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THE FAR INFRARED OPTICAL PROPERTIES
OF KCl AND KBr

DISSERTATION

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

By

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The Ohio State University
1967

Approved by

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CHAPTER 1

INTRODUCTION

To study the far infrared optical properties of solids generally implies that one seeks some experimental or theoretical knowledge concerning the real and/or imaginary parts of the frequency dependent dielectric susceptibility tensor or any other mathematically related functions such as the complex dielectric constant or the complex index of refraction. In this paper we wish to examine, in detail, the contributions to these functions that arise from the vibrations of the lattice. Lattice vibrations are often described in terms of phonons; a phonon is simply a normal mode of vibration and it is characterized by two indices. One index describes the wave vector $\vec{k}$ of the phonon and the other is the polarization index j .

During the last forty years or so there has been an enormous effort spent in measuring and interpreting the far infrared optical properties of alkali halide crystals. One obvious reason for this interest is that these crystals possess a rather simple structure with mainly ionic forces interacting between ion pairs and therefore, they are most amenable to theoretical analysis. Secondly, because of their ionic character, the alkali halides

strongly interact with far infrared radiation and they have been investigated extensively by experimenters working in this spectral region. It is the purpose of this work to examine the far infrared optical properties of KCl and KBr by utilizing some of the most recent experimental and theoretical techniques. It is hoped, ultimately, that a reasonable agreement between theory and experiment will yield a more explicit understanding of the physics of these crystals. A good discussion on the far infrared optical properties of crystals and their measurement can be found in a review article by E. E. Bell⁽¹⁾.

By in large, the spectrometer is the conventional tool for measuring the far infrared optical properties of crystals. Using a spectrometer there are many approaches that are available for making these measurements and we will mention only two of them here.

The first method is to measure the power reflected from a single surface of a thick sample as a function of frequency. However, in order to calculate both the real and imaginary parts of the complex index of refraction at a particular spectral frequency, one must secure a second piece of information at this frequency. It is possible to obtain this information by performing another reflection measurement that is reasonably independent from the first one. This can be done by choosing different experimental conditions such as altering the angle of incidence or changing the

¹ E. E. Bell, "Optical Constants and Their Measurement," Encyclopedia of Physics, ed., L. Genzel. (Springer-Verlag, Berlin, 1967), Vol. XXV/2a.

polarization of the radiation. Another, and very popular, method of securing this information is to calculate the phase of the reflected radiation from a complete (over a wide spectral region) reflection spectra by using the Kramers-Kronig dispersion relations⁽²⁾. In practice such an analysis tends to show only the gross aspects of the phase spectra and much of its detailed structure due to phonon interactions is lost. Some of the reasons for this failure will be pointed out in Chapter 2 where the experimental results are presented.

The second technique for obtaining the optical properties of solids is to examine the power transmission spectra. If the sample is thin enough, possesses a small extinction coefficient and the spectrometer has high resolution, the channeled structure that appears in the transmission spectrum can be utilized to determine the complex index of refraction. Alkali halides exhibit a very strong absorption in a rather broad spectral region neighboring their eigenfrequencies, and their indices of refraction are changing rapidly, so that the above mentioned method is not satisfactory. It should be mentioned that in this spectral region the complex index of refraction is strongly influenced by the interactions among phonons and, therefore, this function should be measured as carefully as possible if the phonon-phonon interactions are to be examined in detail.

² T.S. Moss, Optical Properties of Semi-Conductors (Butterworth & Co., Ltd., London, 1961), p. 25.

The technique that we have employed utilizes a far infrared Michelson interferometer. A comprehensive mathematical account of the use of a Michelson interferometer as an instrument for measuring the optical properties of crystals has been given by E.E. Bell⁽³⁾. The detector signal from the Michelson interferometer is recorded as a function of the displacement of the movable mirror when both arms are terminated by mirrors. This function is called an interferogram (or, more precisely, it is called the background interferogram) and it is symmetric about the position in which both arms of the Michelson are optically identical in length (see Figure 1 in section 2.1). The Fourier transform of the background interferogram function yields the spectral power density of the radiation passing through the system; such information constitutes the background spectra. In this instance the Fourier coefficients are real because the background interferogram is both real and symmetric and, therefore, only amplitude information (e.g., the spectral power density) can be extracted.

To measure the optical properties of a crystal by reflection one of the reflecting end mirrors (the one belonging to the stationary arm) is accurately replaced by the well polished, flat crystal that is to be examined. The radiation reflected from the crystal will experience both a phase shift and an amplitude reduction with respect to the incident radiation. For alkali halides both of these

³E.E. Bell, "Measurement of the Far Infrared Optical Properties of Solids with a Michelson Interferometer Used in the Asymmetric Mode: Part I, Mathematical Formulation," Infrared Physics 6, 57 (1966).

quantities are strongly frequency dependent, especially in the spectral region neighboring their eigenfrequencies. Because of the dispersion introduced by the crystal, the resulting interferogram is no longer symmetric and, therefore, possesses a complex Fourier transform (see Figure 1 in section 2.1). The introduction of a crystal into one arm of the Michelson interferometer results in an asymmetric interferogram and the interferometer is said to be operating in an asymmetric mode. Bell⁽³⁾ has shown that the Fourier transform of the asymmetric interferogram yields information about the amplitude and phase of the radiation reflected from the crystal and, by comparing these data with the background spectra, it is possible to extract all of the spectral information about the complex amplitude reflectance function of the crystal. A knowledge of the phase and amplitude of the reflected radiation permits the calculation of both the real and imaginary parts of the complex index of refraction in the spectral region of interest. It is important to note that the phase and amplitude can be obtained from a single experiment by using the Michelson interferometer in this manner.

By the same interferometric technique the optical properties of a crystal can be measured in transmission⁽³⁾. However, the spectral region of interest for alkali halides occurs near the eigenfrequency of the crystal where the extinction coefficient is quite large. In order to measure the complex index of refraction in this region a very thin, flat, and parallel-faced sample must be prepared (which is no trivial task).

The recent surge in the interest of alkali halides has also stemmed from the theoretical developments that have allowed one to calculate their far infrared optical properties from more or less first principles. The early attempts to explain their optical properties were based on a purely classical formalism which considered the response of an ionic lattice to an external electric field. The ions were considered to be bound harmonically to their equilibrium positions and a damping mechanism was provided by including in the equations of motion an ad hoc damping term that was proportional to the velocity of the ions. The coefficient that multiplied the ion velocity was considered to be a constant independent of the driving frequency. There were two serious limitations to this approach. First, the complex index of refraction predicted by this model simply does not agree with the details of experimental results. Secondly, and most important, the model did not provide any significant physical insight into the actual mechanism by which the lattice is capable of absorbing energy.

In the thirties Born and Blackman^(4,5) constructed a model of the lattice in which its normal modes of oscillation could interact with one another. In their work they found that the anharmonicity of the lattice potential was responsible for the damping which

⁴M. Born and M. Blackman, "Über die Feinstruktur der Reststrahlen," Zeit. für Physik 82, 551 (1933).

⁵M. Blackman, "Die Feinstruktur der Reststrahlen," Zeit. für Physik 86, 421 (1933).

meant that the energy of a normal mode was not constant in time but decayed to other normal modes governed by selection rules that conserved energy and momentum of the interacting normal modes. They also found that the damping term coefficient was a function of the frequency of the applied electric wave.

In the early sixties there appeared a number of experimental and theoretical papers that dealt with the problem of finding the normal modes of oscillation in alkali halides. An explicit knowledge of the normal modes is necessary if the optical properties of these crystals are to be calculated in detail. This means that both the eigenvalues (lattice frequencies) and eigenvectors should be known for a rather large number of wave vectors which are, preferably, evenly distributed throughout the first Brillouin zone. A set of papers came from a group at the Chalk River Nuclear Laboratories where neutron spectroscopy techniques were used to measure the dispersion relations (phonon frequency vs. wave vector relations) for KBr and NaI along certain symmetry directions^(6,7,8).

⁶A.D.B. Woods, W. Cochran and B.N. Brockhouse, "Lattice Dynamics of Alkali Halide Crystals," Phys. Rev. 119, 980 (1960).

⁷A.D.B. Woods, B.N. Brockhouse, R.A. Cowley and W. Cochran, "Lattice Dynamics of Alkali Halide Crystals. II. Experimental Studies of KBr and NaI," Phys. Rev. 131, 1025 (1963).

⁸R.A. Cowley, W. Cochran, B.N. Brockhouse and A.D.B. Woods, "Lattice Dynamics of Alkali Halide Crystals. III. Theoretical," Phys. Rev. 131, 1030 (1963).

A second set of purely theoretical papers appeared by Karo and Hardy (9,10,11). They calculated the dispersion relations for a large number of alkali halides by using a 'deformation dipole' model. Their work is of particular interest to us because for each crystal they compiled a comprehensive listing of the frequencies and the associated eigenvectors (or unit polarization vectors) for one thousand evenly-distributed wave vectors lying within the first Brillouin zone.

The first calculation on the far infrared absorption and dispersion of NaCl, LiF and CsBr was performed by Bilz et al⁽¹²⁾. They used a theory which was developed by Born and Huang⁽¹³⁾ and their calculations were based on the eigenvalues provided by Karo. Because they did not have access to computer facilities, their calculations were done 'by hand' and some rather gross approximations were made in order to accomplish this work in a reasonable amount of time.

⁹A.M. Karo, "Lattice Vibrations in Alkali Halide Crystals. I. Lithium and Sodium Halides," J. Chem. Phys. 31, 1489 (1959).

¹⁰A.M. Karo, "Lattice Vibrations in Alkali Halide Crystals. II. Potassium and Rubidium Halides; Cesium Fluoride," J. Chem. Phys. 33, 7 (1960).

¹¹A.M. Karo and J.R. Hardy, "Lattice Dynamics and Specific-Heat Data for Rocksalt-Structure Alkali Halides," Phys. Rev. 129, 2024 (1963).

¹²H. Bilz, L. Genzel and H. Happ, "Zur Ultrarotdispersion der Alkali-Halogenide I. Die Deutung der Spektren Nach der Theorie von Born und Huang," Zeit. für Physik 160, 535 (1960).

¹³M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, Oxford, 1954). Chapt. VII.

In 1962 Bilz and Genzel⁽¹⁴⁾ repeated these calculations for $T=0^\circ\text{K}$ after modifying the theory of Born and Huang. It was this work that provided us with the initial impetus to make such calculations on other alkali halides and then to compare our results with the measured optical properties as obtained by Fourier transform spectroscopy. However, it was felt that a more detailed calculation could be made because of our access to a high speed computer.

In 1961 and 1962 there appeared several papers by Maradudin and Wallis^(15, 16) in which they implicitly used Green's functions and many-body techniques to re-examine the Born and Huang theory of optical absorption in ionic crystals. In their papers they derived theoretical expressions for the complex dielectric susceptibility tensor but they did not evaluate their results for a real crystal.

The first detailed derivation and evaluation of the complex dielectric susceptibility was given by Cowley⁽¹⁷⁾ for KBr and NaI. His theoretical derivation was also based on the Green's function

¹⁴H. Bilz and L. Genzel, "Ultrarotdispersion der Alkalihalogenide II. Zur Theorie der Absorption bei tiefen Temperaturen," Zeit. für Physik 169, 53 (1962).

¹⁵A.A. Maradudin and R.F. Wallis, "Lattice Anharmonicity and Optical Absorption in Polar Crystals. II. Classical Treatment in the Linear Approximation," Phys. Rev. 123, 777 (1961).

¹⁶R.F. Wallis and A.A. Maradudin, "Lattice Anharmonicity and Optical Absorption in Polar Crystals. III. Quantum Mechanical Treatment in the Linear Approximation," Phys. Rev. 125, 1277 (1962).

¹⁷R.A. Cowley, "The Lattice Dynamics of an Anharmonic Crystal," Advances in Physics 12, 421 (1963).

technique although his work extended beyond that of Maradudin and Wallis' by also considering contributions to the susceptibility that came from the higher order terms in the expansion of the crystal dipole moment operator. Using the eigenvalues and eigenvectors as calculated from the shell model^(7,8), and a high speed computer, Cowley was able to perform a rather detailed calculation on the complex index of refraction although he did not have sufficient experimental data with which to meaningfully compare his calculations.

There are also other authors who have attempted to calculate the optical properties of crystals in varying degrees of approximations. Their works are listed below.^(18,19,20,21,22,23)

¹⁸J. Neuberger and R.D. Hatcher, "Infrared Optical Constants of NaCl," J. Chem. Phys. 34, 1733 (1961)

¹⁹I.P. Ipatova, A.A. Maradudin and R.F. Wallis, "Temperature Dependence of the Width of the Fundamental Lattice-Vibration Absorption Peak in Ionic Crystals. II. Approximate Numerical Results," Phys. Rev. 155, 882 (1967)

²⁰V.V. Mitskevich, "Dynamical Theory of NaCl-Type Ionic Crystals. II. Dielectric and Optical Properties." Fiz. Tverd. Tela 3, 3036 (1961) (transl: Soviet Physics-Solid State 3, 2211 (1962)).

²¹V.V. Mitskevich, "Infrared Absorption and Dispersion in LiF and MgO," Fiz. Tverd. Tela 4, 3035 (1962) (transl: Soviet Physics-Solid State 4, 2224 (1963)).

²²R. Wehner, "On the Infra-Red Absorption of Crystals Due to Lattice Vibrations," Phys. Stat. Sol. 15, 725 (1966).

²³R.A. Cowley, "On the Theory of Ferroelectricity and Anharmonic Effects in Crystals," Phil. Mag. 11, 673 (1965).

CHAPTER 2

EXPERIMENTAL PROCEDURE AND RESULTS

2.1 The measurement of the far infrared optical properties of solids by the asymmetric Fourier transform method

In this section a brief account will be given on how the optical properties of KCl and KBr were measured by using a Michelson interferometer operating in an asymmetric mode. The instrument that was employed for these measurements was constructed in this laboratory by Drs. E.E. Bell and E.E. Russell. A rather detailed account of the construction and operation of this particular interferometer can be found in the literature^(1,2,3) and this aspect of the experimental procedure will not be discussed here.

If the Michelson interferometer is to be used for measuring the optical properties of a crystal some thought must be given as to the exact operating conditions of the interferometer so that the

¹E.E. Bell, "Measurement of the Far Infrared Optical Properties of Solids with a Michelson Interferometer Used in the Asymmetric Mode: Part I, Mathematical Formulation," Infrared Physics 6, 57 (1966).

²E.E. Russell and E.E. Bell, "Measurement of the Far Infrared Optical Properties of Solids with a Michelson Interferometer Used in the Asymmetric Mode: Part II, The Vacuum Interferometer," Infrared Physics 6, 75 (1966).

³E.E. Russell, "Measurement of the Optical Constants of Sapphire and Quartz in the Far Infrared with the Asymmetric Fourier Transform Method," Ph.D. thesis, The Department of Physics, The Ohio State University, Columbus, Ohio, 1966.

maximum amount of useful information can be extracted. These considerations will generally include such things as the type of beam splitter to be used, proper filtering of unwanted energy, time required for the measurement of the interferogram and the resolution desired. A more explicit discussion of these conditions is given in section 2.3 and, in the following discussion it will be assumed that they have been properly met.

According to the rules of the game^(1,3) a 'background' run must be made which yields the spectral power density of the electromagnetic radiation passing through the instrument. This run is performed as follows. First, the movable mirror of the interferometer is adjusted until both arms are equal in length. In this position all of the frequency components passing through the system arrive at the detector in phase and a large output signal is produced; this signal is called the 'white light peak'. The position of the 'white light peak' serves as a fiducial point for all subsequent displacements of the movable mirror. The movable mirror is then displaced a distance, say $+X$, away from the white light position. A background interferogram is produced by starting at the position $+X$ and moving the mirror in discrete steps, ΔX , to $-X$ while recording the detector output at each step. This interferogram will be denoted as $P_B(n\Delta X)$ where n is an integer ranging from 0 to $N_{\max}$ such that $N_{\max}\Delta X = 2X$. The top most sketch of Figure 1 shows a typical background interferogram.

In practice it is usually not possible to locate the 'white light' position exactly and the resulting background interferogram is

(A) Background interferogram, $P_B(n \Delta X)$

(B) Sample interferogram (reflection mode), $P_S(n \Delta X)$

Figure 1. Example of a background and a sample interferogram (not drawn to scale).

slightly asymmetric. There are several reasons for this asymmetry. First, the movable mirror is driven by a stepping motor whose smallest translational advance is approximately one-half of a micron. Therefore, the length of the two arms of the interferometer can only be made equal to within one-quarter of a micron. Second, the interferometer is subject to a small amount of thermal instability which causes one arm to thermally expand or contract with respect to the other arm during the time that an interferogram is being produced.

The slight asymmetry in the background interferogram causes $P_B(n\Delta X)$ to possess complex Fourier coefficients, which will be denoted as $\hat{p}_B(\nu) = p_B(\nu)e^{i\phi_B(\nu)}$, where $p_B(\nu)$ is the spectral power of the radiation passing through the instrument and $\phi_B(\nu)$ is the linear phase term resulting from the slightly asymmetric interferogram. Of course, if the background interferogram is completely symmetric, then $\phi_B(\nu)$ would be zero.

Having produced a background interferogram, the end mirror in the stationary arm of the interferometer is then removed and accurately replaced by a well polished, flat crystal whose optical properties are to be measured. A sample interferogram $P_S(n\Delta X)$ is then produced in the identical manner that the background interferogram $P_B(n\Delta X)$ was produced. However, the crystal introduces additional dispersion into the radiation traversing the stationary arm and the resulting interferogram is markedly asymmetric. A typical sample interferogram is sketched in Figure 1.

The sample interferogram also has complex Fourier coefficients which will be denoted as $\hat{p}_S(\nu) = p_S(\nu) e^{i\phi_S(\nu)}$.

Bell⁽¹⁾ has shown that the complex amplitude reflectance function, $\hat{r}(\nu) = r(\nu) e^{i\phi_r(\nu)}$, of the crystal can be found by the relation

$$\hat{r}(\nu) = \frac{\hat{p}_S(\nu)}{\hat{p}_B(\nu)} = \frac{p_S(\nu)}{p_B(\nu)} \cdot e^{i[\phi_S(\nu) - \phi_B(\nu)]}. \quad (2.1.1)$$

Therefore, the amplitude reflectance $r(\nu)$ of the radiation reflected from the crystal is

$$r(\nu) = \frac{p_S(\nu)}{p_B(\nu)}, \quad (2.1.2)$$

and the power reflectance $R(\nu)$ is simply $R(\nu) = r(\nu)^2$.

The phase $\phi_r(\nu)$ of the radiation reflected from the crystal is

$$\phi_r(\nu) = \phi_S(\nu) - \phi_B(\nu) + \pi, \quad (2.1.3)$$

where the factor of π is present because $\phi_S(\nu)$ is measured relative to the phase shift produced by a good metallic mirror (which is π).

Therefore, the Michelson interferometer operating in this manner is capable of yielding both the amplitude and phase of the complex amplitude reflectance.

The complex amplitude reflectance $\hat{r}(\nu)$ can be expressed in terms of the complex index of refraction $\hat{N}(\nu) = N(\nu) + iK(\nu)$ as

$$\hat{r}(\nu) = \frac{-[\hat{N}(\nu) - 1]}{[\hat{N}(\nu) + 1]}, \quad (2.1.4)$$

where $N(\nu)$ is the ordinary index of refraction and $K(\nu)$ is the extinction coefficient. It is possible to invert the last relation and to obtain explicit relations for N and K in terms of r and ϕ_r :

$$N(\nu) = \frac{1 - r^2(\nu)}{1 + r^2(\nu) + 2r(\nu) \cos(\phi_r(\nu))} \quad (2.1.5)$$

$$K(\nu) = \frac{-2r(\nu) \sin(\phi_r(\nu))}{1 + r^2(\nu) + 2r(\nu) \cos(\phi_r(\nu))}. \quad (2.1.6)$$

All data processing, such as performing the Fourier transformations and the calculation of $N(\nu)$ and $K(\nu)$ from $r(\nu)$ and $\phi_r(\nu)$, was done on an IBM 7094 computer using a Scatran compiler.

2.2 Preparation of the KCl and KBr crystals for reflection measurements

It was mentioned in the last section that one of the end mirrors must be accurately replaced by a well polished, flat crystal whose optical properties are to be measured. The preparation of such crystals is not too difficult and a method

that proved to be satisfactory will be outlined here.

Both KBr and KCl were purchased as large single crystals from the Harshaw Chemical Company.^{*} The crystals were cylindrical in shape and were approximately $1\frac{1}{4}$ " in diameter by $1\frac{1}{4}$ " in length. The cylinders were cut up into discs about $1/4$ " thick by a home-made string saw of modest design. This thickness was chosen because it was the largest that the sample changer, located inside the interferometer, could accomodate. The back face of the crystal was canted with respect to the front face to prevent measuring any radiation reflected from the back face.

To polish the front surface of the crystal a slurry was prepared by mixing approximately 10 grams of $1/4$ micron Aluminum Oxide^{**} with a pint of absolute ethyl alcohol. Both KCl and KBr are hygroscopic so care was exercised at all times to prevent any water from contaminating the slurry and working area. The polishing was done on a steel lapping plate 10" in diameter on top of which was mounted a perforated polishing pad called Pad-K.^{***} The crystal was moved back and forth on the slowly rotating lap plate with the slurry being sprayed on at short intervals. This procedure produced an extremely well polished surface although any foreign contaminant introduced onto the lap plate would badly scratch the

^{*} Harshaw Chemical Company, Cleveland, Ohio

^{**} purchased from the Linde Company, East Chicago, Indiana

^{***} purchased from Buehler Limited, Evanston, Illinois

surface. With some care, the center section of approximately 1" to $1\frac{1}{4}$ " in diameter could be made flat to within one or, at most, two fringes of visible light. This area was sufficient for our purposes. However, this technique tended to 'roll' the edges of the crystal and a crystal somewhat larger in diameter, than the area to be made flat, had to be used.

After the crystals were polished they were placed in a desiccator until the time when they were transferred into the interferometer.

2.3 The experimental results of the complex amplitude reflectance and complex index of refraction of KCl and KBr

It was mentioned in the last section that the Michelson interferometer is capable of measuring both the real and imaginary parts of the complex amplitude reflectance in a given spectral region. The width and position of this spectral region depends upon the experimental conditions under which the interferograms are produced. These conditions include the type of beam-splitter, the proper filter combinations which eliminate the aliasing of unwanted power and the window on the Golay detector. Russell⁽⁴⁾ has provided a very useful table that gives the experimental conditions for making measurements in the spectral region of interest.

The measurement of the complex amplitude reflectance of KCl and KBr over a broad region (from approximately 35 cm^{-1} to 360 cm^{-1})

⁴ ibid., p.59.

required working in two different, but overlapping, spectral regions; these regions were approximately 35 cm^{-1} to 180 cm^{-1} and 135 cm^{-1} to 360 cm^{-1} . For future reference, these two regions will be called the quartz region and the diamond region, respectively. (These names were chosen because in the 35 cm^{-1} to 180 cm^{-1} region the quartz window Golay detector was used while in the higher spectral region the diamond window Golay detector was employed.)

In each particular region at least three runs were made for both KCl and KBr at a resolution of 2 cm^{-1} . This resolution was selected for several reasons. First, in the diamond region the total time required to make one background and one sample interferogram was approximately $3\frac{1}{2}$ hours. To increase the resolution to 1 cm^{-1} would have required an operating time of 7 hours which was too long because of the instabilities inherent in the various components of the interferometer. Second, doubling the resolution doubles the number of points that are required to produce an interferogram and this increases the noise on the transformed spectra by a factor of $\sqrt{2}^{(1)}$. The noise associated with the 2 cm^{-1} resolution spectra was rather large and the increase of $\sqrt{2}$ was certainly not desirable.

