Fig 324
11/14
LA-3750

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Lattice Dynamics of Lithium Hydride

MASTER

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This report expresses the opinions of the author or authors and does not necessarily reflect the opinions or views of the Los Alamos Scientific Laboratory.

Printed in the United States of America. Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

LA-3750
UC-34, PHYSICS
TID-4500

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Report written: July 1967

Report distributed: October 24, 1967

Lattice Dynamics of Lithium Hydride*

by

J. Larry Verble

*Also submitted as a dissertation in partial fulfillment of requirements for the degree of Doctor of Philosophy in Physics from Tulane University.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ABSTRACT

Crystalline lithium hydride, with four electrons per primitive unit cell, has the simplest electronic configuration of all ionic crystals with the sodium chloride-type structure and thus represents an excellent test case for existing theories of lattice dynamics of these substances. Lattice vibrations in this system have been studied by measuring the phonon dispersion curves along the three high symmetry directions in a single crystal of ${}^7\text{LiD}$, using the techniques of coherent inelastic scattering of thermal neutrons. The isotopes ${}^7\text{Li}$ and D were chosen over normal Li and H because of their more favorable neutron cross sections. All measurements were taken at room temperature using a triple axis neutron spectrometer operating in the constant $\vec{Q}$ mode. Uncertainties in the measured frequencies are estimated to be no greater than 3-5 percent. The transverse zone center frequency is in excellent agreement with the infrared absorption data. The experimental dispersion curves have been least-squares fitted to several versions of the point ion and shell models of lattice dynamics. A seven parameter shell model, which considers first neighbor and second neighbor negative ion short-range interactions, allows for the negative ion to be polarizable, and uses a variable ionic charge, fits the data to within the experimental accuracy. The model indicates that the negative-negative ion interactions are about 7 percent of the positive-negative ion interactions. In addition, the bond in ${}^7\text{LiD}$ is found to

be about 88 percent ionic, in good agreement with estimates obtained from electronegativity considerations. From the best fit model, the dispersion curves of ${}^7\text{LiH}$ have been calculated assuming that the forces are identical to those for ${}^7\text{LiD}$. To simplify the application of the various models and to aid in classifying the dispersion curve branches, group theory has been applied to the problem of lattice vibrations in the sodium chloride structure.

ACKNOWLEDGEMENTS

The author is deeply grateful to Dr. John L. Yarnell and Dr. Robert H. Morriss under whose co-direction this investigation was conducted. Particular thanks are due Dr. Yarnell for suggesting the problem and for help and guidance during the course of this work. The author is also indebted to Dr. John L. Warren for helpful discussions on the theoretical aspects of this paper; to Mr. Ermil E. Thrasher for preparing the crystal samples; to Dr. Gerald Dolling for making the Chalk River shell model computer code available to us; and to Dr. Stanley P. Marsh for allowing his elastic constant data to be quoted before publication. For financial assistance, gratitude is extended to the U. S. Atomic Energy Commission and the Associated Western Universities.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
I. INTRODUCTION	1
II. THEORY	8
III. EXPERIMENTAL DETAILS	28
IV. RESULTS	40
V. DISCUSSION OF RESULTS	59
VI. SUMMARY	63
APPENDIX	65
LIST OF REFERENCES	97

LIST OF TABLES

Table	Page
1. Phonon frequencies for propagation in the Δ direction of ^7LiD at 300°K (units 10^{13} rad/sec).	41
2. Phonon frequencies for propagation in the Σ direction of ^7LiD at 300°K (units 10^{13} rad/sec).	42
3. Phonon frequencies for propagation in the Λ direction of ^7LiD at 300°K (units 10^{13} rad/sec).	43
4. Model parameters.	55
5. Calculated and observed properties of ^7LiD .	57
A.1 Nearest neighbors to zeroth atom: $l = 0$, $\kappa = 1$.	70
A.2 Rotational matrices for point group T_d .	73
A.3 Interatomic force constant matrices for interaction between the zeroth atom and its first and second nearest neighbors.	77
A.4 Symmetry points and lines in the NaCl (FCC) Brillouin zone.	81
A.5 Matrix elements and characters for propagation along Δ .	83
A.6 Matrix elements and characters for point X.	84
A.7 Matrix elements and characters for Σ , K, U, and S.	85
A.8 Matrix elements and characters for propagation along Λ .	85
A.9 Matrix elements and characters for point L.	86
A.10 Compatibility relations at Γ .	89
A.11 Compatibility relations at X.	89
A.12 Compatibility relations at L.	89

