measurement of one real function of the complex index for all frequencies is sufficient to obtain both its real and imaginary parts, if the dispersion relations are used. The asymmetric Michelson interferometer, however, allows a measurement of two real functions: relative amplitude and phase of an electromagnetic wave transmitted through or reflected from the sample. Thus, both the real and imaginary parts of the complex index can be obtained directly, in a single measurement, with no need for explicit use of dispersion relations.
A major portion of this dissertation is devoted to the theoretical interpretation of the optical constants of potassium iodide. The resonance and strong absorption of alkali halides in the infrared has long been known to be due to motion of the highly charged ions of the lattice, under the influence of the electromagnetic field. If only the quadratic terms in the interionic potential are considered, the ionic motion, in the absence of an external field, is a superposition of contributions from various independent simple harmonic modes of vibration. This is the harmonic approximation. In a strictly periodic crystal, the motion for each mode is that of a wave. The waves are characterized by a wave vector, frequency, and polarization vectors for both $\text{K}^+$ and $\text{I}^-$ ions, in the case of KI. The wave vector is in the propagation direction, and its magnitude is proportional to the reciprocal of the wavelength. The wave vector can take on a number of discreet values equal to the number of unit cells, or ion pairs, in the entire crystal. For future reference, let $N$ denote this number. Six separate waves of different frequency and polarization are possible for each wave vector, corresponding to the six degrees of freedom of the two ions in a unit cell.

In a quantum mechanical, harmonic treatment of the lattice, each of the $6N$ modes has discreet and evenly spaced energy levels, and a stationary state of the entire system can be specified by the set of energy values for all modes. The separation of adjacent
energy levels for a given mode is equal to Planck's constant times the frequency for that mode. Since the energy levels for a given mode are evenly spaced, the total energy for each mode can be specified by an integer. This integer is equal, by definition, to the number of energy quanta, or "phonons" present in this mode. If the lattice interacts with another system, or if anharmonic potential terms are included, such a set of values no longer specifies a stationary state of the system. The complete set of such states can still be used, however, to construct new states, by means of a perturbation method. The interaction results in a probability that energy be exchanged between the modes, or that phonons of some modes disappear, their energy being transferred to other modes, reappearing in the form of new phonons. A phonon, like a quantum mode of an electromagnetic field, or photon, is sometimes called a "quasi-particle," because of its particle-like characteristics.

The interaction considered here, between the electromagnetic field and the lattice, is, in quantum mechanical terms, a photon-phonon interaction, where energy from the electromagnetic field is transferred to a single phonon. Several criteria must be satisfied for a photon to interact with a phonon. Besides having the same frequency and wavelength, the phonon wave must be transverse, as is the photon wave. Also, the photon must interact with a phonon whose wave motion gives rise to a net electrical polarization. It can
be seen that a 100 μ wavelength is very large on the scale of lattice waves, since the shortest possible lattice wave has a wavelength comparable to the ionic separation, about $10^{-4} \mu$.

Therefore, the infrared photon wave vector magnitude can be taken to be zero. At zero wave vector, the lattice modes divide into two types; those for which the positive and negative ions move in the same direction, and those in which they move in opposite directions. Only the latter type give rise to an electrical polarization and are called "optical" modes, while the former are called "acoustical" modes, and have zero frequency for zero wave vector. Of the optical modes, two are transverse, having the same frequency, and one is longitudinal, having a different frequency in the alkali halides. The radiation interacts with only the transverse optical modes, accounting for the resonance at a single frequency. The eigenfrequency can be identified as the transverse optical phonon frequency for zero wave vector.

For wave vectors of non-zero magnitude, the phonon polarizations are not so simply described. However, the classification is still useful, since the frequencies and polarizations are continuous as the wave vector is changed, defining surfaces, or "branches" in wave vector space. The six modes for zero wave vector have frequencies each on one of the six frequency branch surfaces and the same can be said for any other wave vector. The frequency degeneracy for long wavelength transverse waves means
that two separate frequency surfaces coincide for zero wave vector, but not necessarily for other wave vectors. Actually, the two surfaces coincide also for waves along certain other crystallographic symmetry directions (see Figure 7).

A calculation of the optical constants, including only the harmonic part of the lattice potential, predicts a resonance at the eigenfrequency, and a totally opaque, 100 percent reflecting region between the eigenfrequency and the longitudinal optical mode frequency. It predicts an index change, but no absorption. Experimentally, a highly reflecting or "restrahl" region is observed, but the reflectivity never reaches 100 percent, and absorption accompanies the high reflection. The extinction coefficient has a major peak at the eigenfrequency, along with other subsidiary peaks, or structure, in the wings. These subsidiary peaks generally are reduced in magnitude by about a factor of ten or more from the main peak, so they are sometimes not observed. The mechanism which allows energy to be taken away from the optically active mode is the anharmonicity in the interionic potential. In quantum mechanical terms, the optical phonon decays into two or more other phonons of generally non-zero wave vector. Thus, all lattice phonons can be involved in the process. Frequencies of relatively high absorption away from the eigenfrequency correspond to sum and difference frequencies of lattice

\(^3\)Burstein, op. cit.
phonons. Little can be learned about phonon frequencies from the optical constants, however, because of the complicated frequency distribution of the crystal, and the fact that one frequency may correspond to more than one transition between modes of different branches and wave vectors. If the frequencies are known, the optical constants can be calculated and compared with experiment. This is what is done in this work for KI.

The phonon frequencies and polarizations used here were generated from a "shell model" of the harmonic crystal. The physical validity of the model is in doubt in that it does not predict all characteristics of the crystal accurately, but the parameters were chosen by Dolling et al, to give accurate lattice frequencies, as determined by neutron diffraction experiments.

Chapters I and II of this dissertation are devoted to the experimental measurement of the optical constants by transmission and reflection techniques. In Chapters III and IV, attention is turned to the dynamics of the crystal lattice, culminating in a calculation, based on the shell model, of phonon frequencies and polarizations for a set of wave vectors. In Chapter V, the Hamiltonian for the interaction of an external electric field with the crystal is derived, based also on the shell model. In Chapter VI, the optical constants are computed, including the

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effects of temperature and anharmonicity, using the calculated lattice frequencies.

Although other comparisons between theoretical and experimental data have been made for other alkali halides,\(^5\),\(^6\),\(^7\) this particular study is thought to be an improvement in two significant respects. First, the experimental measurements are very reliable. This is partly due to the advantages in the use of an interferometer, particularly the asymmetric mode, as pointed out by Bell.\(^8\) The advantages are that the interferometric method gives a better signal to noise ratio, and, as mentioned above, the asymmetric mode allows a measurement of amplitude and phase of a frequency component, while other methods only allow a measurement of the power, or the square of the amplitude. Also, both transmission and reflection methods supplementing each other were used here. This has not been the case in previous asymmetric mode work, due to the problems in preparing suitable transmission samples.\(^9\) Second, the lattice frequencies used here were obtained from


\(^8\)E. E. Bell, Infrared Physics, 6, 57 (1966).

\(^9\)Johnson, op. cit., p. 5.
neutron diffraction studies and are thought to be more reliable than those used in other work. They are very nearly the actually measured frequencies, and are not simply based on a model fitted to other experimental data. The availability of such data was a major factor in the choice of KI for this investigation.

The results of most of the theoretical developments presented here are not original. The discussions of basic theory were included to establish the notation used here and to provide a sound basis for the understanding of later calculations. For the interferometric measurement technique, the cited references by Bell, and by Russell and Bell should be consulted. For lattice dynamics, the books by Ziman, Maradudin et al., and Born and Huang are among several books presenting theoretical developments. For the lattice-electromagnetic field interaction, the book by Born and Huang is the most complete. In the case of the shell model, many results which are derived here are only quoted in the cited references, and the optical properties of the shell model are treated in a different manner here. For the anharmonic properties, the papers by Cowley, and others, cited in Chapter VI, are relevant.


CHAPTER I

LINEAR RESPONSE FOR TRANSMISSION AND REFLECTION

The dielectric response, or effect of a sample on an electromagnetic wave is dependent upon the inherent properties of the media, and the geometry of the experimental arrangement. This geometry includes not only the size and shape of the sample, but the positions and directions of the entry and exit beams. The response of a sample is always determined by a comparison between signals measured with and without the sample present. Only the intrinsic properties of the media itself are of universal interest, so these properties must in some way be extracted from the measured response.

It is widely known that an electromagnetic wave in free space or in a linear dielectric medium can be expressed as a Fourier integral over component waves in frequency space. The result of the insertion of a sample with linear response into the path of a wave in free space is that each spectral amplitude component is multiplied by a complex number, which is a function of frequency. This function of frequency is called the "spectral response function" in the work that follows. The optical constants entirely
determine the amplitude and wavelength of the wave in the medium, and the boundary conditions on the amplitudes. Thus, from the spectral response function for a given geometry the optical constants can be determined.

In effect, the Michelson interferometer, operated in the asymmetric mode, can measure relative electromagnetic wave amplitudes. Since the source of radiation used in this work has a wide spectral distribution, the effects of all frequencies are present simultaneously. The beam from the source is split into two components, and separated physically by the beam splitter into the two arms of the instrument. The beams are then superimposed again at the beam splitter and directed into the detector. In the first arm is a movable mirror, while a sample can be placed in the second arm. An interferogram is formed by measuring power as a function of the optical path change due to displacement of the mirror. Maximum signal is obtained, without a sample present, when the two arms are of equal optical path length. The position of the mirror for maximum signal is known as the "white light" position, since waves of all wavelengths interfere constructively at this position. In the absence of a sample, the interferogram is symmetric about the white light position, and its Fourier transform yields the spectral power through the instrument. If a sample is placed in the second arm, the interferogram is asymmetric, and a comparison of its transform with the measured
spectral distribution yields the spectral response function of the sample.

All samples considered here are placed in such a way that radiation is incident normal to a flat surface. In the reflection method, radiation which is reflected normal to the surface is measured by the detector. In the transmission method, the sample is made in the form of a thin lamella, with the second face parallel to the first, and radiation which passes through the sample is measured. Transmission samples must be of the appropriate thickness for measurements to be made in a frequency region where the extinction coefficient varies over a particular range of values. Samples too thick would not transmit a measurable amount of radiation, and samples too thin would not give a measurable amount of absorption. Another limitation with transmission samples, using the asymmetric mode, is that any difference in thickness across the face of the sample can affect the measured transmittance, leading to an incorrect determination of the optical constants, if no correction is made. Since it is difficult to prepare samples to the required degree of geometrical perfection, a correction to the spectral response function due to thickness deviation is described in this chapter.
1-1 Review of Fourier Analysis

A brief review of Fourier transform relations is presented here because of the importance of Fourier analysis throughout the remainder of the work. Most of the relations are discussed more thoroughly in a book by Bracewell.¹

The complex Fourier transform \( f(\omega) \) of a real function of time \( F(t) \) is defined in terms of frequency \( \omega \) by

\[
f(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ F(t) \exp(i\omega t).\tag{1.1.1}\]

A necessary condition for existence of the transform \( f(\omega) \) of a function \( F(t) \) is

\[
\lim_{t \to \pm \infty} F(t) = 0.\tag{1.1.2}
\]

Functions dealt with in this dissertation which satisfy (1.1.2) generally have transforms which are analytic functions of complex frequency \( \omega \) in their region of definition. The region of definition is generally the real frequency axis, but in certain important cases it is the upper or lower half frequency plane. If the transform \( f(\omega) \) is analytic along the real axis, the function \( F(t) \)

is given by the inverse to (1.1.1). It is

\[ F(t) = \int_{-\infty}^{\infty} d\omega \, f(\omega) \exp(-i\omega t). \quad (1.1.3) \]

A shorthand notation for (1.1.1) and (1.1.3) is

\[ \mathcal{F}(F(t)) = f(\omega) \]

and

\[ \mathcal{F}^{-1}(f(\omega)) = F(t), \quad (1.1.4) \]

where \( \mathcal{F} \) denotes the Fourier transform operation, and \( \mathcal{F}^{-1} \) its inverse. The convention of using upper-case letters for the functions of time, and the corresponding lower-case letters for their transforms is followed here. It follows from (1.1.1), and the fact that \( F(t) \) is real, that

\[ \mathcal{F}(F(-t)) = f(-\omega) = f^*(\omega), \quad (1.1.5) \]

where the asterisk denotes complex conjugation.

The convolution \( H(t) \), of two functions \( F(t) \) and \( G(t) \) is defined as

\[ H(t) = \int_{-\infty}^{\infty} F(t-t')G(t') \, dt'. \quad (1.1.6) \]

A shorthand notation for the convolution is
\[ H(t) = F(t) \star G(t). \] (1.1.7)

The convolution operation for transforms is defined in the same manner. The convolution operation obeys associative and commutative laws also. An important result is that the transform (or inverse transform) of the convolution is the product of the transforms (or inverse transforms):

\[ \mathcal{F}(F(t) \star G(t)) = f(\omega)g(\omega), \] (1.1.8)

\[ \mathcal{F}^{-1}(f(\omega) \star g(\omega)) = F(t)G(t). \]

Many commonly used functions \( F(t) \) do not satisfy the condition (1.1.2), so that they do not have a Fourier transform. In this case it is frequently possible to define a function \( F^\gamma (t) \) such that

\[ \lim_{t \to \pm \infty} F^\gamma (t) = 0 \quad \text{for } \gamma > 0 \] (1.1.9)

and

\[ \lim_{\gamma \to 0} F^\gamma (t) = F(t). \]

The first equation in (1.1.9) is the condition (1.1.2) for the function \( F^\gamma (t) \), so that it has a transform \( f^\gamma (\omega) \). Using the second equation in (1.1.9), \( F(t) \) is

\[ F(t) = \lim_{\gamma \to 0} \mathcal{F}^{-1}(f^\gamma (\omega)) \]
Within the context of (1.1.10), a transform of $F(t)$ can frequently be given, as a prescription for carrying out the integral in the region of singularities which exist in $f_\eta(\omega)$ in the limit $\eta \to 0$. For the concept to be sensible, the prescription must be independent of the actual representation, or function $F_\eta(t)$ chosen, as long as the conditions (1.1.9) are satisfied. Similar "prescriptions" can be used for one of the functions in the convolution operation.

It is the usual practice to choose $F_\eta(t) = \Xi_\eta(t)F(t)$, where $\Xi_\eta(t)$ is a "window function," for which

$$\lim_{t \to t_\omega} \Xi_\eta(t) = 0 \quad \text{for} \quad \eta > 0$$

and

$$\lim_{\eta \to 0} \Xi_\eta(t) = 1.$$  (1.1.11)

Examples of such functions, which will be useful in this work, for this and other purposes, are the functions $\exp(-\eta|t|)$, and $w_\eta(t)$, where
Here, $1/T$ plays the role of $\gamma$.

Another very useful function is the "step function," defined by

$$\Theta(t) = \begin{cases} 1, & t > 0 \\ 0, & t \leq 0 \end{cases} \quad (1.1.13)$$

The transforms of $\Theta(t)$ and $\Theta(-t)$, when multiplied by a suitable window function, are analytic in the upper and lower half frequency planes, respectively. The same holds for $F(t) \Theta(t)$ and $F(t) \Theta(-t)$, where $F(t)$ is a function having a Fourier transform defined along the real axis. For Fourier transform purposes, $F(t)$ can be written

$$F(t) = \Theta(t)F(t) + \Theta(-t)F(t). \quad (1.1.14)$$

Using window functions $\exp(-\gamma |t|)$ and $W_T(t)$ respectively, the transforms of $\Theta(\pm t)$ are given by

$$\mathcal{F}[\exp(-\gamma |t|) \Theta(\pm t)] = \frac{\pm i}{2\pi} \frac{1}{\omega \pm i\gamma} = \frac{\pm i}{2\pi} \frac{\omega \mp i\gamma}{\omega^2 + \gamma^2},$$

$$\mathcal{F}[W_T(t) \Theta(\pm t)] = \frac{\pm i}{2\pi\omega} (1 - \cos(\omega T) \mp \sin(\omega T)). \quad (1.1.15)$$
Using the analyticity properties mentioned above, a prescription for the transform of $\Theta(\pm t)$, as defined in (1.1.10), is

$$\mathcal{F}(\Theta(\pm t)) = \frac{\pm i}{2\pi} \left( \frac{1}{\omega} \right)_p \mp i \delta(\omega),$$

(1.1.16)

where the subscript $p$ denotes that the Cauchy principal value of the integral is taken, and $\delta(\omega)$ is the Dirac delta function.

Using (1.1.14), the transforms of the window functions are

$$\mathcal{F}(\exp(-\eta |t|)) = \frac{1}{\pi} \frac{\eta}{\eta^2 + \omega^2} \rightarrow \delta(\omega),$$

and

$$\mathcal{F}(w_T(t)) = w_T(\omega) = \frac{\sin(\omega T)}{\pi \omega} \rightarrow \delta(\omega),$$

(1.1.17)

where the arrow indicates the behavior in the $\eta \rightarrow 0$ and $1/T \rightarrow 0$ limits, from (1.1.16). It follows also from (1.1.16) that

$$\mathcal{F}(\exp(\omega_0 t)) = \delta(\omega + \omega_0).$$

(1.1.18)
1-2 Electromagnetic plane waves

For reasons of mathematical simplicity, and usefulness in describing physically simple and approximately realizable situations, the plane wave mode of an electric field is of widespread use in discussions of optical phenomena. There is no loss of generality in the use of plane waves, because a more general wave can be treated as a superposition of plane waves. The beams in the arms of the interferometer used in the experiments to be described later can very nearly be described as plane waves. The optical constants, for a given frequency, determine the velocity and rate of decrease in amplitude of a plane wave propagating in a medium.

Plane waves in free space, and in linear isotropic media are always transverse. Consider a linearly polarized wave in free space propagating along an axis, where \( x \) is the coordinate measuring distance in the direction of propagation. The field in the polarization direction, perpendicular to the \( x \) axis is a function of \( x \) and of time \( t \) only and has the form:

\[
E(x,t) = E_t(t-x/c),
\]

or

\[ (1.2.1) \]

\[ E(x,t) = E_x(x-ct), \]

where the subscripts \( t \) and \( x \) indicate that the argument has dimensions of time or distance, respectively, and \( c \) is the velocity of light.

A Fourier transform of the first equation in (1.2.1) can be defined for the argument \( t-x/c \) by

\[ E(x,t) = \]

\[ \int_{-\infty}^{\infty} \omega e_{\omega}(\omega) \exp(1\omega(x/c-t)), \]

where \( e_{\omega}(\omega) \) is the Fourier transform of \( E_x(t-x/c) \), the amplitude of the \( \omega \) frequency component. It is convenient to define a transform with respect to the distance variable in terms of wave number \( \nu \), writing

\[ E(x,t) = \]

\[ \int_{-\infty}^{\infty} \nu e_{\nu}(\nu) \exp(2\pi i \nu(x-ct)), \]

whose inverse is
\[ E(x,t) = \int_{-\infty}^{\infty} dx \, E(x,t) \exp(-2 \pi i \nu(x-ct)). \quad (1.2.4) \]

By comparison of (1.2.2) and (1.2.3) it is obvious that

\[ \nu = \omega / 2\pi c \quad (1.2.5) \]

and

\[ e_x(\omega) = (1/2\pi c) e_x(\omega/2\pi c). \]

In the analysis in the following sections, the subscripts on \( e_x(\omega) \) and \( e_x(\nu) \) will usually be omitted, leaving only the arguments to distinguish the functions. The wave number will usually be referred to as frequency also. Frequencies will also occasionally be expressed in units of cycles per second (cps), or \( \omega/2\pi c \).

Due to the finite time of measurement in spectroscopic work, and the requirement (1.1.2) for the existence of a transform, the function \( E(t) \) in (1.2.2) must be considered a "truncated" function

\[ E_T(t) = W_T(t) E(t). \quad (1.2.6) \]

Here \( W_T(t) \) is the window function (1.1.12), \( 2T \) is the total measurement time, and \( E(t) \) is the "true" function, for infinite time of measurement. In the limit \( T \gg 1/\omega \) for all frequencies \( \omega \) present in the spectrum, the delta function limit in (1.1.17) is applicable, and the transforms \( e_T(\omega) \) and \( e(\omega) \) are identical.
The restriction to linearly polarized radiation will be carried through this entire dissertation, since the response of the interferometer, and of the isotropic media to be considered, is independent of polarization.

1-3 Linear, time invariant response

Consider a polarized electromagnetic wave of the form (1.2.2) traveling from a source to a detector some distance away. The electric field at the detector can be specified by a function of time, \(E(t)\). If a change in the geometry of the beam between the source and detector is brought about, such as by introducing a sample, or moving a mirror, the new field or "response" can be described by a function, \(E'(t)\). The relationship between the two fields can be expressed, in general, as

\[ E'(t) = G_{op} E(t), \quad (1.3.1) \]

where \(G_{op}\) is an operator acting on \(E(t)\), which expresses the effect of the change in geometry.

The properties of linearity and time invariance hold for all operators to be considered in this work. Using these properties,
$E'(t)$ in (1.3.1) can be expressed as a convolution of a function $G(t)$ with $E(t)$. A simple, but not mathematically rigorous way of obtaining this result, is to first write

$$E(t) = \int_{-\infty}^{\infty} dt' E(t') \delta(t-t'). \quad (1.3.2)$$

Recalling that an integral is defined as the limit of a sum, and applying the linearity property to this sum and the corresponding integral, it is apparent that

$$E'(t) = \int_{-\infty}^{\infty} dt' \hat{G}(t,t')E(t'), \quad (1.3.3)$$

where

$$\hat{G}(t,t') = G_{op} \delta(t-t'). \quad (1.3.4)$$

Equation (1.3.3) can be viewed as a Hilbert space matrix expression, where $E(t)$ and $E'(t)$ are components of vectors, in $t$-space, and $\hat{G}(t,t')$ is an element of a square matrix in $t$-space, representing a linear operator. The Hilbert space representation is frequently used in quantum mechanics, although in terms of position rather than time variables.

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The meaning of time invariance is that if \( G \circ E(t) = E'(t) \), then \( G \circ E(t-t_o) = E'(t-t_o) \), where \( t_o \) is an arbitrary time. This requires that

\[
\hat{G}(t, t') = G(t-t'). \tag{1.3.5}
\]

Because \( G(t) \), according to (1.3.4) and (1.3.5), is given by application of \( G \circ \) to a delta function, or unit impulse, it is called the "impulse response function." In terms of \( G(t) \), (1.3.3) becomes

\[
E'(t) = \int_{-\infty}^{\infty} G(t-t') E(t') \, dt', \tag{1.3.6}
\]

or

\[
E'(t) = G(t) \star E(t), \tag{1.3.7}
\]

which is the convolution operation.

The convolution expression (1.3.6) can be transformed to give

\[
e'(\omega) = g(\omega) e(\omega), \tag{1.3.8}
\]

where \( g(\omega) \) is the "spectral response function," the transform of the impulse response function. Equation (1.3.8) can be viewed as the "diagonal" form of (1.3.3), by analogy to the corresponding situation in the algebra of matrices having discrete elements.
There is one other restriction necessary for the operator to be physically sensible, namely that of causality. To assure that the response (effect) cannot precede the applied impulse (cause), \( G(t) \) must satisfy the equation

\[
G(t) = \Theta(t) G(t), \tag{1.3.9}
\]

where \( \Theta(t) \) is the step function, given in (1.1.13). As a result of this restriction, the real and imaginary parts of the transform \( g(\omega) \) for real \( \omega \) must satisfy the Kramers-Kronig dispersion relations,

\[
\mathcal{R}e \ g(\omega) = \frac{2 \pi}{\omega} \int_0^\infty \frac{\omega' \mathcal{I}m g(\omega') d\omega'}{\omega^2 - \omega'^2},
\]

and

\[
\mathcal{I}m \ g(\omega) = \frac{-2 \omega}{\pi} \int_0^\infty \frac{\mathcal{R}e g(\omega') d\omega'}{\omega^2 - \omega'^2}, \tag{1.3.10}
\]

where the symbols \( \mathcal{R}e \) and \( \mathcal{I}m \) denote real and imaginary parts, respectively. The relations follow by taking the transform of (1.3.9) and applying the convolution rule to the right-hand side, using \( \mathcal{I} \)(\( -\Theta(t) \)) as given in (1.1.16).
1-4 The Michelson interferometer

The interferometer has been discussed in detail by Bell, but the mathematical development necessary for this work is presented here, for continuity.

The electric fields $E_A(t)$ and $E_B(t)$ from the two arms of the interferometer add together at the detector, where the superimposed beams from both arms are focused. The total power at the detector is thus proportional to

$$\int_{-\infty}^{\infty} dt \left[ E_A(t) + E_B(t) \right]^2$$

(1.4.1)

$$= \int_{-\infty}^{\infty} dt \left[ E_A^2(t) + E_B^2(t) + 2E_A(t) E_B(t) \right] .$$

The electric fields used here are of the truncated form (1.2.6), so that the limits $\pm \infty$ in the integral can be used.

Let arm A be the arm with the movable mirror, and arm B the sample arm. For displacement of the mirror such that the optical path increases from that for the white light position (the position for equal optical path in the two arms in the

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4Introduction, footnote 8.
absence of a sample) by a distance \( x \), the field from arm \( A \), due to the wave property of the radiation, is

\[
E_A(t) = E(t - \gamma),
\]

(1.4.2)

where \( \gamma = x/c \), and \( E(t) \) is the field for the white light position. With no sample present in arm \( B \), \( E_B(t) = E(t) \), while with a sample present, \( E_B(t) \) is given by convolution of the impulse response function \( G(t) \) of the sample with \( E(t) \).

Only the interference term in (1.4.1) containing \( E_A(t) \) \( E_B(t) \), is a function of \( \gamma \), and it is proportional to the interferogram function

\[
P(\gamma) = \int_{-\infty}^{\infty} E(t - \gamma) E_B(t) \, dt.
\]

(1.4.3)

This relation can be expressed in convolution form, as

\[
P(\gamma) = E(-\gamma) \ast E_B(\gamma).
\]

(1.4.4)

Denoting the background interferogram by \( P_1(\gamma) \) and the sample interferogram by \( P_2(\gamma) \), it follows, using the appropriate values of \( E_B(t) \), that
\[ p_1(\tau) = E(-\tau) \star E(\tau), \]

and

\[ p_2(\tau) = E(-\tau) \star (G(\tau) \star E(\tau)) = G(\tau) \star p_1(\tau). \]

The Fourier transforms of the expressions in (1.4.5) are

\[ p_1(\omega) = |e(\omega)|^2 \]

and

\[ p_2(\omega) = |e(\omega)|^2 g(\omega) = p_1(\omega) g(\omega), \]

so that the transform of the background interferogram is proportional to the spectral power at the detector, and the spectral response function is given by the ratio of sample to background interferogram transforms. From the results of section 1-2, the same relations hold with \( \nu \) as the frequency variable;

\[ p_1(\nu) = |e(\nu)|^2 \]

and

\[ p_2(\nu) = |e(\nu)|^2 g(\nu) = p_1(\nu) g(\nu), \]

where the interferograms are expressed in terms of optical path \( x \), and transformed according to (1.2.4). This form will be used in the actual calculations.
1-5 The measured interferogram

An interferogram can be considered a function $P(x)$ of a continuous variable $x$, where $x$ extends from minus to plus infinity. To use digital computation methods to compute the Fourier transform of $P(x)$ by (1.2.4), a finite number of points at which to sample the interferogram must be chosen. These points in this work are chosen an increment $\Delta x$ apart, and they extend only over a finite region of the $x$ axis, from $-x_0$ to $+x_0$. This necessarily limits the information which is obtained, and causes a corresponding limitation in the Fourier transform of the interferogram because of this sampling procedure. A very detailed summary of these effects has been given by Mme. J. Connes.\(^5\)

The effect of incremental sampling is to make the Fourier transform periodic, of period $1/\Delta x$. The portion of the transform in the interval $\nu < \nu_m$ is identical to that in the limit $\Delta x = 0$, provided there are no actual components present for frequencies greater than $\nu_m$, where

$$\nu_m \leq (1/2 \Delta x).$$  \hspace{1cm} (1.5.1)

This limitation must be considered in choosing the increment, $\Delta x$, and the filters in the system.