Three methods were employed to reduce the amount of noise associated with the amplitude and phase spectra of KCl and KBr. The first method was to increase the length of time spent in integrating the detector signal at each interferogram point. Normally a one second integration time was used although the read-out

system had a maximum effective integration time of six seconds. This longer integration time was used when operating in the lower frequency region ($35 \text{ cm}^{-1} - 180 \text{ cm}^{-1}$) and a decrease of $\sqrt{6}$ in the noise level was realized. However, the longer integration time was not used in the diamond region because the total time spent in producing the background and sample interferograms was too long for the instrument to remain reasonably stable.

The second method of reducing the noise was to decrease the resolution to 4 cm^{-1} which halved the number of points in the interferograms as compared with those made at 2 cm^{-1} resolution; the corresponding reduction in noise was $\sqrt{2}$. It was found that the 4 cm^{-1} resolution was generally sufficient to resolve the structure present in the complex index of refraction except in the spectral region immediately neighboring the eigenfrequencies of the crystals.

The third method simply involved making many runs with fixed experimental conditions and then averaging the transformed phase and amplitude spectra. To be sure, this technique is not the best one for reducing the noise because it involves inefficient use of the interferometer measurement time and increases the computational cost because each run must now be Fourier analyzed. However, we have used this method to examine the reproducibility of the spectra which mitigated the above objections. In fact, one method of estimating the errors present in the transformed spectra was to examine the range of non-reproducibility of the many runs.

In each of the two spectral regions, quartz and diamond, at least three runs at 2 cm^{-1} resolution and three additional runs at 4 cm^{-1} were made so that a minimum of twelve runs were used to map the complex amplitude reflectance for both KCl and KBr. The final amplitude reflectance was then obtained by averaging the amplitude reflectance from all the runs and hand drawing a smooth curve through the averaged data points.

The results of the power reflectance (amplitude reflectance squared) are given at selected frequencies in Table 1 for KCl and in Table 2 for KBr and the power reflectance curves are respectively drawn in Figures 2 and 5. Figure 4 shows the power reflectance for KCl and KBr on an expanded vertical scale in the region where the power reflectance is less than three percent.

The determination of the phase curve was slightly more complicated because a misalignment resulted when the end mirror of the interferometer was replaced by the crystal whose optical properties were to be measured. The reason for this misalignment is to be found in the end-mirror assembly ⁽⁵⁾ where the sample is positioned by horizontally resting on three vertical posts whose top surfaces are slightly convex. At the points of contact these three convex surfaces tended to produce indentations in the relatively soft KCl and KBr crystals; the indentations were estimated to be approximately 1 or 2 microns in depth. The effect of this misalignment is to introduce an extra term into the phase spectra that

⁵ibid., p.34.

Figure 2. The experimentally measured power reflectance $r^2(\nu)$ and the phase spectrum, $\phi_r(\nu) - \pi$, for KCl.

Figure 3. The experimentally determined index of refraction $N(\nu)$ and the extinction coefficient $K(\nu)$ for KCl.

Figure 4. The experimentally measured power reflectance $r^2(\gamma)$ for KCl and KBr in the spectral region where the power reflectance is less than 0.03.

TABLE 1
THE EXPERIMENTAL RESULTS OF THE POWER REFLECTANCE, PHASE,
INDEX OF REFRACTION AND EXTINCTION
COEFFICIENT FOR KCl

Frequency cm ⁻¹	Power reflectance	Phase	Index of refraction	Extinction coefficient
43.1	0.146	-----	2.24	-----
47.6	0.144	-----	2.22	-----
52.2	0.150	0.022	2.27	0.046
56.7	0.149	0.021	2.26	0.043
61.2	0.150	0.025	2.26	0.051
65.8	0.157	0.037	2.31	0.079
70.3	0.155	0.043	2.29	0.092
74.8	0.160	0.047	2.33	0.103
79.4	0.167	0.042	2.37	0.098
83.9	0.170	0.046	2.40	0.108
88.4	0.177	0.030	2.45	0.075
93.0	0.183	0.025	2.49	0.065
97.5	0.195	0.036	2.58	0.101
102.0	0.201	0.040	2.62	0.118
106.6	0.211	0.045	2.69	0.140
111.1	0.228	0.045	2.82	0.156
114.5	0.243	0.043	2.93	0.164
117.9	0.259	0.043	3.06	0.180
121.3	0.280	0.041	3.23	0.195
124.7	0.309	0.043	3.49	0.242
128.1	0.344	0.040	3.82	0.270
131.5	0.386	0.053	4.23	0.455
133.8	0.426	0.070	4.63	0.737
136.1	0.484	0.085	5.28	1.22
138.1	0.563	0.113	6.08	2.36
139.5	0.618	0.140	6.36	3.53
140.6	0.669	0.172	5.78	4.89
142.9	0.762	0.248	3.46	6.16

TABLE 1 (Contd.)

Frequency cm ⁻¹	Power reflectance	Phase	Index of refraction	Extinction coefficient
145.1	0.821	0.331	1.67	5.50
147.4	0.849	0.414	0.932	4.58
149.7	0.873	0.490	0.567	3.92
151.9	0.888	0.566	0.376	3.40
154.2	0.899	0.639	0.266	3.00
156.5	0.899	0.707	0.210	2.69
158.7	0.895	0.774	0.193	2.44
161.0	0.895	0.839	0.167	2.23
163.3	0.886	0.909	0.157	2.04
165.5	0.877	0.984	0.147	1.86
167.8	0.853	1.06	0.154	1.70
170.1	0.821	1.14	0.169	1.55
172.4	0.778	1.21	0.191	1.42
174.6	0.737	1.29	0.208	1.31
176.9	0.675	1.37	0.240	1.19
179.2	0.598	1.45	0.286	1.09
181.4	0.531	1.51	0.325	1.01
183.7	0.477	1.57	0.355	0.939
185.9	0.427	1.62	0.383	0.873
188.2	0.392	1.66	0.404	0.830
190.5	0.354	1.72	0.421	0.767
192.8	0.311	1.78	0.445	0.705
195.0	0.269	1.83	0.477	0.654
197.3	0.225	1.89	0.509	0.591
199.6	0.184	1.91	0.554	0.549
201.8	0.153	1.91	0.599	0.520
204.1	0.129	1.90	0.640	0.501
206.4	0.115	1.85	0.679	0.499
208.6	0.109	1.81	0.705	0.508
210.9	0.115	1.76	0.711	0.535
213.2	0.132	1.76	0.683	0.562
215.4	0.161	1.85	0.607	0.557
217.7	0.171	2.05	0.534	0.474
220.0	0.142	2.28	0.524	0.348
222.2	0.096	2.44	0.575	0.254
224.5	0.063	2.50	0.639	0.204
226.8	0.043	2.49	0.695	0.182
229.0	0.031	2.45	0.742	0.172
231.3	0.024	2.41	0.777	0.167

TABLE 1 (Contd.)

Frequency cm ⁻¹	Power reflectance	Phase	Index of refraction	Extinction coefficient
233.6	0.020	2.35	0.804	0.165
235.8	0.017	2.31	0.824	0.162
238.1	0.015	2.28	0.840	0.156
240.4	0.013	2.27	0.849	0.151
242.6	0.012	2.29	0.857	0.141
244.9	0.0093	2.36	0.865	0.119
247.2	0.0077	2.38	0.882	0.100
249.4	0.0058	2.37	0.901	0.087
251.7	0.0035	2.33	0.919	0.078
254.0	0.0022	2.30	0.937	0.067
256.3	0.0013	2.21	0.957	0.055
258.5	0.0008	2.02	0.974	0.050
260.8	0.0005	1.77	0.990	0.043
263.1	0.0004	1.43	1.00	0.038
265.3	0.0005	0.897	1.04	0.035
267.6	0.0006	0.621	1.04	0.030
269.9	0.0007	0.486	1.05	0.026
273.3	0.0013	0.335	1.07	0.026
276.7	0.0016	0.282	1.08	0.025
280.1	0.0024	0.235	1.10	0.024
283.5	0.0029	0.141	1.11	0.017
286.9	0.0032	0.085	1.12	0.011
290.3	0.0042	0.045	1.14	0.007
293.7	0.0045	0.036	1.14	0.005
297.1	0.0058	0.015	1.17	0.003
303.9	0.0072	-----	1.19	-----
310.7	0.0090	-----	1.21	-----
317.5	0.0099	-----	1.22	-----
324.3	0.012	-----	1.24	-----
331.1	0.012	-----	1.25	-----
337.9	0.015	-----	1.28	-----
344.7	0.016	-----	1.29	-----
351.5	0.018	-----	1.31	-----
358.3	0.019	-----	1.32	-----
365.1	0.020	-----	1.33	-----
371.9	0.024	-----	1.37	-----
374.2	0.023	-----	1.36	-----

Figure 5. The experimentally measured power reflectance $r^2(\nu)$ and the phase spectrum, $\phi_r(\nu) - \pi$, for KBr.

Figure 6. The experimentally determined index of refraction $N(\nu)$ and the extinction coefficient $K(\nu)$ for KBr.

TABLE 2

THE EXPERIMENTAL RESULTS OF THE POWER REFLECTANCE, PHASE,
INDEX OF REFRACTION AND EXTINCTION
COEFFICIENT FOR KBr

Frequency cm ⁻¹	Power reflectance	Phase	Index of refraction	Extinction coefficient
36.3	0.156	-----	2.30	-----
40.8	0.161	-----	2.34	-----
45.4	0.161	0.050	2.34	0.112
49.9	0.162	0.044	2.34	0.099
54.4	0.166	0.049	2.37	0.114
59.0	0.169	0.062	2.38	0.145
63.5	0.173	0.061	2.41	0.148
68.0	0.180	0.059	2.46	0.150
72.6	0.185	0.059	2.50	0.156
77.1	0.192	0.061	2.55	0.168
81.6	0.203	0.058	2.63	0.173
86.2	0.216	0.054	2.72	0.176
90.7	0.235	0.054	2.87	0.195
94.1	0.253	0.061	3.00	0.249
96.4	0.267	0.063	3.11	0.278
98.6	0.285	0.066	3.26	0.322
100.9	0.306	0.068	3.43	0.374
103.2	0.331	0.071	3.65	0.443
105.5	0.365	0.075	3.97	0.569
107.7	0.413	0.083	4.45	0.809
110.0	0.484	0.102	5.17	1.42
112.3	0.587	0.144	5.86	3.13
114.5	0.701	0.243	3.96	5.33
116.8	0.797	0.346	1.73	5.16
119.1	0.834	0.479	0.780	3.95
121.3	0.837	0.578	0.536	3.28
123.6	0.837	0.671	0.403	2.82
125.9	0.825	0.772	0.334	2.42
128.1	0.811	0.841	0.310	2.20

TABLE 2 (Contd.,)

Frequency cm ⁻¹	Power reflectance	Phase	Index of refraction	Extinction coefficient
130.4	0.786	0.934	0.292	1.95
132.7	0.755	1.02	0.287	1.74
134.9	0.727	1.12	0.279	1.57
136.1	0.706	1.15	0.287	1.50
138.3	0.655	1.25	0.300	1.34
140.6	0.594	1.35	0.321	1.19
142.9	0.521	1.46	0.353	1.06
145.1	0.444	1.54	0.396	0.949
147.4	0.370	1.62	0.439	0.847
149.7	0.307	1.70	0.478	0.759
151.9	0.248	1.77	0.522	0.677
154.2	0.193	1.82	0.574	0.606
156.5	0.149	1.85	0.626	0.547
158.7	0.114	1.85	0.683	0.501
161.0	0.090	1.81	0.738	0.472
163.3	0.077	1.77	0.778	0.459
165.5	0.076	1.74	0.793	0.465
167.8	0.078	1.73	0.792	0.473
168.9	0.079	1.74	0.784	0.471
171.2	0.075	1.85	0.754	0.429
173.5	0.064	1.95	0.747	0.375
175.8	0.047	2.08	0.759	0.302
178.0	0.033	2.14	0.788	0.248
180.3	0.024	2.14	0.818	0.220
182.6	0.014	2.06	0.870	0.194
184.8	0.013	1.97	0.896	0.193
187.1	0.013	2.03	0.885	0.185
189.4	0.0086	2.15	0.893	0.140
191.6	0.0049	2.12	0.922	0.111
193.9	0.0026	1.93	0.961	0.092
196.2	0.0014	1.70	0.988	0.074
198.4	0.0008	1.18	1.02	0.054
200.7	0.0011	0.772	1.05	0.048
203.0	0.0014	0.571	1.06	0.044
205.2	0.0020	0.412	1.08	0.039
210.9	0.0038	0.211	1.13	0.029
214.3	0.0050	0.150	1.15	0.024
217.7	0.0057	0.100	1.16	0.018
221.1	0.0069	0.087	1.18	0.017

TABLE 2 (Contd.)

Frequency cm ⁻¹	Power reflectance	Phase	Index of refraction	Extinction coefficient
223.4	0.0081	0.054	1.20	0.012
225.6	0.0082	0.048	1.20	0.010
229.0	0.0097	0.038	1.22	0.009
233.6	0.012	0.020	1.24	0.005
238.1	0.013	0.010	1.26	0.003
244.9	0.015	-----	1.28	-----
251.7	0.018	-----	1.31	-----
258.5	0.019	-----	1.32	-----
265.3	0.020	-----	1.33	-----
272.1	0.023	-----	1.36	-----
278.9	0.023	-----	1.36	-----
285.7	0.025	-----	1.38	-----
292.5	0.026	-----	1.39	-----
299.3	0.028	-----	1.40	-----
306.2	0.029	-----	1.41	-----
313.0	0.029	-----	1.41	-----
319.8	0.029	-----	1.41	-----
326.6	0.030	-----	1.42	-----
333.4	0.029	-----	1.41	-----
340.2	0.030	-----	1.42	-----
347.0	0.032	-----	1.43	-----
353.8	0.033	-----	1.44	-----
360.6	0.030	-----	1.42	-----
362.8	0.031	-----	1.43	-----

is linear in the frequency. It is known from the work of Mentzel⁽⁶⁾ that the extinction coefficient, and hence the phase, is extremely small in the region beginning with 315 cm^{-1} for KCl and 260 cm^{-1} for KBr and extending to higher frequencies. Our measurements in these regions indicated that the extremely small phase values could not be discerned from the noise level. To correct for the phase error due to the misalignment it was assumed that these regions of extremely small phase values had phases identically equal to zero. A linear curve of the form $\Delta\phi = a\nu$ was fitted (in the least squares sense) to each region, where $\Delta\phi$ is the error in the phase caused by the misalignment, ν is the frequency and a is the slope to which a numerical value was assigned by the fitting process. Having determined the slope, a , in this manner, the phase spectra was corrected by subtracting the linear term $\Delta\phi = a\nu$ from each point on the uncorrected phase spectra.

The above procedure was satisfactory for determining the phase error for those measurements that extended to sufficiently high frequencies where the phase returned to zero, (diamond region). However, for those measurements that were made at the lower frequencies, (quartz region), it was not possible to pin down the phase error in the above manner because the phases of KCl and KBr did not return to a zero value at the high frequency end of this region. For these data the linear phase correction term was found

⁶ A. Mentzel, "Untersuchung des Absorptionsverlaufes von KCl und KBr auf der Kurzwelligen Seite Ihrer Ultraroten Eigenschwingen," Zeit. für Physik 88, 178 (1934).

by insisting that the uncorrected phase curves of the 'quartz' region be made to coincide with the corrected phase curves made in the 'diamond' region in the spectral region where they overlapped. The overlap region was approximately 150 cm^{-1} to 190 cm^{-1} for KCl and 115 cm^{-1} to 150 cm^{-1} for KBr. Having found the linear correction term, the phase in the 'quartz' region was corrected by subtracting this term from each point.

The corrected phase spectra are given in Tables 1 and 2 and shown in Figures 2 and 5 for KCl and KBr respectively.

A word is in order at this time concerning the size of the errors that are expected to be present on the measured values of the power reflectance and phase spectra. It was previously mentioned that many experimental runs were made on each crystal and the resulting values for the power reflectance and phase were obtained by averaging these data. The vertical bars drawn on the curves shown in Figures 2, 4 and 5 approximate the range of the peak-to-peak non-reproducibility at various frequencies. The range of reproducibility was not a constant but varied in different spectral regions. In particular, the reproducibility in the power reflectance curves was found to be poorest in the region of maximum reflectivity (approximately 155 cm^{-1} for KCl and 120 cm^{-1} for KBr) and best in the regions of lowest reflectivity (approximately 265 cm^{-1} for KCl and 200 cm^{-1} for KBr). Table 3 gives the values of the peak-to-peak errors in the experimental measurements at selected frequencies for KCl and KBr.

TABLE 3

THE ESTIMATED PEAK-TO-PEAK ERRORS IN THE EXPERIMENTAL
DATA FOR KCL AND KBR AT SELECTED FREQUENCIES

KCL			KBR		
freq. (cm ⁻¹)	peak-to-peak non-reproducibility		freq. (cm ⁻¹)	peak-to-peak non-reproducibility	
	power reflect.	phase		power reflect.	phase
70	0.008	-----	40	0.008	-----
105	0.01	0.025	70	0.015	0.025
140	0.02	0.025	90	0.02	0.025
155	0.03	0.03	110	0.025	0.025
180	0.02	0.03	125	0.035	0.025
200	0.015	0.04	140	0.03	0.025
220	0.01	0.05	155	0.025	0.025
250	0.0005	0.07	175	0.008	0.03
270	0.0005	0.10	205	0.0005	0.05
310	0.0025	0.03	260	0.0015	-----
355	0.005	-----	340	0.0035	-----

Because the final data were determined by averaging at least six experimental runs the power reflectance and phase data are known to better accuracy than the peak-to-peak error limits would indicate. However, because of the small averaging statistics, it is not possible to say that the reflectance and phase curves are known to be accurate to within $\pm \frac{\Delta_{P-P}}{\sqrt{N}}$ of their average values, where Δ_{P-P} is the peak-to-peak error in the experimental data and N is the number of runs that were averaged.

The real and imaginary parts of the complex index of refraction were then calculated from the power reflectance and phase spectra by using equations (2.1.5) and (2.1.6). These results are also tabulated in Tables 1 and 2 and they are drawn in Figures 3 and 6 for KCl and KBr respectively. The values of the extinction coefficient K below 0.1 are probably not accurate because the phase becomes too difficult to measure with any degree of certainty.

Finally, let us point out why it is difficult to use a Kramers-Kronig dispersion analysis to obtain the phase spectra from the power reflectance data.

The Kramers-Kronig relation states that the phase $\phi(\nu_0)$ at a given frequency ν_0 can be obtained from a knowledge of the power reflectance $R(\nu)$ by the following equation:

$$\phi(\nu_0) = -\frac{\nu_0}{\pi} \int_0^{\infty} \frac{\log R(\nu)}{\nu^2 - \nu_0^2} d\nu. \quad (2.3.1)$$

An examination of Figures 2, 4 and 5 shows that the spectral region where the phase spectra has significant structure due to phonon interactions (225 cm^{-1} to 285 cm^{-1} for KCl and 170 cm^{-1} to 220 cm^{-1} for KBr) is also the region where the power reflectance becomes very small (less than 0.05). Using conventional instruments, such as a spectrometer, it is difficult to determine the power reflectance to within 0.01 and the extremely small values of the power reflectance, shown in Figure 4, cannot be accurately determined.

From equation (2.3.1) it can be seen that the largest contributions to the integrand will come from those terms where $\nu \approx \nu_0$ and, if $R(\nu)$ is relatively small in this region (say less than .01), then an inaccurate measurement of $R(\nu)$ will correspondingly produce a rather large inaccuracy in the determination of the phase.

In conclusion, it is not possible then to obtain reliable phase data from the Kramers-Kronig relations in the region where the power reflectance is very small and cannot be measured extremely accurately. The present work on KCl and KBr and some preliminary work on NaI shows that there is considerable phase information in the region of small power reflectance and, therefore, it becomes a moot question as to the usefulness of a Kramers-Kronig analysis when examining the detailed spectra caused by phonon interactions in alkali halides.

CHAPTER 3

THEORETICAL CONSIDERATIONS

3.1 The harmonic and adiabatic approximations

The starting point for an understanding of the far infrared absorption by alkali halides is to first establish the mathematical approximations that are necessary to solve the quantum mechanical problem of a vibrating lattice. These approximations are called the harmonic and adiabatic approximations and they are given a rigorous mathematical development by Born and Huang⁽¹⁾. In this section the essential features of these approximations will be outlined.

Owing to the very large nuclear mass M_0 as compared to the electron mass m the total kinetic energy of the nuclei T_N is small compared to the total electron kinetic energy T_E . Therefore, T_N is treated as a perturbation (with an expansion parameter of $(m/M_0)^{1/4}$) on the zeroth order Hamiltonian H_0 such that

$$H_0 = T_E + U, \quad (3.1.1)$$

where U is the total potential energy of the nuclei and electrons.

¹M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, Oxford, 1954), Chapter IV.

H_0 then represents a system of dynamic electrons and fixed nuclei interacting via Coulomb fields and repulsive overlap potentials.

In zeroth order the total wave function of the system is a product of an electronic wave function and a nuclear wave function. The nuclear wave function is determined by a Hamiltonian that consists of T_N plus an effective potential function in which the nuclei move that is a quadratic function of the nuclear displacements from their equilibrium positions. This zeroth order approximation of the nuclear wave function is called the harmonic approximation and it yields a very elementary description of the vibrating lattice; e.g., the electrons move as though the nuclei were fixed at their equilibrium positions and the nuclei vibrate in an effective quadratic potential.

In practice most calculations of the lattice vibrations are based on the harmonic model in which adjustable parameters are introduced such that the resulting dispersion curves can be made to closely match those that are experimentally measured or to compare favorably with other experimental data^(2,3). In general, however, the harmonic Hamiltonian does not correctly describe a real crystal and some of the more notable deficiencies are:

1. The harmonic crystal exhibits no thermal expansion.

² A.M. Karo and J.R. Hardy, "Lattice Dynamics and Specific-Heat Data for Rocksalt-Structure Alkali Halides," Phys. Rev. 129, 2024 (1963).

³ A.D.B. Woods, W. Cochran and B.N. Brockhouse, "Lattice Dynamics of Alkali Halide Crystals," Phys. Rev. 119, 980 (1960).

2. The elastic constants are independent of temperature and pressure.
3. The adiabatic and isothermal elastic constants are equal.
4. There are no matrix elements that connect one vibration state (phonon) to another so the transition probability for the decay of a phonon into other phonon states is zero.

The last objection is particularly serious to us because it predicts an appreciable absorption of electromagnetic energy by the harmonic crystal only in a very narrow spectral region close to the eigenfrequency; experiments indicate strong absorption with secondary maxima over a rather broad region with a peak at the eigenfrequency.

The objections cited above may be removed by including higher order terms in the effective potential function (cubic, quartic, etc.) in which the nuclei move. However, the inclusion of these higher order terms removes us from the harmonic approximation and into the adiabatic or Born-Oppenheimer approximation. The adiabatic approximation is simply a higher order solution to the above mentioned perturbation calculation. In this case the total wave function is still a product of the nuclear wave function and the electronic wave function, however, each is now determined to second order (as contrasted to zeroth order for the harmonic approximation).

An examination of the electronic wave function shows that the electrons move as though the nuclei were held fixed at their instantaneous positions (not necessarily at their equilibrium positions), and

the electrons are said to follow the nuclear motion adiabatically. A sufficient condition for the validity of this approximation is that the maximum lattice vibration frequency be much smaller than the energy gap between the electronic ground state and the first excited state. The nuclear vibrations do not cause electronic transitions but simply deform the electronic state in an adiabatic manner. Alkali halides have electronic excitation frequencies several orders of magnitude greater than the vibrating nuclei and, therefore, the adiabatic approximation is quite valid for these crystals.