LIST OF FIGURES

Figure	Page
1. Shell model short-range interaction.	23
2. The short-range interaction polarization.	26
3. Schematic diagram of the triple axis spectrometer.	33
4. The (011) plane of the reciprocal lattice showing a typical inelastic scattering process.	36
5. A neutron group corresponding to a transverse acoustic phonon propagating in the [100] direction.	37
6. Phonon dispersion curves of ^7LiD at 300°K , compared to calculated curves based on Model I.	44
7. Phonon dispersion curves of ^7LiD at 300°K , compared to calculated curves based on Model II.	45
8. Phonon dispersion curves of ^7LiD at 300°K , compared to calculated curves based on Model III.	46
9. Phonon dispersion curves of ^7LiD at 300°K , compared to calculated curves based on Model IV.	47
10. Phonon dispersion curves of ^7LiH calculated using the parameter values of Model IV for ^7LiD .	58
A.1. Primitive unit cell for the sodium chloride crystal structure.	68
A.2. Brillouin zone for the face-centered cubic lattice.	80

I. INTRODUCTION

General Considerations

Lattice vibrations result because of thermal excitation when the atoms in a solid execute small oscillations about their equilibrium positions. In the case of a perfect crystal, these atomic motions can be analyzed in considerable detail if the crystal boundaries are neglected and one assumes that the forces between atoms are harmonic. For a crystal with N atoms, one obtains for the equations of motion of the system a set of $3N$ coupled harmonic oscillator equations. A transformation to normal coordinates allows this set of equations to be uncoupled, and as a result, the $3N$ normal modes of vibration of the system are described as plane waves. If the wave motion is then quantized, the quantum associated with a normal mode can be considered as an elementary excitation of the lattice, and this quantum is known as a phonon.

The interatomic forces in a solid are responsible for the characteristic way in which the atoms move under thermal excitation. In principle, if the interatomic potentials were known, the forces due to arbitrary displacements of the atoms could be determined. From this information the entire dynamics of the crystal system could be calculated. Unfortunately, for most solids the interatomic potentials and forces are not known analytically. However, from experimental studies of lattice vibrations one can often work in reverse to obtain

information about the interatomic forces.

Lattice waves can be characterized by three basic quantities:

(1) the wave vector $\vec{q}$, (2) the angular frequency $\omega(\vec{q})$, and (3) the polarization vectors $\vec{\xi}(\vec{q})$. The wave vector specifies the direction of wave propagation and has a magnitude $|\vec{q}| = 2\pi/\lambda$, where λ is the wavelength. The relation between the frequency and wave vector $\omega = \omega(\vec{q})$ is known as the dispersion relation. The polarization vectors determine the displacements of the atoms in a typical unit cell.

In the case of a three dimensional crystal, the dispersion relation is a multivalued function in wave vector space. For a crystal with s atoms in the primitive unit cell and for a given wave vector $\vec{q}$, $\omega(\vec{q})$ will have $3s$ values, some of which may be degenerate. Along a selected direction in wave vector space the dispersion relation corresponds to a set of curves with $3s$ branches, called the dispersion curves. To specify a particular branch, the dispersion curves $\omega_j(\vec{q})$ are labeled with a branch index j , ($j = 1 \dots 3s$).

The atomic displacements will, in general, be in different directions and at various angles to the direction of propagation for the various atoms in a given unit cell. For wave propagation along highly symmetric directions, however, the crystal symmetry often requires that all displacements occur along lines which are either perpendicular or parallel to the direction of propagation. Such cases correspond to "pure" modes of vibration, and one can speak of the polarization of the dispersion curve branches as either pure transverse or pure longitudinal. A complete determination of the dispersion relation therefore involves not only a determination of the frequencies, but also an identification

of the branches according to their polarization.

Interest in the field of lattice dynamics has increased steadily over the past ten years, primarily because of the development of methods which allow the dispersion relation to be obtained experimentally. The most common technique utilizes the coherent inelastic scattering of thermal neutrons from a single crystal [1]. Experimental conditions may be chosen so that processes in which the scattered neutron creates or annihilates a single phonon predominate. In this case a peak in the neutron counting rate corresponds to a phonon of wave vector $\vec{q}$ and frequency $\omega = \omega(\vec{q})$. Such a peak will be observed when the conservation of wave vector and energy equations

$$\vec{Q} \equiv \vec{k} - \vec{k}' = \vec{G} \pm \vec{q} \quad (1.1a)$$

$$E - E' = \pm \hbar\omega \quad (1.1b)$$

are satisfied. The meaning of the symbols is as follows:

$\vec{Q}$ = wave vector transfer vector

$\vec{k}$ = incident neutron wave vector

$\vec{k}'$ = scattered neutron wave vector

$\vec{G}$ = reciprocal lattice vector¹

E = incident neutron energy

E' = scattered neutron energy.