The effect of restriction to the finite sampling interval, and a shift $+L$ of this sampling interval is that a function

$$P'(x, L) = \hat{W}_x^o(x) P(x + L)$$

(1.5.2)

is actually measured, where $\hat{W}_x^o(x)$ is the window function defined in (1.1.12). The Fourier transform of the measured interferogram is then

$$p'(-\nu, L) = \int_{-\infty}^{\infty} d\nu' \hat{W}_x^o(-\nu + \nu')P(-\nu')\exp(-2\pi i\nu L)$$

(1.5.3)

$$\approx p(-\nu)\exp(-2\pi i\nu L).$$

In the limit $x_0 \to \infty$, the transform of the window function becomes a delta function, and the approximate equality becomes true equality. The width of the actual transform limits the resolution, but by an amount which can be estimated. The half width of the base of the central peak of this transform is $1/2x_0$. The rather large positive and negative peaks on both sides of the central maximum further destroy the resolution. These "feet" can be reduced by using the "apodized" window function

*This shift is generally used for transmission samples, discussed in section 1-7. Where it is not used, $L = 0$, and $P'(x, 0) = P(x)\hat{W}_x^o(x) \equiv P'(x)$. For background interferograms, $P'(x) \approx P(x), x_0$
\[ A_{x_0}(x) = (0.54 + 0.46 \cos(\pi x/x_0))u_{x_0}(x). \]  

Using this window function, the measured interferogram transform is

\[ p'(\nu, L) = \int_{-\infty}^{\infty} d\nu' a_{x_0}(\nu - \nu')p(\nu')\exp(-2\pi i\nu'L). \]

This, however, doubles the width of the central peak. The resolution interval \( \Delta \nu \) is then defined by

\[ \Delta \nu = 1/x_0. \]

1-6 The optical constants

The electric field in free space, as expressed in (1.2.3) is a sum of component waves of different frequencies. Each wave has the same velocity of propagation, c. This fact, together with only the assumptions of samples having linear and time invariant response, has been used to show how the spectral response function of a sample \( g(\nu) \) can be measured, using a Michelson interferometer

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(within the limits of resolution). The function \( g(\nu) \) depends on the geometry and composition of the particular sample.

In a linear, isotropic medium, the component waves for each frequency have different velocities and thus different wavelengths. Also, the waves are diminished in amplitude by absorption in propagating through the medium. The electric field in this case is more general than that given by \((1.2.3)\). It is

\[
E(x,t) = \int_{-\infty}^{\infty} d\nu \, e(\nu) \exp(2\pi i \nu (\mathcal{N}(\nu) x - ct)), \quad (1.6.1)
\]

where \( \mathcal{N}(\nu) \) is the complex index of refraction,

\[
\mathcal{N}(\nu) = n(\nu) + ik(\nu), \quad (1.6.2)
\]

where \( n \) and \( k \) are the real index of refraction, and extinction coefficient, respectively. The index \( n \) determines the wavelength of the wave, and \( k \) the rate of extinction, or absorption. The expression \((1.6.1)\) obviously is not of the form \((1.2.1)\), in general.

To determine \( g(\nu) \), as a function of \( \mathcal{N}(\nu) \) for plane-faced samples, \((1.6.1)\) must be used, in addition to relations giving the reflectivity and transmissivity of the surfaces of the sample, since waves are partially reflected and partially transmitted at the surfaces. The amplitude reflectivity for normal incidence external to the sample is

\[
r(\nu) = \frac{1 - \mathcal{N}(\nu)}{1 + \mathcal{N}(\nu)}, \quad (1.6.3)
\]
For incidence internal to the sample,

\[ r_{\text{int}}(\nu) = -r(\nu) \]  \hspace{1cm} (1.6.4)

The amplitude transmissivities are given by

\[ t(\nu) = 1 + r(\nu) \]  \hspace{1cm} (1.6.5)

and

\[ t_{\text{int}}(\nu) = 1 + r_{\text{int}}(\nu) = 1 - r(\nu). \]

1-7 The spectral response function for transmission

Consider a sample in the form of a lamella of thickness b. The complex amplitude transmittance, \( t^s(\nu) \), or the ratio of the complex amplitude at the exit surface to that at the entrance surface, can be derived by consideration of radiation traveling through the sample and being partially transmitted and reflected from the surfaces. The result, using equations (1.6.1) and (1.6.3) through (1.6.5) above is\(^7\,^8\)


\(^8\) E. E. Bell, Méthodes Nouvelles de Spectroscopie Instrumentale, Colloque C2, p. 18 (1967), No. 161, Éditions du Centre National de la Recherche Scientifique, (also printed as Supplément au Journal de Physique).
This rather complicated expression is in the form of a sum of "partial waves." The $\lambda = 0$ term, the first partial wave, is due to radiation which passes through the sample only once. The remaining terms are due to radiation reflected back between the two surfaces at least once, then in the direction of the exit beam. These terms give rise to a "ripple" effect in the amplitude transmittance for low absorption, known as "channeled spectrum." The $\lambda = 1$ term is considered the first channeled spectrum term.

The insertion spectral response, obtained by comparison with an air space of length $b$, is

$$g(b, \nu) = t^5(\nu)\exp(-2\pi i\nu b)$$

(1.7.2)

$$= \sum_{\lambda=0}^{\infty} g_{\lambda}(b, \nu),$$

where $g_{\lambda}(b, \nu)$ is the response function for the $\lambda$'th partial wave:

$$g_{\lambda}(b, \nu) = (1-r^2(\nu))r^{2\lambda}(\nu)\exp(ib\Gamma_{\lambda}(\nu)),$$

(1.7.3)

where $\Gamma_{\lambda}(\nu)$ is defined by

$$\Gamma_{\lambda}(\nu) = 2\pi \nu((2\lambda+1)N(\nu) - 1).$$

(1.7.4)
Consider a sample for which absorption is small, and for which index is nearly constant. It follows, by transforming (1.7.2), and using (1.3.6), that if an impulse is applied to the sample, with the spectral response function (1.7.2), the response for the \( \ell \) th partial wave consists of an impulse shifted by an optical path of length \( (2\ell + 1)n-1)b \) from the applied impulse. This relation gives the approximate shift in position for each partial wave in the interferogram if the index is relatively constant, since the background interferogram usually can be approximately described as a single impulse. This approximation can be used as a guide in choosing a distance, \( L \) in (1.5.2), to shift the interferogram to center it on the major contribution, for \( \ell = 0 \). Also, it can be seen that higher order waves are shifted far enough, eventually, so that their contribution is out of the sampling region. This is sometimes a help in determining the optical constants, since the series can be terminated at a finite value of \( \ell \) for computation with the experimental data.

1-8 Corrections to the spectral response function for transmission

Consider first the correction for geometrical imperfection. The term "imperfect" here will be taken to mean that the sample geometry deviates from that of a flat, parallel-faced sample. The deviation may be either because one or both of the surfaces are not flat, the two surfaces are not parallel, or that both of these
conditions are true. For both of these conditions there is a slight difference in sample thickness at various points across the area through which radiation passes. Considering a circular region of the sample, the thickness may be specified by a function, \( b(r, \phi) \), where \( r \) and \( \phi \) are polar coordinates in the plane of the crystal faces. From \( b(r, \phi) \), one can define a thickness distribution function \( f(b) \) by

\[
f(b)\,db = dA/A,
\]

(1.8.1)

where \( dA \) is the area with thickness in the interval \( db \) about \( b \). This function is normalized to unity:

\[
\int_0^\infty f(b)\,db = 1.
\]

(1.8.2)

The effect of this distribution on the response function can be determined by integrating the amplitude from all area elements, so that the true response function is

\[
g(\nu) = \int_0^\infty db \, f(b)g(b, \nu).
\]

(1.8.3)

It is convenient to expand \( g(\nu) \) in the form of a sum over partial waves,

\[
g(\nu) = \sum_k g_k(\nu),
\]

(1.8.4)
as with \( g(b, \nu) \) in (1.7.2). It then follows that the correction can be applied to each partial wave separately:

\[
g_f (\nu) = \int_{-\infty}^{\infty} db f(b)g(b, \nu). \tag{1.8.5}
\]

Defining an arbitrary thickness, \( b_0 \), this can be written

\[
g_f (\nu) = g_f (b_0, \nu) \Delta_f (\nu), \tag{1.8.6}
\]

where

\[
\Delta_f (\nu) = \int_{-\infty}^{\infty} dx f(b_0 + x)\exp(i \int_f (\nu)x). \tag{1.8.7}
\]

The result is that each term in the series is modified by a complex multiplying function of frequency \( \Delta_f (\nu) \). Higher frequencies and higher orders lead to more severe effects, because they lead to faster variations of the exponential function in (1.8.7). If the distribution is symmetric about \( b_0 \), then \( \Delta_f (\nu) \) is real, and the phase of each partial wave is unaltered.

A simple case is the uniform thickness distribution:

\[
f(b) = \begin{cases} \frac{1}{\Delta b}, & |b-b_0| < \Delta b/2 \\ 0, & |b-b_0| \geq \Delta b/2 \end{cases}, \tag{1.8.8}
\]

where \( b_0 \) is the average thickness, and \( \Delta b \) the total deviation from the average. For \( f(b) \) in (1.8.8),
This applies to a rectangular wedged sample, or to a circular sample with slightly concave or convex surfaces. If the actual distribution for a sample is quite narrow, and nearly symmetric about $b_0$, this serves as a good approximate function to use in accounting for imperfections. In practice, it is not profitable to find the actual distribution.

Frequently, samples may have flat, but non-parallel surfaces. For a circular aperture, and a total thickness deviation, $\Delta b$, the exact correction is derived in Appendix A, and the result is in the form of a Bessel function of the first kind, of order one:

$$\Delta_1(\nu) = 2 \frac{J_1(\nu \Delta b/2)}{J'_1(\nu) \Delta b/2}.$$ (1.8.10)

The effect of convergence of the beam which passes through the sample is similar to that due to sample imperfection, so that the value of $\Delta b$ used can be assumed to contain a contribution due to convergence. This effect is small for the instrument used in the present work.  

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The spectral response function considered up to this point is that which would be measured only under perfect resolution. The effect on an interferogram transform of the window function limiting the resolution has been discussed in section 1-5. Assuming that the background interferogram has its values localized enough toward the center so that it is not affected by the window function, and using (1.5.5) and (1.4.7), the actually measured sample interferogram transform can be written

\[ p_2'(\nu, L) = \]

\[ \int_{-\infty}^{\infty} d\nu' \int_{-\infty}^{\infty} A_{\nu_0}(\nu - \nu') g(\nu') p_1(\nu') \exp(-2\pi i L \nu') \cdot \]

Using the spectral response function (1.8.4), for an imperfect sample, and making the approximation that \( p_1(\nu') \) and \( N(\nu') \) (and therefore \( r(\nu') \), \( \Gamma_A(\nu') \) and \( \Delta_A(\nu') \)) are constant over the small interval where \( A_{x_0}(\nu - \nu') \) has appreciable values, the integral can be carried out. It is

\[ p_2'(\nu, L) = p_1(\nu) \exp(-2\pi i \nu L) \]

\[ (1.8.12) \]

\[ \sum_{\ell = 0}^{\infty} \left[ \int_{-\infty}^{\infty} g_\ell(b_0, \nu) \Delta_A(\nu) A_{x_0} \left( \frac{b_0 \Gamma_A(\nu)}{2\pi \nu} - 1 \right) \right] . \]
It should be noted that $A(x)$ here has a complex argument, whereas it was defined in (1.5.4) for only real arguments. In the computer program to be described in section 2-1, which was used for the work on KI, only the real part of the argument was included. Since the correction was small, it was not worth while to evaluate the actual function.

In (1.8.12) the window function correction can be expressed as a part of the response function itself. Defining a modified correction factor for each partial wave,

$$\Delta_4'(\nu) = \Delta_2'(\nu) A_x(\frac{b_0 \Gamma_2(\nu)}{2\pi \nu} - L), \quad (1.8.13)$$

(1.8.12) can be written

$$p^*_2(\nu, L) = g'(\nu)p_1(\nu) \exp(-2\pi i \nu L), \quad (1.8.14)$$

where $g'(\nu)$ is the response function obtained by using $\Delta_4'(\nu)$ instead of $\Delta_4(\nu)$ in (1.8.6) and (1.8.4). The result, in terms of the impulses mentioned in section 1-7, is that each impulse is weighted according to the value of the window function at its position.
1-9 The spectral response function for reflection

The complex amplitude reflectance of a planar surface between free space and a dielectric medium has been given in terms of the complex index of refraction by (1.6.3). The component of radiation considered in this expression is only the primary reflected component, since, in general, there will be other components due to reflection from other surfaces of the sample. Samples in which the other components are suppressed or deflected will be called "reflection samples."

A convenient way of measuring the reflectivity is to compare the interferogram transform taken with the sample in place with that taken with the sample replaced by a mirror. Recalling that the reflectance of a perfect mirror is -1, the response function, for reflection, is given by

\[ g_R(\nu) = \frac{1 - \mathcal{N}(\nu)}{1 + \mathcal{N}(\nu)} , \]  \hspace{1cm} (1.9.1)

which can be solved to give the index:

\[ \mathcal{N}(\nu) = \frac{1 + g_R(\nu)}{1 - g_R(\nu)} . \]  \hspace{1cm} (1.9.2)
In practical situations, it is generally impossible to precisely replace the mirror by the sample, so that there is a difference in optical path between them, denoted by $D$. A shift in optical path of $+D$ for the sample with respect to the mirror results in a phase shift of $+2\pi D$ in the sample interferogram. Thus

$$p_2(\nu) = p_1(\nu)g_R(\nu)e^{2\pi i D \nu}.$$  \hspace{1cm} (1.9.3)

If $D$ is known, the function $g_R(\nu)$, as found by (1.9.3), can be substituted into (1.9.2) to give the complex index. A method of determining $D$ is discussed in section 2-3.
CHAPTER II

MEASUREMENT OF THE OPTICAL CONSTANTS OF KI

The purpose of the present chapter is to describe the actual procedure used in determining the optical constants of KI, in the far infrared. The basic formulas which were used have been developed in Chapter I. The computer program for computation of the optical constants from transmission data, and the preparation of suitable samples for transmission measurements are described here preceding a description of the actual results.

2-1 Transmission optical constants computer program

The expression for the spectral response function in terms of the complex index and the transforms of the background and sample interferograms, in the case of transmission, is very complicated, and cannot be explicitly solved for the complex index. The iteration method to be described here, of finding the index, is essentially the same as that described by Russell.¹

For a given frequency, \( \nu \), the corrected spectral response function, from the results of section 1-8 can be written

¹Russell, op. cit., pp. 22-23.
\[ g'(\nu) = (1 - r^2(\nu)) \exp(2\pi i (N(\nu) - 1) \nu b_0) \Lambda'(\nu), \]  

(2.1.1)

where \( \Lambda'(\nu) \) is a function of \( \nu \) and \( N(\nu) \), given by

\[ \Lambda'(\nu) = \sum_{\lambda = 0}^{\lambda_{\text{max}}} r^{2\lambda}(\nu) \Delta_{\lambda}'(\nu) \exp(4\pi i \lambda \nu b_0 N(\nu)), \]  

(2.1.2)

where \( \lambda_{\text{max}} \) corresponds to the highest order partial wave with a contribution in the sampling region. In terms of the background and sample interferogram transforms \( p_1'(\nu) \) and \( p_2'(\nu, L) \), (1.8.14) gives

\[ N(\nu) = 1 - \frac{1}{\nu b_0} \left[ m + \nu L \right] \]  

(2.1.3)

\[ + \frac{1}{2\pi 1\nu b_0} \times \log \left\{ \frac{p_2'(\nu, L)}{p_1'(\nu) \Lambda'(\nu)} \right\}, \]

where \( L \) is the optical path shift in the interferogram. The complex index, \( N(\nu) \) was evaluated, using (2.1.3), by an iteration procedure at each spectral point in a given frequency interval.

Consider first the initial spectral point in the interval for which \( N(\nu) \) was computed. Knowing \( n \) approximately at this point, the proper value of the integer \( n \) was found, before beginning the
program, and read into the program as input data. A sequence of iterations were made, numbered by an index \( j \), where

\[ j = 1, 2, \ldots, j_m. \]  

(2.1.4)

Output index values \( N_j^0 \) were obtained from the left-hand side of (2.1.3) using input values \( N_j^1 \) on the right-hand side. To begin the process \( N_1^0 \) was computed by setting \( N_1^1 = 1.0 \). For the next calculation, \( j = 2 \), the value \( N_2^1 = N_1^0 \) was used as the input value. The sequence was continued in this manner, setting

\[ N_j^1 = N_{j-1}^0, \]  

(2.1.5)

until consistent values, for which \( N_{j_m}^0 = N_{j_m-1}^0 \) were obtained.

For a point adjacent to the initial point, it was not necessary to compute \( N_2^1 \) in the above manner, but rather, it was set equal to the final value for the initial computed point. Likewise, a new value of \( m \) was not needed, since trial logic in the program was designed to choose \( m \) such that only the trial index value closest to that from the preceding point was accepted. It was only necessary to try the values for \( m \) differing by unity from that for the initial point.

For the remainder of the interval, the procedure for going from a given point to an adjacent point was the same as described in the preceding paragraph. Since the spectrum covered in the measurements consisted of isolated regions where usable data
existed, and since the initial value of \( m \) had to be determined from experimental data, the initial point was chosen at the center of the interval. The program proceeded point by point from the center point to that for maximum frequency. Then, returning to the point adjacent to the center point, on the low frequency side, it proceeded to that for the lowest frequency in the interval.

2-2 Preparation of samples for transmission measurements

The preparation of samples for transmission was a challenge because of the thickness required (about 100 \( \mu \)) and the small tolerable deviation (a few microns) in thickness across the optically usable area. A circular area of 3/4" diameter was optimum for use in the interferometer. Salt crystals of this diameter, and 100 \( \mu \) thickness are extremely fragile.

Samples used in these measurements were prepared by grinding and polishing bulk pieces of crystalline KI. The bulk pieces were cylindrical, of diameter 1.5". They were purchased from the Harshaw Chemical Company. The problems of support in polishing, eliminating wedging of the sample, and handling after preparation were overcome by epoxying one flat, polished surface permanently to a brass plate, as shown in Fig. 1. The center, circular hole in the plate, through which radiation could pass when the preparation was completed, was filled by the disk, of the same thickness as the plate, during the grinding operation. A small amount of
Figure 1. The assembly for support of transmission samples during grinding. The disk, plate, and crystal diameters are 3/4", 2", and 1 1/2", respectively.
epoxy was applied only to the plate. The cylinder, with the plate and disk secured to it with screws, could be moved along the center axis with respect to the casing.

Before the crystal was applied to the plate, the reference surface, plate surface, and disk surface were cut and ground flat and parallel to each other. The center disk was then removed by removing, then replacing the plate, and the crystal was applied to the plate surface with epoxy, as mentioned previously. The center disk was replaced after the epoxy had cured. The excess bulk of the salt cylinder was then removed, using a string saw with a slight amount of water. In the grinding operation, the cylinder was first moved in, with respect to the casing, so that only a slight amount of salt extended beyond the reference surface. Material was then ground away by placing the entire system against a rotating lap plate, using an abrasive suspended in ethyl alcohol. The cylinder was worked down until the desired thickness of salt was reached. This thickness was the distance between the plate and reference surfaces at completion, which was measured with a depth micrometer.

The method described here was found to be satisfactory for producing samples of 100\(\mu\) in thickness, for both KBr and KI, with relative ease. Uniformity in thickness across the surface, however, was difficult to obtain. The principal difficulties seemed to be that the crystal did not hold firm against the center
disk across its entire area in the final grinding, and the fact that dust particles between the sample and disk left their imprint on the final product. To reduce problems due to the epoxy thickness over the plate, but not over the disk, an attempt was made to keep the epoxy entirely in a very shallow groove, as shown in Fig. 1, leaving a narrow ridge between the groove and the disk. To reduce grinding of the reference surface, an alternate casing was used until the final thickness was nearly reached.

The o-ring under the plate in Fig. 1 was to keep alcohol from reaching the under-surface of the crystal during grinding. Alcohol had to be removed from the polished surface, with a clean, soft tissue, immediately after lifting it from the polishing pad, to prevent etching of the surface. The air holes shown in Fig. 1 were to facilitate removal of the plate and sample after polishing.

2-3 Experimental results for KI

The optical constants of KI were determined from both transmission and reflection measurements with the Michelson interferometer, using the Fourier transforms of interferograms apodized according to (1.5.4). A given technique (reflection or transmission, single or double beam), sample, and set of filters and beam splitter could generally yield usable data only in a set of isolated frequency intervals, many times only in one narrow interval. Many separate measurements were thus necessary to determine n and k over a wide, continuous spectral region. In the following
discussion, the major emphasis will be on the KI samples themselves, since the appropriate filters and beam splitter combinations were, in most cases, known from previous work.\textsuperscript{2, 3}

Three samples of different thicknesses were used for transmission measurements. The average thicknesses, \( b_0 \), together with identification numbers, and deviations in thickness, \( \Delta b \), for these samples are listed in Table 1. The determination of \( b_0 \) and \( \Delta b \) is described later in this section. Two reflection samples, SA1 and SA2, were used. These were similar to the samples used by Johnson.\textsuperscript{4} They were very thick (about 1/4"), with one flat and highly polished surface. The spectral intervals used, with appropriate filters, beam splitter, and sample, are given in Table 2. The quantities \( \Delta x \) and \( \Delta \nu \), the step increment and resolution, respectively, were defined in section 1-5.

Figure 2 shows the amplitude transmittance and phase for one of the thin samples, SD3. The eigenfrequency (see Introduction) is indicated by \( \nu_0 \). Even for a sample this thin, 119\( \mu \) , the absorption is too great in the region 90-150cm\(^{-1} \) for there to be measurable transmitted power. In the region from 200cm\(^{-1} \) upward, \( k \) cannot be accurately measured.

\begin{itemize}
  \item \textsuperscript{2}Russell, op. cit., p. 59.
  \item \textsuperscript{3}Johnson, op. cit., p. 19.
  \item \textsuperscript{4}Johnson, op. cit., pp. 16-18.
\end{itemize}
since absorption is too small, and the transmittance is more strongly dependent on channeled spectrum, and the precise geometry of the sample. In the region below 50cm$^{-1}$, the transmittance should reach nearly 100 percent also, but a thicker sample was used to determine the optical constants in this region, so the transmittance of this sample was not measured.

**TABLE 1**

TRANSMISSION SAMPLE GEOMETRICAL DATA

<table>
<thead>
<tr>
<th>Sample</th>
<th>$b_0$, $\mu$ average thickness</th>
<th>$\Delta b_0$, $\mu$ thickness deviation over sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD1</td>
<td>101.0 ± 0.50</td>
<td>7.3 ± 2.0</td>
</tr>
<tr>
<td>SD3</td>
<td>119.15 ± 0.50</td>
<td>3.0 ± 1.0</td>
</tr>
<tr>
<td>SD4</td>
<td>720.0 ± 2.0</td>
<td>5.5 ± 1.5</td>
</tr>
</tbody>
</table>

The power reflectivity and phase are shown in Fig. 3. The reflected power peaks in the region of high absorption. The phase has large values in this region also, but drops very sharply below the eigenfrequency. The small reflection phase values in the region below $\nu_0$ do not yield accurate values of $k$, particularly since the absolute phase varies between different runs, because of the variation in the position of the sample with respect to the reference mirror.
### TABLE 2

**SPECTRAL REGIONS AND CONDITIONS FOR INTERFEROMETRIC MEASUREMENTS ON KI**

<table>
<thead>
<tr>
<th>Spectral Region, cm⁻¹</th>
<th>Filters*</th>
<th>Technique</th>
<th>Samples</th>
<th>Δ x, μ</th>
<th>Δ v, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-50</td>
<td>Quartz, 250 lines per inch metal mesh, KBr+BaF₂+LiF</td>
<td>Single, double beam transmission</td>
<td>SD4</td>
<td>30 x 1.024</td>
<td>5.0</td>
</tr>
<tr>
<td>45-90 and 160-195</td>
<td>Quartz, 1/2 mil mylar, LiF</td>
<td>Single beam transmission</td>
<td>SD1, SD3</td>
<td>18</td>
<td>5.0</td>
</tr>
<tr>
<td>85-170</td>
<td>Quartz, 1/2 mil and 1/4 mil mylar, LiF</td>
<td>Reflection (single beam)</td>
<td>SA1, SA2</td>
<td>18, 15</td>
<td>5.0</td>
</tr>
<tr>
<td>190-225</td>
<td>Quartz, 1/4 mil mylar, LiF</td>
<td>Single, double beam transmission</td>
<td>SD4</td>
<td>15</td>
<td>5.0</td>
</tr>
<tr>
<td>160-700</td>
<td>Diamond, 1/10 mil mylar</td>
<td>Single beam transmission</td>
<td>SD1, SD3</td>
<td>4</td>
<td>10.0</td>
</tr>
<tr>
<td>190-700</td>
<td>Diamond, 1/10 mil mylar</td>
<td>Single, double beam transmission</td>
<td>SD4</td>
<td>4</td>
<td>10.0</td>
</tr>
</tbody>
</table>

*Filters are detector window, beam splitter, and powders in polyethelene, in that order. About 2mm black polyethelene was used in addition, for all spectral regions. Where no powders are indicated, none were used.
Figure 2. The amplitude transmittance, $|g'(\nu)|$, and phase, $\arg(g'(\nu))$, for a KI sample of average thickness $b_0 = 119.15\mu$. Resolution and approximate error ranges are indicated. The eigenfrequency is indicated by $\nu_0$. 
Figure 3. The averaged power reflectance, $|g_R(\nu)|^2$, and phase, $\arg(g_R(\nu))$, for two thick polished KI samples. Resolution and approximate error ranges are indicated. The absolute phase was established by comparison with transmission measurements, as discussed in the text.
The reflected power compares favorably with that measured by Yoshinaga et al. Hadni et al. have also measured the power reflectivity, and have calculated the phase and optical constants from the power reflectivity by means of a Kramers-Kronig analysis, and also by a "dispersion analysis." In a dispersion analysis, the reflectivity is used to find parameters for a best fit to an ad hoc dispersion formula, and the optical constants computed on the basis of this formula. The optical constants obtained by Hadni compare favorably in magnitude with those of this measurement, in the range favorable to reflectivity measurements, but the structure is less pronounced in his results. In fact, all subsidiary structure in the phase, distinctly seen in Fig. 3, was entirely missed by the Kramers-Kronig analysis.