The nuclear motion in the adiabatic approximation is determined by a Hamiltonian that includes the kinetic energy of the nuclei plus an effective potential which includes terms up to the fourth power in the nuclear displacements. The inclusion of the cubic and quartic potential terms gives rise to the phonon-phonon interactions that are largely responsible for the details of the far infrared optical properties of solids. It should be noted that it is not mathematically permissible to consider the nuclear motion on the basis of an effective potential that contains terms higher than quartic. If the potential function contains quintic and higher order terms Born and Huang⁽¹⁾ have shown that it is no longer possible to separate the total wave function into a product of a nuclear wave function and an electronic wave function. In this case the total wave function represents an electron-phonon interaction.

There is one final point that should be mentioned regarding the kind of lattice model that Karo and Hardy employ for calculating the dispersion relations for alkali halides.⁽²⁾ The adiabatic approximation concerns itself with the nuclear displacements, nuclear mass and an effective potential in which the nuclei vibrate. The Karo and Hardy model tacitly assumes that the nucleus is so constrained in its motion by the surrounding electronic cloud that the effective nuclear potential is identical to the potential in which the entire ion moves. In other words, the nucleus and its electronic cloud move in phase much as a rigid ion would do and so one can speak of an ionic effective potential, ionic displacements and ionic masses rather than the corresponding nuclear nomenclature. This approximation enormously simplifies the analysis.

3.2 Crystal structure and the reciprocal lattice

KBr and KCl crystallize into the well known sodium chloride structure shown in Figure 7. The space lattice of this structure is face-centered cubic with a basis of one positive and one negative ion. The distance between the nearest unlike ions is the lattice constant r_0 and has the numerical value of $3.14 \text{ \AA}$ for KCl and $3.30 \text{ \AA}$ for KBr.

In order to construct the reciprocal lattice for this space structure it is necessary to define the unit cell which contains the basis ions. The construction of this unit cell is somewhat arbitrary although it is necessary to keep its volume equal to $2r_0^3$.

Figure 7. The sodium chloride crystal structure.

To each ion in the lattice can be assigned a volume $v_i = r_o^3$ such that the total number of ions times v_i equals the volume of the crystal. Therefore, the volume of the unit cell containing two ions must be $2r_o^3$.

Three appropriate vectors for generating a unit cell are shown in Figure 7 and are given by

$$\begin{aligned} \underline{a}_1 &= r_o [\underline{e}_y + \underline{e}_z] \\ \underline{a}_2 &= r_o [\underline{e}_x + \underline{e}_z] \\ \underline{a}_3 &= r_o [\underline{e}_x + \underline{e}_y] , \end{aligned} \quad (3.2.1)$$

where $\underline{e}_i$ is a unit vector in the i^{th} cartesian direction. It is easily verified that the unit cell volume v_a ($v_a = \underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3$) is equal to $2r_o^3$. The generating vectors for the reciprocal lattice $\underline{b}_i$ can be constructed from the $\underline{a}_i$ by the following relations⁽⁴⁾:

$$\begin{aligned} \underline{b}_1 &= \frac{\underline{a}_2 \times \underline{a}_3}{v_a} = \frac{1}{2r_o} [-\underline{e}_x + \underline{e}_y + \underline{e}_z] \\ \underline{b}_2 &= \frac{\underline{a}_3 \times \underline{a}_1}{v_a} = \frac{1}{2r_o} [\underline{e}_x - \underline{e}_y + \underline{e}_z] \\ \underline{b}_3 &= \frac{\underline{a}_1 \times \underline{a}_2}{v_a} = \frac{1}{2r_o} [\underline{e}_x + \underline{e}_y - \underline{e}_z] . \end{aligned} \quad (3.2.2)$$

The three vectors given by equation (3.2.2) then generate a body-centered cubic reciprocal lattice as shown in Figure 8.

⁴ J.M.Ziman, Principles of the Theory of Solids (Cambridge University Press, Cambridge, 1964), Chapter I.

Figure 8. The reciprocal lattice and the first Brillouin zone for the sodium chloride structure.

It should be pointed out that we have chosen the three unit cell vectors $\underline{a}_i$ merely as an aid for constructing the reciprocal lattice. In an actual calculation, when sums over the lattice are being performed, it turns out that a more convenient choice for the unit cell of the real lattice is a Wigner-Seitz cell that encloses both a positive and a negative ion and whose origin is taken to be at the equilibrium position of one of these ions. It is also convenient to use a Wigner-Seitz cell for the unit cell in reciprocal space called the first Brillouin zone, which is the truncated octahedron shown in Figure 8. If $\underline{k}$ is a vector in the reciprocal lattice with components k_x , k_y , and k_z such that

$$\underline{k} = \frac{1}{2r_0} [k_x \underline{e}_x + k_y \underline{e}_y + k_z \underline{e}_z] , \quad (3.2.3)$$

then the first Brillouin zone shown in Figure 8 has the boundaries⁽⁵⁾

$$\begin{aligned} k_x = \pm 1 ; \quad k_y = \pm 1 ; \quad k_z = \pm 1 ; \\ \pm k_x \pm k_y \pm k_z = \pm \frac{3}{2} . \end{aligned} \quad (3.2.4)$$

The reason for using the first Brillouin zone construction, rather than the unit cell generated by $\underline{b}_1$, $\underline{b}_2$, and $\underline{b}_3$ is that the choice of the Wigner-Seitz cell is compatible with the notation adopted by Karo⁽⁶⁾.

⁵R.A. Smith, Wave Mechanics of Crystalline Solids (John Wiley & Sons, Inc., New York, 1961), Section 6.8.

⁶A.M. Karo, "Lattice Vibrations in Alkali Halide Crystals. I. Lithium and Sodium Halides," J. Chem. Phys. 31, 1489 (1959).

Any vector between two points of the reciprocal lattice is called a reciprocal lattice vector and it is generally designated as $\underline{G}$. Because the reciprocal lattice is a body-centered cubic lattice, $\underline{G}$ will be of the form

$$\underline{G} = \frac{1}{2r_0} [l_x \underline{e}_x + l_y \underline{e}_y + l_z \underline{e}_z] , \quad (3.2.5)$$

where l_x , l_y , and l_z are integers which are all even or all odd.

3.3 The work of Karo and Hardy on the lattice dynamics of alkali halide crystals

In a series of papers Karo and Hardy have calculated the lattice dynamics of alkali halides using several models^(2,6,7,8,9). Their work is of particular importance because a detailed calculation of the optical properties requires a rather complete knowledge of the eigenvalues and eigenvectors for a large number of wave vectors lying within the first Brillouin zone.

Karo and Hardy worked within the harmonic approximation by only keeping terms in the potential function that are proportional

⁷A.M. Karo, "Lattice Vibrations in Alkali Halide Crystals. II. Potassium and Rubidium Halides; Cesium Fluoride," J. Chem. Phys. 33, 7 (1960).

⁸J.R. Hardy, "Lattice Dynamics of Alkali Halide Crystals in Relation to Specific Heat Data," Phil. Mag. 7, 315 (1962).

⁹A.M. Karo and J.R. Hardy, "Precise Vibrational Frequency Distributions and the Second-Order Raman Spectrum and Specific Heat of NaCl," Phys. Rev. 141, 696 (1966).

to the quadratic displacement terms. Their calculations were based on the 'deformation dipole' model and were carried out for 0° K and for room temperature. In each instance parameters were introduced into the assumed potential function which were evaluated by relating the potential and its derivatives to such experimentally observed quantities as the lattice constant and compressibility^(2,6).

The eigenvalues and eigenvectors that have been used in calculating the far infrared optical properties of KCl have been determined in a manner described in reference 2 and tabulated in a report that was kindly sent to us by Dr. Karo⁽¹⁰⁾. The eigendata were obtained for one thousand wave vectors evenly distributed throughout the first Brillouin zone. For each wave vector six frequencies were obtained, of which three were assigned to acoustic branches and three to optical branches. Because of the symmetry possessed by the first zone the calculation of the eigendata could be restricted to a volume that was one forty-eighth of the Brillouin zone (called the irreducible zone) that contained exactly forty-eight wave vectors. The eigenvalues and eigenvectors for wave vectors lying outside the irreducible zone are generated by applying the appropriate symmetry operation to the points within the zone⁽¹¹⁾.

¹⁰ A.M. Karo and J.R. Hardy, "Lattice Dynamics of Rocksalt-Structure Alkali Halides: Eigenvectors and Eigenfrequencies," U. of California Lawrence Radiation Laboratory, Report No. UCRL-14822 (1966).

¹¹ J. Neuberger and R.D. Hatcher, "Infrared Optical Constants of NaCl," J. Chem. Phys. 34, 1733 (1961), p. 1739.

As an example, consider a wave vector $\mathbf{k}_2$, restricted to the irreducible zone, with components $k_{2x} = 0.6$, $k_{2y} = 0.4$, and $k_{2z} = 0.2$ in units of $\frac{1}{2r_0}$ (see section 3.2). There are a total of forty-seven wave vectors lying outside the irreducible zone, but still within the first Brillouin zone, that are related to $\mathbf{k}_2$ by a symmetry operation. The forty-eight symmetry-related wave vectors are (including $\mathbf{k}_2$ itself):

1.	0.6	0.4	0.2	13.	0.2	0.4	0.6
2.	0.6	0.4	-0.2	14.	0.2	0.4	-0.6
3.	0.6	-0.4	0.2	15.	0.2	-0.4	0.6
4.	0.6	-0.4	-0.2	16.	0.2	-0.4	-0.6
5.	0.6	0.2	0.4	17.	0.4	0.6	0.2
6.	0.6	0.2	-0.4	18.	0.4	0.6	-0.2
7.	0.6	-0.2	0.4	19.	0.4	-0.6	0.2
8.	0.6	-0.2	-0.4	20.	0.4	-0.6	-0.2
9.	0.2	0.6	0.4	21.	0.4	0.2	0.6
10.	0.2	0.6	-0.4	22.	0.4	0.2	-0.6
11.	0.2	-0.6	0.4	23.	0.4	-0.2	0.6
12.	0.2	-0.6	-0.4	24.	0.4	-0.2	-0.6

(3.3.1)

PLUS

[twenty-four additional wave vectors which have the signs of all of the components of the above wave vectors changed.]

The eigenvectors and eigenvalues for those symmetry-related wave vectors lying outside of the irreducible zone are related to

the eigenvectors and eigenvalues of the wave vector lying in the irreducible zone. These relations have been established by Neuberger and Hatcher⁽¹¹⁾ and their results are summarized below.

Suppose that $\mathbf{k}_{\mathbf{N}2}$ is a vector of the irreducible zone. Then the eigenvector $\boldsymbol{\eta}(\mathbf{k}_{\mathbf{N}2}j)$ for the mode $(\mathbf{k}_{\mathbf{N}2}j)$ has the form⁽¹⁰⁾

$$\boldsymbol{\eta}(\mathbf{k}_{\mathbf{N}2}j) = \begin{bmatrix} m_x(\mathbf{k}_{\mathbf{N}2}j/0) \\ m_x(\mathbf{k}_{\mathbf{N}2}j/1) \\ m_y(\mathbf{k}_{\mathbf{N}2}j/0) \\ m_y(\mathbf{k}_{\mathbf{N}2}j/1) \\ m_z(\mathbf{k}_{\mathbf{N}2}j/0) \\ m_z(\mathbf{k}_{\mathbf{N}2}j/1) \end{bmatrix}, \quad (3.3.2)$$

where $m_x(\mathbf{k}_{\mathbf{N}2}j/0)$ is the x component of the eigenvector belonging to the mode $(\mathbf{k}_{\mathbf{N}2}j)$ and associated with the $K = 0$ particle in the unit cell, while $m_x(\mathbf{k}_{\mathbf{N}2}j/1)$ is associated with the $K = 1$ particle in the unit cell. Similar interpretations hold for the remaining four components of $\boldsymbol{\eta}(\mathbf{k}_{\mathbf{N}2}j)$.

If a new, symmetry-related, wave vector $\mathbf{k}_{\mathbf{N}2}'$ is created by simply interchanging two components of $\mathbf{k}_{\mathbf{N}2}$, say the x and y components, such that

$$\begin{aligned} k_{2x}' &= k_{2y} , \\ k_{2y}' &= k_{2x} , \\ \text{and } k_{2z}' &= k_{2z} , \end{aligned} \quad (3.3.3)$$

then the new eigenvector $\boldsymbol{\eta}'(\mathbf{k}_{\mathbf{N}2}'j)$ corresponding to $\mathbf{k}_{\mathbf{N}2}'$ will be

identical to $\eta(k_2 j)$ except the x' and y components will be interchanged, e.g.,

$$\eta'(k_2' j) = \begin{bmatrix} m_y(k_2 j/0) \\ m_y(k_2 j/1) \\ m_x(k_2 j/0) \\ m_x(k_2 j/1) \\ m_z(k_2 j/0) \\ m_z(k_2 j/1) \end{bmatrix} \quad (3.3.4)$$

The eigenvalues remain invariant under this operation, e.g.,

$$\omega(k_2 j) = \omega(k_2' j).$$

Similarly, it can be shown that a change in the sign of one or more of the components of k_2 results in a new wave vector k_2'' that has its corresponding eigenvector components changed in sign. For example, if

$$\begin{aligned} k_{2x}'' &= -k_{2x} , \\ k_{2y}'' &= +k_{2y} , \\ \text{and } k_{2z}'' &= -k_{2z} , \end{aligned} \quad (3.3.5)$$

then

$$\eta''(k_2'' j) = \begin{bmatrix} -m_x(k_2 j/0) \\ -m_x(k_2 j/1) \\ +m_y(k_2 j/0) \\ +m_y(k_2 j/1) \\ -m_z(k_2 j/0) \\ -m_z(k_2 j/1) \end{bmatrix} \quad (3.3.6)$$

The eigenvalues also remain invariant under a change in sign of any or all of the components of $\underline{k}_2$.

Therefore, it can be concluded that any wave vector lying outside of the irreducible zone has the same eigenvalue as does the symmetry-related wave vector which lies within the irreducible zone. In particular, all of the wave vectors in equation (3.3.1) have the same eigenvalues.

Karo and Hardy also calculated the heat capacity and the Debye temperature for KCl. The heat capacity predicted by their model at 260 °K is 11.47 cal/mole·degree K, where as the experimental value is 11.56 cal/mole·degree K. The calculated Debye temperature of approximately 225 °K is slightly higher than the observed value of 210 °K.

3.4 The crystal Hamiltonian and dipole moment operators

In accordance with the adiabatic approximation the following Hamiltonian for a vibrating lattice will be used. The Hamiltonian consists of a kinetic energy part and an effective potential function in which the ions move of the form

$$H = \frac{1}{2} \sum_{L,K} \sum_{\alpha} M_K \dot{u}_{\alpha}^2(LK) + \frac{1}{2} \sum_{L,K} \sum_{L',K'}' \phi [|\underline{r}(LK;L'K')|] . \quad (3.4.1)$$

In this expression $u_\alpha(LK)$ is the α -Cartesian component of the displacement of the K^{th} ion in the L^{th} unit cell from its equilibrium position, and M_K is the mass of the K^{th} ion. L ranges over the N unit cells in the crystal and $K = 1, 2$ designates the particular ion (of the two ions) in the unit cell. The second term on the right hand side of equation (3.4.1) represents the total potential energy of the lattice and it is expressed as a double sum over the two-body potentials $\phi[|\vec{r}(LK; L'K')|]$. $\phi[|\vec{r}(LK; L'K')|]$ represents a central potential between two ions, one of which has its displaced position located at $\vec{r}(LK) = \vec{r}_0(LK) + \vec{u}(LK)$ and the other at $\vec{r}(L'K') = \vec{r}_0(L'K') + \vec{u}(L'K')$ where $\vec{r}_0(LK)$ is the vector from an arbitrary origin of the lattice to the equilibrium position of the ion (LK) . The vector $\vec{r}(LK; L'K')$ then represents the difference between $\vec{r}(LK)$ and $\vec{r}(L'K')$ e.g.,

$$\begin{aligned} \vec{r}(LK; L'K') &\equiv \vec{r}(LK) - \vec{r}(L'K') = [\vec{r}_0(LK) - \vec{r}_0(L'K')] + \\ &+ [\vec{u}(LK) - \vec{u}(L'K')] \equiv \vec{r}_0(LK; L'K') + \vec{u}(LK; L'K'). \end{aligned} \quad (3.4.2)$$

The prime on the summation symbol, $\sum'_{L'K'}$, means that terms in the double sum with $(LK) = (L'K')$ are to be excluded.

The next step is to represent the potential function appearing in equation (3.4.1) by a Taylor series expansion in powers of $[\vec{u}(LK) - \vec{u}(L'K')]$ up to quartic terms (remember that the inclusion of quintic and higher order terms violates the adiabatic approximation):

$$\begin{aligned}
\Phi &= \frac{1}{2} \sum_{LK} \sum'_{L'K'} \phi(|\underline{r}(LK;L'K')|) = \\
&= \frac{1}{2} \sum_{LK} \sum'_{L'K'} \left[\phi(|\underline{r}_0(LK;L'K')|) + \right. \\
&\quad + \sum_{\alpha} \phi_{\alpha}(LK;L'K') [u_{\alpha}(LK) - u_{\alpha}(L'K')] + \\
&\quad + \frac{1}{2} \sum_{\alpha, \beta} \phi_{\alpha\beta}(LK;L'K') [u_{\alpha}(LK) - u_{\alpha}(L'K')] \times \\
&\quad \times [u_{\beta}(LK) - u_{\beta}(L'K')] + \frac{1}{6} \sum_{\alpha\beta\gamma} \phi_{\alpha\beta\gamma}(LK;L'K') \times \\
&\quad \times [u_{\alpha}(LK) - u_{\alpha}(L'K')] [u_{\beta}(LK) - u_{\beta}(L'K')] \times \\
&\quad \times [u_{\gamma}(LK) - u_{\gamma}(L'K')] + \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \phi_{\alpha\beta\gamma\delta}(LK;L'K') \times \\
&\quad \times [u_{\alpha}(LK) - u_{\alpha}(L'K')] [u_{\beta}(LK) - u_{\beta}(L'K')] \times \\
&\quad \times [u_{\gamma}(LK) - u_{\gamma}(L'K')] [u_{\delta}(LK) - u_{\delta}(L'K')] + \\
&\quad \left. + \dots \dots \dots \text{plus higher order terms} \right] . \quad (3.4.3)
\end{aligned}$$

The sums over α, β, γ , and δ each extend over the three Cartesian indicies x, y , and z . For notation simplicity let the distance between two ions be designated as $|\underline{r}(LK;L'K')| \equiv r$ which has components r_x, r_y , and r_z . Then the expansion coefficients

$\phi_{\alpha\beta\dots}(\mathbf{L}\mathbf{K}; \mathbf{L}'\mathbf{K}')$ appearing in equation (3.4.3) are given explicitly by

$$\phi_x = \left. \frac{\partial \phi(\lambda)}{\partial \lambda_x} \right|_{\lambda=\lambda_0} = \frac{\lambda_x}{\lambda} \phi'(\lambda) \Big|_{\lambda=\lambda_0}, \quad (3.4.4a)$$

$$\begin{aligned} \phi_{xy} = \left. \frac{\partial^2 \phi(\lambda)}{\partial \lambda_x \partial \lambda_y} \right|_{\lambda=\lambda_0} &= \left[\frac{\lambda_x \lambda_y}{\lambda^2} \left(\phi''(\lambda) - \frac{\phi'(\lambda)}{\lambda} \right) + \right. \\ &\quad \left. + \frac{\delta_{xy}}{\lambda} \phi'(\lambda) \right] \Big|_{\lambda=\lambda_0}, \end{aligned} \quad (3.4.4b)$$

$$\begin{aligned} \phi_{xyz} = \left. \frac{\partial^3 \phi(\lambda)}{\partial \lambda_x \partial \lambda_y \partial \lambda_z} \right|_{\lambda=\lambda_0} &= \\ &= \left\{ \frac{\lambda_x \lambda_y \lambda_z}{\lambda^3} \left(\phi'''(\lambda) - \frac{3}{\lambda} \phi''(\lambda) + \frac{3}{\lambda^2} \phi'(\lambda) \right) + \right. \\ &\quad + \left(\delta_{xy} \frac{\lambda_z}{\lambda^2} + \delta_{yz} \frac{\lambda_x}{\lambda^2} + \delta_{zx} \frac{\lambda_y}{\lambda^2} \right) \left[\phi''(\lambda) - \right. \\ &\quad \left. \left. - \frac{1}{\lambda} \phi'(\lambda) \right] \right\} \Big|_{\lambda=\lambda_0}, \end{aligned} \quad (3.4.4c)$$

and

$$\begin{aligned}
 \phi_{xyzw} &= \frac{\partial^4 \phi(\lambda)}{\partial \lambda_x \partial \lambda_y \partial \lambda_z \partial \lambda_w} \Big|_{\lambda=\lambda_0} = \\
 &= \left\{ \frac{\lambda_x \lambda_y \lambda_z \lambda_w}{\lambda^4} \left[\phi^{IV}(\lambda) - \frac{6}{\lambda} \phi'''(\lambda) + \frac{15}{\lambda^2} \phi''(\lambda) - \right. \right. \\
 &\quad \left. \left. - \frac{15}{\lambda^3} \phi'(\lambda) \right] + \left(\lambda_x \lambda_y \delta_{zw} + \lambda_x \lambda_z \delta_{yw} + \right. \right. \\
 &\quad \left. \left. + \lambda_x \lambda_w \delta_{yz} + \lambda_y \lambda_z \delta_{xw} + \lambda_y \lambda_w \delta_{xz} + \right. \right. \\
 &\quad \left. \left. + \lambda_z \lambda_w \delta_{xy} \right) \left(\frac{1}{\lambda^3} \right) \left[\phi'''(\lambda) - \frac{3}{\lambda} \phi''(\lambda) + \right. \right. \\
 &\quad \left. \left. + \frac{3}{\lambda^2} \phi'(\lambda) \right] + \left(\delta_{xy} \delta_{zw} + \delta_{yz} \delta_{xw} + \delta_{xz} \delta_{yw} \right) \right. \\
 &\quad \left. \times \left(\frac{1}{\lambda^2} \right) \left[\phi''(\lambda) - \frac{1}{\lambda} \phi'(\lambda) \right] \right\} \Big|_{\lambda=\lambda_0} . \tag{3.4.4d}
 \end{aligned}$$

The above expressions can be somewhat simplified because $\phi'(r_0) = 0$.

A normal coordinate transformation is now made in which the ionic displacement operators $u_{\mathbf{L}\mathbf{K}}$ are expressed in terms of the phonon creation and annihilation operators. This transformation casts the Hamiltonian into a new form which is often referred to as the second quantization representation and it is in this representation that all subsequent analysis will be carried out. The normal mode transformation is written as

$$u_x(LK) = \left(\frac{\hbar}{2NM_K} \right)^{1/2} \sum_{\underline{k}}^N \sum_{j=1}^6 \frac{m_x(\underline{k}j|K)}{\omega(\underline{k}j)^{1/2}} \times \quad 57$$

$$\times e^{2\pi i \underline{k} \cdot [\underline{X}(L) + \underline{X}(K)]} [a_{\underline{k}j} + a_{-\underline{k}j}^+] , \quad (3.4.5)$$

where $\sum_{\underline{k}}^N \sum_{j=1}^6$ is a sum over all the quantized normal modes of the lattice, $\underline{k}$ being the wave vector of the mode and j identifies the particular branch of the dispersion curve to which that mode belongs; for notation convenience this double sum will be represented as $\sum_{\underline{k}j}$. $\underline{X}(L)$ is a vector from the origin of the lattice to the origin of the L^{th} unit cell and $\underline{X}(K)$ is a vector from the origin of the unit cell to the K^{th} ion within the cell. $a_{\underline{k}j}$ is a destruction operator that annihilates a phonon of wave vector $\underline{k}$ belonging to the branch j while $a_{-\underline{k}j}^+$ creates a phonon characterized by the parameters $-\underline{k}, j$. $\omega(\underline{k}j)$ is the angular frequency of the mode $(\underline{k}j)$ in the harmonic crystal and $m_x(\underline{k}j|K)$ is the x-component of the corresponding eigenvector or unit polarization vector which is associated with the K^{th} ion in the unit cell. These eigenvectors are identical to those defined by Karo and Hardy⁽⁶⁾ and they are related to the eigenvectors $e_x(\underline{k}j|K)$ used by Born and Huang⁽¹²⁾;

$$m_x(\underline{k}j|K) = e_x(\underline{k}j|K) e^{-2\pi i \underline{k} \cdot \underline{X}(K)} . \quad (3.4.6)$$

¹² Born and Huang, op. cit., p. 297.