In these equations the plus signs are used for phonon creation and

¹The factor of 2π has been included in the definition of $\vec{G}$.

the minus signs for phonon annihilation. For a monoenergetic neutron beam, E and $\vec{k}$ are known. By analyzing the scattered neutrons in energy and wave vector, the frequency and wave vector of the phonons can be inferred. Repeated observations at various energy and wave vector transfers then allow the dispersion relation to be obtained for phonon propagation along selected directions in the crystal.

The dispersion relation is of interest for a number of reasons. In the first place, it can lead to an understanding of many physical properties of solids including, for example, thermal properties such as the specific heat, infrared and optical properties, dielectric properties of insulators, and electrical transport properties of conductors. Secondly, the dispersion relation provides the necessary experimental information required to test various theories of lattice dynamics. This is perhaps its most interesting aspect.

Interpretation of the experimentally determined dispersion curves is usually carried out within the framework of the general Born-von Karman theory of lattice dynamics. The procedure most often followed involves the construction of a force model which considers interactions between some selected number of neighboring atoms. Interatomic force constants are used to describe the interactions and are left as adjustable parameters to be determined by fitting the model to the experimental data. For forces which are sufficiently short-ranged, the number of unknown parameters can be kept to a minimum by considering interactions between some small number of neighbors. In this case the values of the parameters so obtained yield information about the strength of the interatomic forces. The range of

these forces is indicated by the number of interacting neighbors the model requires to give a reasonable fit to the data.

For long-ranged forces, on the other hand, one must either have added information about the interatomic potential or else be confronted with an unmanageable number of parameters. In the latter case, one has almost no hope of extracting physical meaning from a force model and should, perhaps, use a more fundamental approach.

A model which can reproduce the experimental dispersion curves can be useful in yet another respect, and that is in the determination of the frequency distribution function $g(\omega)$. The function $g(\omega)$ gives the density of allowed vibrational states of the crystal, or put another way, the quantity $g(\omega)\Delta\omega$ represents the number of allowed normal modes occurring between a frequency ω and $\omega + \Delta\omega$. From the distribution function it is possible to determine most of the important thermal properties of the solid including, for example, the temperature dependence of the specific heat.

Review of Previous Work

Because of its simple electronic structure, crystalline lithium hydride represents probably the simplest ionic solid. In this substance both the Li^+ and H^- ions take on the closed-shell electronic configuration of the He atom. Consequently, the H^- ion may be considered as the first ion in the halogen series, and LiH may thus be treated as one of the alkali halides. Crystalline LiH has the sodium chloride structure; hence, there are two ions with four electrons contained in the primitive unit cell.

This simplified electronic structure has led to much theoretical interest in the LiH molecule and solid. Ewing and Seitz [2] have applied the Hartree-Fock method to the study of the electronic states of solid LiH. Calculations of the cohesive energy of the solid have been made by several investigators [3], assuming complete ionic bonding. The discrepancy between these calculations and the observed cohesive energy seems to indicate that a certain amount of covalent bonding is present. The calculation of Morita and Takahashi [4], where homopolar bonding is taken into account, removes the discrepancy. Recent theoretical studies of the lattice dynamics of LiH include the results of Brodsky and Burstein [5] who have used certain observed properties of LiH to calculate various parameters occurring in the shell model of lattice dynamics.

On the experimental side, Calder et al. [6] have performed an x-ray and neutron diffraction analysis of LiH to determine electron distributions and structure factors. Woods et al. [7] have determined the energy distribution of thermal neutrons inelastically scattered from polycrystalline LiH. They state that peaks in their energy distribution possibly correspond to peaks in the frequency distribution function. Along similar lines, Zemlianov et al. [8] have observed the incoherent inelastic scattering of cold neutrons from polycrystalline samples of ^7LiH and ^7LiD . From a point ion model they calculate the energy dependence of the polarization vectors and the Debye-Waller factors. These results are then compared to experiment to deduce the frequency distribution functions for the two substances.