Fig. 4 shows the power reflectance in the region where it is very close to zero. This region is shown to a much larger scale than in Fig. 3 so that it can be read to the accuracy of the measured data. Since amplitude, rather than power (the square of the amplitude) was measured, power ratios much lower than those usually measured in power spectroscopy could be determined. The same was true in the case of the transmission measurements. This


Figure 4. The power reflectance of KI, $|g_{R}(\nu)|^2$, in the region of very low reflectance.
meant that sample thicknesses could be twice the values that would be needed for the same power measurement in power spectroscopy.

A description of the method of determining the optical constants is best begun with the high frequency region, above the absorption band. In this region, $k$ is too small to be measured with crystals as thin as those used here. The index, $n$, can be measured very well, provided the thickness of the sample is known accurately, and the phase cycle can be established. The thickness was not known, at the outset, to the accuracy required, since it is very difficult to measure the thickness of such fragile samples. Fortunately, however, index values in this region were known from prism measurements in the near infrared, so that the thickness could be determined, knowing an approximate value to establish the phase cycle. In the absence of absorption, and at points where the phase correction due to channeled spectrum is zero, the phase of $p_2^*(\nu, L)/p_1(\nu)$, from (1.8.14), is given by

$$\arg(p_2^*(\nu, L)/p_1(\nu)) = \arg(g^*(\nu)) - 2\pi (\nu L + m)$$

Here, $m$ is an integer specifying the phase cycle. This formula holds where the power variation due to channeled spectrum is at a maximum or minimum (see (2.3.3)). The thickness distribution $f(b)$ (section 1-8) is assumed to be symmetric about the average

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7K. Korth, Zeit. f. Phys. 84, 677 (1933).
thickness $b_0$, so that all $\Delta_f (\nu)$ are real. Due to (2.3.1),
either the index or thickness can be determined if the other and
the integer $m$ are known. The integer $m$ can be determined if an
approximate thickness and the index are known. The approximate
thickness was determined by a micrometer reading in some cases
and by the sample's weight and area, and the known density in
other cases. Using the value of $m$ and index values at several
points in the region $350-700 \text{cm}^{-1}$, it was possible to get a
consistent, accurate value for the thickness, within one micron.
The thicknesses $b_0$ so determined, for each of the transmission
samples, are those recorded in Table 1, and used in the subsequent
determination of the optical constants.

Another interesting feature of the high frequency region is
that here the effects of sample geometry imperfection appear most
noticeably, so that the quality of the sample can be checked. For
some samples the channeled spectrum power was "washed out" at
higher frequencies, and even power in the first partial wave was
decreased, where it should reach a constant value. When this was
too serious, the sample was rejected, but when it was not prohibi-
tively bad, a parameter, $\Delta b$, was determined and (1.8.9) was used
to correct for the effects. For the determination of $\Delta b$, and to
provide an indication of the effects of geometry imperfections,
it is useful to expand (1.8.9):
Because of the dependence on the square of \( f_{\lambda} (\nu) \) and thus of \( \nu \), it can be seen that at lower frequencies, effects may be far less serious, so that it is not necessary to have perfection at high frequencies. It also can be seen how much more drastically higher-order terms in the series are affected. This is not serious in highly absorbing regions, since the contribution of the higher-order terms is small.

It can be seen by (1.7,2) that the channeled spectrum amplitude, or power, should have a maximum for

\[
2nb_{o} \nu = \text{integer}
\]

and a minimum for

\[
2nb_{o} \nu = \text{half odd integer}.
\]

This was not true with some samples. This may be an indication of an asymmetric distribution in thickness. It was necessary, in most of this work, to reduce the size of the aperture at the sample to correct the situation. The image of the source, which appeared at this point, was not circular, and did not fill the ordinarily used 3/4" diameter aperture here. Reducing the aperture to 3/8" diameter reduced the signal only by a factor of two, and caused the channeled spectrum to appear much better, both in magnitude and position of the maxima and minima.
There was a serious problem in the use of the asymmetric mode, for thick samples, such as SD4 here. Amplitude data could not be reliably used to determine \( k \). The reason for this was not fully investigated. The deviation in thickness for SD4 was estimated by careful micrometer measurements of the thickness of the brass plate at many points, and of the total thickness of the plate plus the sample. The value of \( \Delta b \) so determined, given in Table 1, is less than that for SD1, for which good data was obtained. Changing the aperture size did not have a significant effect, which seemed to rule out both the effect of geometry imperfections and that of aberrations due to convergence of the beam, suggested by Russell.\(^8,9\)

The problem was circumvented by using only phase data from the asymmetric measurements, and power data obtained by placing the sample in the detector beam. This is the "double beam" method of Table 2, while the "single beam" refers to the asymmetric mode. In the low frequency region, good agreement between single and double beam results was obtained.

In all transmission measurements other than those just discussed, the asymmetric mode was used, and \( n \) and \( k \) were determined using the computer program discussed in section 2-1 and \( b_0 \) and \( \Delta b \) from Table 1. For the very thin transmission samples, SD1

\(^8\)Russell, op. cit., p. 73 and p. 85.

\(^9\)Chapter I, footnote 10.
and SD3, the contribution from the first channeled spectrum term was important. The second term was included in the calculations, but was quite small. For SD4, channeled spectrum was not present in the interferogram, using the resolution 5cm$^{-1}$. The criterion used in determining $\ell_{\text{max}}$ in (2.1.2) was

$$\left(2\ell_{\text{max}} + 1\right)\frac{n}{m} - 1 \geq b_o > x_o - L, \quad (2.3.4)$$

where $\frac{n}{m}$ is the minimum value of $n$ in the interval for which the computation was made. $L$ was generally chosen such that

$$L \geq (n_{av} - 1)b_o, \quad (2.3.5)$$

where $n_{av}$ is the average value of $n$ in the interval. The reasons for these choices were discussed in section 1-7.

The computation of $N$ from reflection data was comparatively simple. A point by point program based on (1.9.2) and (1.9.3) was used. The value of the optical path shift, $D$, was determined by computing $g_R$ from (1.9.1), using a value of $N$ measured in transmission, and solving (1.9.3) for $D$. This was done at a frequency of 85cm$^{-1}$, as discussed below.

Fig. 5 shows the optical constants, $n$ and $k$, resulting from consideration of all measurements made. Generally, at least two separate runs were made for each set of experimental conditions. The choice of which technique to rely upon when different techniques gave different results was based on consistency between the
Figure 5. The experimentally determined index of refraction, $n(v)$, and extinction coefficient $k(v)$ for KI. The values given are average values from many measurements in transmission and reflection, as discussed in the text.
separate runs, and on the reliability of the amplitude and phase data. The regions of overlap between good reflection and transmission data were quite narrow. Use of thinner transmission samples could have widened these regions, but this would not be easy, since a great effort was needed to prepare samples as thin as the ones used here. The value of \( 85 \text{cm}^{-1} \), where the reflection phase was established by transmission results, is in the low frequency overlap region. With the phase established here, consistent results were obtained in the high frequency overlap region, 160-170cm\(^{-1}\). Similar overlap regions existed between data taken from transmission measurements with different sample thicknesses and between single and double beam measurements at the low frequencies. The eigenfrequency, \( V_0 \), was taken as the frequency of maximum \( n k \), in the region near the maxima in \( n \) and \( k \) (see section 6-4).

The values of \( n \) and \( k \) used in Figure 5 are also given in Table 7, Appendix C. This table should be consulted for more accurate numerical values. The values determined by transmission measurements are generally more reliable than those of the reflection measurements. This is particularly true of the index values, which are dependent entirely on the phase in regions where absorption is small.

Selected values of \( n \) in the high frequency transmission region, extending to frequencies of very low absorption, are given in Table 3. The values were obtained using sample SD3.
TABLE 3

THE INDEX OF REFRACTION OF KI FOR SELECTED FREQUENCIES

ABOVE THE EIGENFREQUENCY

<table>
<thead>
<tr>
<th>$\nu$, cm$^{-1}$</th>
<th>n</th>
<th>$\nu$, cm$^{-1}$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>156.2</td>
<td>0.897</td>
<td>345</td>
<td>1.557</td>
</tr>
<tr>
<td>158.7</td>
<td>0.937</td>
<td>357</td>
<td>1.563</td>
</tr>
<tr>
<td>161.3</td>
<td>0.990</td>
<td>370</td>
<td>1.568</td>
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<tr>
<td>163.8</td>
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<td>384</td>
<td>1.573</td>
</tr>
<tr>
<td>166.3</td>
<td>1.082</td>
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<td>168.8</td>
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<td>171.3</td>
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<td>1.580</td>
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<td>456.6</td>
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<td>476.6</td>
<td>1.594</td>
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</tr>
<tr>
<td>627.2</td>
<td>1.609</td>
<td></td>
<td></td>
</tr>
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</table>
from the prism data mentioned previously are also included. This cannot be considered a comparison between two separate measurements, since the prism values were used to establish the thickness, b_0. However, the table does give an indication of the accuracy with which b_0 was determined, and of the consistency between two methods of measurement over the frequency interval.

Values of n for frequencies in the transmission region below \( \nu_0 \) are plotted in Fig. 6 as a function of the square of frequency. This choice of scale was made because, on the basis of the approximate formula for the optical constants derived in Chapter V (see equations (5.1.6) and (5.6.4)), \( n(\nu) \) should be a linear function of \( \nu^2 \) for very low frequencies. Thus, by extrapolation, \( n(0) \), a constant of significance in the theories in Chapters V and VI, could be determined. The value so determined here for KI is \( n(0) = 2.24 \pm .01 \).
Figure 6. The low frequency index of refraction \( n(\nu) \) of KI, extrapolated to zero frequency. The abscissa is proportional to the square of frequency.
CHAPTER III

REVIEW OF LATTICE DYNAMICS

Potassium iodide, at room temperature, is an ionic, crystalline solid, whose crystal structure is of the NaCl type. In the equilibrium, or zero temperature state of the crystal, each nucleus is situated on a particular site of the lattice. The study of the slight motion of the nuclei from their equilibrium sites, due to the presence of small amounts of energy above the zero point energy, is known as lattice dynamics. The motion of the electrons due to the nuclear motion has to be taken into account. In the adiabatic approximation, the coordinates and momenta of the electrons are not explicitly considered in the Hamiltonian (and equations of motion) for lattice motion, but the change in energy due to electronic motion is expressed in terms of the nuclear coordinates and included in the potential energy of the lattice. A correct solution to the lattice dynamical problem, in the adiabatic approximation, would require an electronic


wave function, expressed as a function of the lattice configuration. In practice, simplified models of the electronic configuration, as a function of lattice configuration are used. In the case of ionic solids, such as KI, the electron wave functions are, to a good approximation, well localized about the nuclei as they move about their respective lattice sites.

Various models have been proposed to describe the motion of the electrons of an ion with respect to the nucleus. The simplest such model is the "rigid ion model" in which the electron cloud is assumed to move in such a way that it remains undistorted and concentric with the nucleus. The rigid ion model does not take into account the effects of the electrical polarizability of the ion itself. To account for the effects of ionic polarizability in lattice dynamical work, a "shell model" has been proposed. It is used in this work for KI. In the shell model, the nucleus and inner electrons form a single, spherical, charged entity, the core. The outer electrons form a similar entity, the shell. Forces are exerted between core and shell tending to keep them

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concentric, so that the ion itself has a polarizability, but not a permanent dipole moment. Assuming zero mass for the shell, the shell coordinates can, in accordance with the adiabatic principle, be eliminated from the Hamiltonian for ionic motion. The core motion will, in this discussion, be referred to as the ionic motion, since the shell very nearly follows the core. In the limit of very strong core-shell forces, the rigid ion model is approached.

The first step in the solution of a lattice dynamical problem is generally that of finding a set of coordinates in terms of which the equations of motion are uncoupled, in the harmonic approximation. The coordinates, known as normal coordinates, are linear combinations of the cartesian ionic displacement coordinates. In the harmonic approximation, only the quadratic terms in the expansion of the inter-ionic potential in terms of ionic cartesian coordinates are included. The matrix of coefficients, the dynamical matrix, is generally non-diagonal. It can be diagonalized by a transformation to a new set of coordinates. The normal coordinates are those which diagonalize the dynamical matrix and also keep the kinetic energy matrix diagonal. In the case of a periodic lattice, each mode represents a wave, so the general motion is a superposition of waves.

The dynamical matrix for KI is \( 6N \) dimensional, where \( N \) is the number of unit cells in the entire crystal. The unit cell
contains one $K^+$ and one $I^-$ ion. There are thus six degrees of freedom per unit cell. The result of periodicity is that the dynamical matrix can be transformed so that it breaks up into $N$ 6x6 matrices, each corresponding to a particular wave vector. The 6x6 matrix for a given wave vector is known as the Fourier transformed dynamical matrix. The diagonalization of the transformed dynamical matrix for a given wave vector then gives the classical frequencies squared as eigenvalues, and an eigenvector, specifying polarization, corresponding to each frequency.

In this chapter, the harmonic Hamiltonian is expressed in terms of the total Hamiltonian, or energy of the lattice. The actual form of the potential energy is not specified in this chapter. It is shown, from the harmonicity alone, that normal coordinates can be found, in principle. Then, assuming periodicity, the process of finding the normal coordinates is reduced to a manageable problem, using the wave technique. It is important to note that the usefulness of the number representation, as discussed in section 3-6 is not in any way a result of the periodicity of the lattice.

Finally, it must be noted that, although the harmonic approximation implies only vibration of the ions, the introduction of anharmonicity causes thermal expansion of the lattice. The motion at high temperatures can approximately be described as a vibration about new average positions. The dynamical matrix used to fit the
experimental frequencies at room temperature may be different from
the true harmonic dynamical matrix. The model of the lattice
assumed by considering the average separation of ions to be the
equilibrium separation is referred to here as "quasi-harmonic,"
although the term means different things to different authors. As
defined here, the quasi-harmonic frequencies are the proper
frequencies to use in the calculation of the optical constants
described in Chapter VI.

3-1 The NaCl type lattice

The KI lattice is of the NaCl type. The NaCl lattice can
be defined as the set of points specifying the set of lattice
vectors \( \vec{r} \) of cartesian components \( d_n^1, d_n^2, \) and \( d_n^3 \), or

\[
\vec{r} = d(n_1, n_2, n_3),
\]

(3.1.1)

where \( n_1, n_2, \) and \( n_3 \) are integers such that

\[
n_1 + n_2 + n_3 \text{ is even,}
\]

(3.1.2)

and \( d \) is half the lattice constant. The origin point, for \( \vec{r} = 0 \),
is also a lattice point. The coordinate axes implied here will
be called the "crystallographic" axes. It is convenient, for a
finite lattice, to associate with each lattice vector \( \vec{r} \) an integer
\( \ell \), where
\[ \ell = 0, 1, \ldots, N - 1, \]  
\[ (3.1.3) \]

taking \( \lambda = 0 \) for \( \tilde{\lambda} = 0 \).

At each lattice point there is a primitive unit cell, containing an ion pair. Let \( s \) denote the particular ion in the cell, and \( \vec{s} \) a vector from the lattice point to the \( s \)'th ion. The ions take the following positions:

\[
\text{for } s = 1, \quad \vec{s} = 0, \quad \text{and for } s = 2, \quad \vec{s} = (0, 0, d). 
\]  
\[ (3.1.4) \]

For KI, the \( s = 1 \) ion will be \( K^+ \) and the \( s = 2 \) ion \( I^- \).

The cubic unit cell has an edge of length \( 2d \). This is not a primitive cell, since there are four ion pairs within the cell. The volume of the primitive cell is \( v_c = (2d)^3/4 = 2d^3 \). The cubic cell is a face-centered cubic (fcc). Kittel\(^6\) presents a more complete discussion of this, and a variety of other structures.

The reciprocal lattice\(^7\) is defined as the set of points specifying the vectors \( \vec{g} \) such that

\[ \vec{g} \cdot \vec{\lambda} = 2\pi \text{ times an integer}, \]  
\[ (3.1.5) \]


\(^7\)Ziman, op. cit., pp. 1-15.
where \( \mathbf{L} \) is any lattice vector. For the NaCl lattice, the reciprocal lattice vectors are given by

\[ g = \left( \frac{\pi}{d} \right)(h_1, h_2, h_3) . \tag{3.1.6} \]

The integers are those such that

\[ h_1, h_2, \text{and} h_3 \text{ are all even or all odd.} \tag{3.1.7} \]

This reciprocal lattice has a body-centered cubic (bcc) cell of dimension \( 2\pi/d \).

The displacement of the \( s \)'th ion in the \( \mathbf{L} \)'th cell from its equilibrium position is denoted by the vector \( \mathbf{r}_s(\mathbf{L}) \) and its \( \alpha \) cartesian coordinate (\( \alpha = x, y, \text{or} z \)) by \( u_{\alpha s}(\mathbf{L}) \). The position with respect to the origin is

\[ \mathbf{r}_s(\mathbf{L}) = \mathbf{L} + \mathbf{s} + \mathbf{u}_s(\mathbf{L}) = \mathbf{r}_s^0(\mathbf{L}) + \mathbf{u}_s(\mathbf{L}) . \tag{3.1.8} \]

When time development of the coordinates is considered in later chapters, the displacements will be denoted by \( \mathbf{u}_s(\mathbf{L} | t) \), and similarly for the other coordinates.

3-2 The lattice Hamiltonian

Writing the momentum conjugate to \( u_{\alpha s}(\mathbf{L}) \) as \( p_{\alpha s}(\mathbf{L}) \), the Hamiltonian is the sum of kinetic and potential energy:
\[ H = (1/2) \sum_{\alpha s \lambda} p_{\alpha s \lambda}^2 \frac{\left( \vec{\alpha} \right)^2}{m_s} + U, \]  

(3.2.1)

where \( U \) is the total potential energy due to displacement of ions from their equilibrium positions, a function of all ionic coordinates \( \vec{r}_s (\vec{X}) \), and thus of all \( u_{\alpha s} (\vec{X}) \).

The potential energy can be expanded in a Taylor series about the ionic equilibrium positions:

\[
U = \sum_{\alpha s \lambda} \phi_{\alpha s} (\vec{X}) \ u_{\alpha s} (\vec{X}) \\
+ \left( \frac{1}{2!} \right) \sum_{\alpha s \lambda} \left( \sum_{\alpha' s' \lambda'} \phi_{\alpha s \alpha' s'} (\vec{X}, \vec{X}') \ u_{\alpha s} (\vec{X}) \ u_{\alpha' s'} (\vec{X}') \right) \\
+ \left( \frac{1}{3!} \right) \sum_{\alpha s \lambda} \left( \sum_{\alpha' s' \lambda'} \sum_{\alpha'' s'' \lambda''} \phi_{\alpha s \alpha' s' \alpha'' s''} (\vec{X}, \vec{X}', \vec{X}'') \ u_{\alpha s} (\vec{X}) \ u_{\alpha' s'} (\vec{X}') \ u_{\alpha'' s''} (\vec{X}'') \right) + \ldots
\]

(3.2.2)

where the coefficients are derivatives of the total potential energy:

\[
\phi_{\alpha_1 \alpha_2 \ldots \alpha_n} (\vec{X}_1, \ldots, \vec{X}_n) = \left. \frac{\partial^n U}{\partial u_{\alpha_1 s_1} (\vec{X}_1) \ldots \partial u_{\alpha_n s_n} (\vec{X}_n)} \right|_{\text{all } u_{\alpha s} (\vec{X}) = 0}.
\]

The first summation in (3.2.2) vanishes since the lattice is postulated to be at equilibrium when all \( u_{\alpha s} (\vec{X}) \) are zero. The
second summation is the harmonic part. The third and higher order terms are the anharmonic contributions.

The periodicity of the lattice implies that the potential coefficients are also periodic; so that

\[ \phi \propto_1 s_1 \cdots \propto_n s_n (\vec{r}_1, \ldots, \vec{r}_n) = \]

\[ \phi \propto_1 s_1 \cdots \propto_n s_n (\vec{r}_1 + \vec{r}, \ldots, \vec{r}_n + \vec{r}), \]

where \( \vec{r} \) is any lattice vector, \( \vec{r}_i = \vec{r}_i - \vec{r}_j \), for all \( i \) and \( j \).

In the case of harmonic coefficients this takes the form

\[ \phi \propto_1 s_1 \propto_2 s_2 (\vec{r}_1, \vec{r}_2) = \phi \propto_1 s_1 \propto_2 s_2 (0, \vec{r}_2 - \vec{r}_1) \]

\[ = \phi \propto_1 s_1 \propto_2 s_2 (\vec{r}_2 - \vec{r}_1), \]

so that the function of two lattice vectors depends only on their difference. This is similar to the result of time invariance, applied to the response function in (1.3.5); and it will aid in the diagonalization of the matrix in much the same way that a Fourier transformation diagonalizes the response function.

3-3 Normal coordinates

The harmonic Hamiltonian is the kinetic energy plus the harmonic part of the potential energy:
The coordinates and momenta are real functions of time in the classical case. In the quantum mechanical case, they are Hermitean operators. Consider first the classical case. Introducing a $6N$ vector matrix, $u$, and corresponding matrices for other quantities, the harmonic Hamiltonian can be written

$$H_0 = (1/2) \left\{ \sum_{\kappa} p_{\kappa}^2 (\vec{\lambda}_\kappa) / m_\kappa + \sum_{\kappa} \sum_{\kappa'} \phi_{\kappa}^{\kappa'} (\vec{\lambda}_\kappa, \vec{\lambda}_{\kappa'}) u_{\kappa}^{\kappa'} (\vec{\lambda}_\kappa) \right\}. \quad (3.3.1)$$

where a bar over a matrix denotes the Hermitean adjoint, or transposed conjugate of the matrix, and $(1/m)$ is the reciprocal mass diagonal matrix.* The use of the transposed conjugate rather than simply the transpose is unnecessary at this point, since the coordinates are real; $u_{\kappa}^{\kappa'} (\vec{\lambda}_\kappa) = u_{\kappa}^{\kappa'} (\vec{\lambda}_\kappa)$. In the analysis which follows, however, complex unitary transformations will be considered, so that the more general invariant form is convenient.

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* Diagonal matrices such as this will frequently be formed from quantities depending on only one set of the integers $(\kappa,s,\lambda)$. The parentheses will be left off the matrices when there is no ambiguity in doing so.
The quantum mechanical form of (3.3.2) is identical to the classical form except that the coordinates become operators. The operators corresponding to the coordinates, which will be referred to as coordinates in the following analysis, are Hermitean operators: \( u_\alpha^\dagger(\vec{\xi}) = u_\alpha(\vec{\xi}^*), \) where the \( \dagger \) denotes Hermitean conjugate. A quantum mechanical operator can be expressed as a matrix in a Hilbert space. The Hermitean adjoint of that matrix gives the matrix corresponding to the Hermitean conjugate of the original operator. In so far as this dissertation is concerned, the transition from classical to quantum mechanics can be made by substituting a dagger (\( \dagger \)) for an asterisk (\( \ast \)), when an asterisk appears on the coordinates themselves, and conversely. A bar appearing over a vector matrix means, in the quantum mechanical case, that Hermitean conjugates of the component operators are taken.

Consider the problem of finding a canonical transformation to new coordinates such that both kinetic and potential energy are diagonal. This can be found by first applying the canonical transformation

\[
\begin{align*}
 u' &= \left(1/\sqrt{m}\right) u, \text{ and } p' = \left(\sqrt{m}\right) p, \\
\end{align*}
\]

so that the Hamiltonian becomes:

\[
\begin{align*}
 H_0 &= \frac{1}{2} \left( p^\prime p^\prime + \bar{u}'(1/\sqrt{m}) \phi (1/\sqrt{m}) u' \right). 
\end{align*}
\]
The matrix \((1/\sqrt{m}) \phi (1/\sqrt{m})\) is symmetric, and can be diagonalized by a unitary transformation. Consider the vectors \(u'(\lambda)\), the normalized solutions (or eigenvectors) of the characteristic equation

\[
(\omega^2(\lambda) - (1/\sqrt{m}) \phi (1/\sqrt{m})) u'(\lambda) = 0, 
\]

where the index \(\lambda\) enumerates the \(6N\) solutions and \(\omega^2(\lambda)\) is the eigenvalue for the \(\lambda\) eigenvector. The characteristic equation can be written in terms of the cartesian ionic coordinate matrix as

\[
(m \omega^2(\lambda) - \phi) u(\lambda) = 0, 
\]

although the solutions of this equation are not normalized. The transformation

\[
u' = VQ, 
\]

where \(V\) is a matrix whose columns are the vectors \(u'(\lambda)\), and \(Q\) is the normal mode matrix, then diagonalizes \((1/\sqrt{m}) \phi (1/\sqrt{m})\), according to a well known theorem in matrix algebra. The elements of the transformed matrix are the eigenvalues, \(\omega^2(\lambda)\), the squares of the classical frequencies. The transformation \(V\) can always be real, but in the case of degeneracies there is freedom in the

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choice of eigenvectors, so it could be complex. Such is the case for the lattice waves considered in the next section.

In terms of elements of the matrices, the transformation from the normal coordinates to the cartesian coordinates, from (3.3.3) and (3.3.7), is

\[ u_{\alpha s} (\vec{x}) = \frac{1}{\sqrt{m_s}} \sum_{\lambda} v_{\alpha s} (\vec{r}, \lambda) q(\lambda). \] (3.3.8)

The inverse follows from the fact that V is unitary; so that \( V^{-1} = \overline{V} \). Thus

\[ q(\lambda) = \sum_{\alpha s \lambda} v_{\alpha s}^* (\vec{r}, \lambda) \sqrt{m_s} u_{\alpha s} (\vec{x}). \] (3.3.9)

The momentum \( P(\lambda) \) conjugate to \( Q(\lambda) \) must be chosen so that the transformation is canonical, and the commutation relations are preserved. It is,

\[ P(\lambda) = \sum_{\alpha s \lambda} \left( v_{\alpha s} (\vec{r}, \lambda) p_{\alpha s} (\vec{x}) / \sqrt{m_s} \right). \] (3.3.10)

It is obvious that neither \( Q(\lambda) \) nor \( P(\lambda) \) are Hermitean, unless \( V \) is real.