The Karo and Hardy eigenvectors are chosen because they have been explicitly evaluated for many of the alkali halides⁽¹⁰⁾.

They are real for a crystal every ion of which is at a center of inversion symmetry and they satisfy the usual orthonormality and closure relations:

$$\sum_{K\alpha} m_{\alpha}(\underline{k}_j|K) m_{\alpha}(\underline{k}_{j'}|K) = \delta_{jj'} \quad (3.4.7a)$$

$$\sum_j m_{\alpha}(\underline{k}_j|K) m_{\beta}(\underline{k}_j|K') = \delta_{\alpha\beta} \delta_{KK'} \quad (3.4.7b)$$

If the transformation given by equation (3.4.5) is substituted in the Hamiltonian (3.4.1) it is found that H can be separated into a harmonic part H_0 (which contains the kinetic energy and quadratic potential term) and into an anharmonic term H_A (containing the cubic and quartic potential terms) such that $H = H_0 + H_A$ where

$$H_0 = \sum_{\underline{k}_j} \frac{1}{2} \hbar \omega(\underline{k}_j) [a_{\underline{k}_j} a_{\underline{k}_j}^{\dagger} + a_{\underline{k}_j}^{\dagger} a_{\underline{k}_j}], \quad (3.4.8)$$

and

$$\begin{aligned}
 H_A = & \frac{1}{6} \left(\frac{\hbar}{2N^{1/3}} \right)^{3/2} \sum_{\underline{k}_1 \underline{k}_2 \underline{k}_3} \sum_{j_1 j_2 j_3} \Delta(\underline{k}_1 + \underline{k}_2 + \underline{k}_3) \times \\
 & \times \frac{\Phi^{(3)}(\underline{k}_1 j_1 ; \underline{k}_2 j_2 ; \underline{k}_3 j_3)}{[\omega(\underline{k}_1 j_1) \omega(\underline{k}_2 j_2) \omega(\underline{k}_3 j_3)]^{1/2}} \prod_{i=1}^3 [a_{\underline{k}_i j_i} + a_{-\underline{k}_i j_i}^\dagger] + \\
 & + \frac{\hbar^2}{96N} \sum_{\underline{k}_1 \underline{k}_2 \underline{k}_3 \underline{k}_4} \sum_{j_1 j_2 j_3 j_4} \Delta(\underline{k}_1 + \underline{k}_2 + \underline{k}_3 + \underline{k}_4) \times \\
 & \times \frac{\Phi^{(4)}(\underline{k}_1 j_1 ; \underline{k}_2 j_2 ; \underline{k}_3 j_3 ; \underline{k}_4 j_4)}{[\omega(\underline{k}_1 j_1) \omega(\underline{k}_2 j_2) \omega(\underline{k}_3 j_3) \omega(\underline{k}_4 j_4)]^{1/2}} \times \prod_{i=1}^4 [a_{\underline{k}_i j_i} + a_{-\underline{k}_i j_i}^\dagger] .
 \end{aligned}
 \tag{3.4.9}$$

The delta functions appearing in equation (3.4.9) conserve the phonon wave vectors and are defined as

$$\Delta(\underline{k}_1 \cdots + \underline{k}_m) = \begin{cases} 1 & \text{if } (\underline{k}_1 + \cdots + \underline{k}_m) = 0 \text{ or } \underline{G} \text{ where} \\ & \underline{G} \text{ is a reciprocal lattice vector} \\ & \text{(see equation (3.2.5))} \\ 0 & \text{otherwise.} \end{cases}
 \tag{3.4.10}$$

The n^{th} order coupling coefficient $\Phi^{(m)}(\underline{k}_1 j_1 \cdots \underline{k}_m j_m)$ has an explicit form given by

$$\begin{aligned}
\Phi^{(m)}(\underline{k}_1 j_1 \cdots \underline{k}_m j_m) &= \frac{1}{2} \sum_K \sum_{L'K'}' \sum_{\alpha_1 \cdots \alpha_m} \times \\
&\times \phi_{\alpha_1 \cdots \alpha_m}(0K; L'K') \prod_{i=1}^m \left(\frac{m_{\alpha_i}(\underline{k}_{ij_i}|K)}{\sqrt{M_K}} \times \right. \\
&\times e^{2\pi i \underline{k}_{ij_i} \cdot \underline{\chi}(K)} - \frac{m_{\alpha_i}(\underline{k}_{ij_i}|K')}{\sqrt{M_{K'}}} e^{2\pi i \underline{k}_{ij_i} \cdot [\underline{\chi}(L') + \underline{\chi}(K')]} \left. \right).
\end{aligned}
\tag{3.4.11}$$

In arriving at equation (3.4.11) the origin of the lattice was chosen to coincide with the origin of the $L = 0$ unit cell and hence $\underline{\chi}(L=0) = 0$.

Two final notation changes will now be made that will result in a Hamiltonian of the simplest possible form. Upon introducing a new operator

$$A_{\underline{k}j} \equiv a_{\underline{k}j} + a_{-\underline{k}j}^{\dagger}, \tag{3.4.12}$$

and also defining a new n^{th} order coupling coefficient such that

$$\begin{aligned}
 V^{(m)}(\underline{k}_1 j_1 \cdots \underline{k}_m j_m) &= \frac{1}{m! N^{(m/2 - 1)}} \times \\
 &\times \Delta(\underline{k}_1 + \cdots + \underline{k}_m) \left[\frac{\hbar^m}{2^m \omega(\underline{k}_1 j_1) \cdots \omega(\underline{k}_m j_m)} \right]^{1/2} \times \\
 &\times \Phi^{(m)}(\underline{k}_1 j_1 \cdots \underline{k}_m j_m), \quad (3.4.13)
 \end{aligned}$$

the crystal Hamiltonian, $H = H_0 + H_A$, takes the following form:

$$H_0 = \sum_{\underline{k}j} \frac{1}{2} \hbar \omega(\underline{k}j) [a_{\underline{k}j} a_{\underline{k}j}^\dagger + a_{\underline{k}j}^\dagger a_{\underline{k}j}], \quad (3.4.14)$$

$$\begin{aligned}
 H_A &= \sum_{\underline{k}_1 j_1} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} V^{(3)}(\underline{k}_1 j_1; \underline{k}_2 j_2; \underline{k}_3 j_3) \times \\
 &\times A_{\underline{k}_1 j_1} A_{\underline{k}_2 j_2} A_{\underline{k}_3 j_3} + \\
 &+ \sum_{\underline{k}_1 j_1} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} \sum_{\underline{k}_4 j_4} V^{(4)}(\underline{k}_1 j_1; \underline{k}_2 j_2; \underline{k}_3 j_3; \underline{k}_4 j_4) \times \\
 &\times A_{\underline{k}_1 j_1} A_{\underline{k}_2 j_2} A_{\underline{k}_3 j_3} A_{\underline{k}_4 j_4}. \quad (3.4.15)
 \end{aligned}$$

The form of H is now identical with that obtained by Cowley⁽¹³⁾.

Expansion of the dipole moment operator

In an ionic crystal that possesses a first order electric moment the α -Cartesian component of the dipole moment operator M_α can be expanded in terms of the ionic displacements by a Taylor series as⁽¹⁴⁾

$$\begin{aligned}
 M_\alpha = & \sum_{LK} \sum_{\beta} M_{\alpha,\beta}(LK) u_\beta(LK) + \\
 & + \frac{1}{2} \sum_{LK} \sum_{L'K'}' \sum_{\beta\gamma} M_{\alpha,\beta\gamma}(LK; L'K') u_\beta(LK) u_\gamma(L'K') + \\
 & + \dots \text{higher order terms,}
 \end{aligned}
 \tag{3.4.16}$$

where $u_\alpha(LK)$ is the α -Cartesian component of the displacement of the K^{th} ion in the L^{th} unit cell from its equilibrium position.

If the second-quantized transformation given by equations (3.4.5) and (3.4.12) is substituted into the above expression it is found that the dipole moment operator can be written as

¹³R.A.Cowley, "The Lattice Dynamics of an Anharmonic Crystal," Advances in Physics 12, 421 (1963).

¹⁴Born and Huang, op. cit., p.219 and p. 305.

$$\begin{aligned}
 M_\alpha = & \sum_j M_\alpha(oj) A_{oj} + \\
 & + \sum_{\underline{k}_1 j_1} \sum_{j_2} M_\alpha(\underline{k}_1 j_1 ; -\underline{k}_1 j_2) A_{\underline{k}_1 j_1} A_{-\underline{k}_1 j_2} .
 \end{aligned}
 \tag{3.4.17}$$

The expansion coefficients used in (3.4.17) have the following form:

$$M_\alpha(oj) = \left(\frac{N\hbar}{2\omega(oj)} \right)^{1/2} \sum_K \sum_\beta \frac{M_{\alpha,\beta}(K)}{\sqrt{M_K}} m_\alpha(oj|K)
 \tag{3.4.18}$$

$$\begin{aligned}
 M_\alpha(\underline{k}_1 j_1 ; -\underline{k}_1 j_2) = & \frac{\hbar}{4} \frac{1}{[\omega(\underline{k}_1 j_1) \omega(-\underline{k}_1 j_2)]^{1/2}} \times \\
 & \times \sum_K \sum_{L'K'} \sum_{\beta\gamma} \frac{M_{\alpha,\beta\gamma}(OK; L'K')}{\sqrt{M_K M_{K'}}} m_\beta(\underline{k}_1 j_1 | K) \times \\
 & \times m_\gamma(-\underline{k}_1 j_2 | K') e^{-2\pi i \underline{k}_1 \cdot \underline{x}(L')} e^{2\pi i \underline{k}_1 \cdot [\underline{x}(K) - \underline{x}(K')]} .
 \end{aligned}
 \tag{3.4.19}$$

As previously mentioned, $m_p(k_1 j_1 / K)$ etc., are the Karo and Hardy eigenvectors which are related to the eigenvectors defined by Born and Huang⁽¹²⁾ by equation (3.4.6).

The calculations of the dielectric constants by Cowley on KBr and NaI⁽¹³⁾ and by Ipatova et al.⁽¹⁵⁾ on LiF and NaCl show that the dominant contribution to the far infrared dielectric constants is that associated with the first term on the right hand side of equation (3.4.17). Because of this reason, and the fact that an enormous savings in computation time can be affected, only the linear term in the dipole moment operator will be used in the analysis of KCl.

3.5 Derivation of the complex dielectric susceptibility from the Green's function approach

The starting point for the derivation of the optical properties of a solid is to establish the correct Hamiltonian which describes the interaction between the external electromagnetic radiation and the phonon field. As pointed out in the last section the time independent Hamiltonian H for the crystal can be written as the sum of a harmonic part H_0 and an anharmonic contribution H_A such that

$$H = H_0 + H_A . \quad (3.5.1)$$

¹⁵I.P. Ipatova, A.A. Maradudin and R.F. Wallis, "Temperature Dependence of the Width of the Fundamental Lattice-Vibration Absorption Peak in Ionic Crystals. II. Approximate Numerical Results," Phys. Rev. 155, 882 (1967).

It is assumed that at $t = -\infty$ the system was in a state of thermal equilibrium described by a canonical distribution and at that time an external electric field $\vec{E}(t)$ was turned on. A dipole interaction between the electric field and the crystal occurs which is of the form

$$H_I(t) = - \vec{M} \cdot \vec{E}(t) , \quad (3.5.2)$$

where $\vec{M}$ is the electric dipole moment operator of the crystal and it is given explicitly by equations (3.4.16) and (3.4.17). The electric field of frequency ω is described by the equation

$$\vec{E}(t) = \lim_{\substack{\epsilon \rightarrow 0 \\ (\epsilon > 0)}} e^{\epsilon t} \vec{E}_0 e^{i\omega t} , \quad (3.5.3)$$

where the factor $e^{\epsilon t}$ is introduced to adiabatically turn on the field for $t < 0$ and to serve as a boundary condition that $\vec{E}(-\infty) = 0$.

The total Hamiltonian of the perturbed system is time dependent and can be written as

$$H_T = H + H_I(t) , \quad (3.5.4)$$

where all of the operators appearing in equation (3.5.4) are expressed in the Schrodinger representation.

The next step is to calculate the ensemble average of the expectation value of the α^{th} -Cartesian component of the dipole moment operator $\langle\langle M_\alpha \rangle\rangle_{H_T}$ and then to look for a linear relation

between $\langle\langle M_\alpha \rangle\rangle_{H_T}$ and the β -component of the external field $E_\beta(t)$ of the form

$$\langle\langle M_\alpha \rangle\rangle_{H_T} = \sum_\beta \hat{\chi}_{\alpha\beta}(\omega) \left[E_{0\beta} e^{\varepsilon t} e^{i\omega t} \right]. \quad (3.5.5)$$

$\hat{\chi}_{\alpha\beta}(\omega)$ is the frequency dependent complex dielectric susceptibility tensor and $\langle\langle M_\alpha \rangle\rangle_{H_T}$ is the shorthand notation for the canonical ensemble average of M_α taken with respect to the total time dependent Hamiltonian $H_T(t)$, e.g.,

$$\langle\langle M_\alpha \rangle\rangle_{H_T} \equiv \frac{\text{trace} \left[e^{-\beta H_T} M_\alpha \right]}{\text{trace} \left[e^{-\beta H_T} \right]}, \quad (3.5.6)$$

where β is the usual $1/k_B T$. It should be noted that in the absence of the external field $E(t)$ an ionic crystal possesses no permanent electric dipole moment so that $\langle\langle M_\alpha \rangle\rangle_{H_T}$ represents the induced dipole moment and is, therefore, a function of time.

The evaluation of the α -th component of the induced dipole moment has been outlined by Kubo⁽¹⁶⁾ and Zubarev⁽¹⁷⁾ and only the results of their work will be given.

¹⁶R. Kubo, "Statistical-Mechanical Theory of Irreversible Processes. I.," Journal of the Physical Society of Japan 12, 570 (1957).

¹⁷D.N. Zubarev, "Double-Time Green Functions in Statistical Physics," Usp. Fiz. Nauk 71, 71 (1960) [transl: Soviet Physics-Uspokhi 3, 320 (1960)].

$$\langle\langle M_\alpha \rangle\rangle_{H_T} = -\frac{i}{\hbar} \lim_{\substack{\epsilon \rightarrow 0 \\ (\epsilon > 0)}} e^{i\Omega t + \epsilon t} \int_{-\infty}^{+\infty} e^{-i(\Omega + i\epsilon)\tau} d\tau \quad (3.5.6)$$

$$\times \left\{ \theta(\tau) \langle\langle M_\alpha(\tau), -\vec{M}(0) \cdot \vec{E}_0 \rangle\rangle_H \right\} d\tau. \quad (3.5.7)$$

The operators appearing in this expression are written in the Heisenberg picture, e.g.,

$$M_\alpha(\tau) = e^{iH\tau/\hbar} M_\alpha e^{-iH\tau/\hbar}, \quad (3.5.8)$$

and $\theta(\tau)$ is a unit step function defined by the relation

$$\theta(\tau) \equiv \begin{cases} 1 & \text{if } \tau > 0 \\ 0 & \text{if } \tau < 0 \\ \text{undefined at } \tau = 0. \end{cases} \quad (3.5.9)$$

The integrand factor $\langle\langle [M_\alpha(\tau), -\vec{M}(0) \cdot \vec{E}_0] \rangle\rangle_H$ represents the canonical ensemble average of the commutator of two operators taken with respect to the time independent crystal Hamiltonian H .

If the dot product appearing in equation (3.5.7) is expanded as

$$\vec{M}(0) \cdot \vec{E}_0 = \sum_{\beta} M_{\beta}(0) E_{0\beta} \quad (3.5.10)$$

and only the linear term in the dipole moment operator expansion (3.4.17) is kept then it immediately follows from equation (3.5.7) that a linear relation exists between the induced dipole moment and the driving electric field:

$$\langle\langle M_\alpha \rangle\rangle_{HT} = \sum_{\beta} \hat{\chi}_{\alpha\beta}(\omega) [E_{0\beta} e^{i\omega t + \epsilon t}]. \quad (3.5.11)$$

$\hat{\chi}_{\alpha\beta}(\omega)$ is the α, β -component of the complex dielectric susceptibility tensor and has an explicit form that can be obtained from equations (3.5.7) and (3.5.10):

$$\begin{aligned} \hat{\chi}_{\alpha\beta}(\omega) = & \frac{-i}{Nv\hbar} \sum_{jj'} M_\alpha(0j) M_\beta(0j') \times \\ & \lim_{\substack{\epsilon \rightarrow 0 \\ (\epsilon > 0)}} \int_{-\infty}^{+\infty} e^{-i(\omega + i\epsilon)\tau} \left\{ \theta(\tau) \times \right. \\ & \left. \times \langle\langle A_{0j}(\tau), A_{0j'}(0) \rangle\rangle_H \right\} d\tau, \end{aligned} \quad (3.5.12)$$

where $M_\alpha(0j)$ is defined by equations (3.4.17) and (3.4.18).

The factor Nv is the total volume of the crystal and it is present in equation (3.5.12) because $\hat{\chi}_{\alpha\beta}(\omega)$ is defined as the dielectric susceptibility per unit volume.

The quantity in brackets $\{ \dots \}$ in equation (3.5.12) is defined as the retarded Green's function $G^R(0j; 0j'; \tau)$ and it is simply the ensemble average of the commutator of two time-ordered

Heisenberg operators. Equation (3.5.12) shows that $\hat{\chi}_{\alpha\beta}(\omega)$ is proportional to the Fourier transform of the retarded Green's function $G^R(0j; 0j'; \omega + i\epsilon)$ and this is expressed formally as

$$\hat{\chi}_{\alpha\beta}(\omega) = \lim_{\substack{\epsilon \rightarrow 0 \\ (\epsilon > 0)}} \left(\frac{-i}{N\omega\hbar} \right) \sum_{jj'} M_{\alpha}(0j) M_{\beta}(0j') \times \\ \times G^R(0j; 0j'; \omega + i\epsilon), \quad (3.5.13)$$

where

$$G^R(0j; 0j'; \omega + i\epsilon) = \int_{-\infty}^{+\infty} G^R(0j; 0j'; \tau) e^{-i(\omega + i\epsilon)\tau} d\tau. \quad (3.5.14)$$

The advantage in using this formalism is that all of the operators appearing in the retarded Green's function (3.5.12) are defined with respect to the time independent crystal Hamiltonian H where as equation (3.5.6) involves the total time dependent Hamiltonian $H_T(t)$. However, the retarded Green's function should ultimately be evaluated in terms of the harmonic Hamiltonian H_0 whose eigenfunctions and eigenvalues are exactly known.

In order to carry out this program it is convenient to introduce the thermodynamic Green's functions which are defined as the thermal average of two time-ordered operators taken with respect to the crystal Hamiltonian H :

$$G(oj; oj'; u) \equiv \langle\langle T A_{oj}(u) A_{oj'}(0) \rangle\rangle_H. \quad (3.5.15)$$

In this expression $u = it/\hbar$, $A_{oj}(u) \equiv e^{uH} A_{oj} e^{-uH}$, and T is a time ordering operator with the property that

$$\langle\langle T A_{oj}(u) A_{oj'}(0) \rangle\rangle_H = \begin{cases} \langle\langle A_{oj}(u) A_{oj'}(0) \rangle\rangle_H & \text{for } u > 0 \\ \langle\langle A_{oj'}(0) A_{oj}(u) \rangle\rangle_H & \text{for } u < 0. \end{cases} \quad (3.5.16)$$

It is apparent that the thermodynamic Green's function is somewhat similar to the retarded Green's function and this similarity becomes more evident if the Fourier coefficients of these two functions are compared. The motivation for working with the thermodynamic Green's function is the following. Equation (3.5.13) shows that the dielectric susceptibility, and hence the far infrared optical properties, is directly proportional to the Fourier coefficients of the retarded Green's function. In practice, these coefficients are relatively difficult to calculate. However, it turns out that the evaluation of the Fourier coefficients of the thermodynamic Green's function by perturbation theory is considerably easier and there exists a direct relationship between these coefficients and the dielectric susceptibility; therefore, it becomes important to establish these coefficients.

The thermodynamic Green's function is analytic in the region $-\beta < u < +\beta$ for $\beta = 1/k_B T$ where k_B is the Boltzmann constant and T is the absolute temperature; this region is sufficient for

the determination of the excited states of the thermodynamic system. In this region $G(0j; 0j'; u)$ can be expanded as a Fourier series in the u direction⁽¹³⁾:

$$G(0j; 0j'; u) = \sum_{m=-\infty}^{+\infty} G(0j; 0j'; i\omega_m) e^{+i\hbar\omega_m u}, \quad (3.5.17)$$

where $\omega_n = \frac{2\pi}{\hbar\beta} n$ and n is an integer. The Fourier coefficients of the thermodynamic Green's function are given explicitly by

$$G(0j; 0j'; i\omega_m) = \frac{1}{2\beta} \int_{-\beta}^{+\beta} G(0j; 0j'; u) e^{-i\hbar\omega_m u} du, \quad (3.5.18)$$

and these coefficients are referred to as the phonon propagators.

As indicated by equation (3.5.14) the Fourier coefficients of the retarded Green's function $G^R(0j; 0j'; \omega + i\epsilon)$ are continuous functions of the frequency ω . It is possible to show that⁽¹⁸⁾

$$G^R(0j; 0j'; \omega + i\epsilon) = i\beta\hbar G(0j; 0j'; i\omega_m) \quad (3.5.19)$$

if $i\omega_m = \omega + i\epsilon$.

This means that the two Fourier coefficients are identical (apart from the multiplying constants) at the points $i\omega_n$ in the complex

¹⁸W. Cochran and R.A. Cowley, "Phonons in Perfect Crystals," Encyclopedia of Physics, ed., L. Genzel (Springer-Verlag, Berlin, 1967), vol. XXV/2a.

plane where the thermodynamic Green's function is defined. Therefore, the retarded Green's function can be obtained by first calculating the Fourier coefficients of the thermodynamic Green's function at the discrete points $i\omega_n$, and then analytically continuing $i\omega_n$ to the upper half of the complex ω plane. In general, this analytic continuation is not unique; however, in this case it can be done uniquely with no difficulties⁽¹⁹⁾.

The susceptibility tensor is then given by

$$\hat{\chi}_{\alpha\beta}(\omega) = \frac{\beta}{NV} \lim_{\substack{\epsilon \rightarrow 0 \\ (\epsilon > 0)}} \sum_{jj'} M_{\alpha}(oj) M_{\beta}(oj') \times \\ \times G(oj; oj'; \omega + i\epsilon). \quad (3.5.20)$$

The explicit evaluation of $G(oj; oj'; i\omega_n)$ is carried out conveniently by means of the diagram technique and Dyson's equation. Since these techniques have been developed rather extensively in the literature^(17, 20, 21, 22, 23) the detailed analysis will not be

¹⁹G. Baym and N.D. Mermin, "Determination of Thermodynamic Green's Functions," J. Math. Phys. 2, 232 (1961).