Scope of this Work

The purpose of the present work is to present a study of the lattice dynamics of the LiH-LiD systems. Toward this end, the phonon dispersion curves have been measured along three high symmetry directions in a single crystal of ^7LiD by the techniques of coherent inelastic scattering of thermal neutrons. The choice of ^7LiD as a sample rather than normal LiH or LiD depends on two factors: (1) Normal Li contains about 7.5% ^6Li , which has an undesirably large absorption cross section for thermal neutrons, whereas that for ^7Li is considerably less; and (2) the undesirable incoherent scattering from H is much greater than that for D.

The measured dispersion curves are compared to two models of lattice dynamics, the point ion model and the shell model, both of which have been widely applied to other alkali halides. In addition, group theoretical methods are used to simplify the application of these models and to help in classifying the branches of the dispersion curves. Finally, using the results of the shell model for ^7LiD , the dispersion curves of ^7LiH are calculated under the assumption that in the two substances, the forces are the same.

II. THEORY

In this section several theories of lattice dynamics of perfect crystals are presented. After discussing the assumptions which form the framework of the general Born-von Karman theory, the results of this theory are developed. Later in the section specialized models are presented for application to ionic crystals.

Several excellent books and review articles exist which discuss in more detail the results to be presented here. Noteworthy are the works of Maradudin, Montroll, and Weiss [9], Dolling and Woods [10], and Cochran [11].

General Harmonic Theory of Lattice Dynamics

In dealing with any solid state phenomenon, one is faced with a problem involving of the order of 10^{23} interacting particles. This immediately precludes the possibility of exact solutions and makes the use of simplifying assumptions and approximations a necessity. The Born-von Karman theory of lattice dynamics is no exception. In fact, the whole theory has as its framework three assumptions which are fundamental to almost all of solid state theory. These are:

1. The assumption of periodic boundary conditions
2. The adiabatic or Born-Oppenheimer approximation
3. The harmonic approximation.

Before developing the Born-von Karman theory, each of these will be discussed individually.

Periodic Boundary Conditions. -- In considering wave motion which propagates through a lattice, it is desirable to be able to ignore the crystal surfaces entirely. One obvious way of doing this is to assume the crystal to be infinitely extended in space. This approach, however, is physically unsuitable because it leads to an infinite number of atoms, an infinite number of vibrational modes, and ultimately, to a divergent crystal energy.

One scheme for keeping the crystal finite, yet allowing the surfaces to be neglected, involves the use of periodic boundary conditions. Here it is assumed that the three dimensional crystal has dimensions $L_1\vec{a}_1$, $L_2\vec{a}_2$, $L_3\vec{a}_3$, where $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are the primitive translational vectors for the lattice and $L_1 \times L_2 \times L_3$ gives the number of unit cells in the crystal. It is further assumed that any function $\psi(\vec{r})$ of position in the lattice is periodic along each of the three dimensions of the crystal. This can be expressed as

$$\left. \begin{aligned} \psi(\vec{r} + L_1\vec{a}_1) &= \psi(\vec{r}) \\ \psi(\vec{r} + L_2\vec{a}_2) &= \psi(\vec{r}) \\ \psi(\vec{r} + L_3\vec{a}_3) &= \psi(\vec{r}). \end{aligned} \right\} (2.1)$$

Imposing periodic boundary conditions can be thought of in the following way: The original crystal block is built up into an infinite lattice by adding identical blocks of the same size and shape to fill all space. The boundary conditions of Eq. (2.1) require that the displacements of two particles at corresponding points in any two blocks be the same. For the purpose of counting normal modes, only

the atoms contained in the original sample are considered as being in the system.

It should be emphasized that the assumption of periodic boundary conditions is merely a convenient mathematical device which allows one to avoid consideration of the boundaries. The use of the assumption is certainly justified when the following conditions are satisfied: (1) the crystal is of macroscopic size, (2) it has a reasonable geometric shape, and (3) the interatomic forces are sufficiently short-ranged. When long-ranged Coulomb forces exist, however, the assumption can perhaps break down. And yet experience has shown that even in these cases, the use of the assumption leads to reasonable results. Therefore, even when Coulomb forces are present, the assumption is retained. Its justification under these conditions involves the fact that regions in the crystal, having volumes containing several unit cells, must be electrically neutral, thus effectively reducing the range of the forces.