From (3.3.8) and the inverse to (3.3.10), it follows that the Hamiltonian is given by

\[ H_0 = \frac{1}{2} \sum_{\lambda} (p^*(\lambda) P(\lambda) + \omega^2(\lambda) Q^*(\lambda) Q(\lambda)), \] (Classical)

(3.3.11)

\[ H_0 = \frac{1}{2} \sum_{\lambda} (p^\dagger(\lambda) P(\lambda) + \omega^2(\lambda) Q^\dagger(\lambda) Q(\lambda)). \] (Quantum)
If $V$ is real, the coordinates and momenta are Hermitean (real in the classical case), and the Hamiltonian is the sum of separate harmonic oscillator Hamiltonians for each of the normal modes. In the case of lattice waves, however, the modes must be treated in pairs. One cannot apply the classical Hamilton's equations at this point, since the relationship between a given $Q^\alpha(\lambda)$ and actual coordinates of the system $Q(\lambda)$ is not yet specified.

3-4 The consequences of periodicity

In the previous section the harmonic Hamiltonian was cast into matrix form, and matrix operations were applied to show that it is possible to diagonalize the Hamiltonian. The matrices were all of dimension $6N$, because there are $6N$ combinations of the set of indices $\alpha$, $s$, and $\lambda$. It is convenient, because of lattice periodicity, to display the $\lambda$ index explicitly, defining matrices only over the indices $\alpha$ and $s$. These matrices are 6 dimensional, and $N$ of them are required to specify all of the coordinates. The Hamiltonian becomes

$$H_0 = \frac{1}{2} \sum_{\lambda} \sum_{\lambda'} (\bar{p}(\lambda) (1/m) p(\lambda')) + \bar{u}(\lambda) \delta(\lambda, \lambda') u(\lambda').$$

(3.4.1)
Each six dimensional matrix can now be thought of as an element of an N dimensional matrix specified by $\mathbf{A}$ or $\mathbf{X}$. In this N dimensional space a unitary transformation can be applied to diagonalize the Hamiltonian (3.4.1). The periodicity condition (3.2.5) will aid in finding the transformation.

Consider the transformation

$$u(\mathbf{X}) = (1/N)^{1/N} \sum_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{X}) u^0(\mathbf{k}),$$

$$p(\mathbf{X}) = (1/N)^{1/N} \sum_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{X}) p^0(\mathbf{k}),$$

(3.4.2)

where the set of N vectors $\mathbf{k}$ define points in reciprocal space.

Under the conditions of cyclic boundary conditions discussed by Ziman,$^9$ and Maradudin et. al.,$^{10}$ the N points defined by the $\mathbf{k}$ vectors are uniformly distributed in a unit cell in reciprocal space, and satisfy the equations

$$\sum_{\mathbf{k}} \exp(\pm i\mathbf{k} \cdot \mathbf{X}) = N \Delta (\mathbf{X}),$$

$$\sum_{\mathbf{X}} \exp(\pm i\mathbf{k} \cdot \mathbf{X}) = N \Delta (\mathbf{k}),$$

(3.4.3)


where the function $\Delta(\vec{k})$ has the value

$$
\Delta(\vec{k}) = \begin{cases} 
1, & \vec{k} = 0 \\
0, & \vec{k} \neq 0,
\end{cases} \tag{3.4.4}
$$

and similarly for $\Delta(\vec{\xi})$. This assures that the transformation is unitary. The vectors $\vec{k}$ are called "wave vectors" for reasons which shall become apparent. They are also called "momentum vectors," because of the conservation laws in multiphonon interactions.

From (3.4.3) and the periodicity condition (3.2.5), the inverse transformation applied to $\phi(\vec{\xi}, \vec{\xi}')$ gives

$$
\phi^0(\vec{k}, \vec{k}') = \phi^0(\vec{\xi}) \Delta(\vec{k} - \vec{k}'), \tag{3.4.5}
$$

where $\phi^0(\vec{\xi})$ is the "Fourier transformed dynamical matrix" defined by

$$
\phi^0(\vec{\xi}) = \sum_{\vec{\xi}'} \phi(\vec{\xi}') \exp(\text{i}\vec{k} \cdot \vec{\xi}'), \tag{3.4.6}
$$

where $\phi(\vec{\xi}')$ is defined as in (3.2.5). The harmonic Hamiltonian then becomes

$$
H_0 = \frac{1}{2} \sum_{\vec{k}} (\vec{p}^0(\vec{k}) (1/m) \vec{p}^0(\vec{k}) + \vec{u}^0(\vec{k}) \phi^0(\vec{k}) \vec{u}^0(\vec{k})), \tag{3.4.7}
$$

which is the diagonalized form, in the N-dimensional space.
The $N$ values of $\mathbf{K}$ are chosen to lie in a particular region of reciprocal space known as the first Brillouin zone. This means that all values of $\mathbf{K}$ satisfy the inequality

$$\mathbf{K} \cdot \mathbf{g} \leq \frac{1}{2} \mathbf{g} \cdot \mathbf{g}, \quad (3.4.8)$$

where $\mathbf{g}$ is any reciprocal lattice vector other than zero. Values of $\mathbf{K}$ outside of this region are effectively a duplication of one value inside, because the addition of a reciprocal lattice vector does not change the function $\exp(i \mathbf{K} \cdot \mathbf{r})$.

It can be noted from the transformation equation (3.4.2) that the Hermitian adjoint of $u(K)$ is obtained by reversing the wave vector:

$$u^0(\mathbf{K}) = u^0(-\mathbf{K}),$$

and

$$p^0(\mathbf{K}) = p^0(-\mathbf{K}). \quad (3.4.9)$$

As with the Hamiltonian, other matrix expressions involving the $6N$ dimensional matrices can be written as a sum over wave vector of $6$ dimensional matrix functions of wave vector. The only requirement for this to be true is that the periodicity conditions and cyclic boundary conditions are satisfied. The conditions are unrealistic, of course, but the theory is nevertheless very useful, for reasonably large, pure single crystals.
The transformation to normal coordinates for a periodic lattice

This section is devoted to the diagonalization of a term in the Hamiltonian (3.4.7) for a single value of \( \vec{k} \). It is convenient to first make the unitary transformation

\[
    u_\alpha S_S(k) = u_\alpha S_S(k) \exp(i \vec{k} \cdot \vec{s}),
\]

so that the transformed dynamical matrix elements become

\[
    \phi_{\alpha' S' S}(k) = \sum \phi_{\alpha' S' S'}(\vec{l}) \exp(i \vec{k} \cdot (\vec{l} + \vec{s'} - \vec{s})).
\]

These elements will frequently be called "coefficients." The advantage of this definition is that the transformed matrix is real, because of the inversion symmetry of the lattice about either ion in the \( \vec{l} = 0 \) cell.

The portion of the total harmonic Hamiltonian for a given wave vector \( \vec{k} \) is

\[
    H_0(k) = \frac{1}{2} \left( \vec{p}(k) (1/m) \vec{p}(k) + \vec{u}(k) \phi(k) u(k) \right).
\]

The Hamiltonian (3.5.3) can then be diagonalized by solving the characteristic equation

\[
    (\omega^2(kj) - (1/\sqrt{m}) \phi(k)(1/\sqrt{m}) \gamma(kj)) = 0,
\]
where the \( \omega^2(\vec{k}j) \) are the eigenvalues, and \( m(\vec{k}j) \) the normalized eigenvectors with real components \( m_\alpha(s|\vec{k}j) \). Then

\[
\begin{align*}
\psi_{\alpha s}(\vec{k}) &= \sum_j \frac{1}{\sqrt{m_s}} m_\alpha(s|\vec{k}j) Q(\vec{k}j).
\end{align*}
\] (3.5.5)

It is then apparent from (3.4.2), (3.5.1), and (3.5.5) that the elements of the matrix \( V \), defined in (3.3.8), are given by

\[
\begin{align*}
V_{\alpha s}(\vec{\lambda}, \vec{k}j) &= \frac{1}{\sqrt{N}} m_\alpha(s|\vec{k}j) \exp(i \vec{k} \cdot (\vec{\lambda} + \vec{s})),
\end{align*}
\] (3.5.6)

where the substitution

\[
\vec{\lambda} = \vec{k}j
\] (3.5.7)

has been made. It is obvious from (3.5.6) that

\[
V_{\alpha s}(\vec{\lambda}, \vec{k}j) = V_{\alpha s}(\vec{\lambda}, -\vec{k}j),
\] (3.5.8)

so that

\[
\omega(\vec{k}j) = \omega(-\vec{k}j)
\]

and

\[
\begin{align*}
Q(\vec{k}j) &= Q(-\vec{k}j) \quad \text{(Quantum),}
Q^*(\vec{k}j) &= Q(-\vec{k}j) \quad \text{(Classical).}
\end{align*}
\] (3.5.9)

The degeneracy between \(-\vec{k}\) and \(\vec{k}\) is a consequence of the inversion symmetry of the lattice, and this is necessary, for the use of a complex transformation \( V \). The Hamiltonian can now be expressed in terms of canonical normal coordinates and momenta, both in classical and quantum mechanics, as
\[ H_0 = \frac{1}{2} \sum_{\overrightarrow{k}_j} (P(-\overrightarrow{k}_j) P(\overrightarrow{k}_j) + \omega^2(\overrightarrow{k}_j) Q(-\overrightarrow{k}_j) Q(\overrightarrow{k}_j)). \quad (3.5.10) \]

A classical solution for the harmonic Hamiltonian is

\[ Q(\overrightarrow{k}_j|t) = Q(\overrightarrow{k}_j|0) \exp(-i\omega(\overrightarrow{k}_j)t). \quad (3.5.11) \]

Now, using expression (3.3.8) for the cartesian coordinates and (3.5.6) for the elements of \( V \),

\[ u_{\alpha s}(\overrightarrow{a}|t) = \]

\[ \frac{1}{\sqrt{n_s}} \sum_{\overrightarrow{k}_j} Q(\overrightarrow{k}_j|0) \gamma(\alpha \overrightarrow{a}|\overrightarrow{k}_j) \exp(i\overrightarrow{k} \cdot (\overrightarrow{a} + \overrightarrow{s}) - \omega(\overrightarrow{k}_j)t), \]

from which it is clear that \( \overrightarrow{k} \) is a wave vector, and the associated wave has a frequency \( \omega(\overrightarrow{k}_j) \) and two polarization vectors \( \overrightarrow{\gamma}(s|\overrightarrow{k}_j) \).

3.6 The number representation

To express the effect of the operators \( Q(\alpha) \) and \( P(\alpha) \) on Hilbert space vectors which define a stationary state of the crystal lattice, in the Harmonic approximation, and to find the energy eigenvalues of such a system, it is convenient to define linear combinations of the operators, known as "annihilation" and "creation" operators. Denoting the annihilation operator for
the mode by \( a(\lambda) \), the creation operator must be the Hermitean conjugate of \( a(\lambda) \), or \( a^\dagger(\lambda) \). For operators \( a(\lambda) \) and \( a^\dagger(\lambda) \) which satisfy the commutation relations

\[
[a(\lambda), a^\dagger(\lambda')] = \delta_{\lambda, \lambda'},
\]

\[
[a(\lambda), a(\lambda')] = [a^\dagger(\lambda), a^\dagger(\lambda')] = 0,
\]

an eigenstate of the "number" operator

\[
N_{\text{op}} = \sum \frac{N_{\text{op}}(\lambda)}{\lambda}, \quad \text{where} \quad N_{\text{op}}(\lambda) = a^\dagger(\lambda)a(\lambda)
\]

(3.6.2)

can be defined as a product over all \( \lambda \) of normalized eigenvectors \( |n(\lambda)\rangle \) of \( N_{\text{op}}(\lambda) \), for which the eigenvalues are the set of positive integers (including zero) \( n(\lambda) \). The creation-annihilation properties also follow. They can be expressed as

\[
a(\lambda)|n(\lambda')\rangle = \delta_{\lambda, \lambda'} (n(\lambda))^{\frac{1}{2}}|n(\lambda) - 1\rangle,
\]

and

\[
a^\dagger(\lambda)|n(\lambda')\rangle = \delta_{\lambda, \lambda'} (n(\lambda) + 1)^{\frac{1}{2}}|n(\lambda) + 1\rangle.
\]

Consider the operators defined by

\[
a(\lambda) = \left(\omega(\lambda)/2\hbar\right)^{\frac{1}{2}} (Q(\lambda) + iP^+(\lambda))
\]

and

\[
b(\lambda) = \left(1/2\omega(\lambda)\hbar\right)^{\frac{1}{2}} (Q(\lambda) - iP^+(\lambda)).
\]

---

In the case where the coordinate and momentum operators $Q(\lambda)$ and $P(\lambda)$ are Hermitean, it follows that $b(\lambda) = a^\dagger(\lambda)$, and the relations (3.6.1) are satisfied by $a(\lambda)$ and $a^\dagger(\lambda)$. However, in the case of traveling wave modes, for which $Q(-\lambda) = Q^\dagger(\lambda)$ and $P(-\lambda) = P^\dagger(\lambda)$ (where $\lambda = \frac{\hbar \omega(\gamma)}{2} j$ and $-\lambda = -\frac{\hbar \omega(\gamma)}{2} j$), it follows that

$$b(\lambda) = a^\dagger(-\lambda),$$

and

$$b(-\lambda) = a^\dagger(\lambda).$$

The operators set $b(\lambda)$ and $b(-\lambda)$ can thus be eliminated in the transformation (3.6.4), and it can be shown that the relations (3.6.1) hold for the operator pairs $(a(\lambda), a^\dagger(\lambda))$ and $(a(-\lambda), a^\dagger(-\lambda))$. In both cases, the total harmonic Hamiltonian is

$$H_0 = \sum_{\text{all } \lambda} \hbar \omega(\gamma)(n_{\text{op}}(\lambda) + \frac{1}{2}),$$

(3.6.6)

so that the eigenvalues of the harmonic Hamiltonian are

$$E_0 = \sum_{\text{all } \lambda} \hbar \omega(\gamma)(n(\lambda) + \frac{1}{2}).$$

(3.6.7)

The inverse of (3.6.4) is, for the Hermitean case

$$Q(\lambda) = (\hbar/\omega(\gamma))^{\frac{1}{2}} (a(\lambda) + a^\dagger(\lambda)),$$

$$P(\lambda) = i(\hbar \omega(\gamma)/2)^{\frac{1}{2}} (a^\dagger(\lambda) - a(\lambda)).$$

(3.6.8)
For the traveling wave case, it is

\begin{equation}
Q(\lambda) = \left( \frac{\hbar}{2\omega(\lambda)} \right)^{\frac{1}{2}} \left( a(\lambda) + a^\dagger(-\lambda) \right),
\end{equation}

(3.6.9)

\begin{equation}
P(\lambda) = i\left( \frac{\hbar}{2\omega(\lambda)} \right)^{\frac{1}{2}} \left( a^\dagger(\lambda) - a(-\lambda) \right).
\end{equation}

For the work described in Chapter VI, where the anharmonic Hamiltonian is written in terms of normal coordinates, it is convenient to define the operator

\begin{equation}
A(\lambda) = \left( \frac{2\omega(\lambda)}{\hbar^2} \right)^{\frac{1}{2}} Q(\lambda) = a(\lambda) + a^\dagger(-\lambda).
\end{equation}

(3.6.10)
CHAPTER IV

THE DIAGONALIZATION OF THE SHELL MODEL HAMILTONIAN FOR KI

To complete the transformation to normal coordinates, by diagonalizing the transformed dynamical matrix $\phi(\vec{k})$, it is necessary to specify the total potential energy explicitly as a function of ionic cartesian coordinates. In the rigid ion model of the lattice, the potential is a sum of interionic bond potentials, each bond potential being expressed as a function of the distance of separation of the two ions forming the bond. In the shell model, the situation is more complicated, because core-core, shell-shell, and shell-core forces, within one ion and between ions, must all be taken into account separately, and the shell coordinates eliminated from the potential, in accordance with the adiabatic approximation.

The forces acting between cores and shells of separate ions are assumed, in this work, to be of two types; Coulomb forces due to the charges on the cores and shells, and repulsive electronic overlap forces due to the exclusion principle. The overlap forces are weak except between a few near neighbors, and are thus called “short range” forces, while the Coulomb forces
are strong enough so that contributions from all ions in the lattice must be considered. The same holds for the harmonic parts of the respective potentials. In the rigid ion model, the total potential energy is simply a sum of Coulomb and short range potentials, and therefore the dynamical matrix \( \phi \) is simply \( \phi = R + \phi_c \), where \( R \) and \( \phi_c \) are dynamical matrices due to short range and Coulomb forces respectively. The matrix \( \phi_c \) is equal to \( ZCZ \), where \( Z \) is a diagonal matrix having the ionic charges as elements, and \( C \) depends only upon the geometry of the lattice. The shell model dynamical matrix is a function of \( R, C, Z \), and also of \( Y \), a matrix specifying shell charges, and \( A \), a matrix specifying the core-shell ionic force constants.

In this chapter, the transformed dynamical matrices \( R(\vec{\xi}) \) and \( C(\vec{\xi}) \) are first found. Next, the shell model is introduced, and the harmonic potential energy of the 12N dimensional system consisting of coordinates of cores and shells of all ions is written. Then it is shown how the adiabatic approximation allows the separation of the energy into two parts, only one of which contains the core, or "ionic" coordinates and momenta. The result is a derivation of the shell model dynamical matrix. This transformed dynamical matrix is then used to compute frequencies and eigenvectors for the KI lattice.
The short range dynamical matrix will be expressed in terms of certain parameters specifying the first and second derivatives of the short range nearest and next-nearest neighbor interionic potentials. The short range transformed dynamical matrix is defined as in (3.5.2) as

\[ R_{\alpha'\alpha s',s}(\vec{r}) = \sum_{\vec{r}'} R_{\alpha'\alpha s',s}^{s'}(\vec{r}') \exp(i\vec{r} \cdot (\vec{q} + \vec{q}' - \vec{s})), \]  

(4.1.1)

The elements of \( R(\vec{q}') \) are the second derivatives of \( U_{R} \), the total potential energy due to short range forces. Thus

\[ R_{\alpha'\alpha s',s}(\vec{r}') = \frac{\frac{1}{2} U_{R}}{\gamma u_{\alpha'\alpha s}(0)} | u_{\alpha'\alpha s}(\vec{r}') |^2 \bigg|_{u = 0}, \]  

(4.1.2)

where \( U_{R} \) is a sum of interionic short range potentials:

\[ U_{R} = \frac{1}{2} \sum_{s_1} \sum_{s_2} \sqrt{R} R_{s_1s_2}^{s_1s_2} \left| \vec{r}_{s_1} (\vec{x}_{s_1}) - \vec{r}_{s_2} (\vec{x}_{s_2}) \right|. \]  

(4.1.3)

The form of the interionic potential, \( \sqrt{R} R_{s_1s_2}^{s_1s_2} (r) \), depends only on \( s_1 \) and \( s_2 \) because only nearest and next-nearest neighbor bonds are considered. For nearest neighbors, \( s_1 \neq s_2 \), while for next nearest neighbors \( s_1 = s_2 = 1 \) or \( 2 \) for cation-cation or anion-anion bonds, respectively.
Carrying out the differentiation,

\[ R_{\alpha \alpha'}(\vec{r}) = -R_{\alpha \alpha'}^{ss'}(\vec{r}' + \vec{s}' - \vec{s}) \]  
\[ + \delta_{ss'} \delta_{\lambda'0} \sum_{s''} \lambda'' R_{\alpha \alpha'}^{ss''}(\vec{\lambda}'' + \vec{s}'' - \vec{s}) , \]

where

\[ R_{\alpha \alpha'}^{ss'}(\vec{r}_0) = \frac{\partial^2}{\partial r_{\alpha'}^2} \left. \sqrt{R_{ss'}}(r) \right|_{r_0} \]
\[ = \left. \frac{r_0}{r^2_0} \right|_{r_0} \left. \frac{\partial}{\partial r^2} \sqrt{R_{ss'}}(r) \right|_{r_0} \]
\[ + \frac{1}{r_0} \left. \left( \delta_{\alpha \alpha'} - \frac{r_0}{r^2_0} \right) \right|_{r_0} \left. \frac{\partial \sqrt{R_{ss'}}(r)}{\partial r} \right|_{r_0} \]

for \( \vec{r}_0 \neq 0 \), and

\[ R_{\alpha \alpha'}^{ss'}(\vec{r}_0) = 0 \] for \( \vec{r}_0 = 0 \),

where \( r = |\vec{r}| \), and similarly for \( r_0 \).

The transformed dynamical matrix can then be written

\[ R_{\alpha \alpha'}(\vec{k}) = -\sum_{\lambda''} R_{\alpha \alpha'}^{ss'}(\vec{\lambda}'' + \vec{s}'' - \vec{s}) \exp(ik \cdot (\vec{\lambda}'' + \vec{s}'' - \vec{s})) \]
\[ + \delta_{ss'} \sum_{\lambda''} R_{\alpha \alpha'}^{ss''}(\vec{\lambda}'' + \vec{s}'' - \vec{s}) . \]
From (4.1.6), it follows that

$$\lim_{|k| \to 0} \sum_{s'} R_{\alpha s \alpha' s'}(k) = 0.$$  \hfill (4.1.7)

A dynamical matrix must satisfy this equation for there to be solutions describing translation of the entire lattice with no relative motion between ions (acoustical modes), as can be seen from the characteristic equation (3.5.4). This condition also assures the existence of optical modes.

Equation (4.1.6) is a sum over bonds, each bond between an ion in the \( \mathcal{I} = 0 \) cell, and another ion in the lattice. For any given bond, there are two terms which contribute; one \( k \)-dependent, from the first summation, and the other \( k \)-independent, from the second summation. Due to (4.1.7), the \( k \)-independent part can easily be found from the \( k \)-dependent part. The \( k \)-independent part, for any bond, always appears for elements of \( R_{\alpha s \alpha' s'}(k) \) for which \( s = s' \), and in such a way that (4.1.7) is satisfied.

Symmetry can be used to simplify the evaluation considerably. The bond specified \( \vec{r}_o \), where \( \vec{r}_o = \vec{a} + \vec{s}' - \vec{s} \), can be included along with that for \( +\vec{r}_o \) by substituting \( 2 \cos(k \cdot \vec{r}_o) \) for \( \exp(+ik \cdot \vec{r}_o) \). Since all bonds under consideration are in one of the planes normal to the crystallographic axes, only those in one plane need be considered explicitly, and the contributions from the rest can be evaluated by a permutation of the indices. Finally,
the \( s = s' = 2 \) part is the same, except for the values of the parameters, as the \( s = s' = 1 \) part. This is because the cation-cation and anion-anion bonds are geometrically equivalent, but may involve different forces. Making full use of symmetry, one can derive the entire matrix by explicit consideration of only the following bond pairs:

- **Bond pair a**, nearest neighbor; \( \vec{r}_o^a = (\pm d, 0, 0) \),
- **Bond pair b**, next-nearest neighbor; \( \vec{r}_o^b = (\pm d, 0, \pm d) \),
- **Bond pair c**, next-nearest neighbor; \( \vec{r}_o^c = (\pm d, 0, \mp d) \).

Bond pair a has \( \vec{k} \)-dependent parts for \( s \neq s' \), while pairs b and c have \( \vec{k} \)-dependent parts for \( s = s' = 1 \).

For the following evaluation it is convenient to partition the \( 6 \times 6 \) matrix \( R(\vec{k}) \) into four \( 3 \times 3 \) matrices \( R_{s,s'}(\vec{k}) \) whose elements are specified by \( (\alpha, \alpha') \). Consider the contribution due to the bond pair a. From (4.1.6) and (4.1.5)

\[
R^{a}_{1,2}(\vec{k}) = \begin{bmatrix}
-A_{12} & 0 & 0 \\
0 & -B_{12} & 0 \\
0 & 0 & -B_{12}
\end{bmatrix} \cos(\vec{k} \cdot d), \quad (4.1.8)
\]

where the superscript denotes the bond pair a, and the parameters are defined by

\[
A_{ss'} = 2 \left\{ \frac{\nabla^R_{ss'}(r)}{2r^2} \right\}_{r_o}, \quad (4.1.9)
\]
Since the matrix is symmetrical,

\[ R_{2,1}^{a}(\vec{k}) = R_{1,2}^{a}(\vec{k}) \]  \hspace{1cm} (4.1.10)

Considering (4.1.7) for this bond pair, it follows that

\[ R_{1,1}^{a}(\vec{k}) = R_{2,2}^{a}(\vec{k}) = -R_{1,2}^{a}(0). \]  \hspace{1cm} (4.1.11)

For bonds \( b \) and \( c \),

\[ R_{1,2}^{b}(\vec{k}) = R_{1,2}^{c}(\vec{k}) = 0, \]  \hspace{1cm} (4.1.12)

so that their contributions must vanish at \( \vec{k} = 0 \), for (4.1.7) to be satisfied. For bond pair \( b \),

\[
R_{1,1}^{b}(k) = \begin{bmatrix}
\frac{1}{2}(A_{11} + B_{11}) & 0 & \frac{1}{2}(A_{11} - B_{11}) \\
0 & B_{11} & 0 \\
\frac{1}{2}(A_{11} - B_{11}) & 0 & \frac{1}{2}(A_{11} + B_{11})
\end{bmatrix}
\]  \hspace{1cm} (4.1.13)

\[ \times (1 - \cos((k_x + k_z)d)). \]

For bond pair \( c \),
Considering all contributions found by a cyclic permutation of the coordinate axes, the final result is

\[ R_{\alpha_1 \alpha_2}(k) = \begin{bmatrix} \frac{1}{2}(A_{11} + B_{11}) & 0 & -\frac{1}{2}(A_{11} - B_{11}) \\ 0 & B_{11} & 0 \\ -\frac{1}{2}(A_{11} - B_{11}) & 0 & \frac{1}{2}(A_{11} + B_{11}) \end{bmatrix} X \left( 1 - \cos\left( (k_x - k_z) d \right) \right). \]

(4.1.14)

where \((\alpha, \beta, \gamma) = (x, y, z), (y, z, x), \) or \((z, x, y)\). The \(s = s' = 2\) elements are easily derived from the \(s = s' = 1\) elements when \(A_{11} \) and \(B_{11}\) are replaced by \(A_{22}\) and \(B_{22}\) respectively, giving
a total of six parameters required to specify the $R$ matrix. This result is given by Cochran, et. al.\textsuperscript{1}

4-2 The Coulomb coefficients

The total Coulomb potential energy, for the rigid ion model, is

$$U_c = \frac{1}{2} \sum_{s_1 l_1} \sum_{s_2 l_2} \frac{Z_{s_1} Z_{s_2}}{r_{s_1}^2 (l_1) - r_{s_2}^2 (l_2)}.$$ (4.2.1)

From this potential, corresponding coefficients can be defined in the same manner as for the short range coefficients. It is useful to write the dynamical matrix for Coulomb forces as

$$\phi_C \alpha_s \alpha'_s, (\vec{l}, \vec{l}') = Z_s Z_s C_{\alpha s \alpha'_s,}, (\vec{l}, \vec{l}'),$$ (4.2.2)

where $Z_s$ is the ionic charge, for which $Z_1 = -Z_2$, and $C$ is the "Coulomb" matrix, given by

$$C_{\alpha s \alpha'_s,} (\vec{l}) = - \left[ 1 - \Delta (\vec{l} + \vec{s}' - \vec{s}) \right]$$ \textsuperscript{2}

$$\left. \frac{\partial^2}{\partial x_{\alpha} \partial x_{\alpha'}} \left( \frac{1}{|\vec{l} + \vec{s}' - \vec{s} - \vec{x}|} \right) \right|_{\vec{x} = 0}$$

$$+ \Delta (\vec{l}' + \vec{s}' - \vec{s}) \sum_{s' \alpha'' l''} \left( \frac{Z_{s''}}{Z_s} \right)$$


\textsuperscript{2}X. X. X. X. X. X.
where \( \vec{x} \) here is a dummy vector variable. The second term vanishes for cubic symmetry.\(^2\) The Coulomb coefficients are then

\[
C_{\alpha' \beta' \gamma' \delta'}(\vec{k}) = \exp(ik \cdot (\vec{s}' - \vec{s}))
\]

\[
x \sum_{\lambda'} \left\{ \left[ 1 - \Delta (\vec{\lambda}' + \vec{s}' - \vec{s}) \right] \right.
\]

\[
\left. \frac{\partial^2}{\partial x_{\alpha'} \partial x_{\lambda'}} \left( \frac{1}{|\vec{\lambda}' + \vec{s}' - \vec{s} - \vec{x}|} \right) \right|_{\vec{x} = 0},
\]

The summation here cannot be limited to a few near neighbors, because of the slow convergence. The summation can be carried out by means of a mathematical transformation described by Kellerman\(^2\) and by Ziman.\(^3\) It is known as the Ewald method. Consider the identity

\[
\frac{1}{r} = \frac{2}{\sqrt{\pi}} \left\{ \int_0^\infty \exp(-r^2 \rho^2) \, d\rho + \int_0^\infty \exp(-r^2 \rho^2) \, d\rho \right\},
\]

\(^2\)E. W. Kellerman, Phil. Trans. A 238, 513 (1940).