²⁰A.I. Alekseev, "The Application of the Methods of Quantum Field Theory in Statistical Physics," Usp. Fiz. Nauk 73, 41 (1961) (transl: Soviet Physics-Uspekhi 4, 23 (1961)).

²¹D.J. Thouless, The Quantum Mechanics of Many-Body Systems (Academic Press, New York, 1961).

²²A.A. Abrikosov, L.P. Gorkov and I.E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963).

²³R.L. Mills, "Field-Theory Methods," Physics of Many-Particle Systems, ed. E. Meeron (Gordon and Breach, to be published).

presented here although the results are given below.

If the phonon propagator $G(0j;0j'; i\omega_n)$ (see equation (3.5.18)) is regarded as a 6×6 matrix in the branch indices j and j' then it can be shown that the elements of the phonon propagator are solutions of the Dyson equation^(24,25):

$$G(0j;0j'; i\omega_m) = \delta_{jj'} G^0(0j; i\omega_m) + G^0(0j; i\omega_m) \times \\ \times \sum_{j_1} P(0j;0j_1; i\omega_m) G(0j_1;0j'; i\omega_m), \quad (3.5.21)$$

where j, j' and j_1 each run from one to six and $P(0j;0j_1; i\omega_n)$ is called the proper self-energy matrix of the $\vec{k} = 0$ phonon.

$P(0j;0j_1; i\omega_n)$ is discussed in some detail by Maradudin and Fein⁽²⁵⁾.

$G^0(0j; i\omega_n)$ is called the free phonon propagator and it is simply the Fourier transform of the harmonic thermodynamic Green's function:

$$G^0(0j; i\omega_m) = \frac{1}{2\beta} \int_{-\beta}^{+\beta} \langle\langle T A_{0j}(u) A_{0j}(0) \rangle\rangle_{H_0} \times \\ \times e^{-i\hbar\omega_m u} du, \quad (3.5.22)$$

²⁴ L.E. Gurevich and I.P. Ipatova, "Temperature Dependence of the Line Width of Resonance Absorption by the Lattice of Ionic Crystals," J. Exptl. Theoret. Phys. (U.S.S.R.) 45, 231 (1963)(transl: Soviet Physics-JETP 18, 162 (1964)).

²⁵ A.A. Maradudin and A.E. Fein, "Scattering of Neutrons by an Anharmonic Crystal," Phys. Rev. 128, 2589 (1962), p. 2597.

$$G^o(oj; i\omega_m) = \frac{2\omega(oj)}{\beta\hbar} \cdot \left(\frac{1}{\omega(oj)^2 + \omega_m^2} \right). \quad (3.5.23)$$

It is important to mention two points about equation (3.5.22). First, the thermal average of the Green's function is calculated with respect to the harmonic Hamiltonian H_0 and, secondly, this harmonic averaging is diagonal in the branch index j . This is not generally true when the averaging is done with respect to the crystal Hamiltonian⁽²⁶⁾.

Wallis et al.⁽²⁷⁾ have shown that the self-energy matrix $P(oj; oj_1; i\omega_n)$ is diagonal in the branch indices j and j_1 such that

$$P(oj; oj_1; i\omega_m) = \delta_{jj_1} P(oj; oj_1; i\omega_m) \equiv P(oj; i\omega_m). \quad (3.5.24)$$

From equations (3.5.21), (3.5.23) and (3.5.24) $G(oj; oj'; i\omega_n)$ can be written as

$$G(oj; oj'; i\omega_m) = \delta_{jj'} \left(\frac{2\omega(oj)}{\beta\hbar} \right) \left(\frac{1}{\omega(oj)^2 + \omega_m^2 - \frac{2\omega(oj)}{\beta\hbar} P(oj; i\omega_m)} \right). \quad (3.5.25)$$

²⁶ibid., p. 2596.

²⁷R.F. Wallis, I.P. Ipatova and A.A. Maradudin, "Temperature Dependence of the Width of the Fundamental Lattice Vibration Absorption Peak in Ionic Crystals," Fiz. Tverd. Tela 8, 1064 (1966) (transl: Soviet Physics-Solid State 8, 850 (1966)), Appendix A.

The last equation shows that the diagonal part ($j = j'$) of the self-energy matrix has the effect of altering the frequency $\omega(0j)$ of the mode $(0j)$ and it is in this context that $P(0j;0j'; i\omega_n)$ derives its name as the 'self-energy matrix'. Equation (3.2.25) shows that the Fourier coefficients of the thermodynamic Green's function $G(0j;0j'; i\omega_n)$ are functions of the $\underline{k} = 0$ self-energy matrix $P(0j; i\omega_n)$.

According to equations (3.5.13) and (3.5.19) and (3.5.20) the complex dielectric susceptibility tensor $\hat{\chi}_{\alpha\beta}(\omega)$ can be obtained from the Fourier coefficients of the thermodynamic Green's function $G(0j;0j'; i\omega_n)$ by replacing the discrete variable $i\omega_n$ by the continuous variable $\omega + i\epsilon$ such that

$$\hat{\chi}_{\alpha\beta}(\omega) = \left(\frac{-i}{N\omega\hbar} \right) \sum_{jj'} M_{\alpha}(0j) M_{\beta}(0j') \times$$

$$\times \left\{ \lim_{\substack{\epsilon \rightarrow 0 \\ (\epsilon > 0)}} G^R(0j;0j'; \omega + i\epsilon) \right\} \quad (3.5.26)$$

$$= \left(\frac{\beta}{N\omega} \right) \sum_{jj'} M_{\alpha}(0j) M_{\beta}(0j') \times$$

$$\times \left\{ \lim_{\substack{\epsilon \rightarrow 0 \\ (\epsilon > 0)}} G(0j;0j'; \omega + i\epsilon) \right\}. \quad (3.5.27)$$

An examination of equation (3.5.25) shows that the analytic continuation of $G(0j;0j'; i\omega_n)$ to the upper-half of the complex ω

plane results in the following relation:

$$G(\omega_j; \omega_j'; \omega + i\varepsilon) = \delta_{jj'} \left(\frac{2\omega(\omega_j)}{\beta\hbar} \right) \times$$

$$\times \frac{1}{\omega(\omega_j)^2 - (\omega + i\varepsilon)^2 - \frac{2\omega(\omega_j)}{\beta\hbar} P(\omega_j; \omega + i\varepsilon)}.$$

(3.5.28)

When $P(\omega_j; i\omega_n)$ is analytically continued to $P(\omega_j; \omega + i\varepsilon)$ the usual procedure is to divide the $P(\omega_j; \omega + i\varepsilon)$ matrix into an Hermitean part $\Delta(\omega_j; \omega)$ plus an anti-Hermitean matrix $\Gamma(\omega_j; \omega)$ such that

$$\lim_{\substack{\varepsilon \rightarrow 0 \\ (\varepsilon > 0)}} P(\omega_j; \omega + i\varepsilon) = -\beta\hbar \Delta(\omega_j; \omega) + i\beta\hbar \Gamma(\omega_j; \omega).$$

(3.5.29)

The α, β -component of the dielectric susceptibility tensor can now be written by combining equations (3.5.25), (3.5.27) and (3.5.29) to obtain

$$\hat{\chi}_{\alpha\beta}(\omega) = \chi_{\alpha\beta}^E +$$

$$+ \frac{1}{N\omega\hbar} \sum_j \frac{2\omega(\omega_j) M_\alpha(\omega_j) M_\beta(\omega_j)}{\omega(\omega_j)^2 - \omega^2 + 2\omega(\omega_j) [\Delta(\omega_j; \omega) - i\Gamma(\omega_j; \omega)]},$$

(3.5.30)

where $\chi_{\alpha\beta}^E$ has been added to account for the electronic contribution to the susceptibility. It is apparent that $\Delta(0j;\omega)$ gives rise to the change in frequency of the normal mode, $\omega(0j)$, and $\Gamma(0j;\omega)$ determines the lifetime of the $\underline{k} = 0$ mode. Both of these quantities are functions of temperature and of the applied frequency; in the harmonic approximation $\Delta(0j;\omega)$ and $\Gamma(0j;\omega)$ are both zero.

3.6 Evaluation of the $\underline{k} = 0$ phonon self-energy matrix

In order to properly evaluate the self-energy matrix, the anharmonicities of the potential function and the effects of thermal expansion must be included. The thermal expansion becomes important because the equilibrium distance between the ions, and hence the forces between them, changes as the temperature is changed. The effect of thermal expansion is to produce a homogenous deformation of the crystal and this deformation adds additional terms to the potential energy of the crystal^(18,28,29). The thermal expansion contribution to the Hamiltonian will be designated as H_{TE} . Cochran and Cowley⁽³⁰⁾ give an explicit expression for H_{TE} and it will not be repeated here because it will be shown later that thermal expansion effects are to be neglected in calculating the dielectric susceptibility.

²⁸Born and Huang. op. cit., chapter III.

²⁹A.A. Maradudin, "Thermal Expansion and Phonon Frequency Shifts," Phys. Stat. Sol. 2, 1493 (1962).

³⁰Cochran and Cowley, op. cit., p. 114.

The anharmonic plus the thermal expansion Hamiltonian can be written by using equation (3.4.15) as

$$\begin{aligned}
 H_{TE} + \sum_{\underline{k}_1 j_1} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} V^{(3)}(\underline{k}_1 j_1; \underline{k}_2 j_2; \underline{k}_3 j_3) \times \\
 \times A_{\underline{k}_1 j_1} A_{\underline{k}_2 j_2} A_{\underline{k}_3 j_3} + \sum_{\underline{k}_1 j_1} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} \sum_{\underline{k}_4 j_4} \times \\
 \times V^{(4)}(\underline{k}_1 j_1; \underline{k}_2 j_2; \underline{k}_3 j_3; \underline{k}_4 j_4) A_{\underline{k}_1 j_1} A_{\underline{k}_2 j_2} A_{\underline{k}_3 j_3} A_{\underline{k}_4 j_4} \cdot
 \end{aligned}
 \tag{3.6.1}$$

The $V^{(n)}$ -coefficients are explicitly written out in equations (3.4.11) and (3.4.13). The explicit calculation of the Hermitean $\Delta(0j; \Omega)$ and anti-Hermitean $\Gamma(0j; \Omega)$ parts of the self-energy matrix has been outlined in detail by Maradudin and Fein⁽²⁵⁾ and by Cowley⁽¹³⁾ by means of the diagram technique. Their results are:

$$\begin{aligned}
 \Delta(0j; \Omega) = \Delta_1 + \Delta_2 + \Delta_3 = \hbar_{TE} + \\
 + \frac{12}{\hbar} \sum_{\underline{k}_1 j_1} V^{(4)}(0j; 0j; \underline{k}_1 j_1; -\underline{k}_1 j_1) [2m(\underline{k}_1 j_1) + 1] - \\
 - \frac{18}{\hbar^2} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} |V^{(3)}(0j; \underline{k}_2 j_2; \underline{k}_3 j_3)|^2 \times
 \end{aligned}$$

$$\begin{aligned}
& \times \left[\frac{n(\underline{k}_2 j_2) + n(\underline{k}_3 j_3) + 1}{(\Omega + \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3))_P} + \frac{n(\underline{k}_2 j_2) + n(\underline{k}_3 j_3) + 1}{(\omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3) - \Omega)_P} + \right. \\
& \left. + \frac{n(\underline{k}_3 j_3) - n(\underline{k}_2 j_2)}{(\omega(\underline{k}_2 j_2) - \omega(\underline{k}_3 j_3) - \Omega)_P} + \frac{n(\underline{k}_2 j_2) - n(\underline{k}_3 j_3)}{(\omega(\underline{k}_3 j_3) - \omega(\underline{k}_2 j_2) - \Omega)_P} \right], \\
& (3.6.2)
\end{aligned}$$

and

$$\begin{aligned}
\Gamma(0j; \Omega) &= \frac{18\pi}{\hbar^2} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} |V^{(3)}(0j; \underline{k}_2 j_2; \underline{k}_3 j_3)|^2 \times \\
& \times \left[- (n(\underline{k}_2 j_2) + n(\underline{k}_3 j_3) + 1) \left\{ \delta(\Omega + \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3)) - \right. \right. \\
& \left. \left. - \delta(\Omega - \omega(\underline{k}_2 j_2) - \omega(\underline{k}_3 j_3)) \right\} - (n(\underline{k}_2 j_2) - n(\underline{k}_3 j_3)) \times \right. \\
& \left. \times \left\{ \delta(\Omega - \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3)) - \delta(\Omega + \omega(\underline{k}_2 j_2) - \omega(\underline{k}_3 j_3)) \right\} \right]. \\
& (3.6.3)
\end{aligned}$$

In these expressions Δ_1 , Δ_2 , and Δ_3 represent the first, second, and third terms respectively on the right hand side of equation

(3.6.2). $\hbar_{TE}$ is the frequency independent contribution to

$\Delta(0j; \Omega)$ from the thermal expansion term in the Hamiltonian H_{TE}

and it is given explicitly by Cochran and Cowley⁽¹⁸⁾. $n(\underline{k}_1 j_1)$ is

the occupation number for the phonon state $(\underline{k}_1 j_1)$ and it is given by

$$m(k, j_i) = \left[e^{\beta \hbar \omega(k, j_i)} - 1 \right]^{-1}. \quad (3.6.4)$$

The notation $\frac{1}{(X)_P}$ means the principal part of X and $\delta(X)$ is the usual Dirac delta function. It should be noted that only the cubic coupling term $V^{(3)}$ gives rise to frequency dependent terms in $\Delta(0j; \mathcal{L})$ and $\Gamma(0j; \mathcal{L})$ while $\hbar_{TE}$ and the fourth-order coupling coefficient $V^{(4)}$ yield frequency independent contributions.

Equations (3.6.2) and (3.6.3) giving $\Delta(0j; \mathcal{L})$ and $\Gamma(0j; \mathcal{L})$ along with equation (3.5.30) constitute a formal solution to the problem of calculating the optical properties of alkali halides.

3.7 Renormalization of the $k = 0$ phonon self-energy matrix

The expression given by equation (3.5.30) for the complex dielectric susceptibility implies that the eigenfrequencies and eigenvectors for a harmonic lattice are known. However, the frequencies that have been calculated by Karo and Hardy are presumably the actual lattice frequencies, i.e., those that would be measured by performing an inelastic neutron scattering experiment. Therefore, the room temperature frequencies given by Karo and Hardy, which will be designated by ω_{KH} , already have the effects of anharmonicity and thermal expansion included in them and they are not acceptable as the unperturbed eigenvalues required for the evaluation of $\Delta(0j; \mathcal{L})$ and $\Gamma(0j; \mathcal{L})$.

Cowley⁽¹³⁾ has proposed a scheme to renormalize the harmonic frequencies such that the complex dielectric susceptibility

expression will involve the experimentally measured frequencies (ω_{KH} , for example). He has shown that it is a reasonable approximation to replace the harmonic frequencies appearing in the expressions for $\Delta(0j; \Omega)$ and $\Gamma(0j; \Omega)$ by the calculated frequencies of Karo and Hardy $\omega_{KH}(kj)$. The actual lattice frequencies, $\omega_{KH}(kj)$, are called, by Cowley, the quasi-harmonic frequencies and they are related, approximately, to the harmonic frequencies by⁽³¹⁾

$$\omega_{KH}^2(kj) \approx \omega^2(kj) + 2\omega(kj) \Delta[kj; \omega_{KH}(kj)], \quad (3.7.1)$$

and hence

$$\omega(kj) \approx \omega_{KH}(kj) - \Delta[kj; \omega_{KH}(kj)], \quad (3.7.2)$$

where $\Delta(kj; \omega_{KH}(kj))$ is the Hermitean part of the self-energy matrix evaluated at the specific frequency $\Omega = \omega_{KH}(kj)$.

Therefore, according to Cowley's renormalization program, the proper self-energy matrix can be calculated by using the so-called quasi-harmonic frequencies $\omega_{KH}(kj)$ in place of the harmonic frequencies $\omega(kj)$.

However, care must be exercised in calculating the dielectric susceptibility by using the quasi-harmonic frequencies. From

³¹E.R. Cowley and R.A. Cowley, "Anharmonic Interactions in Alkali Halides. I," Proc. Roy. Soc. (London) A 287, 259 (1965).

equation (3.5.30) it is seen that $\hat{\chi}_{\alpha\beta}(\omega)$ has a denominator of the form

$$\omega(0j)^2 - \omega^2 + 2\omega(0j) [\Delta(0j; \omega) - i\Gamma(0j; \omega)], \quad (3.7.3)$$

and the frequency dependence of $\hat{\chi}_{\alpha\beta}(\omega)$ depends, in part, on the frequency dependence of the $k = 0$ proper self-energy matrix $(\Delta(0j; \omega) - i\Gamma(0j; \omega))$. $\omega(0j)$ cannot simply be replaced by $\omega_{KH}(0j)$ in this denominator; equations (3.7.1) and (3.7.2) must be used.

In equation (3.6.2) it was shown that $\Delta(0j; \omega)$ is a sum of three terms Δ_1, Δ_2 , and Δ_3 , the first two of which are frequency independent and arise from the thermal expansion and fourth order anharmonic contributions, respectively. Δ_3 is the frequency dependent term and it will be written as $\Delta_3(0j; \omega)$. Cowley and Cowley⁽³²⁾ have shown for KBr that Δ_1 and Δ_2 tend to be very nearly equal in magnitude but opposite in sign so the two almost cancel each other. It will be assumed for KCl that $\Delta_1 + \Delta_2 \approx 0$ (or $\Delta_1 + \Delta_2 \ll \Delta_3$) and this approximation will obviate calculating these two terms.

If equations (3.7.1) and (3.7.2) are substituted into equation (3.5.30) the renormalized dielectric susceptibility becomes

³²E.R.Cowley and R.A. Cowley, "Anharmonic Interactions in Alkali Halides. II," Proc. Roy. Soc. (London) A 292, 209 (1966).

$$\hat{\chi}_{\alpha\beta}(\omega) = \chi_{\alpha\beta}^E + \left(\frac{1}{N\hbar} \right) \sum_j \frac{M_{\alpha}(0j)M_{\beta}(0j) 2[\omega_{KH}(0j) + \Delta_3(0j; \omega_{KH}(0j))]}{DENOMINATOR}, \quad (3.7.4)$$

where

$$DENOMINATOR = \omega_{KH}^2(0j) - \omega^2 + 2[\omega_{KH}(0j) + \Delta_3(0j; \omega_{KH}(0j))] \times \\ \times [\Delta_3(0j; \omega) - \Delta_3(0j; \omega_{KH}(0j)) - i\Gamma(0j; \omega)]. \quad (3.7.5)$$

The frequencies used in the evaluation of $\Delta_3(0j; \omega)$ and $\Gamma(0j; \omega)$ are those of Karo and Hardy, $\omega_{KH}(\mathbf{k}j)$.

3.8 The complex index of refraction

In the preceding work the complex dielectric susceptibility $\hat{\chi}(\omega)$ was derived and from this the complex dielectric constant $\hat{\epsilon}(\omega)$ can easily be obtained:

$$\hat{\epsilon}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = 4\pi\hat{\chi}(\omega). \quad (3.8.1)$$

However, our experimental results are given in terms of the complex index of refraction $\hat{N} = N + iK$ (see Chapter 2), where N is the ordinary refractive index and K is the extinction coefficient.

ϵ' and ϵ'' are related to N and K by the relationships

$$\epsilon' = N^2 - K^2 \quad (3.8.2a)$$

$$\text{and} \quad \epsilon'' = 2NK \quad (3.8.2b)$$

These two equations can be inverted to obtain N and K as functions of ϵ' and ϵ'' :

$$N = \left[\frac{\epsilon' + \sqrt{\epsilon'^2 + \epsilon''^2}}{2} \right]^{1/2}, \quad (3.8.3a)$$

$$K = \left[\frac{-\epsilon' + \sqrt{\epsilon'^2 + \epsilon''^2}}{2} \right]^{1/2}. \quad (3.8.3b)$$

CHAPTER 4

THE NUMERICAL CALCULATION OF THE $\tilde{k} = 0$ SELF-ENERGY MATRIX AND COMPLEX INDEX OF REFRACTION OF KCl

The numerical calculation of the $\tilde{k} = 0$ self-energy matrix of KCl was performed on an IBM 7094 computer. This chapter is concerned with the numerical evaluation of the input data, such as the derivatives of the lattice potential, the $\tilde{k} = 0$ eigenvector, the high frequency dielectric constant, etc., and the general procedure that was employed by the computer in evaluating the $\tilde{k} = 0$ self-energy matrix and the complex index of refraction.

4.1 The potential function

In the following calculations the lattice model employed by Karo and Hardy⁽¹⁾ was used. In this model the potential function for each ion is the sum of a long range electrostatic potential and a short range repulsive potential, the latter being of the central force, exponential-type and assumed to act between nearest neighbors only. The potential energy per pair

¹A.M. Karo and J.R. Hardy, "Lattice Dynamics and Specific-Heat Data for Rocksalt - Structure Alkali Halides," Phys. Rev. 129, 2024 (1963).

of ions separated by a distance r_0 is given as

$$\phi(r_0) = -\frac{\alpha e^2}{r_0} + 6Ce^{-r_0/\rho} \quad , \quad (4.1.1)$$

where α is the Madelung constant and C and ρ are parameters that can be calculated by relating the above potential function to experimentally observed values of the lattice constant r_0 and compressibility $\beta^{(2)}$. Once C and ρ have been evaluated for a given temperature it is straightforward to explicitly calculate the second and third derivatives of $\phi(r_0)$; these derivatives will be denoted as $\phi''(r_0)$ and $\phi'''(r_0)$. These data have been collected in Table 4; the room temperature experimental values of r_0 and β are those given by Karo and Hardy.⁽¹⁾

4.2 Evaluation of the x components of the $k = 0$ eigenvector

From equation (A.12) it is seen that the third order coupling coefficient $v^{(3)}(0j_1; k_2 j_2; G -k_2 j_3)$ is proportional to the x components of the $k = 0$ eigenvector:

$$v^{(3)}(0j_1; k_2 j_2; G -k_2 j_3) \propto \left[\frac{m_x(0j_1/0)}{\sqrt{M_0}} - \frac{m_x(0j_1/1)}{\sqrt{M_1}} \right] \quad .(4.2.1)$$

² M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, Oxford, 1954), p.13.

lattice constant	r_o	3.139×10^{-8} cm
compressibility	β	5.63×10^{-12} cm ² /dyne
electron charge	e	4.8×10^{-10} esu
Madelung constant	α	1.7476
screening radius	ρ	0.3236×10^{-8} cm
C		3.597×10^{-9} erg
$\phi''(r_o)$		$+1.0024 \times 10^5$ ergs/cm ²
$\phi''(r_o)/r_o$		$+0.3193 \times 10^{13}$ ergs/cm ³
$\phi'''(r_o)$		-3.6533×10^{13} ergs/cm ³
mass of + ion	M_+	64.916×10^{-24} gm
mass of - ion	M_-	58.867×10^{-24} gm
high frequency dielectric constant	ϵ_∞	2.18
$\left[\frac{m_x(0j_1/0)}{\sqrt{M_0}} - \frac{m_x(0j_1/1)}{\sqrt{M_1}} \right]$		0.1799×10^{12} gm ⁻¹
ionic polarizability	$\begin{cases} \alpha_+ \\ \alpha_- \end{cases}$	$\begin{matrix} 1.201 \\ 2.974 \end{matrix}$
effective charge	e^*/e	0.80

TABLE 4. Room temperature data used in the numerical calculation of the optical properties of KCl.