The Adiabatic Approximation. -- The most general way of considering a solid is in terms of the system of interacting electrons and nuclei of which it is composed. An accurate description of such a system would, in general, require a knowledge of the combined electronic and nuclear motions. Because of the large disparity between the electronic and nuclear masses, however, the adiabatic approximation [12] allows the problems of motion of the two systems to be separated.

The assumption basically is that the Schrödinger wave function Ψ for the system can be approximated by the product

$$\Psi \simeq \phi \psi . \quad (2.2)$$

The function ϕ describes the electronic problem and is evaluated with the nuclei held in fixed positions. The electronic wavefunction thus depends parametrically on the static configuration of the nuclear system, as well as depending upon the electronic coordinates. By solving the electronic Schrödinger equation, the energy of the electronic system is obtained. This energy is then used as part of the potential for the nuclear problem, which is described by the nuclear system wavefunction ψ .

The approximation assumes, in effect, that the electrons respond instantaneously to changes in positions of the nuclei and that the energies involved in this process are not sufficient to cause electronic transitions. The qualitative criteria for the validity of the approximation is that the kinetic energy of the nuclei is much smaller than the separation between electronic energy levels for a given nuclear configuration. Peierls [13] has shown that this condition is well satisfied for rare gas solids and ionic crystals, both being cases where the electronic levels are widely separated. For metals, on the other hand, the energy levels for the outer electrons are almost continuous, and in this case, the approximation is certainly subject to question.

The Harmonic Approximation. -- Consider a crystal of $L_1 \times L_2 \times L_3$ primitive unit cells, with each unit cell containing s ions. The equilibrium position of the l th unit cell with respect to the origin is given by $\vec{r}(l) = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3$. The integers l_1 , l_2 , and l_3

are represented collectively by $\ell = \{\ell_1, \ell_2, \ell_3\}$, and $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the primitive lattice translation vectors. The equilibrium positions of the s ions in a particular unit cell are denoted by $\vec{r}(\kappa)$, ($\kappa = 1 \cdots s$). Thus, a particular ion in the lattice, say the κ th ion in the ℓ th unit cell, has the position $\vec{r}(\kappa)^\ell = \vec{r}(\ell) + \vec{r}(\kappa)$. If the ions are now allowed to deviate from equilibrium, the displacement of the κ th ion in the ℓ th unit cell is represented by $\vec{u}(\kappa)^\ell$. The position of the displaced ion with respect to the origin is then $\vec{r}(\kappa)^\ell + \vec{u}(\kappa)^\ell$.

The total potential energy of the crystal can be written as a function of the positions of all ions, $\Phi(\cdots, \vec{r}(\kappa)^\ell + \vec{u}(\kappa)^\ell, \cdots)$. For small deviations from equilibrium it is reasonable to expand this potential in a Taylor series in the displacements,

$$\begin{aligned} \Phi = \Phi_0 + \sum_{\ell \kappa \alpha} \Phi_{\alpha}(\kappa)^\ell u_{\alpha}(\kappa)^\ell + \\ \frac{1}{2} \sum_{\substack{\ell \kappa \alpha \\ \ell' \kappa' \beta}} \Phi_{\alpha\beta}(\kappa \kappa')^{\ell \ell'} u_{\alpha}(\kappa)^\ell u_{\beta}(\kappa')^{\ell'} + \cdots, \end{aligned} \quad (2.3)$$

where the following notation is defined:

Φ_0 = static potential energy

$$\Phi_{\alpha}(\kappa)^\ell = \left. \frac{\partial \Phi}{\partial u_{\alpha}(\kappa)^\ell} \right|_0 \quad (2.4a)$$

$$\Phi_{\alpha\beta}(\kappa \kappa')^{\ell \ell'} = \left. \frac{\partial^2 \Phi}{\partial u_{\alpha}(\kappa)^\ell \partial u_{\beta}(\kappa')^{\ell'}} \right|_0. \quad (2.4b)$$

The zero subscripts indicate that the derivatives are evaluated at

equilibrium, while the α and β subscripts denote the α th and β th ($\alpha, \beta = 1, 2, 3$) Cartesian components of $\vec{u}_\kappa^{(l)}$.

In the harmonic approximation all terms beyond second order in Eq. (2.3) are neglected. The potential energy in this form allows for only harmonic atomic motions, with the higher order terms corresponding to anharmonic contributions. Within this approximation the lattice vibrations are treated as a set of independent normal modes or, in the quantum case, as a set of non-interacting phonons.