\(^3\)Ziman, op. cit., pp. 37-42.
where $G$ is a positive number. In the Ewald method this identity, with \( \vec{r} = |\vec{r}' + \vec{s} - \vec{s} - \vec{x}| \), is used to write (4.2.4) as a sum of two integrals, one from zero to $G$, and the other from $G$ to infinity. The integration in the second term is done before the summation, and for large values of $G$, the sum converges rapidly. The summation in the first term is transformed by means of what is called a "theta-function transformation," to a reciprocal lattice summation. This summation converges rapidly for small values of $G$. Kellerman chose a value of $G$ such that both sums converged rapidly enough so that they could be carried out by computational methods of his day. The choice of $G$ made here is one large enough so that the entire lattice sum can be neglected, and the reciprocal lattice sum carried out using a digital computer. The reciprocal lattice summation is (see Appendix B)

\[
C_{\alpha s \alpha' s'}(\vec{k}) = \frac{4\pi}{v_c} \sum_{\vec{g}} \left\{ \exp\left(-i\vec{g} \cdot (\vec{s}' - \vec{s})\right) \right\}
\]

\[
x = \frac{\lambda \alpha \lambda \alpha'}{\lambda^2} \exp\left(-\frac{\lambda^2}{4G^2}\right) \}
\]

\[
= \delta_{\alpha \alpha'} \delta_{ss'} \frac{4G^3/3}{\pi} ,
\]

where $\vec{g}$ is a reciprocal lattice vector, \( \vec{\lambda}' = \vec{k} + \vec{g} \), \( \lambda = |\vec{\lambda}| \), and $v_c$ is the volume of the primitive unit, $2d^3$. The quantity \( \exp(-i\vec{g} \cdot (\vec{s}' - \vec{s})) \) is equal to +1 for points on the corners of the
bcc reciprocal lattice cell (considering the \( \vec{g} = 0 \) point a corner point) and equal to \((-1)^{s'} - s\) for points interior to the bcc cell.

For computational reasons, and for the later study of the optical properties, it is useful to study the behavior of the Coulomb coefficients in the \(|\vec{k}| = 0\) limit. In this limit, according to (4.2.6),

\[
\lim_{|\vec{k}| \to 0} C_{\alpha'\alpha s'}(\vec{k}) = \frac{4\pi}{v_c} \lim_{|\vec{k}| \to 0} \left( \frac{k_{\alpha} k_{\alpha'}}{k^2} \right) + C_{\perp ss'}(0) \delta_{\alpha'\alpha},
\]

where \(C_{\perp ss'}(0)\), is a component of what is defined here as the 2X2 long wavelength transverse Coulomb dynamical matrix. It is defined for non-zero \(|\vec{k}|\) values in section 4-4. It is given, according to (4.2.6) and (4.2.7), by

\[
C_{\perp ss'}(0) = \frac{4\pi}{v_c} \sum_{\vec{g}} \Delta(\vec{g}) \exp(-I\vec{g} \cdot (\vec{s}' - \vec{s}))) \frac{\vec{g}^2}{v_c^2} \exp(-g^2/4G^2)
\]

\[
\cdot \vec{g}^{3} \cdot 4G^2 / 3\pi^2.
\]

For wave vectors \(\vec{k}\), of small magnitude, directed along a cartesian axis specified by \(\alpha\), the coefficient \(C_{\alpha'\alpha s'}(\vec{k})\) for \(\beta \neq \alpha\) and \(\gamma \neq \alpha\) is \(\delta_{\beta\gamma} C_{\perp ss'}(0)\). The coefficient \(C_{\alpha'\alpha s'}(\vec{k})\) is
C_{\parallel ss'}(0), a component of the 2x2 long wavelength longitudinal Coulomb dynamical matrix, given, according to (4.2.7) by

$$C_{\parallel ss'}(0) = \frac{4\pi}{v_c} + C_{\parallel ss'}(0). \quad (4.2.9)$$

The condition (4.1.7) applied to $\phi_C$, recalling that $Z_1 = -Z_2$ demands that

$$C_{\perp 11}(0) = C_{\perp 12}(0),$$

$$C_{\perp 21}(0) = C_{\perp 22}(0), \quad (4.2.10)$$

and similarly for $C_{\parallel ss'}(0)$. Due to this result, and the fact that the matrices are symmetrical, all four elements of each matrix are identical. From explicit computer calculations to be described shortly, the value $C_{\parallel ss'}(0) = -4\pi/3v_c$ was found. Taking this as the correct value, it follows from (4.2.9), that

$$C_{\parallel ss'}(0) = \frac{8\pi}{3v_c}. \quad (4.2.11)$$

Now, (4.2.8) can be written

$$C_{\perp ss'}(0) =$$

$$\frac{4\pi}{v_c} \sum_{\vec{g}_{\text{ext}}} \Delta \left( \frac{\vec{g}}{g} \right) \left( \frac{\vec{g}_x^2}{g^2} \right) \exp \left( -\frac{g^2}{4G^2} \right)$$

$$+ \sum_{\vec{g}_{\text{int}}} (-1)^{s'} s \left( \frac{\vec{g}_x^2}{g^2} \right) \exp \left( -\frac{g^2}{4G^2} \right)$$

$$- \int_{ss'} \frac{4G^3}{3\pi},$$

where
where the symbols "ext" and "int" mean points external (on the corners) and internal to the bcc cell respectively. From (4.2.10) and (4.2.11) it follows that

\[
\frac{4G^3}{3\sqrt{\pi}} = 2 \frac{4\pi}{V_c} \sum_{\vec{g}_{\text{int}}} \frac{g^2}{g^2} \exp(-g^2/4G^2).
\]

(4.2.12)

Using this result, and explicit values for \(\exp(-ig \cdot (\vec{s} - \vec{s}'))\), equation (4.2.5) becomes

\[
C_{\alpha s \alpha' s'}(\vec{\kappa}) = \frac{4\pi}{V_c} \left( \sum_{\vec{g}_{\text{ext}}} \frac{\lambda_{\alpha} \cdot \lambda_{\alpha'}}{\lambda^2} \exp(-\chi^2/4G^2) \right)
+ \left( -1 \right)^{s' - s} \sum_{\vec{g}_{\text{int}}} \frac{\lambda_{\alpha} \cdot \lambda_{\alpha'}}{\lambda^2} \exp(-\chi^2/4G^2)
- \delta_{ss'} \delta_{\alpha\alpha'} 2 \sum_{\vec{g}_{\text{int}}} \frac{g_{\alpha} \cdot g_{\alpha'}}{g^2} \exp(-g^2/4G^2).
\]

(4.2.13)

For computational purposes, it is convenient to define

\[
G' = dG,
\]

and

\[
\vec{g}' = (d/2\pi)\vec{g},
\]

(4.2.14)

and similarly for \(\vec{\kappa}\) and \(\vec{\chi}\). In terms of \(\vec{g}'\), the bcc cell is of edge unity. Thus, (4.2.13) becomes
\[ c_{\alpha s \alpha' s'}(\vec{k}) = \frac{4\pi}{v_c} \sum_{\vec{g}_{\text{ext}}^*} \left( \frac{\lambda_{\alpha} \lambda_{\alpha'}}{\chi'^2} \exp(-\chi'^2 \pi^2 / \sigma^2) \right) \]

\[ + (-1)^{s'-s} \left( \frac{\lambda_{\alpha} + \frac{1}{2}}{\chi' + \frac{\sigma}{2}} \exp(-\pi^2 (\chi' + \frac{\sigma}{2})^2 / \sigma^2) \right) \]

\[ - 2 \sum_{\alpha' \alpha''} \sum_{ss'} \left( \frac{(s_{\alpha' \alpha''} + \frac{1}{2})(s_{ss'}' + \frac{1}{2})}{\left| \vec{g}_{\text{ext}}^* + \frac{\sigma}{2} \right|^2} \exp(-\pi^2 \left| \vec{g}_{\text{ext}}^* + \frac{\sigma}{2} \right|^2 / \sigma^2) \right) \]

where \( \vec{g}_{\text{ext}}^* \) indicates that all vectors \( \vec{g}' \) for which \( |\vec{g}'| > \vec{g}_{\text{m}} \) were omitted, and \( \frac{\sigma}{2} \) is a vector, all of whose components are \( \frac{1}{2} \). The components of all vectors \( \vec{g}_{\text{ext}}^* \) are integers, which facilitated indexing in the computation. The order of summation implied by (4.2.15) is that which was used in the actual computer program. This method was thought to be preferable to that of carrying out a summation for each term separately, since that would involve subtracting large and nearly equal values. In the computation, the exponentials were factored into parts for each cartesian component of \( \vec{g}' \) or \( \vec{g}_{\text{ext}}^* \), and values were pre-computed, and stored for later use. Thus, only 3 \( (2\vec{g}_{\text{m}} + 1) \) exponentials had to be computed for a given \( \vec{k} \).

The condition for neglect of the lattice summation is shown in Appendix B to be
The condition for termination of the reciprocal lattice sum at 
$|g'| = g'_m$ is

$$16 g'_m G'^2 \exp(-\frac{2 g'_m^2}{G'^2}) < 1.$$  \hspace{1cm} (4.2.17)

These relations aided in determining $G'$ and $g'_m$ for the computation.
The computation is discussed, along with that for the complete
harmonic problem in section 4-5.

4-3 The shell model

As explained in the introductory paragraphs to Chapters III
and IV, in the shell model\(^4\) it is assumed that each ion consists of
a core and shell, each having a charge. The system to be considered
is thus $12N$ dimensional, or $12$ dimensional in terms of transformed
matrices. The core coordinates are still denoted by $u$, while $v$
denotes the shell coordinates, specifying displacement of the
shells from their equilibrium positions. A coordinate $w$, specifying
displacement of the shell from the core is defined by

$$w = v - u.$$  \hspace{1cm} (4.3.1)

---

\(^4\)See Chapter III, footnotes 3-5.
The momenta corresponding to the coordinates \( u, v, \) and \( w \) are denoted by \( p_u, p_v, \) and \( p_w \) respectively. The core charges are \( x_1 \) and \( x_2, \) the shell charges \( y_1 \) and \( y_2, \) and the total ionic charges \( z_1 \) and \( z_2 \) as with the rigid ion model. Relations between these charges are:

\[
x_s + y_s = z_s \text{ for } s = 1 \text{ and } 2, \quad \text{and } z_1 + z_2 = 0, \quad (4.3.2)
\]

the latter because each unit cell has zero net charge. Three parameters are thus required to specify the charges. The 6N dimensional dipole moment vector is defined as

\[
M = Xu + Yv = Zu + Yw, \quad (4.3.3)
\]

where \( X, Y, \) and \( Z \) are 6N dimensional diagonal matrices corresponding to the respective charges defined above.

The total shell model harmonic potential energy can be written

\[
U_{SH}^{(2)} = U_R^{(2)} + U_C^{(2)} + U_A^{(2)}, \quad (4.3.4)
\]

where \( U_R^{(2)}, U_C^{(2)}, \) and \( U_A^{(2)} \) are the short range, Coulomb, and ionic core-shell harmonic potentials, respectively. The short range force is assumed to act only between shells.\(^5\) Thus,

\(^5\)Chapter III, footnote 4.
The harmonic Coulomb potential is given in terms of the dipole moment vector $M$ as

$$U^{(2)} = \frac{1}{2} |M|^2. \quad (4.3.5)$$

The core-shell potential can be written

$$U^{(2)} = \frac{1}{2} |A| \cdot w_A \cdot w, \quad (4.3.6)$$

where $A$ is a diagonal matrix, containing ionic force constants $A_1$ and $A_2$ in the $s = 1$ and $s = 2$ positions, respectively. The total potential energy can be expressed entirely in terms of $u$ and $v$ coordinates and momenta. The harmonic Hamiltonian becomes

$$H_0 = \frac{1}{2} \bar{P}_u \left( \frac{1}{m} \right) \bar{p}_u + \frac{1}{2} \bar{P}_v \left( \frac{1}{l m} \right) \bar{p}_v$$

$$+ \frac{1}{2} \bar{v} (R + A + YCY) v + \frac{1}{2} \bar{v} (YCX - A) u$$

$$+ \frac{1}{2} \bar{u} (XCY - A) v + \frac{1}{2} \bar{u} (A + XCX) u,$$

where $(1/l m)$ is the shell reciprocal mass matrix and $(1/m)$ is the core reciprocal mass matrix. The characteristic equation is

$$(m) \omega^2 u = (A + XCX) u + (XCY - A) v \quad (4.3.8)$$

$$(l m) \omega^2 v = (YCY - A) u + (R + A + YCY) v.$$

$$(4.3.9)$$
Using the characteristic equation (4.3.9), the coupled Hamiltonian (4.3.8) can be diagonalized by a linear transformation

\[ u = u(Q, q) \]
\[ v = v(Q, q), \]

where \( Q \) and \( q \) denote separate and independent sets of 6N normal modes.

It is convenient to write (4.3.9) in terms of \( u \) and \( w \) coordinates. Using (4.3.1), and after some manipulation it becomes

\[ m \omega^2 u + \delta m \omega^2 (u + w) = au + bu, \]
\[ \delta m \omega^2 (u + w) = bu + cw, \]

where

\[ a = R + ZCZ, \]
\[ b = R + ZCY, \]
\[ c = R + A + YCY. \]

Due to the difference in magnitude of the elements of \( m \) and \( \delta m \), the spectrum of (4.3.11) consists of two bands widely separated in magnitude. For the low (ionic) frequencies, \( \delta m \omega^2 \) is very small, so that, approximately,
\[ m \omega^2 u = \phi u, \quad (4.3.13) \]
\[ w = r' u, \]

where
\[ r' = c^{-1} B, \]
and
\[ \phi = a + b r' \]

\( \phi \) is the shell model dynamical matrix, which differs from the rigid ion model dynamical matrix by an added term \( b r' \), which is due to shell motion. For the very high electronic frequencies, \( m \omega^2 \) is essentially infinite, so that
\[ u = 0, \quad (4.3.15) \]
\[ m \omega^2 w = cw. \]

Equations (4.3.13) and (4.3.15) can be used to find the separate solutions, or transformations to normal coordinates \( Q \) and \( q \), to the adiabatic approximation:
\[ u^i = (1/\sqrt{m})Q, \quad w^i = r u^i, \quad (4.3.16) \]

and
\[ u^e = 0, \quad w^e = (1/\sqrt{\delta m})S q, \quad (4.3.17) \]
where $V$ and $S$ are the unitary transformation matrices corresponding to dynamical matrices $\phi$ and $c$ respectively. Transformed matrices can be defined corresponding to each of the matrices considered here, and $\phi(\vec{r})$ and $c(\vec{r})$ diagonalized, according to the methods of Chapter III. The superscripts $i$ and $e$ denote "ionic" and "electronic" modes respectively, although the ionic mode involves electronic motion also. The approximate transformation to normal coordinates can be expressed as

$$u = (1/\sqrt{m})Vq,$$  \tag{4.3.18}

$$w = \Gamma(1/\sqrt{m})Vq + (1/\sqrt{m})Sq.$$  

4-4 Symmetry directions and the $|\vec{r}| \to 0$ limit

The $6\times6$ transformed matrices $R(\vec{r})$ and $C(\vec{r})$, and thus the rigid ion model and shell model transformed dynamical matrices, are generally non-diagonal. However, for $\vec{r}$ directed along one of the coordinate axes, taken coincident with the crystallographic axes (see section 3-1), the matrices are diagonal in the cartesian indices. For example, for the $(h, 0, 0)$ direction,

$$\phi_{s's'}((k_x, 0, 0)) =$$  

$$\begin{cases} 
\delta_{\alpha\alpha'}\phi_{s's'}(k_x), & \text{for } \alpha = y \text{ or } z \\
\delta_{\alpha\alpha'}\phi_{s's'}(k_x), & \text{for } \alpha = x, 
\end{cases}$$  \tag{4.4.1}
and similarly for $R(\mathbf{k})$ and $C(\mathbf{k})$. The symbols $\perp$ and $\parallel$ denote transverse, and longitudinal, respectively, as discussed in section 4-2 for the matrix $C(\mathbf{k})$. The six eigenvectors of $\phi((k_x, 0, 0))$ accordingly divide into pairs, each pair corresponding to one of the 2x2 matrices $\phi_\perp(k_x)$ or $\phi_\parallel(k_x)$, associated with one of the cartesian axes. The optical and acoustical modes (see the Introduction and section 4-1) for $\phi_\parallel(k_x)$ are called longitudinal optical (LO) and longitudinal acoustical (LA), respectively. For $\phi_\perp(k_x)$, the optical and acoustical modes are called transverse optical (TO) and transverse acoustical (TA), respectively. For $\mathbf{k}$ along the $(h, h, h)$ direction, the modes can also be classified as either longitudinal or transverse. For $\mathbf{k}$ along the $(h, h, 0)$ direction, however, there are only transverse waves, the others being neither transverse or longitudinal, and non-degenerate.

The "dispersion relations" or, frequencies (in units of cycles per second) as a function of wave vector for KI are given in Fig. 7 for the three directions just mentioned. The arrangement of the graphs for the three directions, and the direction of increasing wave vector, were chosen in such a way that the frequencies were continuous from one graph to the next. Wave vector magnitudes are all plotted to the same scale. In the case of the $(h, h, 0)$ direction, some points outside the first Brillouin zone appear, and the zone boundary is indicated by a dashed line.
Figure 7. The KI room temperature shell model lattice frequencies, for wave vectors directed along three axes, as indicated. The actual wave vector magnitude is \(|\mathbf{K}| = (\pi/d)h\), and the three graphs are drawn to the same wave vector scale. The frequency \(\omega_0\) is the eigenfrequency, \(\omega_0 = \omega(0j)/2\pi\).
The equivalence in frequency of the points \((1, 0, 0)\) and \((1, 1, 0)\) is due to the fact that the two wave vectors are related by subtraction of the reciprocal lattice vector \((1, 1, 1)\) and a symmetry operation, all of which leave the dynamical matrix invariant. The calculation of these values is described in the next section. The frequency \(\omega_o\) in Fig. 7 is the eigenfrequency in units of cps, so that \(\omega_o = c \omega_o/\omega(0j)/2\pi\), where \(\omega(0j)\) is the long wavelength transverse optical frequency, and \(\omega_o\) is the eigenfrequency in \(\text{cm}^{-1}\), determined from the optical constants data.

Up to this point, the cartesian axes used have been taken coincident with the crystallographic axes. In the \(|\kappa| \to 0\) limit, the diagonality in the cartesian coordinates holds for any choice of cartesian coordinate system. This is equivalent to saying that the arbitrary unitary transformation \(\kappa' = T \kappa\) for \(|\kappa| \equiv 0\), results in the new polarization \(u'(\kappa') = Tu(\kappa)\). This will be true if

\[
\lim_{|\kappa| \to 0} \phi(T \kappa) = \lim_{|\kappa| \to 0} T(\kappa) T^\dagger \phi(\kappa) T.
\]

This relation holds for the matrices \(R(\kappa)\) and \(C(\kappa)\), since

\[
\lim_{|\kappa| \to 0} R_{\alpha\alpha'} s_{\alpha\alpha'} (\kappa) = \delta_{\alpha\alpha'} (A_{12} + 2B_{12}) (-1)^s - s',
\]

and

\[
\lim_{|\kappa| \to 0} C_{\alpha\alpha'} s_{\alpha\alpha'} (\kappa) = \frac{4\pi}{\nu_c} \lim_{|\kappa| \to 0} \left( \frac{k_{\alpha\alpha'}}{k^2} \right) + \delta_{\alpha\alpha'} C_{SS'} (0).
\]
where \( c_{ss}\delta(0) = -4\pi/3v_c \). Thus (4.4,2) holds for the rigid ion and shell model dynamical matrices. The result is that the crystal is isotropic for long waves. In particular, the crystal is optically isotropic.

4-5 Shell model computer calculations for KI

The number of separate wave vectors in the first Brillouin zone for a crystal is equal to the number of unit cells in the sample. This, for bulk samples, is the order of Avagadro's number. In the calculations which will be described here, the Brillouin zone is sampled at 1000 points, which are taken to be representative of the entire set of points. Each point chosen actually represents still a very large number of points.

For the purposes of calculation, it is convenient to redefine the wave vector scale so that a wave vector is specified by \((K_1, K_2, K_3)\) where \( K_1 = 10(d/\pi)k_x \), and similarly for the other components. \( K_1 = 10 \) then corresponds to the zone boundary, and there are 1000 wave vectors, within the first Brillouin zone, such that

\[
K_1, K_2, \text{ and } K_3 \text{ are even integers}
\]

or \( K_1, K_2, \text{ and } K_3 \text{ are odd integers}. \)
In other words, the set of points defined by these integers corresponds to a (bcc) lattice. The calculation was limited to this set of points. Due to cubic symmetry, however, only those points in an irreducible element of $1/48$ the volume of the entire zone were considered. This is because one can derive the eigenvectors of the rest by symmetry operations, and the eigenvectors so generated have the same eigenvalues as their corresponding points in the irreducible element. The element chosen here contains the points for which

\[ K_1, K_2, \text{ and } K_3 \geq 0 \]
\[ K_1 \geq K_2, \tag{4.5.2} \]
\[ K_2 \geq K_3. \]

The requirement (3.4.8) that the points be inside the Brillouin zone leads to

\[ K_1 \leq 10, \]
\[ K_1 + K_2 \leq 20, \tag{4.5.3} \]
\[ K_1 + K_2 + K_3 \leq 15, \]

for the reciprocal lattice vectors $(20, 0, 0)$, $(20, 20, 0)$ and $(10, 10, 10)$, respectively.

There are 48 points satisfying the restrictions (4.5.1), (4.5.2), and (4.5.3). This choice was originally due to Kellerman,\textsuperscript{2} and has been used by many others since his work appeared.
The problem, in the case of $Kl$, was first to compute the dynamical matrix for each of these 48 vectors. The dynamical matrix $(4.3.14)$, based on the shell model was used. In terms of $C(\vec{r}), R(\vec{r}), A, Z$, and $Y$, the transformed dynamical matrix is

\[
\phi(\vec{r}) = (R(\vec{r}) + ZC(\vec{r})Z)^{-1} (R(\vec{r}) + A + YC(\vec{r})Y) (R(\vec{r}) + ZC(\vec{r})Z).
\]

Then, using the secular equation $(3.5.4)$, the eigenvectors $\vec{m}(\vec{k}_j)$ and eigenvalues $\omega^2(\vec{k}_j)$ were computed by standard matrix algebra techniques. Computer programs were already in existence to carry out this task.

Since the Coulomb coefficients, or elements of the Coulomb transformed dynamical matrix contain no parameters other than the factor $1/v_c$, it was desirable to compute them first and record them once and for all on cards, so that they could be read into the shell model calculation. Although the values published by Kellerman could have been used, it was decided to recalculate the values using modern computational methods. The computation was done according to $(4.2.15)$ as discussed in section 4-2. The $6X6$ matrix $C(\vec{r})$ was partitioned into four $3X3$ matrices denoted by $C_{s,s'}(\vec{k})$, as with $R(\vec{r})$ in section 4-1. It follows from $(4.2.15)$ that $C_{1,2}(\vec{r}) = C_{2,1}(\vec{r})$ and $C_{1,1}(\vec{r}) = C_{2,2}(\vec{r})$ so that only 18 elements need be computed. Furthermore, each of these matrices are
symmetric, which reduces the number of distinct elements to 12. A set of output cards for each wave vector contained the integers \( K_1, K_2, \) and \( K_3 \), and the 12 distinct Coulomb coefficients for that wave vector. The factor \( 1/v_c \) was neglected in the computation, and inserted, along with other numerical data at a later stage of the shell model calculation.