Maradudin et al.⁽³⁾ have shown that the two components of the $k = 0$ eigenvector are related to each other by the equation

$$\sqrt{M_1} m_x(0j_1/1) = -\sqrt{M_0} m_x(0j_1/0). \quad (4.2.2)$$

If the orthogonality condition given by equation (3.4.7b) is used, then it is found that

$$m_x^2(0j_1/0) + m_x^2(0j_1/1) = 1. \quad (4.2.3)$$

Combining the last two equations yields

$$m_x(0j_1/0) = + \sqrt{\frac{M_1}{M_0 + M_1}}, \quad (4.2.4)$$

and

$$m_x(0j_1/1) = - \sqrt{\frac{M_0}{M_1 + M_0}}. \quad (4.2.5)$$

Therefore,

$$\left[\frac{m_x(0j_1/0)}{\sqrt{M_0}} - \frac{m_x(0j_1/1)}{\sqrt{M_1}} \right] = \sqrt{\frac{M_1 + M_0}{M_1 M_0}} = 0.18 \times 10^{12} \text{ gm}^{-1}. \quad (4.2.6)$$

³A.A. Maradudin, E.W. Montroll and G.H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation (Academic Press, New York, 1963), p. 14.

4.3 Representations for the delta function and principle value function

From equations (3.6.2) and (3.6.3) it is seen that the Hermitean part of the self-energy matrix $\Delta(0j, \mathcal{N})$ involves principle values of the form $\frac{1}{[x]_p}$ while the anti-Hermitean part $\Gamma(0j, \mathcal{N})$ contains delta functions $\delta(x)$. In order to evaluate these expressions by an electronic computer it is necessary to use an analytical realization for $\frac{1}{[x]_p}$ and $\delta(x)$. The following representations have been chosen:

$$\delta(x) = \frac{\epsilon}{\pi} \frac{1}{x^2 + \epsilon^2}, \quad (4.3.1)$$

and

$$\frac{1}{[x]_p} = \frac{x}{x^2 + \epsilon^2}, \quad (4.3.2)$$

where $\frac{\epsilon}{\pi}$ is a normalization factor chosen such that

$$\frac{\epsilon}{\pi} \int_{-\infty}^{+\infty} \frac{dx}{x^2 + \epsilon^2} = 1. \quad (4.3.3)$$

In the computer the integrations involving $\delta(x)$ and $\frac{1}{[x]_p}$ are replaced by summations with an increment in the frequency of $\Delta\mathcal{N}$. The size of $\Delta\mathcal{N}$ was chosen so that many points across the

$\delta(x)$ and $\frac{1}{[x]_P}$ functions were utilized; $\Delta\mathcal{N}$ of about one-eighth of $2\mathcal{E}$ was used.

From equation (4.3.1) it can be shown that the width of the delta function peak at half height is $2\mathcal{E}$. The value of $\mathcal{E}$ must be entered into the computer as input data before the calculation is performed. There is some difficulty in choosing the optimum size of $\mathcal{E}$; if it is chosen too large, the delta function and principle value representation become very broad with the result that $\Gamma(0j, \mathcal{N})$ and $\Delta(0j, \mathcal{N})$ are greatly smoothed. If $\mathcal{E}$ is chosen too small then erratic fluctuations in these functions will occur because there will be too few values of $\Delta\mathcal{N}$ within any interval $2\mathcal{E}$ to give the statistically accurate representation. In the calculations $\mathcal{E}$ was chosen to be approximately $1\frac{1}{2} \text{ cm}^{-1}$.

4.4 Evaluation of the $M_\alpha(0j)$ coefficient and the high-frequency dielectric constant ϵ_∞

$M_\alpha(0j)$ has been defined by equation (3.4.18) and only the x component $M_x(0j)$ need be evaluated because of the assumption that the incident electric wave was polarized along the x direction and, therefore, only interacted with the transverse optic phonon mode whose polarization was in the same direction (see Appendix). Therefore,

$$M_x(0j) = \left[\frac{N\hbar}{2\omega(0j)} \right]^{1/2} \sum_K \sum_\beta \frac{M_{x,\beta}(K)}{\sqrt{MK}} m_x(0j|K). \quad (4.4.1)$$

The multiplying term $\left[\frac{N\hbar}{2\omega(0j)} \right]^{1/2}$ need not be evaluated because when $M_x(0j)$ is substituted into the expression for the dielectric susceptibility (equation(3.5.30)) this multiplying term will cancel out; only the double sum appearing in (4.4.1) need be evaluated.

Wallis et al.⁽⁴⁾ have shown that for an ionic crystal of the NaCl type the tensor $M_{x,\beta}(K)$ is given by

$$M_{x,\beta}(K) = \epsilon_K \delta_{x\beta}, \quad (4.4.2)$$

where

$$\epsilon_K = \frac{e_K^*}{1 - \frac{4\pi}{3} \left(\frac{\alpha_+ + \alpha_-}{\nu} \right)}, \quad (4.4.3)$$

e_K^* is the Szigeti effective charge of the K^{th} ion in the unit cell, α_+ and α_- are the ionic polarizabilities of the positive and negative ions, respectively, and ν is the volume of the unit cell. e_K^* has the same magnitude for both ions in the unit cell and it is positive when K refers to the positive ion and e_K^* is negative when K refers to the negative ion.

Using the values of e_K^* , α_+ , α_- and ν as given by Karo and Hardy,⁽¹⁾ and tabulated in Table 4, it is found that

$$\epsilon \equiv |\epsilon_K| = 5.53 \times 10^{-10} \text{ esu}. \quad (4.4.4)$$

⁴ R.F. Wallis, I.P. Ipatova and A.A. Maradudin, "On the Temperature Dependence of the Width of the Fundamental Lattice Vibration Absorption Peak in Ionic Crystals", Fiz. Tverd. Tela 8, 1064 (1966)(transl: Soviet Physics - Solid State 8, 850 (1966)).

Equation (4.4.1) can now be expanded to yield

$$M_x(oj) = \left[\frac{N\hbar}{2\omega(oj)} \right]^{1/2} \left[\frac{m_x(oj|0)}{\sqrt{M_0}} - \frac{m_x(oj|1)}{\sqrt{M_1}} \right] \epsilon, \quad (4.4.5)$$

and using the values in equation (4.4.4), (4.2.6) gives

$$M_x(oj) = 96.309 \left[\frac{N\hbar}{2\omega(oj)} \right]^{1/2}. \quad (4.4.6)$$

Wallis, Ipatova and Maradudin⁽⁴⁾ have also shown that the high-frequency dielectric constant ϵ_∞ is given by the expression

$$\epsilon_\infty = \frac{2\epsilon}{e^*} - 2. \quad (4.4.7)$$

Using the above values for ϵ and e^* it is found that

$$\epsilon_\infty = 2.18. \quad (4.4.8)$$

(The experimental value of ϵ_∞ for KCl is 2.14).

4.5 An approximation for summing over all the allowed wave vectors in the first Brillouin zone

The calculation of the proper self-energy matrix as given by equations (3.6.2) and (3.6.3) involves a sum over all the allowed wave vectors $\underline{k}_2$ of the type $\sum_{\underline{k}_2}^N$ where N is the number of unit

cells in the crystal. N is obviously an extremely large number being in the order of Avagadro's number. Our calculations were based on a summation over one-thousand evenly-spaced wave vectors rather than the summation over N wave vectors, and so each term in the sum was weighted by a factor $\frac{N}{1000}$;

$$\sum_{\vec{k}_2}^N \quad \text{was replaced by} \quad \frac{N}{1000} \sum_{\vec{k}_2}^{1000} . \quad (4.5.1)$$

4.6 Invariance possessed by the cubic coupling coefficient $v^{(3)}(0j; \vec{k}_2 j_2; \vec{G} - \vec{k}_2 j_3)$ with respect to certain wave vectors that are symmetry-related to $\vec{k}_2$

If the cubic coupling coefficient $v^{(3)}(0j; \vec{k}_2 j_2; \vec{G} - \vec{k}_2 j_3)$ is examined (see equation (A.12) in Appendix A) it becomes evident that this coefficient is invariant in magnitude with respect to a certain subset of those wave vectors $\vec{k}'_2$ which are symmetry-related to $\vec{k}_2$, e.g.,

$$\left| v^{(3)}(0j; \vec{k}'_2 j_2; \vec{G} - \vec{k}'_2 j_3) \right| = \left| v^{(3)}(0j; \vec{k}_2 j_2; \vec{G} - \vec{k}_2 j_3) \right| \quad (4.6.1)$$

for this subset. For a discussion on symmetry-related wave vectors, the eigenvectors and eigenvalues see section 3.3. It is important to note that not all wave vectors $\vec{k}'_2$ that are symmetry-related to $\vec{k}_2$ have cubic coupling coefficients that are equal in magnitude.

The manner in which $\vec{k}'_2$ must be related to $\vec{k}_2$ such that their cubic coupling coefficients are equal in magnitude, will now be discussed:

(1) If the wave vector $\vec{k}'_2$ is symmetry-related to $\vec{k}_2$ by a change in sign of one or more of the components of $\vec{k}_2$, then these wave vectors will have cubic coupling coefficients equal in magnitude.

(2) If $\vec{k}'_2$ is symmetry-related to $\vec{k}_2$ by the interchange of the Y and Z components of $\vec{k}_2$, then $\vec{k}'_2$ and $\vec{k}_2$ have cubic coupling coefficients which are equal in magnitude. However, the magnitude invariance of $V^{(3)}$ does not hold if $\vec{k}'_2$ is related to $\vec{k}_2$ by an interchange of the X and Y or the X and Z components of $\vec{k}_2$.

The reason that $V^{(3)}$ does not remain invariant when the X and Y or X and Z components of $\vec{k}_2$ are interchanged is because of the assumption in the derivation that the incident electric wave was polarized along the +x direction and, therefore, interacted with the transverse optic phonon mode of the same polarization. Because this condition was imposed on the incident electric wave, the cubic coupling coefficient $V^{(3)}$ is not symmetric with respect to an interchange in the X and Y or the X and Z components of the wave vector $\vec{k}_2$. However, $V^{(3)}$ remains symmetric with respect to an interchange of the Y and Z components of $\vec{k}_2$.

Those symmetry-related wave vectors that have the properties outlined in (1) and (2) above are called equivalent wave vectors because they give rise to cubic coupling coefficients equal in

magnitude. Note that all equivalent wave vectors are symmetry-related but not all symmetry-related wave vectors are equivalent.

As an example, consider the irreducible wave vector $\underline{k}_2$ that has components (in units of $\frac{1}{2r_0}$) $k_{2x} = 0.6$, $k_{2y} = 0.4$ and $k_{2z} = 0.2$. Then, for this case, there are a total of sixteen symmetry-related, equivalent, wave vectors lying within the first Brillouin zone that have cubic coupling coefficients that are equal in magnitude. According to the previous discussion these sixteen equivalent wave vectors are:

1.	0.6	0.4	0.2
2.	0.6	0.4	-0.2
3.	0.6	-0.4	0.2
4.	-0.6	0.4	0.2
5.	0.6	-0.4	-0.2
6.	-0.6	-0.4	0.2
7.	-0.6	-0.4	-0.2
8.	-0.6	-0.4	-0.2
9.	0.6	0.2	0.4
10.	0.6	0.2	-0.4
11.	0.6	-0.2	0.4
12.	-0.6	0.2	0.4
13.	0.6	-0.2	-0.4
14.	-0.6	-0.2	0.4
15.	-0.6	0.2	-0.4
16.	-0.6	-0.2	-0.4

This number is only one-third of the total number of wave vectors symmetry-related to $\underline{k}_2$ (see section 3.3).

One final word concerning the relationship between the number of equivalent wave vectors and the number of symmetry-related wave vectors is in order. Suppose that a wave vector $\underline{k}_2$ belonging to the irreducible zone is selected and consider the following two symmetry-related, but not equivalent, wave vectors $\underline{k}'_2$ and $\underline{k}''_2$:

$$\begin{array}{ll}
 k'_{2x} = k_{2y} & k''_{2x} = k_{2z} \\
 k'_{2y} = k_{2x} \quad \text{and} & k''_{2y} = k_{2y} \\
 k'_{2z} = k_{2z} & k''_{2z} = k_{2x}
 \end{array}$$

If N , N' and N'' are the number of wave vectors equivalent to k_2 , k'_2 and k''_2 respectively, then it can be shown that $N = N' = N''$, and $N + N' + N''$ equals the total number of wave vectors symmetry-related to k_2 (including k_2 itself).

4.7 The organization of the KCl eigendata within the computer

The numerical calculation of the KCl self-energy matrix and the complex index of refraction was performed on an IBM 7094 computer. The program itself was rather lengthy and, in large part, reflected the programmer's idiosyncrasies, which unfortunately, do not enjoy universal appeal. Therefore, the discussion that follows will be primarily concerned with the general organization and structure of this program rather than a presentation of the exact details of its logic elements.

It has been mentioned in section 3.3 that the work of Karo and Hardy provided the room temperature eigenvalues and eigenvectors for forty-eight evenly-spaced wave vectors lying within the irreducible volume of the first Brillouin zone. Actually, the square of the eigenfrequencies, rather than the frequencies

themselves, was given.

For a given wave vector there exists a total of six lattice frequencies and six associated eigenvectors. The six frequencies correspond to the branches of the dispersion curves and, according to equation (3.3.2), each associated eigenvector is composed of six components. In total there were approximately two thousand numbers that comprised the eigendata for KCl and these numbers had to be punched onto cards and stored within the computer in some logical fashion.

To accomplish this storage 48 two-dimensional (10×6) matrices were developed in the memory and each matrix contained all of the eigenvectors and eigenvalues associated with a given wave vector of the irreducible zone. An example of one such two-dimensional matrix is shown in Table 5.

The six eigenvectors belonging to the given wave vector were stored as six matrices each of dimension 6×1 . These six, column matrices were located in the upper most part of the large 10×6 matrix; the columns of which identified the particular branches and the first six rows identified the components of each eigenvector (see Table 5).

The seventh row contained the square of the eigenfrequencies which corresponded to the eigenvectors written immediately above them. The computer extracted the square root of each of the squared eigenfrequencies and placed the results in row eight.

	1	2	3	4	5	6
1	$m_x(k_1/0)$	$m_x(k_2/0)$	$m_x(k_3/0)$	$m_x(k_4/0)$	$m_x(k_5/0)$	$m_x(k_6/0)$
2	$m_x(k_1/1)$	$m_x(k_2/1)$	$m_x(k_3/1)$	$m_x(k_4/1)$	$m_x(k_5/1)$	$m_x(k_6/1)$
3	$m_y(k_1/0)$	$m_y(k_2/0)$	$m_y(k_3/0)$	$m_y(k_4/0)$	$m_y(k_5/0)$	$m_y(k_6/0)$
4	$m_y(k_1/1)$	$m_y(k_2/1)$	$m_y(k_3/1)$	$m_y(k_4/1)$	$m_y(k_5/1)$	$m_y(k_6/1)$
5	$m_z(k_1/0)$	$m_z(k_2/0)$	$m_z(k_3/0)$	$m_z(k_4/0)$	$m_z(k_5/0)$	$m_z(k_6/0)$
6	$m_z(k_1/1)$	$m_z(k_2/1)$	$m_z(k_3/1)$	$m_z(k_4/1)$	$m_z(k_5/1)$	$m_z(k_6/1)$
7	$w^2(k_1)$	$w^2(k_2)$	$w^2(k_3)$	$w^2(k_4)$	$w^2(k_5)$	$w^2(k_6)$
8	$w(k_1)$	$w(k_2)$	$w(k_3)$	$w(k_4)$	$w(k_5)$	$w(k_6)$
9	$n(k_1)$	$n(k_2)$	$n(k_3)$	$n(k_4)$	$n(k_5)$	$n(k_6)$
10	K2X	K2Y	K2Z	MULTIP	ROUTE	-----

TABLE 5. The matrix representation of the eigendata stored in the computer for a fixed wave vector $\underline{k}$.

The occupation number of each mode $n(\underline{k}j)$ was calculated for $T = 300^\circ\text{K}$ and stored in row nine:

$$n(\underline{k}j) = \left[e^{\hbar\omega(\underline{k}j)/kT} - 1 \right]^{-1}. \quad (4.7.1)$$

Finally, the tenth row of the matrix was filled with information which aided the program logic. This information was predetermined for each of the forty-eight wave vectors, punched onto cards, and then read into the tenth row of each of the forty-eight matrices. The locations (10,1), (10, 2) and (10, 3) were called K2X, K2Y, and K2Z respectively, and they contained the Cartesian components of the specific wave vector $\underline{k}_2$ to which the matrix belonged.

Location (10,4) was called MULTIP, which was an abbreviation for multiplicity, and it contained the number of wave vectors equivalent to $\underline{k}_2$. That is, MULTIP contained the number of wave vectors related to $\underline{k}_2$ by a symmetry operation of the lattice which had third order coupling coefficients identical in magnitude to that of $\underline{k}_2$. The concept of equivalent wave-vectors is discussed in section 4.6.

The program distinguished between the wave vectors lying totally within the first Brillouin zone and those lying on the zone boundary. There are thirty-nine wave vectors in the irreducible volume of the first Brillouin zone that lie entirely inside the zone. Each of these thirty-nine wave vectors was assigned a value

of +1 in the location called ROUTE. The remaining nine wave vectors lay on the zone boundary and these were assigned values from two to ten in the ROUTE location. The reasons for these assignments will be explained later.

4.8 The procedure for numerically calculating the $k = 0$ proper self-energy matrix of KCl

All of the relations that will be used in calculating the far infrared optical properties of KCl will now be written down. Equation (3.7.4) gives the expression for the complex dielectric susceptibility tensor $\hat{\chi}_{\alpha\beta}(\omega)$. For a crystal that possesses cubic symmetry $\hat{\chi}_{\alpha\beta}(\omega)$ is diagonal in the α and β indices such that

$$\hat{\chi}_{\alpha\beta}(\omega) = \hat{\chi}_{\alpha\beta}(\omega) \delta_{\alpha\beta} \equiv \hat{\chi}(\omega). \quad (4.8.1)$$

Equation (3.7.4) can be rewritten in terms of the complex dielectric constant $\hat{\epsilon}(\omega) = 4\pi\hat{\chi}(\omega)$

$$\hat{\epsilon}(\omega) = \epsilon_{\infty} + \frac{4\pi}{N\omega\hbar} \left[\frac{M_x^2 (\text{DENOMINATOR}_3(\omega_j; \omega(\omega_j)))}{\text{DENOMINATOR}} \right],$$

$$\begin{aligned} \text{DENOMINATOR} = & \omega^2(\omega_j) - \omega^2 + 2 [\omega(\omega_j) + \Delta_3(\omega_j; \omega(\omega_j))] \times \\ & \times \{ \Delta_3(\omega_j; \omega) - \Delta_3(\omega_j; \omega(\omega_j)) - i\Gamma(\omega_j; \omega) \}. \end{aligned}$$

(4.8.2)

In going from equation (3.7.4) to equation (4.8.2) $\omega_{KH}(0j)$ has been replaced by $\omega(0j)$ for notation convenience (in this instance $\omega(0j)$ does not represent the harmonic frequencies). $\sum_j$ takes only the one value corresponding to the particular transverse optic branch with which the $\underline{k} = 0$ incident electric wave can interact. In the appendix it was assumed that this wave was polarized in the $\pm x$ direction and that it interacted with the $\underline{k} = 0$ phonon mode of the same polarization. The eigenvector of this phonon mode has only x components as shown in equation (A.5). Equation (4.4.5) shows that $M_\alpha(0j)$ is proportional to the x components of this eigenvector and, therefore, $M_\alpha(0j) = M_x(0j)$.

$\Delta_3(0j; \Omega)$ is the frequency dependent term of the Hermitean part of the self-energy matrix and, from equation (3.6.2) is written as

$$\begin{aligned} \Delta_3(0j; \Omega) = & \frac{-18}{\hbar^2} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} |V^{(3)}(0j; \underline{k}_2 j_2; \underline{k}_3 j_3)|^2 \times \\ & \times \left[(m(\underline{k}_2 j_2) + m(\underline{k}_3 j_3) + 1) \left\{ \frac{1}{[-\Omega + \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3)]_\rho} + \right. \right. \\ & \left. \left. + \frac{1}{[-\Omega + \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3)]} \right\} + (m(\underline{k}_2 j_2) - m(\underline{k}_3 j_3)) \times \right. \\ & \left. \times \left\{ \frac{-1}{[-\Omega + \omega(\underline{k}_2 j_2) - \omega(\underline{k}_3 j_3)]_\rho} + \frac{1}{[-\Omega - \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3)]_\rho} \right\} \right]. \end{aligned} \quad (4.8.3)$$

$\Gamma(0j; \Omega)$ is the anti-Hermitean part of the self-energy matrix:

$$\begin{aligned} \Gamma(0j; \Omega) = & \frac{18\pi}{\hbar^2} \sum_{\underline{k}_2 j_2} \sum_{\underline{k}_3 j_3} |V^{(3)}(0j; \underline{k}_2 j_2, \underline{k}_3 j_3)|^2 \times \\ & \times \left[- (m(\underline{k}_2 j_2) + m(\underline{k}_3 j_3) + 1) \left\{ \delta(\Omega + \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3)) - \right. \right. \\ & - \delta(\Omega - \omega(\underline{k}_2 j_2) - \omega(\underline{k}_3 j_3)) \left. \right\} - (m(\underline{k}_2 j_2) - m(\underline{k}_3 j_3)) \times \\ & \times \left\{ \delta(\Omega - \omega(\underline{k}_2 j_2) + \omega(\underline{k}_3 j_3)) - \delta(\Omega + \omega(\underline{k}_2 j_2) - \omega(\underline{k}_3 j_3)) \right\} \left. \right] . \end{aligned} \quad (4.8.4)$$

Looking at the last three equations, it should be apparent that there is an enormous amount of arithmetic involved in the calculations; it took me about seven minutes to complete the problem.

In order to calculate the Hermitean and anti-Hermitean parts of the $\underline{k} = 0$ KCl self-energy matrix according to equations (4.8.3) and (4.8.4) it is necessary, among other things, to evaluate such sums over normal modes as $\sum_{\underline{k}_2} \sum_{j_2} \sum_{j_3}$ (the sum over the wave vector $\underline{k}_3$, $\sum_{\underline{k}_3}$, is not an independent summation because $\underline{k}_3 = \underline{G} - \underline{k}_2$). The sum $\sum_{\underline{k}_2}$ ranges over the one-thousand wave vectors lying in the first Brillouin zone, which were provided by the work of Karo and Hardy⁽¹⁾, and j_2 is an index labeling the six phonon branches associated with the wave vector $\underline{k}_2$; j_2 runs from one to six. j_3 also runs from one to six and it identifies the phonon

branch associated with the dependent wave vector $\underline{k}_3 = \underline{G} - \underline{k}_2$.

Therefore, for a given value of $\underline{k}_2$, there are a total of

thirty-six terms associated with the double sum $\sum_{j_2} \sum_{j_3}$.

At first glance there appears to be approximately $1000 \times 6 \times 6 = 36,000$ terms in the triple sum $\sum_{\underline{k}_2} \sum_{j_2} \sum_{j_3}$ and, therefore, there would be this number of cubic coupling coefficients

$V^{(3)}(0j_1; \underline{k}_2 j_2; \underline{G} - \underline{k}_2 j_3)$ to evaluate. However, some reduction in this number can be achieved because many of the wave vectors $\underline{k}_2$ give rise to identical coefficients because of the symmetry possessed by $V^{(3)}(0j_1; \underline{k}_2 j_2; \underline{G} - \underline{k}_2 j_3)$ as discussed in section 4.6. It turns out that there are approximately 140 wave vectors, out of the original number of 1000, that give rise to distinct third order coupling coefficients.