Development of General Harmonic Theory. -- The interpretation of Eqs. (2.4) is as follows: $\Phi_{\alpha\kappa}^{(l)}$ represents the negative of the force in the α -direction on the (κ) th atom evaluated at the equilibrium; but since at equilibrium the force on the particle must vanish, this quantity must be zero. If one defines

$$K_{\alpha\beta}^{(ll')\kappa\kappa'} \equiv - \Phi_{\alpha\beta}^{(ll')\kappa\kappa'}, \quad (2.5)$$

then $K_{\alpha\beta}^{(ll')\kappa\kappa'}$ represents an interatomic force constant. If the atom at $\vec{r}_\kappa^{(l)}$ is displaced a unit distance in the β -direction, then $K_{\alpha\beta}^{(ll')\kappa\kappa'}$ is the resulting force in the α -direction on the atom at $\vec{r}_\kappa^{(l)}$.

Two important properties of the force constants can be established. By interchanging the order of differentiation in Eq. (2.4b), one obtains

$$K_{\alpha\beta}^{(ll')\kappa\kappa'} = K_{\beta\alpha}^{(l'l)\kappa'\kappa}. \quad (2.6)$$

From the translational invariance of the lattice it follows that $K_{\alpha\beta}^{(ll')\kappa\kappa'}$ does not depend upon κ and κ' separately, but only on the

difference $l-l'$,

$$K_{\alpha\beta}^{(ll')} = K_{\alpha\beta}^{(l-l')} . \quad (2.7)$$

It is now possible to deduce the equations of motion for the system. The total kinetic energy of the crystal is

$$T = \frac{1}{2} \sum_{l\kappa\alpha} m_{\kappa} \dot{u}_{\alpha}^{(l)}{}^2, \quad (2.8)$$

so that the classical Hamiltonian becomes

$$H = \Phi_0 + \frac{1}{2} \sum_{l\kappa\alpha} m_{\kappa} \dot{u}_{\alpha}^{(l)}{}^2 - \frac{1}{2} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta}} K_{\alpha\beta}^{(ll')} u_{\alpha}^{(l)} u_{\beta}^{(l')}. \quad (2.9)$$

The application of Hamilton's canonical equations

$$\dot{u}_{\alpha} = \frac{\partial H}{\partial p_{\alpha}} \quad (2.10a)$$

$$\dot{p}_{\alpha} = - \frac{\partial H}{\partial u_{\alpha}} \quad (2.10b)$$

leads to the equation of motion for the $(\frac{l}{\kappa})$ th atom

$$\dot{p}_{\alpha} = m_{\kappa} \ddot{u}_{\alpha} = - \frac{\partial H}{\partial u_{\alpha}^{(l)}} = - \sum_{l'\kappa'\beta} K_{\alpha\beta}^{(ll')} u_{\beta}^{(l')}. \quad (2.11)$$

Plane wave solutions to Eq. (2.11) can be constructed as

$$u_{\alpha}(\kappa) = U_{\alpha}(\kappa | \vec{q}_j) \exp\{i[\vec{q} \cdot \vec{r}(\kappa) - \omega_j(\vec{q})t]\}, \quad (2.12)$$

where $U_{\alpha}(\kappa | \vec{q}_j)$ represents a wave amplitude whose components define to within a constant factor the polarization vectors $\vec{\xi}(\kappa | \vec{q}_j)$. The $\vec{\xi}$'s can in general be complex and are chosen so they are orthonormal and satisfy closure [9]. When Eq. (2.12) is substituted into Eq. (2.11) one obtains

$$m_{\kappa} \omega_j^2(\vec{q}) U_{\alpha}(\kappa | \vec{q}_j) = \sum_{\kappa' \beta} D_{\alpha\beta}(\vec{q}, \kappa \kappa') U_{\beta}(\kappa' | \vec{q}_j), \quad (2.13)$$

where

$$D_{\alpha\beta}(\vec{q}, \kappa \kappa') \equiv - \sum_{\ell \ell'} K_{\alpha\beta}(\kappa \kappa', \ell \ell') \exp\{i\vec{q} \cdot [\vec{r}(\kappa, \ell) - \vec{r}(\kappa', \ell')]\} \quad (2.14)$$

defines the elements of the so-called dynamical matrix. The above definition of the dynamical matrix is by no means universal; here Cochran's definition [11] has been used.