To make the neglected lattice sum smaller than \( 10^{-10} 1/v_c \), it was decided, using (4.2.16) to choose \( G' = 5.5 \). This required a value of \( g_m' = 10 \), using (4.2.17), to reduce the neglected portion of the reciprocal lattice sum to a similar order of magnitude. This required calculating the order of 8000 terms for each of the 12 elements and all of this for each of the 48 points! The entire calculation, for all 48 points, was done in 6.6 minutes on the IBM 7094 of the OSU Computer Center. This was the longest single calculation done in all of this work. Values obtained were, with few exceptions, within a few parts in one thousand of those of Kellerman.²

A computer program, here called the "shell model program" was used to compute the shell model dynamical matrix (4.5.4) for each wave vector \( \mathbf{K} \), from the parameters of Table 4, and the Coulomb coefficients. The short range coefficients, the elements of \( R(\mathbf{K}) \), were calculated from (4.1.15), using the appropriate parameters listed in Table 4. The values given there are those of Dolling et al.,⁶ except for a temperature correction. This correction

---

⁶ Dolling et al., op. cit.
<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
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<tr>
<td>lattice constant</td>
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<tr>
<td>potassium mass</td>
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<td>iodine mass</td>
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<td>3.03 (\times 10^{12}) (\text{cps})</td>
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<tr>
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<td>(0.92\mathbf{e})</td>
</tr>
<tr>
<td>(A_{12})</td>
<td></td>
<td>(12.4^* \times e^2/\nu_c)</td>
</tr>
<tr>
<td>(B_{12})</td>
<td></td>
<td>(-0.924^*)</td>
</tr>
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</tr>
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<td>force constants</td>
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<td>(A_{22})</td>
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</table>

*These values are different from the 90°K values of Dolling (see text).*
was necessary, since Dolling's values were chosen to give the correct lattice frequencies at 90°K, while this work was done at room temperature. It was assumed that only the short range forces are modified by thermal expansion. Parameters $A_{12}$ and $B_{12}$ in Table 4 were reduced, by a factor 0.924 from those given by Dolling, in order to give the correct room temperature eigenfrequency as the $k^2 = 0$ transverse optical mode frequency. The shell charges and ionic force constants are given in terms of the polarizability parameters $^4$ by

$$
Y_s = -\frac{\kappa_s R^s}{d_s}, \quad A_s = -R_0 + Y_s^2 / \kappa_s
$$

with

$$
R_0 = \frac{(A_{12} + 2B_{12})}{0.924},
$$

where $A_{12}$ and $B_{12}$ are the room temperature values of Table 4. The factor 0.924 appears here because Dolling's values for 90°K are appropriate here, in view of the assumption that the charges and ionic force constants are independent of temperature.

The computation of $\phi(\vec{k})$ involved a matrix inversion, which was done using a standard library routine. The matrix

$$(1/\sqrt{m}) \phi(\vec{k}) (1/\sqrt{m})$$

was then formed, using $\phi(\vec{k})$ and the appropriate masses. This matrix was then punched into cards and read into a Scatran program which called a library routine to diagonalize
the matrix. The rest of the program was done in the Fortran language, but this step in Scatran was necessary because no suitable Fortran program to accomplish this task was available at the time the work was done. The resulting frequencies and eigenvectors, along with the wave vector integers, were then punched into another set of cards to be used as an input to the program for calculating the optical constants, described in Chapter VI.
CHAPTER V

INTERACTION OF THE LATTICE WITH AN ELECTROMAGNETIC FIELD

The linear optical properties of a dielectric medium, KI in particular, have been discussed in Chapters I and II. The electric field for each spectral component was treated as a wave propagating through the medium, being partially reflected and partially transmitted at surfaces between the medium and free space. The electric field considered there is the field which is generally called the "macroscopic" field. It is not equal to the actual "microscopic" field, which varies from point to point in a much more complex manner, depending upon the actual charge distribution resulting from the wave functions of all the nuclei and electrons in the crystal.

The concept of a macroscopic field is based on the Maxwell theory of macroscopic linear dielectric media.¹ In this theory, the state of polarization of the medium is described by a continuous function of the position coordinates of points in the medium. It is assumed that the average polarization per unit volume of any macroscopically small volume element is proportional to the

¹Ziman, op. cit., p. 220.
macroscopic field evaluated at the position of the volume element. In order that the polarization function be continuous, it is obvious that the volume elements under consideration, over which the field is essentially constant, must contain several unit cells. Since the field for a spectral component has been assumed to be sinusoidal in form, the polarization must be that corresponding to a displacement of the ions and electrons in the form of a lattice wave, of wavelength equal to that of the electric field. The condition for applicability of the theory then, is that the wavelength of the field wave be very long compared to the unit cell dimension, 2d. This is certainly true in the case of infrared radiation.

In the present chapter, the electrical properties of the shell model are considered, and appropriate quantities are related to those of the Maxwell theory, so that the optical constants can be calculated. The medium is assumed to have zero magnetic susceptibility, so that the magnetic field need not appear in this analysis, although it is present, according to the Maxwell theory. KI is considered to be optically isotropic, since the properties of the crystal are independent of its orientation, for the limiting case of zero magnitude wave vector, which is appropriate for the interaction with infrared radiation. The isotropy for zero wave vector was discussed in section 4-4.
5.1 Review of the Maxwell theory for macroscopic, linear, isotropic, dielectric media

The electric field waves in an isotropic medium are transverse. As in Chapter I, consider the wave to be polarized in a single direction, here the z direction, with the x direction as the direction of propagation. The cartesian coordinate of the field is then

\[ E_\omega(\mathbf{r}, t) = \delta_{\omega z} \int_{-\infty}^{\infty} d\omega e(\omega) \exp(i(\mathbf{K}(\omega) \cdot \mathbf{r} - \omega t)), \]

where \( \mathbf{K}(\omega) \) is the wave vector, taken parallel (or antiparallel) to the x axis;

\[ K_x(\omega) = (\omega/c) N(\omega), \quad K_y = K_z = 0, \]

where \( N(\omega) \) is the complex index. The component wave for the frequency \( \omega \) is

\[ E^{\omega}_x(\mathbf{r}, t) = \delta_{\omega z} e(\omega) \exp(i(\mathbf{K}(\omega) \cdot \mathbf{r} - \omega t)). \]

The polarization due to this field is also a wave

\[ P^{\omega}_z(\mathbf{r}, t) = \delta_{\omega z} m(\omega) \exp(i(\mathbf{K}(\omega) \cdot \mathbf{r} - \omega t)), \]

where \( m(\omega) \) is proportional to \( e(\omega) \).
\( m(\omega) = \chi(\omega)\sigma(\omega), \) \hspace{1cm} (5.1.5)

where \( \chi(\omega) \) is the complex dielectric susceptibility.

Maxwell's equations lead to the very important result \(^1\) that

\[ N(\omega) = \xi^{1/2}(\omega), \] \hspace{1cm} (5.1.6)

where \( \xi(\omega) \) is the complex dielectric constant,

\[ \xi(\omega) = 1 + 4\pi\chi(\omega). \] \hspace{1cm} (5.1.7)

The significance of (5.1.6) and (5.1.7) is that the complex index of refraction can be calculated from the polarization of the crystal under the influence of a wave of the type given in (5.1.3).

The remainder of this dissertation is devoted to such a calculation.

5-2 The electrical properties of lattice waves

Before considering the effect of an external electric field on the lattice, it is profitable to examine the electric fields produced by the harmonic displacement of the cores and shells from their equilibrium positions in the lattice. The field can be evaluated at lattice points, from the Coulomb part of the harmonic potential energy.

The Coulomb part of the harmonic potential energy, from (4.3.6) is
The cartesian component of the electric field at the \((s, \lambda)\) site, due to displacement of the cores and shells at all other lattice sites is

\[
\langle x \rangle = - \frac{U_c^{(2)}}{M_{\alpha s}(\lambda)}
\]

(5.2.1)

where the superscript "har" denotes the harmonic field. A 6N-vector \(E_{\text{har}}\) can be formed from the field also. It is, from (5.2.2)

\[
E_{\text{har}} = -CM_s
\]

(5.2.3)

The field vector, \(E_{\text{har}}\) can be transformed to wave vector form,

\[
E_{\text{har}}(\vec{x}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} E_{\text{har}}(\vec{k}) \exp(i(\vec{k} \cdot (\vec{x} + \vec{z})))
\]

(5.2.4)

in the same manner as can the other 6N-vectors. Equations (5.2.1) and (5.2.3) then become,
where the equations hold for all \( N \) wave vectors \( \vec{k} \), and the matrices are 6 dimensional.

It must be emphasized that the quantity \( \frac{1}{\sqrt{N}} E^{\text{har}}(\vec{k}) \) in (5.2.4) is the amplitude of a wave for a given wave vector \( \vec{k} \). The presence of the factor \( \frac{1}{\sqrt{N}} \) is necessary in order that the transformation to wave vector form be unitary.

5-3 The interaction of external electromagnetic waves with lattice waves

To compute the polarization resulting from an electromagnetic wave, it is necessary first to find the lattice motion resulting from the field wave, and then find the polarization resulting from this lattice motion. The actual equations of motion depend on the system of mechanics used (classical or quantum mechanical), the actual Hamiltonian of the lattice (anharmonic terms possibly included), and the initial state (temperature) of the crystal when the field is applied. The basic form of the interaction
portion of the Hamiltonian, however, is independent of such questions. Accordingly, in this section the Hamiltonian for interaction between an electric field wave and a lattice wave, and the polarization per unit volume resulting from the lattice wave are given. In section 5-5, these quantities are expressed in terms of normal coordinates.

The presence of external sources modifies the expression (5.2,3) for the field at an ionic site, since there is an interaction field $\Delta E$, not due to the motion of other ions. The total effective field is

$$E^{\text{eff}} = E^{\text{har}} + \Delta E = -\mathcal{CM} + \Delta E.$$  \hspace{1cm} (5.3.1)

An additional energy results from the field $\Delta E$, so that the total electrical part of the Hamiltonian is

$$H_E = U^{(2)} + H_{\text{INT}},$$ \hspace{1cm} (5.3.2)

where $H_{\text{INT}}$ is the interaction part,

$$H_{\text{INT}} = -N \Delta E.$$ \hspace{1cm} (5.3.3)

Consider the field $\Delta E^\omega$, for a single frequency component, assuming that $\Delta E^\omega (\vec{r}, t)$ is proportional to $E^\omega (\vec{T} + \vec{s}, t)$ in (5.1,3). Then
\[ \Delta E^\omega_s (\mathbf{r}_1 | t) \]
\[ = \int \varepsilon \Delta e(\omega) \exp(i(\mathbf{K}(\omega) \cdot (\mathbf{r}_1 + \mathbf{r}_2) - \mathbf{r}_1), \quad (5.3.4) \]

where \( \Delta e(\omega) \) is proportional to \( e(\omega) \). In wave vector form,

\[ \Delta E^\omega_s (\mathbf{r}_1 | t) \]
\[ = \int \varepsilon \Delta e(\omega) \Delta (\mathbf{K}(\omega) - \mathbf{K}_0) \exp(-i\mathbf{K}_0), \quad (5.3.5) \]

so that the Hamiltonian for interaction between the field wave of frequency \( \omega \) and the lattice wave with wave vector \( \mathbf{K}_0 \) is

\[ H^\omega_{\text{INT}} (\mathbf{r}_1 | t) = \sqrt{N} \Delta e(\omega) \exp(-i\mathbf{K}_0) \]
\[ \times \Delta (\mathbf{K}(\omega) - \mathbf{K}_0) \sum_s H_{zs}(\mathbf{r}_1 | t). \quad (5.3.6) \]

The total interaction Hamiltonian for the \( \omega \) component, \( H^\omega_{\text{INT}}(t) \), is obtained by summing \( H^\omega_{\text{INT}} (\mathbf{r}_1 | t) \) over all wave vectors \( \mathbf{K}_0 \). If \( \mathbf{K}(\omega) \) is real, which is true for a purely harmonic crystal, as shown in section 5-6, then only the term for \( \mathbf{K} = \mathbf{K}(\omega) \) contributes, as is obvious from the expression (3.4.4) for \( \Delta (\mathbf{K} - \mathbf{K}(\omega)) \). In the more general case where \( \mathbf{K}(\omega) \) is complex, it cannot, of course, be equal to a real lattice wave vector. The wave vector \( \mathbf{K}(\omega) \) may interact with a distribution of lattice wave vectors \( \mathbf{K}_0 \) such that
\[ \hat{\mathbf{r}} = \hat{\mathbf{r}}_r(\omega), \] where the \( r \) denotes the real part. We assume that the distribution is sharply peaked enough at \( \hat{\mathbf{r}} = \hat{\mathbf{r}}_r(\omega) \) that it is valid to write

\[ H^\omega_{\text{INT}}(t) = H^\omega_{\text{INT}}(\hat{\mathbf{r}}_r(\omega)|t). \] (5.3.7)

The \( z \) component of the polarization per unit volume, \( \mathcal{M}_z(\mathbf{r},t) \), evaluated at a unit cell specified by a lattice vector \( \mathbf{r} \), under the long wavelength conditions for which \( \mathcal{M}_z(\mathbf{r},t) \) is defined, is

\[ \mathcal{M}_z(\mathbf{r},t) = \frac{1}{v_c} \sum_s M_z(s|t). \] (5.3.8)

By expanding \( \mathcal{M}_z(\mathbf{r},t) \) in wave vector form,

\[ \mathcal{M}_z(\mathbf{r},t) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \mathcal{M}_z(\mathbf{k}|t) \exp(i(\mathbf{k} \cdot \mathbf{r})), \] (5.3.9)

it follows that

\[ \mathcal{M}_z(\mathcal{R}|t) = \sum_s \frac{1}{v_c} M_{zs}(\mathcal{R}|t), \] (5.3.10)

so that the Hamiltonian (5.3.7) becomes

\[ H^\omega_{\text{INT}}(t) = -\sqrt{N} v_c A e(\omega) \exp(-i\omega t) \mathcal{M}_z(-\hat{\mathbf{r}}_r(\omega)|t). \] (5.3.11)
Comparing (5.3.9) with (5.1.4) and using $\mathbf{k} = \mathbf{k}_F(\omega)$, it follows that

$$m(\omega)\exp(-i\omega t) = \frac{1}{\sqrt{N}} M_z(\mathbf{k}_F(\omega)|t). \quad (5.3.12)$$

This relation allows the susceptibility to be found after the equations of motion have been solved for $M_z(\mathbf{k}_F(\omega)|t)$.

5.4 Identification of the interaction field

The interaction field $\Delta E$ must be chosen such that the total effective field at the ionic sites has the correct value. The effective field at a point in a macroscopic medium can be computed by dividing the medium into two regions, the first region consisting of a macroscopically small sphere centered on the point, and the second region consisting of the remaining parts of the medium and external sources. In this manner, for cubic crystals, Kittel\(^2\) shows that the effective field at an equilibrium ionic site is

$$E_{\text{eff}}^\alpha (\mathbf{r}|t) = E_\alpha (\mathbf{r},t) + \frac{4\pi}{3} M_\alpha (\mathbf{r},t) \quad (5.4.1)$$

$$= E_\alpha (\mathbf{r},t) + \frac{4\pi}{3v_c} \sum_{s'} M_{\alpha s'} (\mathbf{r}|t).$$

\(^2\)Kittel, op. cit., p. 160.
Expressing the macroscopic field in terms of component frequencies, and the lattice vectors in terms of component wave vectors, and making the correspondence between frequency and wave vector as in the preceding section gives

\[ E_{\alpha s}^{\text{eff}}(\mathbf{r}, \omega) |t\rangle = \sqrt{N} e(\omega) \exp(-i\omega t) \]

\[ - \sum_{s'} C_{\alpha s's'}(0) H_{\alpha s'}(\mathbf{R}_T(\omega) |t\rangle, \]

where the explicit value of the Coulomb coefficient has been made use of. For \( \alpha = z \), a comparison of (5.4.2) with (5.3.1) yields

\[ \Delta E_{zs}^{\omega}(\mathbf{r}, \omega) |t\rangle = \sqrt{N} e(\omega) \exp(-i\omega t), \]

or

\[ \Delta e(\omega) = e(\omega), \]

so that, at the lattice sites, the \( z \) component of the interaction field is equal to the macroscopic field.

5-5 The interaction in terms of normal coordinates

In this section the polarization per unit volume \( \mathcal{M}_z(\mathbf{r}, |t\rangle \) as in (5.3.11) and (5.3.12) is expressed in terms of normal coordinates \( Q(\mathbf{R}, |t\rangle, \) The wave vector form of the shell model polarization matrix, \( M(\mathbf{R}) \), is given, from (4.3.3), by
The coordinates \( u(\vec{k}) \) and \( w(\vec{k}) \) can be expressed as linear combinations of \( Q(\vec{k}j) \) and \( q(\vec{k}j) \), according to the results of section 4-3. Therefore \( M(\vec{k}) \) is a sum of "ionic" and "electronic" parts,

\[
M(\vec{k}) = N^1(\vec{k}) + N^e(\vec{k}),
\]

and the same applies to \( M_z(\vec{k}) \), the Hamiltonian, and therefore to the dielectric constant.

The electronic part of the dielectric constant is independent of frequency in the infrared. The constant value is derived in section 5-6, but here only the ionic part is considered. The polarization matrix due to "ionic" motion is

\[
M^1(\vec{k}) = Z(\vec{k}) u^1(\vec{k}),
\]

where \( Z(\vec{k}) \) is the effective charge matrix,

\[
Z(\vec{k}) = Z + Y f(\vec{k}),
\]

where \( f(\vec{k}) \) is defined in (4.3.14). From the transformation of \( u(\vec{k}) \) to normal coordinates and (5.3.10), it follows that

\[
M^1_z(\vec{k} | t) = \sum_j M^1_z(\vec{k}_j) Q(\vec{k}_j | t),
\]
where the polarization coefficient $\mathcal{M}_z(\mathbf{k}_j)$ is given by

$$
\mathcal{M}_z(\mathbf{k}_j) = \frac{1}{v_c} \sum_{s} \sum_{s'} \frac{\tilde{z}_{zs} \alpha_{s'}(\mathbf{k})}{\sqrt{n_s}} \frac{m_{s'}(s'|\mathbf{k}_j)}{n_s}. \tag{5.5.6}
$$

Since only wave vectors $\mathbf{k} = \mathbf{k}_i(\omega)$ for which $|\mathbf{k}| \gg 0$ are used, the $|\mathbf{k}| \to 0$ form of the frequencies and eigenvectors can be used (see section 4-4). Then, for the transverse mode,

$$
\mathcal{M}_z(0j) = \frac{1}{v_c} \sum_{s'} \tilde{z}_{ss'} \frac{m_{s'}(s'|0j)}{\sqrt{n_s}}, \tag{5.5.7}
$$

where the "0" argument denotes a small-magnitude vector in the x direction. $\tilde{z}_{ss'}$ is the "effective charge" for the s' ion,

$$
\tilde{z}_{ss'} = \sum_{s} \tilde{z}_{ssss'}(0), \tag{5.5.8}
$$

where $\tilde{z}(0)$ has been partitioned into 2x2 matrices $\tilde{z}_\perp(0)$ and $\tilde{z}_\parallel(0)$, in the same manner as for $C(0)$ and $R(0)$ in sections 4-2 and 4-4, so that

$$
\tilde{z}_\perp(0) = \mathbf{Z} + \gamma \Gamma_\perp(0), \tag{5.5.9}
$$

and similarly for $Z_{\parallel}(0)$. It follows easily from the fact that $\tilde{b}_{\perp 11}(0) = -\tilde{b}_{\perp 12}(0)$ that
so that an effective charge

\[ \vec{Z}_1 = |\vec{Z}_{1,1}| = |\vec{Z}_{1,2}| \]  

(5.5.11)

can be defined, in analogy with rigid ion model, where \( Z_1 = -Z_2 \).

The eigenvectors for \( \vec{K} = 0 \) are determined by the condition (4.1.7), which holds both in the rigid ion and shell models. It then follows that for the TO mode

\[ M_z^{(0,j)} = \frac{\vec{Z}_1}{v_c} \frac{1}{\sqrt{\mu}} \]  

(5.5.12)

where \( \mu \) is the reduced mass, defined by

\[ \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \]  

(5.5.13)

The coefficient vanishes for the LO mode.

The Hamiltonian (5.3.11) is therefore finally,

\[ H_{\text{INT}}^{\omega,1}(t) \]

(5.5.14)

\[ = -\sqrt{\frac{N}{\mu}} \vec{Z}_1 e(\omega) \exp(-i\omega t) Q(-\vec{K}_1(\omega)) j|t). \]

The polarization amplitude (5.3.12) is
where \( j \) refers to the TO mode for motion along the \( z \) axis.

5.6 The harmonic lattice model and the high and low frequency dielectric constants

A solution to the equations of motion for a harmonic crystal interacting with the electric field not only serves to illustrate the use of the many quantities which have been defined, but gives nearly the correct values of the index (or dielectric constant) in the low and high frequency limits.

The total Hamiltonian for the \( |\vec{K}| = |\vec{K}(\omega)| \) modes is, from (3.5.10) and (5.5.14),

\[
\begin{align*}
\mathcal{H}(-\vec{K}(\omega)j|t)\mathcal{H}(\vec{K}(\omega)j|t) \\
&+ \omega^2(0j)Q(-\vec{K}(\omega)j|t)Q(\vec{K}(\omega)j|t) \\
&\quad - \sqrt{\frac{N}{\mu}} \tilde{Z}_\perp \omega(\omega) \exp(-i\omega t)Q(-\vec{K}(\omega)j|t).
\end{align*}
\]

The frequency \( \omega(0j) \) is the quasi-harmonic frequency for the long-wavelength transverse optical phonon, or the eigenfrequency. From Hamilton's canonical equations for the \( -\vec{K}(\omega) \) mode, the steady
state solution to the resulting equation for $Q(\tilde{R}(\omega)j|t)$ is

$$Q(\tilde{R}(\omega)j|t) = \frac{\sqrt{N} z_1 e(\omega) \exp(-i\omega t)}{\omega^2(0j) - \omega^2}.$$  

(5.6.2)

Therefore, the ionic dielectric susceptibility for frequency $\omega$, from (5.5.15) and (5.1.5) is

$$\chi^1(\omega) = \frac{z_1^2}{\mu v_c} \frac{1}{\omega^2(0j) - \omega^2}.$$  

(5.6.3)

Equation (5.6.3) gives only the ionic part of the susceptibility. Just as this reaches a constant value for comparatively low frequencies (microwave or radio frequencies), the electronic susceptibility is constant throughout the infrared, since the resonances for electronic motion are of much higher frequency. Therefore, using (5.1.7)

$$\varepsilon(\omega) = \frac{4\pi z_1^2}{\mu v_c(\omega^2(0j) - \omega^2)} + \varepsilon(\infty),$$  

(5.6.4)

where $\varepsilon(\infty)$ is the dielectric constant due to electronic processes. The low frequency dielectric constant is
In a similar manner, $\varepsilon(\infty)$ is the low frequency value for purely electronic motion. From the characteristic equation (3.5.4), and assuming that the condition (4.1.7) holds for the dynamical matrix $\phi(\mathbf{r})$, it follows that

$$\mu \omega^2(0) = |\phi_{ss}(0)|. \quad (5.6.6)$$

This means, from (5.6.5), that the low frequency dielectric constant is actually independent of the core masses.

A direct method of finding the high frequency dielectric constant $\varepsilon(\infty)$ would be to carry out a solution for the electronic motion, using (4.3.15), as done here for the electronic motion. A serious drawback of this procedure is that it is difficult to derive an expression which does not involve the shell masses. That is, to the shell model approximation, the expression derived in this manner is apparently not independent of $\xi m$.

Woods et al. and Cowley et al. avoid this problem by neglecting the short range coupling between shells of adjacent ions, so that each ion is independently polarizable. The approach to be

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$^3$Chapter III, footnote 3.

$^4$Chapter IV, footnote 4.
described here requires no such approximation, and no assumption about the shell masses.

The interaction field in (5.3.1) can be modified by addition of terms proportional to the polarization, provided those terms are subtracted from the harmonic part. Adding $4\pi m(\omega)$ to $\delta e(\omega)$, so that

$$
\delta e(\omega) = e(\omega) + 4\pi m(\omega) \equiv d(\omega), \quad (5.6.7)
$$

where $d(\omega)$ is the "displacement" field, causes $C_{ss}(0) = -\frac{4\pi}{3\nu_c}$ to be replaced by $C_{ss}(0) = \frac{8\pi}{3\nu_c}$ in the harmonic part of the Hamiltonian. Thus, one can carry out steps using, $\delta e(\omega) = d(\omega)$, similar to those already carried out in this chapter for $\delta e(\omega) = e(\omega)$, giving

$$
\frac{m_1^1(\omega)}{d(\omega)} = \frac{4\pi z_2^2}{\mu \nu_c (\omega_2^2 - \omega^2)}, \quad (5.6.8)
$$

where $\omega_2$ is the frequency for the LO mode, and $z_2$ the effective charge for this mode. Dividing (5.6.7) by $d(\omega)$ then gives

$$
\varepsilon(\omega) = \frac{1}{\frac{1}{\varepsilon(\infty)} - \frac{4\pi z_2^2}{\mu \nu_c (\omega_2^2 - \omega^2)}}, \quad (5.6.9)
$$

Denoting $\omega_0(\omega)$ here by $\omega_1$, we have, from (5.6.4) and (5.6.9)
\[
\epsilon (\omega) = \frac{4\pi \frac{Z_2^2}{\mu v_c}}{\omega_\perp^2 - \omega^2} + \epsilon (\infty) \left( \omega_\parallel^2 - \omega^2 \right) \\
= \frac{\epsilon (\infty) \left( \omega_\parallel^2 - \omega^2 \right)}{\omega_\parallel^2 - \omega^2 - \epsilon (\infty) \frac{4\pi \frac{Z_2^2}{\mu v_c}}{\epsilon (\infty)}}.
\]

For this equality to hold,

\[
\omega_\parallel^2 - \omega_\perp^2 = \epsilon (\infty) \frac{4\pi \frac{Z_2^2}{\mu v_c}}{\epsilon (\infty)} = \frac{4\pi \frac{Z_2^2}{\mu v_c}}{\epsilon (\infty)}
\]

so that \( \epsilon (\infty) \) is given by

\[
\epsilon (\infty) = \frac{Z_\perp}{Z_\parallel}.
\]

From (5.6.5) and (5.6.11), the Lyddane-Sachs Teller (LST) relation \(^5\)

\[
\epsilon (0) = \frac{\omega_\parallel^2}{\omega_\perp^2} \epsilon (\infty)
\]

results. It would certainly be much more difficult to prove this relation directly from the expressions for \( \epsilon (0) \) and \( \epsilon (\infty) \) derived as discussed earlier. Some approximations would have to be made, since, as discussed in section 4-3, the diagonalization

\(^5\)M. Born and K. Huang, op. cit., p. 87.
method used is not strictly correct. The LST relation, as derived here, is strictly a result of a harmonic model, with no approximations made. Equation (5.6.12), for \( \varepsilon(\infty) \), is exact also, although, in practice, the adiabatic approximation is used in calculating \( \bar{Z}_\perp \) and \( \bar{Z}_\parallel \).

Table 5 shows calculated values for KI of the quantities just discussed, compared with experimental values, for the dielectric constants. The charges \( \bar{Z}_\perp \) and \( \bar{Z}_\parallel \) were calculated using (5.5.9), and using the parameters of Table 4 in the matrices. \( \varepsilon(\infty) \) was calculated from (5.6.12) and \( \varepsilon(0) \) from (5.6.6).