The order for evaluating the triple sum $\sum_{\underline{k}_2} \sum_{j_2} \sum_{j_3}$ appearing in equations (4.8.3) and (4.8.4) will be as follows:

$$\sum_{\substack{\text{all wave} \\ \text{vectors } \underline{k}_2 \\ \text{in the irreducible} \\ \text{zone}}} \left(\sum_{j_2} \sum_{j_3} \left\{ \sum_{\substack{\text{all wave} \\ \text{vectors symmetry-} \\ \text{related to } \underline{k}_2}} \right\} \right) . \quad (4.8.5)$$

This notation means that a wave vector $\underline{k}_2$ belonging to the irreducible zone is first selected. Then the branch indices j_2 and j_3 are fixed and finally the sum over all the wave vectors that are symmetry-related to $\underline{k}_2$ is carried out. The program evaluates these sums in the order indicated by the parenthesis.

To evaluate the $\mathbf{k} = 0$ proper self-energy matrix, the computer first selected one of the forty-eight wave vectors (called $\mathbf{k}_2$) belonging to the irreducible volume of the first Brillouin zone. The X, Y and Z components of the irreducible wave vector $\mathbf{k}_2$ were stored in the memory locations labeled K2X, K2Y and K2Z which were contained in the 6 x 10 matrix associated with the wave vector $\mathbf{k}_2$ and shown in Table 5. The computer next examined the contents of the location within this matrix called ROUTE. If ROUTE contained a +1 then the computer knew that the irreducible wave vector $\mathbf{k}_2$ did not lie on the boundary of the first Brillouin zone; if ROUTE contained any number other than a +1, $\mathbf{k}_2$ was to be considered as lying on the Brillouin zone boundary and the computer was to transfer to another part of the program for special instructions. These two cases will now be examined.

Case I. The wave vector does not lie on the boundary of the first Brillouin zone (ROUTE = 1) and, therefore, $\mathbf{k}_3 = \mathbf{G} - \mathbf{k}_2 = -\mathbf{k}_2$ because $\mathbf{G} = 0$. All of the eigenvector components associated with the wave vector $\mathbf{k}_3$ appearing in the expression for $v^{(3)}(0j_1; \mathbf{k}_2 j_2; -\mathbf{k}_2 j_3)$ (see equation A.12) become

$$m_{\alpha}(\mathbf{G} - \mathbf{k}_2 j_3 / 0) = m_{\alpha}(-\mathbf{k}_2 j_3 / 0) = -m_{\alpha}(\mathbf{k}_2 j_3 / 0) \quad (4.8.6)$$

and

$$m_{\alpha}(\mathbf{G} - \mathbf{k}_2 j_3 / 1) = m_{\alpha}(-\mathbf{k}_2 j_3 / 1) = -m_{\alpha}(\mathbf{k}_2 j_3 / 1). \quad (4.8.7)$$

The associated eigenvalues become

$$\omega(\underline{G} - \underline{k}_2 j_3) = \omega(-\underline{k}_2 j_3) = +\omega(+\underline{k}_2 j_3), \quad (4.8.8)$$

because the lattice frequencies are always even functions of the wave vectors. Also, the factor $\cos(2\pi \underline{G} \cdot \underline{r}_0 \cdot \underline{e}_\alpha)$ appearing in equation (A.12) equals +1 because $\underline{G} = 0$; here $\underline{e}_\alpha$ is a unit vector in the X, Y or Z direction.

Case II. The wave vector $\underline{k}_2$ lies on the boundary of the first Brillouin zone ($\text{ROUTE} \neq 1$) and $\underline{G}$ does not equal zero. Of the forty-eight wave vectors belonging to the irreducible zone there are a total of nine that lie on the boundary of the Brillouin zone. Each of these nine wave vectors was assigned a different number in the ROUTE location and this number instructed the computer to transfer to a special section of the program where the values of $\underline{G}$, $\underline{k}_3 = \underline{G} - \underline{k}_2$ and $\cos(2\pi \underline{G} \cdot \underline{r}_0 \cdot \underline{e}_\alpha)$ were found. These values are given in Table 6. In this manner the computer knew where to locate the eigenvectors and eigenvalues belonging to the wave vector $\underline{k}_3 = \underline{G} - \underline{k}_2$ by simply examining the contents of the location ROUTE.

Having chosen an irreducible wave vector $\underline{k}_2$, the computer selected values for j_2 and j_3 and then began to evaluate the contributions to $\Delta_3(0j; \underline{n})$ and $\Gamma(0j; \underline{n})$ by evaluating the cubic coupling coefficient $V^{(3)}(0j; \underline{k}_2 j_2; \underline{G} - \underline{k}_2 j_3)$ as given by equation (A.12).

	WAVE VECTOR $\vec{k}_2$			$\vec{k}_3 = \vec{G} - \vec{k}_2$			$\vec{G} = \vec{k}_2 + \vec{k}_3$			$\cos(2\pi \vec{r}_0 \cdot \vec{e}_{\alpha} \cdot \vec{G})$ ($\vec{e}_{\alpha} = \vec{e}_{\alpha x}$ or $\vec{e}_{\alpha y}$ or $\vec{e}_{\alpha z}$)
	k_{2x}	k_{2y}	k_{2z}	k_{3x}	k_{3y}	k_{3z}	G_x	G_y	G_z	
1	1	.4	0	1	-.4	0	2	0	0	+1
2	1	.2	.2	1	-.2	-.2	2	0	0	+1
3	1	.2	0	1	-.2	0	2	0	0	+1
4	1	0	0	1	0	0	2	0	0	+1
5	.9	.5	.1	.1	.5	.9	1	1	1	-1
6	.9	.3	.3	.1	.7	.7	1	1	1	-1
7	.7	.7	.1	.3	.3	.9	1	1	1	-1
8	.7	.5	.3	.3	.5	.7	1	1	1	-1
9	.5	.5	.5	.5	.5	.5	1	1	1	-1

TABLE 6. The nine wave vectors $\vec{k}_2$ that lie on the zone boundary and the corresponding values of the dependent wave vector $\vec{k}_3$, the reciprocal lattice vector $\vec{G}$ and the cosine factor.

The calculation of $V^{(3)}(0j; k_2 j_2; G - k_2 j_3)$ proceeded in a very straightforward manner and the values of the constants multiplying $V^{(3)}$, such as $\phi'''(\rho_0)$, $\frac{\phi''(\rho_0)}{\rho_0}$, M_0 , M_1 and $\left[\frac{m_X(0j_1/0)}{\sqrt{M_0}} - \frac{m_X(0j_1/1)}{\sqrt{M_1}} \right]$, are given in Table 4 of section 4.1. The factor $N^{1/2}$ in the denominator of $V^{(3)}$ will cancel later.

Having evaluated $V^{(3)}$, the computer gave its attention to the calculation of the delta functions and principle value functions that appear in the expressions for $\Delta_3(0j; \rho)$ and $\Gamma(0j; \rho)$ given in equations (4.8.3) and (4.8.4). $\Delta_3(0j; \rho)$ and $\Gamma(0j; \rho)$ were calculated at evenly spaced, discrete frequency intervals $\rho_p = p(0.5) \text{ cm}^{-1}$, where p is an integer beginning with zero and extending to 800. To indicate the method by which the computer evaluated the delta functions and principle values, the calculation of $\Delta(0j; \rho_p)$ will be considered as an example.

An examination of equation (4.8.3) shows that there are four principal value functions to be calculated for $\Delta_3(0j; \rho_p)$. In section 4.3 it was stated that the principal value function was to be represented as (equation (4.3.2))

$$\frac{1}{[x]_p} \Rightarrow \frac{x}{x^2 + \epsilon^2} \quad (4.8.9)$$

The computer selected some starting frequency ρ_1 , and calculated the contribution to $\Delta_3(0j; \rho_1)$ by the relation

$$\begin{aligned}
& -\frac{18}{\hbar^2} |V^{(3)}(0j; \underline{k}_2 j_2; \underline{G} - \underline{k}_2 j_3)|^2 \Delta \Omega \times \\
& \times \left\{ (m(\underline{k}_2 j_2) + m(\underline{G} - \underline{k}_2 j_3) + 1) \times \right. \\
& \times \left(\frac{-\Omega_1 + \omega(\underline{k}_2 j_2) + \omega(\underline{G} - \underline{k}_2 j_3)}{[-\Omega_1 + \omega(\underline{k}_2 j_2) + \omega(\underline{G} - \underline{k}_2 j_3)]^2 + \epsilon^2} + \right. \\
& \left. \left. + \frac{-\Omega_1 + \omega(\underline{k}_2 j_2) + \omega(\underline{G} - \underline{k}_2 j_3)}{[-\Omega_1 + \omega(\underline{k}_2 j_2) + \omega(\underline{G} - \underline{k}_2 j_3)]^2 + \epsilon^2} \right) + \right. \\
& + (m(\underline{k}_2 j_2) - m(\underline{G} - \underline{k}_2 j_3)) \left(\frac{-\Omega_1 - \omega(\underline{k}_2 j_2) + \omega(\underline{G} - \underline{k}_2 j_3)}{[-\Omega_1 - \omega(\underline{k}_2 j_2) + \omega(\underline{G} - \underline{k}_2 j_3)]^2 + \epsilon^2} - \right. \\
& \left. \left. - \frac{-\Omega_1 + \omega(\underline{k}_2 j_2) - \omega(\underline{G} - \underline{k}_2 j_3)}{[-\Omega_1 + \omega(\underline{k}_2 j_2) - \omega(\underline{G} - \underline{k}_2 j_3)]^2 + \epsilon^2} \right) \right\} , \quad (4.8.10)
\end{aligned}$$

where $\Delta \Omega$ is the frequency interval of 0.5 cm^{-1} that was used (see section 4.3).

A new frequency Ω_2 was selected such that $\Omega_2 = \Omega_1 + \Delta \Omega$ and the above procedure was repeated to find the contribution to

$\Delta_3(0j; \Omega_2)$. This procedure was repeated until the highest frequency of 400 cm^{-1} was reached, and the contribution to

$\Delta_3(0j; \Omega_p)$ from each frequency Ω_p was stored in a linear array inside the computer.

Therefore, for a fixed wave vector, $\underline{k}_2$ and branch indices j_2 and j_3 , the above method yielded the contribution to $\Delta_3(0j; \underline{\omega}_p)$ for discrete frequencies $\underline{\omega}_p$ running from zero to a maximum of 400 cm^{-1} .

The calculation of $\Gamma(0j; \underline{\omega}_p)$ proceeded in an identical fashion except the delta function representation was used (equation (4.3.1)).

It is at this point that the concept of symmetry-related and equivalent wave vectors becomes useful. It is stated in section 4.6 that all equivalent wave vectors have cubic coupling coefficients that are equal in magnitude (providing, of course that the branch indices j_2 and j_3 remain fixed). These equivalent wave vectors also have identical eigenfrequencies (see section 3.3) which means that their population factors, $n(\underline{k}_2 j_2) = \left[e^{\hbar \omega(\underline{k}_2 j_2)/kT} - 1 \right]^{-1}$, are also equal. Therefore, the contributions to $\Delta_3(0j, \underline{\omega}_p)$ and $\Gamma(0j; \underline{\omega}_p)$ have the same value for all equivalent wave vectors and so the computer calculated this value for one of these wave vectors and then multiplied the result by the number of equivalent wave vectors. This number is contained in the location MULTIP. It was mentioned earlier in this section that all the contributions to $\Delta_3(0j; \underline{\omega}_p)$ and $\Gamma(0j; \underline{\omega}_p)$ from those wave vectors symmetry-related to the irreducible wave vector $\underline{k}_2$ would be calculated before further evaluating the double sum $\sum_{j_2} \sum_{j_3}$.

According to the discussion in section 4.6 the number of wave vectors equivalent to the irreducible wave vector $\underline{k}_2$ only equals one-third of the number of wave vectors symmetry-related to $\underline{k}_2$.

Therefore, the computer constructed two wave vectors symmetry-related, but not equivalent to k_2 of the form

$$\begin{array}{ll} k_{2x}' = k_{2y} & k_{2x}'' = k_{2z} \\ k_{2y}' = k_{2x} & \text{and} \quad k_{2y}'' = k_{2y} \\ k_{2z}' = k_{2z} & k_{2z}'' = k_{2x} \end{array}$$

In each of these two cases the coupling coefficients,

$$\left| v^{(3)}(0j_1; k_2' j_2; G - k_2' j_3) \right|^2 \quad \text{and} \quad \left| v^{(3)}(0j_1; k_2'' j_2; G - k_2'' j_3) \right|^2,$$

were calculated and the contributions to $\Delta_3(0j; \mathcal{N}_p)$ and $\Gamma(0j; \mathcal{N}_p)$ were evaluated for all frequencies $\mathcal{N}_p$ by the method outlined above. In each case the result was multiplied by the contents of the location MULTIP to account for the identical contributions arising from the wave vectors equivalent to k_2' and k_2'' . It should be remembered that k_2 , k_2' and k_2'' all have the same number of equivalent wave vectors (see section 4.6).

So far the computer has evaluated the contributions to

$\Delta_3(0j; \mathcal{N}_p)$ and $\Gamma(0j; \mathcal{N}_p)$ from all of the wave vectors symmetry-related to the irreducible wave vector k_2 for fixed branch indices j_2 and j_3 . The computer then repeated the identical calculation outlined above for each value of j_2 and j_3 ($j_2, j_3 = 1, \dots, 6$).

The contributions to the functions $\Delta_3(0j; \mathcal{N}_p)$ and $\Gamma(0j; \mathcal{N}_p)$ for each successively chosen value of j_2 and j_3 were added to the previously stored values of $\Delta_3(0j; \mathcal{N}_p)$ and $\Gamma(0j; \mathcal{N}_p)$, respectively;

these stored values of $\Delta_3(0j; \Omega_p)$ and $\Gamma(0j; \Omega_p)$ resulted from previously calculated contributions from other irreducible wave vectors k_2 and branches j_2 and j_3 . At the end of the computation $\Delta_3(0j; \Omega_p)$ and $\Gamma(0j; \Omega_p)$ contained all possible contributions from the triple sum $\sum_{k_2} \sum_{j_2} \sum_{j_3}$. When this was completed the computer selected a new wave vector from the irreducible zone and repeated the entire process of summations (see (4.8.5)).

It should be clear by now that the evaluation of the Hermitean and anti-Hermitean parts of the self-energy matrix, $\Delta_3(0j; \Omega_p)$ and $\Gamma(0j; \Omega_p)$, is no trivial task which literally involved tens-of-millions of arithmetic computations. The results of the calculations are shown in Figures 9 and 10 for $\Delta_3(0j; \Omega_p)$ and $\Gamma(0j; \Omega_p)$.

It was relatively simple to calculate the complex dielectric constant $\hat{\epsilon}(\Omega_p)$ by substituting the calculated values of $\Delta_3(0j; \Omega_p)$ and $\Gamma(0j; \Omega_p)$ into equation (4.8.2). Using equations (3.8.3a) and (3.8.3b) the real and imaginary parts of the complex index of refraction were found. These results are shown in Figures 11 and 12.

Figure 9. The frequency dependent, Hermitean part of the $\tilde{k} = 0$ self-energy matrix for KCl.

Figure 10. The anti-Hermitian part of the $k_z = 0$ self-energy matrix for KCl.

Figure 11. The experimental and calculated curves of the index of refraction for KCl.

Figure 12. The experimental and calculated curves of the extinction coefficient for KCl.

CHAPTER 5

DISCUSSION AND CONCLUSIONS

In the last section the theoretical calculations for the real and imaginary parts of the frequency dependent complex index of refraction were presented. In this chapter some conclusions will be drawn on the calculations and suggestions will be offered on how the results could be improved.

It was previously mentioned that the calculations of $\Delta_3(0j;\mathcal{L})$ and $\Gamma(0j;\mathcal{L})$ were based, in large measure, on the work of Karo and Hardy⁽¹⁾ in which they calculated the eigenvectors and eigenvalues for KCl for one thousand evenly-distributed wave vectors lying within the first Brillouin zone. Some of the gross features of our calculations can be directly identified by examining the density-of-states curve associated with the eigenvalues⁽²⁾ and, for future reference, this curve has been reproduced in Figure 13. To our knowledge no other theoretical or experimental (by neutron diffraction techniques) data exists on the determination of the dispersion curves for KCl and, therefore, it is difficult to judge the adequacy of the deformation dipole model used by Karo and Hardy. The eigenvalues obtained from the deformation dipole model have only been

¹See section 3.3.

²

A.M. Karo and J.R. Hardy, "Lattice Dynamics and Specific-Heat Data for Rocksalt-Structure Alkali Halides," Phys. Rev. 129, 2024 (1963).

Figure 13. The density-of-states curve for KCl.

indirectly checked by comparing theoretical calculations with such experimentally measured quantities as the specific heat or Debye temperature.⁽²⁾

To be completely consistent all of the numerical values used in the calculations of N and K, such as the lattice constant, compressibility, screening radius, electronic polarizabilities, etc., were taken from the work of Karo and Hardy⁽²⁾ (see Table 4 in section 4.2). Any additional information needed in the calculation, such as $M_x(0j)$, ϵ_∞ , $\phi''(r_0)$, $\phi'''(r_0)$, etc., were evaluated by using the above mentioned constants. No adjustable parameters were introduced into the calculations for either N or K.

Looking at Figures 11 and 12 of the last section, it can be seen that there is very reasonable agreement between the experimental and calculated curves for N and K.* In the following discussion attention will be focused mainly on curves for the extinction coefficient K because these curves are the easiest to examine for discrepancies between theory and experiment.

It is also helpful to examine $\Gamma(0j; \mathcal{N})$ and so, for convenience, Figures 10 and 12 from the last section are shown as Figures 14 and 15 of this section.

Looking at Figure 14 for the extinction coefficient it can be seen that most of the qualitative features of the experimental curve are reproduced, especially on the high-frequency side of the

* In calculations of this type which are, at best, extremely long and involved, and which begin with more-or-less first principles (i.e., the known lattice potential), it is surprising that there is any agreement at all between theory and experiment!

Figure 14. The experimental and calculated curves of the extinction coefficient for KCl.

Figure 15. The anti-Hermitian part of the $k=0$ self-energy matrix for KCl.

fundamental lattice absorption peak where the agreement is best. In this region the qualitative and quantitative features of the three subsidiary maxima, labeled 7, 9 and 10, seem to be in reasonable agreement although the calculated curve gives the positions of these three secondary maxima some 15 to 20 cm^{-1} below the experimental positions.

The discrepancies that occur in the spectral positions of the secondary maxima of K can, in large part, be traced to the work of Karo and Hardy. Examining the KCl density-of-states curve shown in Figure 13, it can be assumed that there are roughly four peaks in this curve as indicated by the arrows. To be sure, this density-of-states curve is not very detailed and it tends to show only the gross features. The reason for the coarseness is because of the relatively small number of frequencies (6,000) that Karo and Hardy use in their calculation. These four maxima in the density of states occur at the approximate frequencies given below:

- 1) $\omega_A \approx 42 \text{ cm}^{-1}$
- 2) $\omega_B \approx 86 \text{ cm}^{-1}$
- 3) $\omega_C \approx 111 \text{ cm}^{-1}$
- 4) $\omega_D \approx 138 \text{ cm}^{-1}$

From these four frequencies the sum and difference frequencies for any pair can be constructed and Table 7 gives these combinations.

sum frequencies (cm ⁻¹)	label	difference frequencies (cm ⁻¹)	label
$\omega_A + \omega_B = 128$	1	$\omega_B - \omega_A = 44$	7
$\omega_A + \omega_C = 153$	2	$\omega_C - \omega_A = 69$	8
$\omega_A + \omega_D = 180$	3	$\omega_D - \omega_A = 96$	9
$\omega_B + \omega_C = 197$	4	$\omega_C - \omega_B = 25$	10
$\omega_B + \omega_D = 224$	5	$\omega_D - \omega_B = 52$	11
$\omega_C + \omega_D = 249$	6	$\omega_D - \omega_C = 27$	12

Table 7. The sum and difference frequencies for the four maxima occurring in the KCl density-of-states curve.

An examination of Figure 14 shows that the three secondary maxima in K occurring on the high-frequency side of the fundamental peak correspond to sum bands in the maxima of the density-of-states. Also, the two peaks in K occurring near 70 cm⁻¹ and 95 cm⁻¹ can be explained as difference bands corresponding to differences in frequencies associated with the maxima in the density-of-states.

All of the assignments given in Table 7 seem plausible when the curve for $\Gamma(0j; \omega)$ is examined (see Figure 15). The curve for $\Gamma(0j; \omega)$ shows these sum and difference frequencies because it contains delta functions of the form $\delta[\omega \pm \omega(k_2 j_2) \pm \omega(q-k_2 j_3)]$ (see equation(4.8.4)). Most of the structure appearing on $\Gamma(0j; \omega)$ can be accounted for by the assignments made in Table 7. If the density-of-states curve were more detailed, the sum and difference assignments would have been more accurate and all of the

structure appearing on $\Gamma(0j; \mathcal{L})$ could have been accounted for. At any rate, the above discussion indicates that the discrepancies occurring in the spectral position of the various subsidiary maxima can be attributed to the work of Karo and Hardy.

The most obvious discrepancies between the calculated and experimental curves for K occur on the low-frequency side of the fundamental absorption peak; the computed values appear to be a factor of 3 to 5 times too low. We agree with the remark made by Ipatova, Maradudin and Wallis ⁽³⁾ that it is a somewhat curious result that the numerical calculations seem to reproduce the experimental curve for K on the high-frequency side of the fundamental absorption peak much better than they do on the low-frequency side.

An accurate experimental measurement of K (for KCl) is difficult to obtain below 130 cm^{-1} by reflection techniques because the phase in this region becomes very small (see Figure 2 in Chapter 2). The experimental values of K below 130 cm^{-1} can be improved by using transmission techniques. Such measurements should accurately fix the magnitude of the secondary maxima occurring around 80 cm^{-1} and the minima at 91 cm^{-1} both of which are now known only to an accuracy of 15 or 20 percent. A rather general conclusion that can be drawn from this work is that it seems to be more difficult, both experimentally and theoretically, to obtain the extinction coefficient K on the low-frequency side of

³ I.P. Ipatova, A.A. Maradudin and R.F. Wallis, "Temperature Dependence of the Width of the Fundamental Lattice-Vibration Absorption Peak in Ionic Crystals II. Approximate Numerical Results," Phys. Rev. 155, 882 (1967), p.894.

the fundamental lattice absorption peak than on the high-frequency side.

It is not clear why the calculated values of K should be so much smaller than the experimental values below 130 cm^{-1} although, almost surely, the trouble lies in the calculation of $\Gamma(0j; \mathcal{N})$. The reason is that in the region below 130 cm^{-1} N is considerably larger than K so that equation (3.8.3b) can be expanded in a Taylor series to yield $K \approx \frac{\epsilon''}{2\sqrt{\epsilon'}}$, where ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant (see equations (3.8.2a) and (3.8.2b)). Since ϵ'' is directly proportional to $\Gamma(0j; \mathcal{N})$ it follows that $K(\mathcal{N}) \propto \Gamma(0j; \mathcal{N})$. Looking at the computed curve for $\Gamma(0j; \mathcal{N})$ in Figure 15 and examining Table 7 it is seen that in the region less than 130 cm^{-1} most of the contributions to $\Gamma(0j; \mathcal{N})$ come from difference frequencies. These difference combinations give rise to the extremely broad region extending from 0 cm^{-1} to approximately 115 cm^{-1} and are of the general form (see equation (4.8.4))

$$[n(k_2 j_2) - n(G - k_2 j_3)] \delta [\mathcal{N} \pm \omega(k_2 j_2) \pm \omega(G - k_2 j_3)] .$$

The computer program has been examined, and re-examined, many times specifically looking for any computational errors that might have caused too low a value to be calculated for the difference combinations.