The dynamical matrix $D(\vec{q})$, in general, has dimensions $3s \times 3s$. Represented in block form it can be written as

$$D(\vec{q}) = \begin{bmatrix} D_{11}(\vec{q}) & \dots & D_{1s}(\vec{q}) \\ \vdots & & \vdots \\ D_{s1}(\vec{q}) & \dots & D_{ss}(\vec{q}) \end{bmatrix}, \quad (2.15)$$

where each of the $D(\vec{q}, \kappa \kappa')$'s are 3×3 sub-matrices having the form

$$D(\vec{q}, \kappa \kappa') = \begin{bmatrix} D_{11}(\vec{q}, \kappa \kappa') & D_{12}(\vec{q}, \kappa \kappa') & D_{13}(\vec{q}, \kappa \kappa') \\ D_{21}(\vec{q}, \kappa \kappa') & D_{22}(\vec{q}, \kappa \kappa') & D_{23}(\vec{q}, \kappa \kappa') \\ D_{31}(\vec{q}, \kappa \kappa') & D_{32}(\vec{q}, \kappa \kappa') & D_{33}(\vec{q}, \kappa \kappa') \end{bmatrix}. \quad (2.16)$$

From Eqs. (2.6) and (2.14) it can be shown that

$$D_{\beta\alpha}(\kappa|\vec{q}) = D_{\alpha\beta}^*(\kappa|\vec{q}), \quad (2.17)$$

and thus, in general, the dynamical matrix is Hermitian.

Equation (2.13) can be written in concise matrix form as

$$D U = \omega^2 m U, \quad (2.18)$$

where m is a $3s \times 3s$ diagonal mass matrix and U is a $3s \times 1$ column matrix constructed from the $U_\alpha(\kappa|\vec{q}_j)$'s in the following way:

$$U = \begin{bmatrix} U(1|\vec{q}_j) \\ \vdots \\ U(s|\vec{q}_j) \end{bmatrix}, \quad U(\kappa|\vec{q}_j) = \begin{bmatrix} U_1(\kappa|\vec{q}_j) \\ U_2(\kappa|\vec{q}_j) \\ U_3(\kappa|\vec{q}_j) \end{bmatrix}. \quad (2.19)$$

The quantity U will be known as the eigenvector. In Eq. (2.18) U could be replaced by the normalized eigenvector E which is constructed from the polarization vectors $\vec{E}(\kappa|\vec{q}_j)$ in a similar fashion. Equation (2.18) has the form of a matrix eigenvalue problem so that the condition for solubility of the set of equations is

$$\det (D - \omega^2 m) = 0. \quad (2.20)$$

Solving the set of equations represented by (2.20) determines the normal mode frequencies $\omega_j(\vec{q})$. As $\vec{q} \rightarrow 0$, there will in general be three values of $\omega_j(\vec{q})$ which vanish. These three modes are known as the acoustic modes; the remaining $3s-3$ modes whose frequencies do

not vanish at $\vec{q} = 0$ are called optical.

Two important properties of $\omega_j(\vec{q})$ are as follows:

1. $\omega_j(\vec{q}) = \omega_j(\vec{q} + \vec{G})$, where $\vec{G}$ is any reciprocal lattice vector. Thus, $\omega_j(\vec{q})$ has the periodicity of the reciprocal lattice, and to specify $\omega_j(\vec{q})$ completely, only wave vectors lying within and on the surface of the first Brillouin zone need be considered.
2. $\omega_j(\vec{q}) = \omega_j(-\vec{q})$. This condition makes it necessary to consider only positive wave vectors.

In order to apply the above theory, a knowledge of the interatomic force constants is required. The force constants usually cannot be obtained directly, since the interatomic potential through which they are defined is most often not available. In most cases, therefore, one must rely on a force model of the solid in which the force constants are regarded as unknowns.

For some types of crystals it is often possible to evaluate some of the force constants from physical measurements such as elastic constants, compressibilities, dielectric constants, etc. More often, however, the force constants are determined by comparing a model to measured dispersion curves.

The results obtained from a particular model will, of course, depend upon the number of neighbors allowed to interact, as well as the specific assumptions made regarding the nature of the interatomic forces. In any case, one can usually use the symmetry of the crystal to reduce the number of independent elements in the force constant matrices. If this is the only restriction imposed, then within the

Born-von Karman framework, the resulting model is the most general possible and is known as the general Born-von Karman or tensor force (TF) model. A further reduction in the number of force constants will require additional assumptions, for example, by assuming axially symmetric or central forces. These particular assumptions lead to the so-called axially symmetric (AS) and central force (CF) models, respectively.