\( \varepsilon(0) \) was also calculated from the LST relation (5.6.13), using \( \omega_n \) as computed in Chapter IV (see Fig. 7). The low frequency index of refraction \( n(0) \) was taken from Fig. 6, and the high frequency value from the data of Korth. The "static" dielectric constant is that measured at radio frequencies, using the material as a dielectric in a capacitor. This value should be equal to \( n^2(0) \). The values of \( \varepsilon_s \) are close to the measured \( n^2(0) \), but the shell model values of \( \varepsilon(\infty) \) and \( \varepsilon(0) \) are significantly lower. The ratio \( \varepsilon(0)/\varepsilon(\infty) \), however, agrees well with the experimental value, indicating, because of the LST relation, and

---

6 This value of \( \varepsilon \) is higher than the square of the highest value of \( n \) in Table 3, because \( n \) continues to increase slowly into the near infrared and visible, where it begins to increase more quickly due to the electronic processes. See the data of Korth; Chapter II, footnote 7.
**TABLE 5**

SHELL MODEL AND EXPERIMENTAL DIELECTRIC DATA FOR KI

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>effective charges</td>
<td>( \overline{Z}_e )</td>
<td>1.032</td>
</tr>
<tr>
<td></td>
<td>( \overline{Z}_m )</td>
<td>0.434</td>
</tr>
<tr>
<td>dielectric constants</td>
<td>( \varepsilon(\infty) )</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>( \varepsilon(0) )</td>
<td>4.35(^a)</td>
</tr>
<tr>
<td></td>
<td>( \varepsilon(0)/\varepsilon(\infty) )</td>
<td>1.82</td>
</tr>
<tr>
<td>frequencies for long waves</td>
<td>( \omega_e/2\pi )</td>
<td>(3.03 \times 10^{12}) cps</td>
</tr>
<tr>
<td></td>
<td>( \omega_m/2\pi )</td>
<td>(4.09 \times 10^{12}) cps</td>
</tr>
<tr>
<td>dielectric constants</td>
<td>( \varepsilon(\infty) = n^2(\infty) )</td>
<td>2.69(^b)</td>
</tr>
<tr>
<td></td>
<td>( \varepsilon(0) = n^2(0) )</td>
<td>5.02 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>( \varepsilon(0)/\varepsilon(\infty) )</td>
<td>1.86</td>
</tr>
<tr>
<td>Other experimental values</td>
<td>static dielectric constant</td>
<td>( \varepsilon_s )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) This value is increased to \( \varepsilon(0) = 4.43 \) due to anharmonicity (see section 6-8). The ratio \( \varepsilon(0)/\varepsilon(\infty) \) then becomes 1.85, although the LST relation does not hold in this case.

\(^b\) See footnote 6.


the fact that \( \omega_A \) was chosen to be the correct value, that the shell model value of \( \omega_H \) is correct. The anharmonic correction to \( \xi(0) \) (see section 6-8) increases \( \xi(0) \) such that the ratio \( \xi(0)/\xi(\infty) \) is closer to the experimental ratio.
CHAPTER VI

THE OPTICAL CONSTANTS OF KI WITH ANHARMONIC DAMPING
OF THE OPTICAL PHONON

The Hamiltonian for interaction between a KI crystal lattice and an electromagnetic wave of a single frequency was derived in Chapter V. The portion of this Hamiltonian corresponding to the motion of the ions was expressed in terms of a single optical phonon coordinate. The problem considered in this chapter is that of finding the time dependence of this coordinate when anharmonic terms are included in the potential energy of the lattice.

Quantum theory is used exclusively in this chapter. The crystal, initially at room temperature, is assumed to undergo a slight disturbance caused by introduction of the interaction. The resulting motion of the optical phonon coordinate is found by the methods of Green's functions. The result, for the dielectric susceptibility, is that an additional complex function of frequency, or "self-energy" is added to the denominator in (5.6.4), resulting from a damping of the motion associated with the optical phonon. The self-energy contains all of the effects of multiphonon

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interactions, which are due to anharmonicity, as mentioned in the introduction. To compute the self-energy, the quasi-harmonic eigenvalues and eigenvectors computed in Chapter IV are used, together with a parameter determining the magnitude of the anharmonicity.

6.1 The anharmonic crystal in thermal equilibrium

The total Hamiltonian of the KI lattice, given in expanded form in (3.2.2), can be written

$$H = H_0 + H_A.$$  \hspace{1cm} (6.1.1)

$H_0$ is the harmonic part, which was transformed to the form (3.5.10), in terms of normal coordinates and momenta $Q(k_j)$ and $P(k_j)$.

$H_A$ is the anharmonic part of the potential energy series, which for the purposes of this chapter, we terminate with the quartic, or fourth order term $H_A^{(4)}$ in the expansion, so that

$$H_A = H_A^{(3)} + H_A^{(4)}.$$  \hspace{1cm} (6.1.2)

Since only the third order, or cubic term $H_A^{(3)}$ will be needed to perform the computation described later in this chapter, we consider that term, written in terms of the normal coordinates.

It is, in terms of coordinates $A(k_j)$ defined in (3.6.10),
\[ H^{(3)}_\Lambda = \sum_{\vec{K}_{11}} \sum_{\vec{K}_{22}} \sum_{\vec{K}_{33}} V(\vec{K}_{11}, \vec{K}_{22}, \vec{K}_{33}) \]

(6.1.3)

\[ \times A(\vec{K}_{11}) A(\vec{K}_{22}) A(\vec{K}_{33}). \]

The coefficients \( V(\vec{K}_{11}, \vec{K}_{22}, \vec{K}_{33}) \) are given by

\[ V(\vec{K}_{11}, \vec{K}_{22}, \vec{K}_{33}) = \left( \frac{\hbar^3}{8 \omega(\vec{K}_{11}) \omega(\vec{K}_{22}) \omega(\vec{K}_{33})} \right)^{\frac{1}{2}} \phi(\vec{K}_{11}, \vec{K}_{22}, \vec{K}_{33}), \]

(6.1.4)

where the coefficients \( \phi(\vec{K}_{11}, \vec{K}_{22}, \vec{K}_{33}) \) are the expansion coefficients for the potential in terms of the coordinates \( Q(\vec{K}) \), and are given by

\[ \phi(\vec{K}_{11}, \vec{K}_{22}, \vec{K}_{33}) = \sum_{\alpha_1} \sum_{\alpha_2} \sum_{\alpha_3} \frac{1}{6N^{3/2}} \]

\[ \times \frac{m_{\alpha_1}(s_1|\vec{K}_{11})}{\sqrt{m_{s_1}}} \frac{m_{\alpha_2}(s_2|\vec{K}_{22})}{\sqrt{m_{s_2}}} \frac{m_{\alpha_3}(s_3|\vec{K}_{33})}{\sqrt{m_{s_3}}} \]

(6.1.5)

\[ \times \exp(i\vec{K}_1 \cdot \vec{L}_1 + i\vec{K}_2 \cdot \vec{L}_2 + i\vec{K}_3 \cdot \vec{L}_3) \]

\[ \times \phi \alpha_1 s_1 \alpha_2 s_2 \alpha_3 s_3 (\vec{L}_1, \vec{L}_2, \vec{L}_3). \]
Due to the periodicity of the lattice, expressed by (3.2.4),

\[ \phi(k_{11}, k_{22}, k_{33}) \]

which is similar to (3.4.5), for the harmonic coefficients. The fourth order, and higher coefficients can be treated in a completely analogous manner.

Consider a crystal, having the total Hamiltonian (6.1.1), in thermal equilibrium at an absolute temperature, T. In the theory of quantum statistical mechanics, the thermal average of any linear operator, \( \mathcal{O} \), can be expressed

\[ \langle \mathcal{O} \rangle = \frac{\text{Tr}(\mathcal{O} \rho)}{\text{Tr}(\rho)} \]

where the triangular brackets \( \langle \rangle \) denote thermal average, and \( \text{Tr} \) denotes trace. \( \rho \) is the density operator,

\[ \rho = \exp(-\beta H). \]

Here \( \beta = 1/k_B T \), where \( k_B \) is the Boltzmann constant.

---

6-2 The dielectric susceptibility in terms of a retarded Green's function

Consider the response of the crystal, initially in thermal equilibrium, under the application of an electric field of frequency $\omega$. The interaction Hamiltonian and polarization per unit volume, as given by (5.5.14) and (5.5.15) take the quantum mechanical form

$$H_{\text{INT}}(t) = -\frac{\hbar}{2 \omega_h(0j)} \mu \frac{\hbar}{2N} A^\dagger(0jt) \exp(-i\omega t)$$

and

$$m^1(\omega) \exp(-i\omega t) = \frac{\tilde{Z}_d}{v_c} \left( \frac{\hbar}{2N\mu \omega(0j)} \right)^{1/2} \langle A(0jt) \rangle,$$

where the $0$, as a vector argument, means a vector of small magnitude in the $x$ direction. The $\hbar$ subscript on $\omega_h(0j)$ is to emphasize that the true harmonic frequency, not the quasi-harmonic frequency, is applicable here. The coordinates are considered to be time dependent operators in the Heisenberg time representation. A Heisenberg operator $\mathcal{O}(t)$ is given in terms of the time independent Schrödinger operator $\mathcal{O}$ by

$$\mathcal{O}(t) = \mathcal{O}(0) \exp\left(-i\int_0^t H_{\text{INT}}(t') dt'\right).$$

---

$^2$Messiah, op. cit., p. 314.
\[ \mathcal{S}(t) = \exp\left(iHt/\hbar\right) \mathcal{S} \exp\left(-iHt/\hbar\right), \quad (6.2.3) \]

where \( H \) is a time independent Schrödinger Hamiltonian, in this case, the total lattice Hamiltonian. The triangular brackets again denote a thermal ensemble average.

Kubo\(^3\) has shown that if a Hamiltonian of the form \( \dot{H}^{\omega}_{\text{INT}}(t) \) in (6.2.1) is applied as a perturbation to a system initially in thermal equilibrium with Hamiltonian \( H \), then the thermal average \( \langle A(0j|t) \rangle \) is given by

\[ \langle A(0j|t) \rangle = -\mathcal{Z}_d \left(-1/\hbar\right) \left( \frac{k_B N}{2\omega_h(0j)\mu} \right) g_R(\omega) \exp(-i\omega t), \quad (6.2.4) \]

where \( g_R(\omega) \) is the Fourier transform of the retarded Green's function, \( G_R(t) \). The retarded Green's function \( G_R(t) \) is defined as

\[ G_R(t) = \Theta(t) \left\langle [A(0j|t), A^\dagger(0j|0)] \right\rangle, \quad (6.2.5) \]

where the average is taken with respect to the lattice Hamiltonian \( H \). The rectangular brackets denote commutation, and \( \Theta(t) \) is the step function given in (1.1.13). In terms of the retarded Green's function then, the susceptibility is, from (6.2.2) and (6.2.4),

\(^3\text{R. Kubo, Phys. Soc. Jap. 12, 570 (1957).}\)
The problem of finding the susceptibility is thus reduced to finding the retarded Green's function.

6-3 Thermodynamic Green's functions

For evaluation of the Fourier transform of the retarded Green's function, it is convenient to define the thermodynamic Green's function of the variable, \( u = \frac{it}{\hbar} \), on the real interval \(-\beta < u < \beta\):

\[
G(u) = \left\langle P(A(0j|\mathcal{H}u/i)A(0j|0)) \rightangle ,
\]

where \( P \) is the time-ordering operator, which orders all operators in decreasing time order, from left to right. The function has a Fourier expansion in its interval of definition:

\[
G(u) = \sum_n g(i\omega_n) \exp(iu\omega_n),
\]

where \( g(i\omega_n) \) is a Fourier coefficient, which can be considered a function of the discreet variable \( i\omega_n \).

Using the representation \( G_R(\gamma) = G_R(t) \exp(-\gamma|t|) \) (see section 1-1), Cowley\(^4\) shows that

\[^4\text{R. A. Cowley, Advances in Physics 12, 421 (1963).}\]
where \( g(\omega + 1\eta) \) is the analytic continuation of \( g(i\omega_n) \). In succeeding work, the subscript \( \eta \) on the retarded Green's function and its transform will be omitted, although it is convenient to use this representation explicitly in the formulas.

6-4 The perturbation expansion and the self-energy

A perturbation expansion to be considered here enables the Green's functions for an anharmonic crystal to be calculated. The "interaction" form of the operator \( \mathcal{V} \) is defined as

\[
\tilde{\mathcal{V}}(u) = \exp(uH_o) \mathcal{V} \exp(-uH_o),
\]

(6.4.1)

where \( H_o \) is the harmonic portion of the Hamiltonian. This definition is analogous to that of the interaction operator used in ordinary quantum mechanics.\(^5\) The operator \( \mathcal{V}(u) \) can, in principle, be found for any operator \( \mathcal{V} \) which can be expanded in terms of the creation and annihilation operators \( a(\vec{k}) \) and \( a^\dagger(\vec{k}) \), due to (3.6.3). The anharmonic Hamiltonian is one such operator, due to (3.6.10) and 6.1.3).

---

\(^5\) Messiah, op. cit., p. 321.
The expansion is

\[ G(u) = \left< P(A(0j|u)A^+(0j|0)) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \right> \]

\[ \times \left< \int_{0}^{\beta} du_1 \cdots \int_{0}^{\beta} du_n H_A(u_1) \cdots H_A(u_n) \right> \]

where the subscript \( o \) indicates that the harmonic Hamiltonian \( H_0 \)
is used in the density operator (6.1.6). The subscript \( c \) denotes
a restriction in the choice of contributions which should be
considered. This is of no concern in the present limited discussion.

Abrikosov et al.\(^6\) consider the evaluation of the expansion
for general types of operators, while Cowley\(^4\) and Maradudin and
Fein\(^7\) discuss the explicit evaluation for the particular lattice
Hamiltonian considered here. Cowley\(^8\) also presents a summary of
the problem of anharmonicity in crystals and the application of
Green's functions.

The procedure in evaluating the expansion is first to expand
the anharmonic Hamiltonian in terms of creation and annihilation

\(^6\)A. A. Abrikosov, L. P. Gor'kov, and I. Ye. Dzyaloshinskii,
Quantum Field Theoretical Methods in Statistical Physics (Pergamon


\(^8\)R. A. Cowley, in Phonons in Perfect Lattices and in Lattices
with Point Imperfections, ed. by R. W. H. Stevenson (Plenum Press,
operators, using (6.1.3) and (3.6.10), as mentioned. Using the properties of the creation and annihilation operators given in (3.6.3), it is shown by Abrikosov et. al.\(^9\) that the average of a time-ordered product of operators can be expressed as a sum of products of time-ordered averages of pairs of operators. Each such pair defines a harmonic Green's function, which can be easily evaluated. To carry out the integration, all Green's functions are expanded in their Fourier series form, and a diagram technique aids in the evaluation of \(g(i\omega_n)\).

The result\(^4\) of consideration of an infinite set of terms in the expansion (6.4.2) is

\[
g(i\omega_n) = \frac{1}{\beta h} \frac{2\omega(0j)}{\omega_h^2(0j) - (i\omega_n)^2 + 2\omega_h(0j)D(0j,i\omega_n)}.
\]  

(6.4.3)

The function \(D(0j,i\omega_n)\) is the "self-energy." It can be expressed as a sum of three parts,

\[
D(0j,i\omega_n) = \Delta_1(0j) + \Delta_2(0j) + D_3(0j,i\omega_n),
\]  

(6.4.4)

where \(\Delta_1(0j)\) and \(\Delta_2(0j)\) are contributions due to thermal expansion and fourth order anharmonicity respectively. Because they are real and independent of frequency, it is not necessary

\(^9\)Abrikosov et. al., op. cit., p. 106.
to compute them in this work, as will be shown later in this section. The function $D_3(\epsilon_j, i\omega_n)$ is due to third order anharmonicity alone. It is

$$D_3(\epsilon_j, i\omega_n) =$$

$$-\frac{18}{\hbar^2} \sum \sum |V(\epsilon_j, \vec{k}_1 j_1, \vec{k}_2 j_2)|^2 F(\omega_1, \omega_2, i\omega_n),$$

where

$$F(\omega_1, \omega_2, i\omega_n)$$

$$= (n_1 + n_2 + 1) \left[ \frac{1}{(\omega_2 + \omega_1 + i\omega_n)} + \frac{1}{(\omega_1 + \omega_2 - i\omega_n)} \right]$$

$$- (n_2 - n_1) \left[ \frac{1}{(\omega_2 - \omega_1 + i\omega_n)} + \frac{1}{(\omega_2 - \omega_1 - i\omega_n)} \right].$$

The frequency $\omega_1$ and population number $n_1$ are

$$\omega_1 = \omega (\vec{k}_1 j_1),$$

$$n_1 = (\exp(\beta \hbar \omega_1) - 1)^{-1},$$

and similarly for $\omega_2$ and $n_2$. The lattice frequencies to be used in this expression are the quasi-harmonic frequencies, which
were calculated in Chapter IV (see the introductory remarks of Chapter III).

On extending the function $g(i\omega_n)$ in (6.4.3) analytically, by substituting $\omega + i\eta$ for $i\omega_n$, the dielectric susceptibility, from (6.2.6) and (6.3.3) becomes

$$\chi^1(\omega) = \frac{\widetilde{Z}_\perp^2}{\mu v_c \left[ \omega_h^2(0j) - \omega^2 + 2\omega_h(0j)\delta(0j, \omega + i\eta) \right]}.$$

This differs from (5.6.4) only by the self-energy contribution. Since $\eta$ is very small, it is obvious from (6.4.6) that there are resonances in the self-energy for frequencies $\omega = \omega_1 \pm \omega_2$.

The interpretation of this in terms of quasi-particles is that an incoming photon interacts directly with the $\mathbf{K} = 0$ optical phonon, which in turn interacts with two lattice phonons, in such a way that energy is conserved for the net process and the initial photon energy is given to one or both of the two lattice phonons. Due to the factor $\Delta(0 + \mathbf{k}_1 + \mathbf{k}_2)$ in the expansion coefficients, wave vector, or momentum, is also conserved. The incoming photon has momentum essentially zero, so the two lattice phonons have momentum equal in magnitude, but opposite in direction. The latter fact simplifies the self-energy, so that the frequency dependent part can be written
The self-energy is usually separated into real and imaginary parts, writing

\[ D_3(0j, \omega + i \eta) = \frac{-18}{\hbar^2} \]

(6.4.9)

\[ \sum_{\vec{k}j_1 j_2} N|v(0j, \vec{k}j_1, -\vec{k}j_2)|^2 F(\omega_1, \omega_2, \omega + i \eta). \]

where \( \Delta(0j, \omega) \) and \( \Gamma(0j, \omega) \) are the frequency shift and damping function, respectively. Separating \( D_3(0j, \omega + i \eta) \) in a similar manner, it follows that

\[ \Delta(0j, \omega) = \Delta_1(0j) + \Delta_2(0j) + \Delta_3(0j, \omega), \]

(6.4.11)

and

\[ \Gamma(0j, \omega) = \Gamma_3(0j, \omega). \]

In the limit \( \eta \to 0 \), the real and imaginary parts of \( D_3(0j, \omega + i \eta) \) are frequently expressed in terms of the principal part and delta function, by applying the formula (see section 1-1)

\[ \lim_{\eta \to 0} \frac{1}{x + i \eta} = \left( \frac{1}{x} \right) -i \pi \delta(x) \]

(6.4.12)

to the reciprocal frequency sums and differences in (6.4.6).
The eigenfrequency was determined from experimental data (see section 2.3) as the frequency for a maximum in the quantity $n_k$, and later identified as the quasi-harmonic TO mode frequency, $\omega(0j)$. Using (5.1.6) and (5.1.7), this frequency must also give the maximum in the susceptibility (6.4.8), so that

$$\omega^2(0j) = \omega^2_h(0j) + 2\omega_h(0j) \Delta(0j, \omega(0j)).$$  \hspace{1cm} (6.4.13)

This is the relation given by Cowley\textsuperscript{4} between the quasi-harmonic frequency $\omega(0j)$, and the true harmonic frequency $\omega_h(0j)$.

Using (6.4.13), (6.4.8) can be written

$$\chi^1(\omega) = \frac{\frac{2^2/\mu}{\nu_c}}{\omega^2(0j) - \omega^2 + 2\omega_h(0j)D'(0j, \omega + i\eta)},$$  \hspace{1cm} (6.4.14)

where

$$D'(0j, \omega + i\eta) = \left[\Delta_3(0j, \omega) - \Delta_3(0j, \omega(0j))\right] = i\Gamma(0j, \omega)$$

$$= \Delta'(0j, \omega) - i\Gamma(0j, \omega).$$  \hspace{1cm} (6.4.15)

The susceptibility (6.4.14) is actually independent of $\omega_h(0j)$, since the self-energy is inversely proportional to $\omega_h(0j)$. 
6-5 The cubic expansion coefficients

In order to compute the self-energy, the cubic expansion coefficient $\phi (0j, \vec{k}_j, -\vec{k}_2)$ must be evaluated from (6.1.5). Again, the "0" vector is in the x-direction, and the index j refers to the transverse optical mode for polarization in the z-direction. Johnson evaluated this coefficient, including only the short range, nearest neighbor potentials. The result is, in compact form,

$$\phi (0j, \vec{k}_j, -\vec{k}_2) = \left( \frac{-1}{3\pi^{3/2} \sqrt{m_1 m_2}} \right) L(\alpha\beta\gamma, \vec{k}_j, \vec{k}_2), \quad (6.5.1)$$

where $L(\alpha\beta\gamma, \vec{k}_j, \vec{k}_2)$ is a function of the wave vector $\vec{k}$, polarization vectors $\vec{m}(\vec{k}_j)$ and $\vec{m}(\vec{k}_2)$, and derivatives of the short range nearest neighbor potential. It is

$$L(\alpha\beta\gamma, \vec{k}_j, \vec{k}_2) = \left[ \left( A_3 / 2 \right) w_{\alpha\omega} (\vec{k}_j, \vec{k}_2) \right.$$

$$+ \left( B_3 / 2 \right) (w_{\rho\beta} (\vec{k}_j, \vec{k}_2) + w_{\gamma\gamma} (\vec{k}_j, \vec{k}_2)) \sin(k_{\alpha} x) \sin(k_{\beta} y) \sin(k_{\gamma} z) \right], \quad (6.5.2)$$

$$+ B_3 \left[ w_{\alpha\rho} (\vec{k}_j, \vec{k}_2) \sin(k_{\beta} x) + w_{\alpha\gamma} (\vec{k}_j, \vec{k}_2) \sin(k_{\gamma} x) \right],$$

where

$^{10}$Johnson, op. cit., p. 138.
\[ \mathcal{W}_{\alpha\alpha'}(R_{j_1j_2}) = \]

\[ \left( m_{\alpha}(1|R_{j_1}) m_{\alpha}(2|R_{j_2}) + m_{\alpha}(1|R_{j_1}) m_{\alpha}(2|R_{j_2}) \right) \]

\[ - \left( m_{\alpha}(2|R_{j_1}) m_{\alpha}(1|R_{j_2}) + m_{\alpha}(2|R_{j_1}) m_{\alpha}(1|R_{j_2}) \right), \]

and the constants \( A_3 \) and \( B_3 \) are given in terms of the nearest neighbor short range potential of section 4-1 by

\[ A_3 = \frac{\frac{\partial^3 V_{12}^R(r)}{\partial r^3}}{d} \]

and

\[ B_3 = \frac{1}{d^2} \left. \frac{\partial^2 V_{12}^R(r)}{\partial r^2} \right|_d - \frac{1}{d} \left. \frac{\partial V_{12}^R(r)}{\partial r} \right|_d - \frac{1}{d} \left. \frac{\partial^2 V_{12}^R(r)}{\partial r^2} \right|_d. \]

The constant \( A_3 \) cannot be determined from the harmonic model alone. However, the short range potential is frequently assumed to have the form

\[ V_{12}^R(r) = C \exp(-Dr), \]

where \( C \) and \( D \) are positive constants. On this basis,

\[ A_3 = A_{12}^2/2dB_{12}. \]
The parameters $A_{12}$ and $B_{12}$ appropriate here are the $0^\circ K$ values, so the $90^\circ K$ values of section 4-5 are better than the room temperature values.

6-6 Simplification of the self-energy due to cubic symmetry

From (6.4.9), (6.1.4), and (6.5.1), the frequency dependent part of the self-energy can be written

$$D_3(0j, \omega + i\gamma) = \frac{-\hbar}{4\mu m_1 m_2 \omega_h(0j)} \sum_{\mathbf{k}} L^2(zxy, \mathbf{R}_{j_1j_2}) F(\omega_1, \omega_2, \omega + i\gamma)/\omega_1 \omega_2.$$ (6.6.1)

The frequencies $\omega_1$ and $\omega_2$ in the function $F(\omega_1, \omega_2, \omega + i\gamma)$ should be the quasi-harmonic frequencies, as mentioned. The frequencies in the denominator, resulting from the transformation (6.1.4) should be the true harmonic frequencies, but the quasi-harmonic values were used in this work.

In the above expression, the $\mathbf{k}$ summation is over the entire Brillouin zone. Denoting by $\{\mathbf{k}\}$ the set of wave vectors in the irreducible element (see section 4-5), (6.6.1) can be written

$$D_3(0j, \omega + i\gamma) = \frac{-\hbar}{4\mu m_1 m_2 \omega_h(0j)} \sum_{\mathbf{k}} \sum_{j_1j_2} \sum_{\sigma} L^2(zxy, \mathbf{R}_{j_1j_2}) F(\omega_1, \omega_2, \omega + i\gamma)/\omega_1 \omega_2.$$ (6.6.2)
where $T_g$ is one of the 48 operators, including the identity operator, which generate quantities for corresponding values of $\vec{k}$ in the entire zone from those in the irreducible element. The frequencies remain invariant, while the eigenvectors undergo the same orthogonal transformation as the wave vector. A careful examination of (6.5.2) and (6.5.3) reveals that there are only three distinct values of $[L(xxy, \vec{k} j_1 j_2)]$, and these are obtained by cyclicly permuting the xyz indices, so that

$$D_3(0j, \omega + i\eta) = \frac{-4\hbar}{N\mu m_1 m_2 \omega_h(0j)} \sum_X \sum_{\{\vec{k}\} j_1 j_2} \sum_{\alpha} L^2(\alpha \beta \gamma, \vec{k} j_1 j_2) \frac{F(\omega_1, \omega_2, \omega + i\eta)}{\omega_1 \omega_2},$$

where it is to be understood that the order of $\alpha \beta \gamma$ is $xyz$, $yze$, and $zxy$, for $\alpha = x, y, \text{ and } z$, respectively.

6-7 **Computer computation of the self-energy**

The computer program which was used to calculate the self-energy was based on (6.6.3) with $F(\omega_1, \omega_2, \omega + i\eta)$ and $L(\alpha \beta \gamma, \vec{k} j_1 j_2)$ defined in (6.4.6) and (6.5.2), respectively. The 48 values of $\vec{k}$ in the irreducible zone element were those...
for which the calculation of the eigenvectors and eigenvalues was described in section 4-5. To account for the fact that some of the volume elements represented by the selected points were not entirely in the irreducible element, but shared by other elements, the contribution for each $\vec{K}$ had to be divided by a quantity called $M(\vec{K})$. The values of this quantity for points on the various boundaries and edges of the element are given in Table 6. For the points on the zone boundary, those for $K_1 = 10$ or $K_1 + K_2 + K_3 \geq 15$, an additional factor of two was required. All points not fitting into any of these categories had $M = 1$.