The calculated results for K seem to indicate that $\Gamma(0j; \mathcal{N})$ is too small only in the spectral region where the difference combinations are important. On the high-frequency side of the fundamental absorption peak (150 cm^{-1} to 200 cm^{-1}) K becomes very large and N is small so that according to equations (3.8.2a) and (3.8.2b) K is once again proportional to $\Gamma(0j; \mathcal{N})$. However, in this region there is very reasonable agreement between the calculated and experimental values of K and they certainly do not differ by the factor of 3 to 5 that occurs on the low-frequency side of the fundamental absorption peak. It should be clear by now that any future work must give careful attention to this problem, both from an experimental and theoretical standpoint.

Some comments are now in order on the improvement of numerical calculations, at least in theory. The first, and most obvious, is to look for better eigendata on KCl which means improved eigenvalues and eigenvectors. The former are probably more important because there are indications that the calculations of N and K are not too sensitive to the values of the eigenvectors⁽³⁾. This area of lattice dynamics is very active today and it should be expected that better dispersion curves will be available either by neutron diffraction techniques or more elaborate theoretical models. It would indeed be interesting to see if the calculated values of K below 130 cm^{-1} could be improved by better data.

Second, in the derivation of the cubic coupling coefficient $v^{(3)}(0j; k_2 j_2; \mathcal{G} - k_2 j_3)$ given in the Appendix, only the nearest

neighbor contributions were calculated. A future calculation might take into account next-nearest neighbors although the resulting expression for $V^{(3)}$ would be much more involved than the one presently being used.

Third, the expressions for the complex dielectric susceptibility as given by equation (3.5.30) were found by calculating the ensemble average of the linear term in the expansion of the dipole moment operator (see equations (3.4.17) and (3.4.18)). The contributions from the second term in this expansion could also be calculated; these have been written out in detail by Cowley.⁽⁴⁾ The additional calculations would be no more difficult to perform than those which have been done in this paper. However, it might be difficult to evaluate the second order coefficient $M_{\alpha}(\mathbf{k}_1 \mathbf{j}_1; -\mathbf{k}_1 \mathbf{j}_2)$ given by equation (3.4.19) because it is not immediately obvious what $M_{\alpha, \beta\alpha}(0\mathbf{K}; \mathbf{L}'\mathbf{K}')$ should be when working with the Karo and Hardy deformation dipole model.

Finally some thought should be given to the inclusion of higher order terms in the evaluation of the proper self-energy matrix such as the frequency dependent terms arising from the quartic coupling coefficient. Ipatova, Maradudin and Wallis^(3,5) have given considerable attention to this problem and they have

⁴R.A. Cowley, "The Lattice Dynamics of An Anharmonic Crystal", *Advances in Physics* 12, 421 (1963), p. 454.

⁵R.F. Wallis, I.P. Ipatova and A.A. Maradudin, "On the Temperature Dependence of the Width of the Fundamental Lattice Vibration Absorption Peak in Ionic Crystals I. Theory", *Fiz. Tverd. Tela* 8, 1064 (1966) (transl: *Soviet Physics - Solid State* 8, 850 (1966)).

shown that the above-mentioned terms give rise to contributions to the self-energy matrix that are proportional to the square of the temperature and may become important at temperatures greater than or equal to the Debye temperature of the crystal.

APPENDIX

EVALUATION OF THE THIRD ORDER COUPLING COEFFICIENT

In this section the third order coupling coefficient $V^{(3)}(0j_1; k_2 j_2; k_3 j_3)$ will be evaluated in terms of a particular lattice model. $V^{(3)}(0j_1; k_2 j_2; k_3 j_3)$ is given by equations (3.4.9), (3.4.11) and (3.4.13) to be

$$\begin{aligned}
 V^{(3)}(0j_1; k_2 j_2; k_3 j_3) = & \frac{1}{6N^{1/2}} \left[\frac{\hbar^3}{8\omega(k_2 j_2)\omega(k_3 j_3)\omega(0j_1)} \right]^{1/2} \times \\
 & \times \Delta(0+k_2+k_3) \left\{ \frac{1}{2} \sum_K \sum_{L'K'}' \sum_{\alpha_1 \alpha_2 \alpha_3} \phi_{\alpha_1 \alpha_2 \alpha_3}(0K; L'K') \times \right. \\
 & \times \prod_{i=1}^3 \left(\frac{m_{\alpha_i}(k_{ij}|K)}{\sqrt{M_K}} e^{2\pi i k_i \cdot \underline{x}(K)} - \right. \\
 & \left. \left. - \frac{m_{\alpha_i}(k_{ij}|K')}{\sqrt{M_{K'}}} e^{2\pi i k_i \cdot [\underline{x}(L') + \underline{x}(K')] } \right) \right\}, \quad (A.1)
 \end{aligned}$$

where the notation occurring in the above expression has been explained in section 3.4. $\phi_{\alpha_1 \alpha_2 \alpha_3}$ is the third derivative of the

two-body potential $\phi(r)$ and it is given explicitly by equation (3.4.4c). The delta function $\Delta(0 + \underline{k}_2 + \underline{k}_3)$ implies that $\underline{k}_3$ is not an independent wave vector but

$$\underline{k}_3 = \underline{G} - \underline{k}_2, \quad (\text{A.2})$$

where $\underline{G}$ is a reciprocal lattice vector that may or may not be equal to zero.

As an aid in evaluating the sums $\sum_{\underline{K}}$ and $\sum'_{\underline{L}'\underline{K}'}$, Figure 16 shows the face-centered cubic lattice of KCl. To designate which pair of ions belongs to a given unit cell a pseudo ellipse has been arbitrarily drawn around some of the ion pairs and the center pair has been chosen to be the $L = 0$ unit cell. The black circle has been selected to represent the $K = 0$ particle in the cell and the open circle to represent the ion designated as $K = 1$. It is also convenient to choose the origin of each unit cell at the position of the $K = 0$ ion such that

$$\underline{X}(\underline{K} = 0) = 0 \quad (\text{A.3a})$$

$$\text{and } \underline{X}(\underline{K} = 1) = r_{0\text{OZ}} \underline{e}_z, \quad (\text{A.3b})$$

where $\underline{X}(\underline{K})$ is the vector from the unit cell origin to the K^{th} particle within the cell. The origin of the lattice is located at the $(L=0, K=0)$ position and the vector from this origin to the origin of the L^{th} unit cell is labeled as $\underline{X}(\underline{L})$. Examples of $\underline{X}(\underline{L}=1)$ and $\underline{X}(\underline{L}=3)$ are shown in Figure 16.

Having established the notation the sums appearing in equation (A.1) can now be evaluated. For a given value of K a model will be

Figure 16. The sodium chloride crystal structure.

used in which only the six nearest neighbors contribute to the sum $\sum_{L'K'}$. To be sure, this approximation neglects the repulsive overlap forces beyond the nearest neighbors. The advantage of this approximation lies in the relative simplicity that the final form of $V^{(3)}$ will have, and hence, the relative ease in programming the computer. $V^{(3)}$ will be evaluated by first summing over the contribution from the nearest neighbors of the $L=0$ unit cell that lie only along the x direction. These will come from the unit cells labeled $L=1, 2, 3$, and 4 as shown in Figure 16. Once this has been done the y and z contributions can be written down immediately by symmetry considerations.

First consider the case where $L=0, K=0$ and $\sum_{L'K'}$ ranges over the two-neighbors of this ion that lie along the x axis, e.g., $(L=1, K=1)$ and $(L=2, K=1)$. The lattice vectors to the origin of the $L=1$ and $L=2$ unit cells are $\vec{X}(L=1) = r_0(\vec{e}_x - \vec{e}_z)$ and $\vec{X}(L=2) = r_0(-\vec{e}_x - \vec{e}_z)$, respectively. The contribution to $V^{(3)}$ from these two cells will be designated as $V_{1,2}^{(3)}(0j_1; k_2j_2; -k_2j_3)$. The ions that lie along the x direction have no y or z components and hence the only terms from $\phi_{\alpha_1\alpha_2\alpha_3}(0K; L'K')$ that will contribute will be (see equation (3.4.4c)):

(1) the diagonal term

$$\phi_{xxx} = \left\{ \frac{\lambda_x^3}{\lambda^3} \phi'''(\lambda) \right\} \Big|_{\lambda=\lambda_0} \quad (\text{A.4a})$$

(2) six off-diagonal terms

$$\begin{aligned} \phi_{xyy} = \phi_{xzz} = \phi_{yxy} = \phi_{zxz} = \phi_{yyx} = \phi_{zzx} = \\ = \left\{ \frac{r_x}{r^2} \phi''(r) \right\} \Big|_{r=r_0}, \end{aligned} \quad (\text{A.4b})$$

where r_x is the x-component of r , e.g., $r = (r_x^2 + r_y^2 + r_z^2)^{1/2}$.

One final simplification can be affected at this time.

Because the crystal possesses cubic symmetry, the optical properties are independent of the polarization direction of the incident photon. This photon has a wave vector very nearly equal to zero, compared to the dimensions of the first Brillouin zone, which will be labeled as $\underline{k} = 0^+$. It will be assumed that the $\underline{k} = 0^+$ incident photon is polarized along the x direction in wave vector space and that it interacts directly with the $\underline{k} = 0^+$ transverse optic phonon mode of the same polarization. Therefore, the eigenvector of this phonon mode will have components only in the x direction and it will be of the form

$$\eta(0^+j_1) = \begin{bmatrix} m_x(0^+j_1/0) \\ m_x(0^+j_1/1) \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \cdot \quad (\text{A.5})$$

Looking at equation (A.1) it can be seen that the α_1 index is always associated with the α_1 -component of the $\underline{k}_1 = 0^+$ eigenvector $m_{\alpha_1}(0^+ j_1/K)$. However, the preceding discussion indicated that the eigenvector of the $\underline{k}_1 = 0^+$ mode has only x components (see (A.5)) and, therefore, the only value that α_1 can take is x. Only two terms, out of the six terms given in equation (A.4b), have the α_1 index equal to x; they are ϕ_{xyy} and ϕ_{xzz} . The other four coefficients are proportional to either the y or z components of the $\underline{k}_1 = 0^+$ eigenvector and these are zero according to equation (A.5).

The contribution to $V^{(3)}$ from the two ions ($L=1, K=1$) and ($L=2, K=1$) is

$$\begin{aligned}
 V_{1,2}^{(3)} \{oj_1 j_2 j_3 | \underline{k}_2 j_2 j_3 | \underline{Q} - \underline{k}_2 j_3\} = & \frac{1}{6N^{1/2}} \left[\frac{1}{8\omega(oj_1)\omega(\underline{k}_2 j_2)\omega(\underline{Q} - \underline{k}_2 j_3)} \right]^{1/2} \\
 & \times \left(\frac{1}{2} \right) \left\{ \phi'''(\lambda_0) \left(\left[\frac{m_x(oj_1|0)}{\sqrt{M_0}} - \frac{m_x(oj_1|1)}{\sqrt{M_1}} \right] \times \right. \right. \\
 & \times \left[\frac{m_x(\underline{k}_2 j_2|0)}{\sqrt{M_0}} - \frac{m_x(\underline{k}_2 j_2|1)}{\sqrt{M_1}} \right] e^{2\pi i \underline{k}_2 \cdot \lambda_0 \underline{e}_x} \left. \left[\frac{m_x(\underline{Q} - \underline{k}_2 j_3|0)}{\sqrt{M_0}} - \right. \right. \\
 & \left. \left. - \frac{m_x(\underline{Q} - \underline{k}_2 j_3|1)}{\sqrt{M_1}} \right] e^{2\pi i (\underline{Q} - \underline{k}_2) \cdot \lambda_0 \underline{e}_x} \right) \right\} +
 \end{aligned}$$

$$\begin{aligned}
& + \frac{\phi''(\lambda_0)}{\lambda_0} \left(\left[\frac{m_x(0j_1|0)}{\sqrt{M_0}} - \frac{m_x(0j_1|1)}{\sqrt{M_1}} \right] \left[\frac{m_y(k_z j_2|0)}{\sqrt{M_0}} - \right. \right. \\
& \left. \left. - \frac{m_y(k_z j_2|1)}{\sqrt{M_1}} \right] e^{2\pi i k_z \cdot \lambda_0 \xi_x} \right] \left[\frac{m_y(\xi - k_z j_3|0)}{\sqrt{M_0}} - \right. \\
& \left. - \frac{m_y(\xi - k_z j_3|1)}{\sqrt{M_1}} \right] e^{2\pi i (\xi - k_z) \cdot \lambda_0 \xi_x} \left. \right] + \left[\frac{m_x(0j_1|0)}{\sqrt{M_0}} - \frac{m_x(0j_1|1)}{\sqrt{M_1}} \right] \times \\
& \times \left[\frac{m_z(k_z j_2|0)}{\sqrt{M_0}} - \frac{m_z(k_z j_2|1)}{\sqrt{M_1}} \right] e^{2\pi i k_z \cdot \lambda_0 \xi_x} \left[\frac{m_z(\xi - k_z j_3|0)}{\sqrt{M_0}} - \right. \\
& \left. - \frac{m_z(\xi - k_z j_3|1)}{\sqrt{M_1}} \right] e^{2\pi i (\xi - k_z) \cdot \lambda_0 \xi_x} \left. \right] \Bigg) - \\
& - \left(\begin{array}{l} \text{a set of terms exactly similar to those given} \\ \text{above except in each exponential there is a minus} \\ \text{sign. These terms come from the ion (L=2, K=1).} \end{array} \right) \Bigg\} \cdot \quad (A.6)
\end{aligned}$$

It can be seen that the term $\left[\frac{m_x(0j_1|0)}{\sqrt{M_0}} - \frac{m_x(0j_1|1)}{\sqrt{M_1}} \right]$ is common to all terms and it can be factored out. For the sake of notation brevity, F_x will be defined to be

$$F_x \equiv \frac{1}{6N^{1/2}} \left[\frac{\hbar^3}{8\omega(oj_1)\omega(\underline{k}_2j_2)\omega(\underline{Q}-\underline{k}_2j_3)} \right]^{1/2} \times$$

$$\times \left(\frac{1}{2} \right) \left[\frac{m_x(oj_1|0)}{\sqrt{M_0}} - \frac{m_x(oj_1|1)}{\sqrt{M_1}} \right]. \quad (A.7)$$

Carrying out the indicated multiplications in (A.6) and combining similar terms it is found that

$$V_{1,2}^{(3)}(oj_1; \underline{k}_2j_2; \underline{Q}-\underline{k}_2j_3) = \frac{-2iF_x \sin[2\pi \underline{k}_2 \cdot \underline{n}_0 \underline{e}_x]}{\sqrt{M_0 M_1}} \times$$

$$\times \left\{ \phi'''(\underline{n}_0) \left(-m_x(\underline{k}_2j_2|0) m_x(\underline{Q}-\underline{k}_2j_3|1) \cos[2\pi \underline{Q} \cdot \underline{n}_0 \underline{e}_x] + \right. \right.$$

$$\left. + m_x(\underline{k}_2j_2|1) m_x(\underline{Q}-\underline{k}_2j_3|0) \right) +$$

$$+ \frac{\phi''(\underline{n}_0)}{\underline{n}_0} \left(-m_y(\underline{k}_2j_2|0) m_y(\underline{Q}-\underline{k}_2j_3|1) \cos[2\pi \underline{Q} \cdot \underline{n}_0 \underline{e}_x] + \right.$$

$$+ m_y(\underline{k}_2j_2|1) m_y(\underline{Q}-\underline{k}_2j_3|0) - m_z(\underline{k}_2j_2|0) \times$$

$$\times m_z(\underline{Q}-\underline{k}_2j_3|1) \cos[2\pi \underline{Q} \cdot \underline{n}_0 \underline{e}_x] + m_z(\underline{k}_2j_2|1) \times$$

$$\times m_z(\underline{Q}-\underline{k}_2j_3|0) \left. \right) \Big\}. \quad (A.8)$$

In simplifying to this expression it was noted that $\sin(2\pi (\underline{G} - \underline{k}_2) \cdot \underline{r}_{o\vec{n}_x})$ can be expanded as

$$-\cos(2\pi \underline{G} \cdot \underline{r}_{o\vec{n}_x}) \sin(2\pi \underline{k}_2 \cdot \underline{r}_{o\vec{n}_x}),$$

because $\sin(2\pi \underline{G} \cdot \underline{r}_{o\vec{n}_x}) = 0$ for all $\underline{G}$ (see equation (3.2.5)).

The contribution to the third order coefficient from the two ions located at $(L=3, K=0)$ and $(L=4, K=0)$ (see Figure 16) will be designated as $V_{3,4}^{(3)}(0j_1; \underline{k}_2 j_2; \underline{G}-\underline{k}_2 j_3)$. It is straight forward to show that this contribution is identical to $V_{1,2}^{(3)}(0j_1; \underline{k}_2 j_2; \underline{G}-\underline{k}_2 j_3)$ as given in equation (A.8);

$$V_{3,4}^{(3)}(0j_1; \underline{k}_2 j_2; \underline{G}-\underline{k}_2 j_3) = V_{1,2}^{(3)}(0j_1; \underline{k}_2 j_2; \underline{G}-\underline{k}_2 j_3). \quad (A.9)$$

The total contribution to $V^{(3)}$ from the ions lying in the x direction is then

$$\begin{aligned} V_{1,2,3,4}^{(3)} &\equiv V_{1,2}^{(3)} + V_{3,4}^{(3)} = \\ &= \frac{-4i F_x \sin[2\pi \underline{k}_2 \cdot \underline{n}_0 \underline{e}_x]}{(M_1 M_0)^{1/2}} \left[\phi'''(\underline{n}_0) \times \right. \\ &\quad \times (m_x(\underline{k}_2 j_2 | 0) m_x(\underline{G}-\underline{k}_2 j_3 | 1) \cos[2\pi \underline{G} \cdot \underline{n}_0 \underline{e}_x] - \\ &\quad \left. - m_x(\underline{k}_2 j_2 | 1) m_x(\underline{G}-\underline{k}_2 j_3 | 0)) \right] + \end{aligned}$$

$$+ \frac{\phi''(\lambda_0)}{\lambda_0} \left(\sum_{\alpha=y,z} \left\{ m_\alpha(k_z j_2 | 0) m_\alpha(\underline{Q} - k_z j_3 | 1) \cos[2\pi \underline{Q} \cdot \lambda_0 \underline{e}_\alpha] - \right. \right. \\ \left. \left. - m_\alpha(k_z j_2 | 1) m_\alpha(\underline{Q} - k_z j_3 | 0) \right\} \right). \quad (\text{A.10})$$

From equation (A.10) the contributions to $V^{(3)}$ from the particles lying along the y and z directions can be immediately written down. These contributions will be designated as $V^{(3)}(\delta = y \text{ or } z)$ where the notation ($\delta = y \text{ or } z$) means that δ is set equal to y or z in the following equation to obtain the contribution to $V^{(3)}$ from the particles lying along the y or z direction. By symmetry considerations from equation (A.10) it follows that

$$V^{(3)}(\delta = y \text{ or } z) = \frac{-4i F_x \sin[2\pi k_z \cdot \lambda_0 \underline{e}_\delta]}{\sqrt{M_0 M_1}} \left(\frac{\phi''(\lambda_0)}{\lambda_0} \right)_x \\ \times \left[m_\delta(k_z j_2 | 0) m_x(\underline{Q} - k_z j_3 | 1) \cos[2\pi \underline{Q} \cdot \lambda_0 \underline{e}_\delta] - \right. \\ \left. - m_\delta(k_z j_2 | 1) m_x(\underline{Q} - k_z j_3 | 0) + m_x(k_z j_2 | 0) m_\delta(\underline{Q} - k_z j_3 | 1) \right. \\ \left. \times \cos[2\pi \underline{Q} \cdot \lambda_0 \underline{e}_\delta] - m_x(k_z j_2 | 1) m_\delta(\underline{Q} - k_z j_3 | 0) \right]. \quad (\text{A.11})$$

Notice that there are no contributions to $V^{(3)}(\delta = y \text{ or } z)$ from the terms containing the third derivative of the potential $\phi'''(r_0)$. It can be seen from equation (A.4a) that the third

derivative of the potential function only enters into the diagonal term of $\phi_{\alpha_1 \alpha_2 \alpha_3}$, e.g.,

$$\phi_{\alpha_1 \alpha_1 \alpha_1} = \left\{ \frac{\lambda_{\alpha_1}^3}{\lambda^3} \phi'''(\lambda) \right\} \Big|_{\lambda=\lambda_0}.$$

For those ions lying only along the y direction $\alpha_1 = y$ and,

similarly, for the ions lying only along the z direction $\alpha_1 = z$.

In the first case $V^{(3)}$ is proportional to $\left[\frac{m_y(0^+ j_1/0)}{\sqrt{M_0}} - \frac{m_y(0^+ j_1/1)}{\sqrt{M_1}} \right]$

and in the second case $V^{(3)}$ is proportional to

$$\left[\frac{m_z(0^+ j_1/0)}{\sqrt{M_0}} - \frac{m_z(0^+ j_1/1)}{\sqrt{M_1}} \right].$$

However, according to equation (A.5),

these components are zero.

Combining equations (A.7), (A.10) and (A.11) the final expression for $V^{(3)}$ can be written as

$$V^{(3)}(0j_1; k_2 j_2; \underline{Q} - k_2 j_3) = \frac{i}{3N^{1/2} (M_1 M_0)^{1/2}} \left[\frac{m_x(0j_1|0)}{\sqrt{M_0}} - \frac{m_x(0j_1|1)}{\sqrt{M_1}} \right]_x$$

$$\times \left[\frac{\hbar^3}{8\omega(0j_1)\omega(k_2 j_2)\omega(\underline{Q} - k_2 j_3)} \right]^{1/2} \left\{ \left[\phi'''(\lambda_0) \times \right.$$

$$\times \left(m_x(k_2 j_2|0) m_x(\underline{Q} - k_2 j_3|1) \cos[2\pi \underline{Q} \cdot \lambda_0 \underline{e}_x] - \right.$$

$$\left. - m_x(k_2 j_2|1) m_x(\underline{Q} - k_2 j_3|0) \right) +$$

$$\begin{aligned}
& + \frac{\phi''(\lambda_0)}{\lambda_0} \sum_{\alpha=\gamma, z} \left(m_\alpha(\underline{k}_2 j_2 | 0) m_\alpha(\underline{G} - \underline{k}_2 j_3 | 1) \times \right. \\
& \times \cos[2\pi \underline{G} \cdot \lambda_0 \underline{e}_x] - m_\alpha(\underline{k}_2 j_2 | 1) m_\alpha(\underline{G} - \underline{k}_2 j_3 | 0) \left. \right) \times \\
& \times \sin[2\pi \underline{k}_2 \cdot \lambda_0 \underline{e}_x] + \frac{\phi''(\lambda_0)}{\lambda_0} \left[\sum_{\delta=\gamma, z} \left(m_\delta(\underline{k}_2 j_2 | 0) \times \right. \right. \\
& \times m_\delta(\underline{G} - \underline{k}_2 j_3 | 1) \cos[2\pi \underline{G} \cdot \lambda_0 \underline{e}_\delta] - m_\delta(\underline{k}_2 j_2 | 1) \times \\
& \times m_\delta(\underline{G} - \underline{k}_2 j_3 | 0) + m_\delta(\underline{k}_2 j_2 | 0) m_\delta(\underline{G} - \underline{k}_2 j_3 | 1) \times \\
& \times \cos[2\pi \underline{G} \cdot \lambda_0 \underline{e}_\delta] - m_\delta(\underline{k}_2 j_2 | 1) m_\delta(\underline{G} - \underline{k}_2 j_3 | 0) \left. \right) \times \\
& \times \sin[2\pi \underline{k}_2 \cdot \lambda_0 \underline{e}_\delta] \left. \right] \} . \tag{A.12}
\end{aligned}$$

This is the explicit form of the third order coupling coefficient that will be used in the numerical calculation of the KCl proper self-energy matrix.

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