**TABLE 6**

**RECIprocal Weights for Wave Vectors in the Irreducible Element of the Brillouin Zone**

<table>
<thead>
<tr>
<th>Wave vector indicies $(K_1 K_2 K_3)$</th>
<th>Reciprocal weight $M^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 0</td>
<td>48</td>
</tr>
<tr>
<td>$K_1$ 0 0</td>
<td>8</td>
</tr>
<tr>
<td>$K_1$ $K_1$ 0</td>
<td>4</td>
</tr>
<tr>
<td>$K_1$ $K_1$ $K_1$</td>
<td>6</td>
</tr>
<tr>
<td>$K_1$ $K_2$ 0 $K_2 \neq K_1$</td>
<td>2</td>
</tr>
<tr>
<td>$K_1$ $K_1$ $K_3$ $K_3 \neq K_1$</td>
<td>2</td>
</tr>
<tr>
<td>$K_1$ $K_2$ $K_2$ $K_2 \neq K_1$</td>
<td>2</td>
</tr>
</tbody>
</table>

*See text above.*
Frequency units of cm\(^{-1}\) were used in the calculation. Using \(\nu\) instead of \(\omega\) for frequencies in these units,

\[
2 \nu_h p_3 (0j, \nu + 1\eta) = \sum_{[\hat{\mathbf{R}}]} \sum_{j_1 j_2} \chi L^2 (\alpha \beta \gamma, \hat{\mathbf{k}}_{j_1 j_2}) \frac{F(\nu_1 \nu_2, \nu + 1\eta)}{\nu_1 \nu_2 \mu(\hat{\mathbf{R}})} ,
\]

where \(\nu_h = \omega_h (0j) / 2\pi c\), and the self-energy is in units of cm\(^{-1}\) also. Taking \(A_3\) and \(B_3\) in units of \(10^8 \times \varepsilon^2 / \nu c\), the constant \(J\) is

\[
J = \frac{8h (10^8 \varepsilon^2 / \nu c)^2}{1000 \mu m_1 m_2 (2\pi c)^5} = 3820 .\]

The constant \(J\) was read into the program after the entire computation was completed. For computation of the population numbers at \(T = 300^\circ\) K,

\[
\sigma \hbar \omega = 2\pi c \sigma \hbar \nu = 0.00475 \nu .\]

The self-energy was computed for a discreet set of frequencies, taken at increments of \(\Delta \nu = 2.5\) cm\(^{-1}\). The real and imaginary parts were computed separately, by taking the real and imaginary parts of the quantity \((x + 1\eta)^{-1}\) as in (1.1.15), where \(x\) here is a lattice frequency sum or difference, as in (6.4.6).
The value $\eta = 2.5\, \text{cm}^{-1}$ was used, giving a half width of the "delta function" peak associated with a given frequency difference as $2\eta = 5\, \text{cm}^{-1}$ (see (6.4.12). The choice of value for $\eta$ was one which would result in "smooth" functions with the limited density of frequency differences available from the 1000 lattice vectors, but not so large as to unduly spread the structure which could be resolved. The effective resolution, $5\, \text{cm}^{-1}$, is the same as the experimental resolution in the frequency interval under consideration (see section 2-3).

The contributions to the self-energy for a given $(\vec{k}_{j_1,j_2})$ were computed for all frequencies $\nu_1$ before proceeding to the next value of $(\vec{k}_{j_1,j_2})$. Storage cells were first defined for the real and imaginary parts of $D_3(0j, \nu_1 + i\eta)$ for each $\nu_1$. Then the wave vector integers $(K_1, K_2, K_3)$, and the eigenvectors and eigenvalues for the first value of $\vec{k}$ were placed in storage.

Consider a given $(j_1,j_2)$ for this wave vector. The contribution to the self-energy for a given frequency $\nu_1$ depends on the eigenvectors $m(\vec{k}_{j_1})$ and $m(\vec{k}_{j_2})$ through $L(\alpha \varphi \sigma, \vec{k}_{j_1,j_2})$ and on the respective frequencies through $F(\nu_1, \nu_2, \nu_1 + i\eta)/\nu_1 \nu_2$

The frequency $\nu_1$ is only involved in the latter, so that the same $L(\alpha \varphi \sigma, \vec{k}_{j_1,j_2})$ was used for all frequencies $\nu_1$ for a given $(j_1,j_2)$. The contribution to the self-energy for frequency $\nu_1$ due to $(j_1,j_2)$ was computed and placed in the appropriate $\nu_1$ storage cell, adding it to the contents from all previous $(j_1,j_2)$
combinations for that $\mathbf{k}$. When all $(j_1 j_2)$ combinations for the wave vector $\mathbf{k}$ were exhausted, the eigendata for the next wave vector was read in, erasing that for the first. The contents of the $\mathcal{U}_i$ cells were, of course, kept, to be added to the contribution for the next $(k_1 j_1 j_2)$. The procedure was repeated until all wave vectors were exhausted.

The computational accuracy was checked by use of a convenient relation,

$$2v_h \int_0^\infty d\nu \Gamma'(0j,\nu) = \sum_{\{k\}} \sum_{j_1 j_2} \sum_{\alpha} \frac{1}{M(k) \nu_1 \nu_2} \frac{L^2(\alpha/\nu, k_1 j_1 j_2)}{(n_1 + n_2 + 1) + |n_2 - n_1|}.$$  

(6.7.4)

This can be proved through use of the relation (6.4.12). The summation on the right side was made along with, and in the same manner as the self-energy summation. The integral on the left was approximated by adding the computed values of $\Gamma'(0j,\nu_i)$ for all 100 frequencies, and multiplying the result by $\Delta\nu = 2.5\text{cm}^{-1}$. The equality was found to hold to within two percent.

The computed results for $\Delta'(0j,\nu)$ and $\Gamma'(0j,\nu)$ are shown in Fig. 8. The values $A_3 = -13.6 \times 10^8 \text{e}^2/\nu_c$ and $B_3 = 2.04 \times 10^8 \text{e}^2/\nu_c$. 


Figure 8. The modified frequency shift, $\Delta'(0j,\nu)$, and damping function, $\Gamma(0j,\nu)$, for the long wavelength transverse optical phonon mode in KI. The significance of $\Delta_3(0j,\nu_0) = -7.47 \text{cm}^{-1}$ is discussed in the text.
were used for the potential derivatives. This choice of the values of $A_3$ and $B_3$ is discussed in the next section. The frequency shift $\Delta'(0,j,\nu)$ was made to be zero at $\nu = \nu_o$ by subtracting $\Delta_3(0,j,\nu_o)$ from $\Delta_3(0,j,\nu)$, as discussed in section 6-4. The value $\Delta_3(0,j,\nu_o) = -7.47\text{cm}^{-1}$ is shown in Fig. 8 also. It is interesting to note that $\Delta'(0,j,\nu)$ is zero at the frequencies where $\Gamma(0,j,\nu)$ has its relative maximum values, for the peaks on both sides of the eigenfrequency. The behavior of the imaginary part looks, to a gross approximation, like two delta function peaks, and the real part shows the principal value behavior accompanying these peaks, in accordance with the Kramers-Kronig relations.

6-8 The optical constants and comparison with experimental data

The infrared complex index of refraction $\mathcal{N}(\nu)$ can be calculated from the ionic dielectric susceptibility, as given in (6.4.14), using the self-energy $\Delta'(0,j,\nu) - \Gamma(0,j,\nu)$, calculated in section 6-7. The resulting expression for $\mathcal{E}(\nu)$, the square of $\mathcal{N}(\nu)$ is

$$
\mathcal{E}(\nu) = \mathcal{E}(\infty)
$$

(6.8.1)

$$
+ \frac{[\mathcal{E}(0) - \mathcal{E}(\infty)](\nu_o^2 + 2\nu_h \Delta'(0,j,0))}{\nu_o^2 - \nu^2 + 2\nu_h \left[ \Delta'(0,j,\nu) - \Gamma(0,j,\nu) \right]},
$$
where, in terms of the shell model parameters,

$$
(\varepsilon(0) - \varepsilon(\infty)) (\nu_0^2 + 2\nu_h \Delta(0j,0)) = \frac{4\pi Z^2_\perp}{\mu v_c^2 (2\pi c)^2} .
$$

(6.8.2)

A point-by-point computer program based on (6.8.1) was written to calculate $\mathcal{N}(\nu)$.

There are three visible adjustable parameters in (6.8.1), namely $\nu_0$, the eigenfrequency, and $\varepsilon(\infty)$ and $\varepsilon(0)$, the high and low frequency dielectric constants. Included in the self-energy are the derivatives of the nearest neighbor short range interionic potential, $A_3$ and $B_3$. The lattice frequencies and polarization vectors are dependent only on the harmonic part of the potential and are considered here to be pre-determined. The constant $B_3$ is dependent only on the first and second derivatives of the potential, and is thus fixed by the harmonic model. The eigenfrequency $\nu_0$ used in the calculation was the experimentally determined value $\nu_0 = 101\text{cm}^{-1}$. The dielectric constants used were $\varepsilon(\infty) = 2.69$ and $\varepsilon(0) = 5.02$; the experimentally determined values also. These values were used, even though the shell model, using the parameters needed to give correct lattice frequencies, predicts lower values for $\varepsilon(\infty)$ and $\varepsilon(0)$ (see Table 5, section 5-6). The parameter $A_3$ was also adjusted to give the best agreement with experiment.
Figures 9 and 10 show the calculated values of \( n(\nu) \) and \( k(\nu) \), compared with the experimental values presented earlier in Fig. 5. The value of the third derivative of the short range potential, \( A_3 = -13.6 \times 10^8 \, e^2/\nu_c = -3.58 \times 10^{12} \, \text{erg-cm}^{-3} \), was used. This was the value needed to give the best fit to the experimental value of \( k \) near and at the eigenfrequency. As an indication of the sensitivity of \( k(\nu_0) \) to \( A_3 \), the ratio

\[
\frac{1}{A_3} \frac{\langle \nu_0 \rangle}{\langle k(\nu_0) \rangle} \approx -0.2 \quad (6.8.3)
\]

was found to hold. Choosing \( A_3 \) to give \( k(\nu_0) \) correctly gave good values for frequencies greater than \( \nu_0 \). The poor agreement at about 190 cm\(^{-1}\) and above is to be expected, since \( \Gamma(0j,\nu) \), when calculated on the basis of only 3-phonon processes (using only \( H_A^{(3)} \)), drops to zero in this range, where higher order processes would be expected to give some contribution. This is because there is a maximum possible frequency sum \( \nu_1 + \nu_2 \), consistent with the selection rules determined by (6.5.3), of about 190 cm\(^{-1}\).

The higher magnitude of the high frequency structure in the calculated \( k \) compared to the experimental \( k \) is consistent with the corresponding results for the index, where the structure in the theoretical curve is much more pronounced. The structure on
Figure 9. The experimental and calculated values of the index of refraction, $n(\nu)$, for KI.
Figure 10. The experimental and calculated values of the extinction coefficient, $k(\nu)$, for KI.
the low frequency side appears only for the calculated \( n \) in Fig. 9, but appears also for the experimental \( n \), for the scale used in Fig. 6, Chapter II. There, the structure for the very low frequencies causes the validity of the linear extrapolation to zero frequency to be questionable. The linear extrapolation is valid, only for frequencies low enough so that the self-energy is very small.

The parameters \( \xi(\infty) \) and \( \xi(0) \), as discussed, were chosen to give good agreement with the experimental data, rather than to be consistent with theoretical predictions based on the shell model. The shell model, then, was actually used only to generate lattice frequencies. The justification for the use of the frequencies so computed is the agreement of these frequencies with those measured in the neutron diffraction experiments of Dolling et. al.\(^{11}\)

In effect then, measured frequencies, and measured values of \( \xi(\infty) \) and \( \xi(0) \) have been used. The shell model, at least in the case of KI, apparently is not a good enough model of the lattice so that a single set of parameters can predict all properties correctly. In the case of KBr and NaI,\(^{12}\) the dielectric constants are predicted much more satisfactorily by a shell model based on lattice frequencies. As noted in section 5-6, the ratio \( \xi(0)/\xi(\infty) \)

\(^{11}\)Dolling et. al., op. cit.

\(^{12}\)Chapter III, footnote 4.
for KI compares favorably with the experimental value. Anharmonicity causes the value of \( \epsilon(0) \) to be modified slightly. According to (6.8.2), \( \epsilon(0) - \epsilon(\infty) \) is inversely proportional to \( \nu_0^2 + 2\nu_h \Delta(0j,0) \) rather than to \( \nu_0^2 \). The corrected value of \( \epsilon(0) \) for the shell model is 4.43, so that \( \epsilon(0)/\epsilon(\infty) = 1.85 \), very close to the experimental value of 1.86.

The general agreement between theory and experiment, with the parameters chosen as discussed above, can be considered quite good. For the low frequency side of \( \nu_0 \), very little improvement is needed in the calculated values. On the high frequency side, the right number of subsidiary peaks appear in the calculated curves, and they fall at very nearly the correct frequencies of 145 and 155\text{ cm}^{-1}, although the magnitudes of n and k are incorrect. The correctness of these frequencies is gratifying, in view of the effort which was necessary to calculate accurate lattice frequencies and eigenvectors. The correct lattice frequencies provide a firm, perhaps necessary, foundation on which to base a serious comparison with experimental data. Unfortunately, however, it is difficult to see how agreement can be improved when it is not good.

Although a particular choice of the parameter \( A \) resulted here in reasonably good agreement, the correctness of the value so determined is in question, since it is reduced in magnitude by nearly a factor of two from that predicted by (6.5.6). Using parameters from the harmonic shell model discussed in Chapter IV,
the value is \( A_3 = -6.70 \times 10^{12} \text{erg-cm}^{-3} \). The value predicted from the parameters published by Born and Huang,\(^{13}\) using the exponential potential (6.5.5), with parameters chosen to give the lattice constant and compressibility, is \( A_3 = -4.45 \times 10^{12} \text{erg-cm}^{-3} \), which is closer to the value determined here. The shell model value, however, according to Dolling,\(^{11}\) predicts the thermal expansion coefficient, and other quantities dependent on anharmonicity to within 10 to 20 percent of the experimental values. Similar results were obtained for KBr and NaI, using shell model parameters.\(^{14,4}\)

The optical constants of KBr, as computed on this basis by Cowley et al.,\(^{14}\) and those of KCl computed by Johnson,\(^{15}\) appear to be in reasonable agreement with the measurements of Johnson\(^{15}\) for these crystals. However, the lack of availability of reliable phonon frequencies for KCl, and the lack of reliable data for the optical constants of KCl in the lower frequency region casts some doubt on the validity of the comparison between experimental and theoretical data.

The low value of \( A_3 \) needed for agreement with the results of this experiment naturally led to questions about the validity of the calculation which was carried out. After a very extensive check of the entire self-energy and optical constants calculations,

\(^{13}\)M. Born and K. Huang, op. cit., p. 26.


\(^{15}\)Johnson et al.
it appears that the calculation was carried out correctly, within the limitations of the theory. Because of the complexity of the calculation, however, it is difficult to be absolutely sure of this.

The limitations of the theory used here, and also used by Johnson, have been discussed by him.\textsuperscript{16} Perhaps the most severe limitation is the restriction to third order anharmonicity in the frequency-dependent part of the self-energy. The effects of higher order terms in the anharmonic Hamiltonian $H_A$ have been included in the theoretical analysis of Wallis et. al.\textsuperscript{17} It is clear that their inclusion would only add to $\Pi(0_j, \nu_0')$, causing an even lower value of $A_3$ to give agreement with experiment. It is reasonable to expect, however, that the inclusion of these terms may improve the agreement on the high frequency side of the eigenfrequency.

The inclusion of Coulomb, as well as short range potentials in the coefficient $V(0_j, \vec{r}_{j_1}, \vec{r}_{j_2})$, and the extension of the summation (6.1.5) beyond nearest neighbors could significantly change the results. No derivation of the resulting coefficient has been carried out, however. Inclusion of the nearest neighbor Coulomb potential in (6.5.4) would change the required value of $A_3$

\textsuperscript{16}Johnson, op. cit., pp. 125-127.

to a value increased by a factor of about 1.3 over that used here. This is considerably less than the factor of about 2.0 necessary for agreement with the shell model value. Also, there is little justification for including only the nearest neighbor part of the Coulomb potential.

If the theory used here is actually as adequate as it appears it should be for predicting the optical constants, and if the calculation was carried out correctly, then the indication is that either the exponential form of the short range potential, or the choice of shell model parameters, is erroneous. The inability of the shell model to give \(\varepsilon(\infty)\) and \(\varepsilon(0)\) correctly, certainly casts doubt on the validity of the model. No serious attempt at readjustment of the parameters has been made, however.

Because the interaction between phonons, on which the self-energy and optical constants depend, involves so many lattice phonons, the calculation is necessarily complex, and it is not wise to rely on this method as a means of actually measuring the anharmonic potential (the constant \(A_2\)). What is needed is one or more experiments in which only a few phonons interact. According to Cowley,\(^8\) the pressure dependence of the normal mode frequencies and dielectric constants, and the non-linear dielectric constants, are among the few experimental quantities depending directly on anharmonicity, without involving summations over all normal modes. It would seem that the asymmetric mode interferometer
used in the present experiment might be uniquely suitable for measurement of the pressure dependence of the dielectric constant, or index of refraction. It is the feeling of the writer of this dissertation that the possibility of such experiments should be investigated by those interested in anharmonicity in solids, and who might be in a position to be able to carry out the experiments.
APPENDIX A

CORRECTION TO THE SPECTRAL RESPONSE FUNCTION
DUE TO WEDGING OF CIRCULAR SAMPLES

For a wedged circular sample of radius $a$, average thickness $b_o$, and total thickness deviation $\Delta b$, the correction to the response function for the $l$'th partial wave can be found by the methods of section 1-8. The thickness, as a function of polar coordinates $\rho = r/a$ and $\Theta$ is

$$b(\rho, \Theta) = b_o + \frac{\Delta b}{2} \rho \cos \Theta. \tag{A.1}$$

The integral in (1.8.7) is equivalent to an integral over area, with thickness expressed as a function of coordinates in the plane of the surface, so that

$$\Delta_l (\nu) = \frac{1}{\pi} \int_0^1 \rho \, d\rho \int_0^{2\pi} d\Theta \exp(-i \int_l (\nu) \frac{\Delta b}{2} \rho \cos \Theta). \tag{A.2}$$

The $\Theta$ integration can be carried out by use of the identity\(^1\)

\(^1\)F. Bowman, Introduction to Bessel Functions (Longmans, Green and Co. LTD., London, 1938) p. 57.
\[ \frac{1}{2\pi} \int_0^{2\pi} \exp(ix \cos \theta) d\theta = J_0(x), \quad (A.3) \]

where \( J_0(x) \) is a Bessel function of the first kind of order zero.

A Bessel function of the first kind of order \( n \), \( J_n(x) \), is defined by

\[ J_n(x) = \sum_{k=0}^{\infty} \frac{(-1)^k}{(k!)^2} \left( \frac{x}{2} \right)^{2k+n}. \quad (A.4) \]

Using (A.3),

\[ \Delta_{\lambda}(\nu) = 2 \int_0^1 \rho^2 \, d\rho \, J_0 \left( \frac{\nu}{\lambda} \right) \frac{\Delta b}{\lambda^2}, \quad (A.5) \]

and using (A.4), the \( \rho \) integration can be carried out:

\[ \Delta_{\lambda}(\nu) = 2 \frac{J_1 \left( \frac{\nu}{\lambda} \right) \frac{\Delta b}{\lambda^2}}{\Gamma_1 \left( \frac{\nu}{\lambda} \right) \frac{\Delta b}{\lambda^2}} \]

\[ = 1 - 1/4 \left( \frac{\nu}{\lambda} \Delta b / 2 \right)^2 + \ldots \quad (A.6) \]

As in (2.3.2), the first order correction is proportional to the square of \( \Gamma_1(\nu) \) and the degree of spread in thickness \( \Delta b \).

\[^2\text{Ibid., p. 1.}\]
APPENDIX B

MATHEMATICAL DETAILS ON THE COULOMB COEFFICIENTS

The Coulomb transformed dynamical matrix was defined in section 4-2, and the Ewald method of performing the lattice sum was discussed briefly. It is the purpose of this appendix to fill in some of the mathematical details omitted in that section. Since the Ewald method is discussed quite thoroughly by Ziman, no attempt is made to duplicate his calculations here. Rather, Ziman's results are adapted to the particular case of the Coulomb dynamical matrix for KI.

The Coulomb coefficients are given by (4,2.4). Using the identity (4.2.5) and the theta-function transformation, Ziman derives the formula

\[
\sum_{\mathbf{k}} \frac{\exp(ik \cdot \mathbf{k})}{|\mathbf{k} + \mathbf{r}|} = \frac{4\pi}{v_c} \sum_{\mathbf{g}} \exp(-\mathbf{g} \cdot \mathbf{r}) \exp(-\mathbf{r}^2/4G^2) / \lambda^2
\]

(B.1)

\[
+ \frac{2}{\sqrt{\pi}} \sum_{\mathbf{k}} \exp(ik \cdot \mathbf{k}) \int_0^\infty \exp(-\rho^2 |\mathbf{k} + \mathbf{r}|^2) d\rho,
\]

\[\text{Ziman, op. cit., pp. 37-42.}\]
\[\text{Ziman, op. cit., p. 41.}\]
where $\mathbf{\lambda}' = \mathbf{k} + \mathbf{g}$.

Applying (B.1) and (4.2.5) to (4.2.4) gives

$$c_{\alpha s, s', \alpha'}(\mathbf{k}) = \exp(i\mathbf{\lambda} \cdot (\mathbf{s}' - \mathbf{s})) \frac{\partial^2}{\partial x_{\alpha} \partial x_{\alpha'}}$$

$$ \left\{ \frac{4\pi}{v_c} \sum_{\mathbf{g}} \exp(-\mathbf{\lambda} \cdot (\mathbf{s}' - \mathbf{s} - \mathbf{x})) \exp(-\lambda^2/4G^2)/\lambda^2 + \frac{2}{\sqrt{\pi}} \sum_{\lambda'} \left[ 1 - \Delta(\lambda' + \mathbf{s} - \mathbf{s}') \right] \exp(i\mathbf{k} \cdot \lambda') \right. $$

$$\left. \left. \int_{G} d\rho \exp(-\rho^2 |\lambda' + \mathbf{s}' - \mathbf{s} - \mathbf{x}|^2) - \frac{2}{\sqrt{\pi}} \sum_{\lambda'} \Delta(\lambda' + \mathbf{s}' - \mathbf{s}) \exp(i\mathbf{k} \cdot \lambda') \left. \int_{0}^{G} \right|_{\lambda = 0} d\rho \exp(-\rho^2 |\lambda' + \mathbf{s}' - \mathbf{s} - \mathbf{x}|^2) \right\} $$

Carrying out the differentiation gives

$$c_{\alpha s, s', \alpha'}(\mathbf{k}) = \frac{4\pi}{v_c} \sum_{\mathbf{g}} \exp(i\mathbf{g} \cdot (\mathbf{s}' - \mathbf{s}))$$

$$x \frac{\lambda_{\alpha} \lambda_{\alpha'}}{\lambda^2} \exp(-\lambda^2/4G^2) - \delta_{\alpha \alpha'} \delta_{ss'} \frac{4G^3}{3\sqrt{\pi}} + \alpha_{\alpha s, s', \alpha'}(\mathbf{k})$$

where the lattice part $\alpha_{\alpha s, s', \alpha'}(\mathbf{k})$ is
Provided the lattice part can be neglected, (B.3) reduces to (4.2.6). The following approximate "order of magnitude" analysis is carried out to estimate the magnitude of the lattice summation and of the neglected infinite portion of the reciprocal lattice summation. The exponentials with imaginary arguments are set to unity. The components of vectors \( \vec{l} + \vec{s} \) and \( \vec{s} \) are replaced by the magnitudes, denoted by \( \lambda \) and \( g \), respectively. The approximations

\[
\sum_{\lambda \geq d} f(\lambda) \approx \frac{1}{v_c} \int_{d}^{\infty} 4\pi \lambda^2 f(\lambda) \, d\lambda \quad (\text{B.5})
\]

and

\[
\sum_{g \geq g_m} f(g) \approx \frac{v_c}{(2\pi)^3} \int_{g_m}^{\infty} 4\pi g^2 f(g) \, dg \quad (\text{B.6})
\]
are made, where \( f \) is an arbitrary function. For all integrals involved, the approximation

\[
\int_{a}^{\infty} x^n \exp(-b \rho^2) \, d\rho \approx \frac{a^{n-1}}{2b} \exp(-ba^2)
\]  

(B.7)

is used.

Applying (B.7) to the integral over \( \rho \) in (B.4) then gives

\[
\mathcal{L} \approx \frac{2G}{\sqrt{\pi}} \sum_{\lambda} \exp(-G^2 \lambda^2) \left(1 - \frac{2G^2 \lambda^2}{\lambda^2} \right) + \frac{8\sqrt{\pi} G}{v_c} \int_{d}^{\infty} (1 - 2G^2 \lambda^2) \exp(-G^2 \lambda^2) \, d\lambda
\]  

(B.8)

where the subscripts and argument have been omitted. Using (B.5) and (B.7),

\[
\mathcal{L} \approx -\frac{8\sqrt{\pi} Gd}{v_c} \left(1 - \frac{1}{2d^2G^2} \right) \exp(-G^2 d^2).
\]  

(B.9)

The magnitudes of the coefficients are about \( 1/v_c \), so that the inequality
\[ 8 \sqrt{\pi} Gd \left| 1 - \frac{1}{2d^2 G^2} \right| \exp(-G^2 d^2) \ll 1 \quad (B.10) \]

must be satisfied for the neglect of the lattice sum. In terms of \( G' \) defined in (4.2.14), (B.10) is the same as (4.2.16).

Applying (B.6) and (B.7) to the reciprocal lattice sum, the neglected portion is

\[ \frac{2}{\pi} \int_{Gm}^{\infty} g^2 \exp(-g^2/4G^2) \, dg \simeq \frac{4G^2}{\pi} \exp(-g_m^2/4G^2) g_m, \quad (B.11) \]

so that the inequality

\[ \frac{4g_m^2 \gamma v}{\pi} \exp(-g_m^2/4G^2) \ll 1 \quad (B.12) \]

must be satisfied for termination of the sum with a value of \( \bar{G} \) for which \(|\bar{G}| = g_m\). With the appropriate substitutions, (B.12) is identical to (4.2.17).
APPENDIX C

THE OPTICAL CONSTANTS OF KI IN TABULATED FORM

The optical constants for KI given in Table 7 below are the averaged values, determined as discussed in section 2-3. The table is given to supplement Figure 5, which is not easily readable to the accuracy with which the data was determined.

TABLE 7

THE EXPERIMENTALLY DETERMINED OPTICAL CONSTANTS OF KI

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<th>Extinction coefficient</th>
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