Point Ion Model

In developing a theory of lattice dynamics for application to a particular class of solids it is often possible to use an assumed form for the interatomic potential. In ionic solids it is well known that the Coulomb potential plays a strong role in the bonding. In addition, there exists an overlap or exchange potential which results in short-ranged repulsive forces between the nearest and perhaps next-nearest neighbors. The overlap of electron wavefunctions for these closest neighbors, in accordance with the Pauli exclusion principle, leads to the exchange forces.

The interatomic potential for ionic solids, if restricted to central, pair-wise interactions, can be written in its simplest form as

$$\Phi = \frac{1}{2} \sum'_{\substack{l, l' \\ \kappa, \kappa'}} \frac{Z_{\kappa} Z_{\kappa'} e^2}{r} + V(r) \quad , \quad (2.21)$$

where the prime on the summation indicates that the term for which $l' = l$ and $\kappa' = \kappa$ is excluded and where Z_{κ} is the ionic charge of

the n th atom in units of e , r is the distance between particles, and $V(r)$ is the overlap potential. The Coulomb potential in the first term is summed over all ions in the crystal. The form of $V(r)$ is usually assumed to be either $A r^{-8}$ or the Born-Mayer potential $B \exp(-r/\rho)$.

Without being quite so restrictive, the repulsive potential could be assumed to be non-central. A more general form of Eq. (2.21) would thus be

$$\Phi = \Phi^{(C)} + \Phi^{(R)}. \quad (2.22)$$

Here the Coulomb potential remains unchanged; $\Phi^{(R)}$ is now no longer required to be central, but is still assumed to be a two-body potential. It is obvious from Eqs. (2.5) and (2.14) that the force constant matrices and the dynamical matrix may be divided into two parts corresponding to the two separate potentials,

$$K_{\alpha\beta}^{(ll')} = K_{\alpha\beta}^{(C)}(ll') + K_{\alpha\beta}^{(R)}(ll') \quad (2.23)$$

and

$$D(\vec{q}) = D^{(C)} + D^{(R)}. \quad (2.24)$$

Also, from Eq. (2.14) it is easily shown that the Coulomb contribution to the dynamical matrix takes the following form,

$$D_{\alpha\beta}^{(C)}(\vec{q}_{\kappa\kappa'}) = Z_{\kappa} Z_{\kappa'} e^2 \exp\{i\vec{q} \cdot [\vec{r}(\kappa') - \vec{r}(\kappa)]\} \times$$

$$\sum_{\ell'} \frac{\partial^2 |\vec{r}(\kappa') - \vec{r}(\ell)|^{-1}}{\partial x_{\alpha}(\kappa) \partial x_{\beta}(\kappa')} \exp\{i\vec{q} \cdot [\vec{r}(\ell') - \vec{r}(\ell)]\}. \quad (2.25)$$

Due to the long-ranged nature of the Coulomb potential, the series in Eq. (2.25) is only conditionally convergent. However, using a method developed by Ewald [14] the series can be transformed into two series, both of which converge much more rapidly. The first involves a summation over a limited region in real space and the second a sum over a region in reciprocal space. Expressions for these summations have been given by Kellerman [15], and they can most easily be evaluated with the aid of a computer. The resulting calculation leads to a set of Coulomb coefficients which can be considered as elements of a matrix $C(\vec{q})$. The Coulomb contribution to the dynamical matrix can then be written in terms of the Coulomb coefficients as

$$D_{\alpha\beta}^{(C)}(\vec{q}_{\kappa\kappa'}) = Z_{\kappa} Z_{\kappa'} C_{\alpha\beta}(\vec{q}_{\kappa\kappa'}). \quad (2.26)$$

The short-range contribution to the dynamical matrix is assumed to be of the tensor force form defined by

$$R_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) \equiv D_{\alpha\beta}^{(R)}(\vec{q}_{\kappa\kappa'}) = - \sum_{\ell'} K_{\alpha\beta}^{(R)}(\ell\ell') \times$$

$$\exp\{i\vec{q} \cdot [\vec{r}(\kappa') - \vec{r}(\kappa)]\}. \quad (2.27)$$

The equations of motion for an ionic crystal then become

$$m_{\kappa} \omega^2(\vec{q}) U_{\alpha}(\kappa|\vec{q}) = \sum_{\kappa'\beta} [R_{\alpha\beta}(\vec{q}_{\kappa\kappa'}) + Z_{\kappa} Z_{\kappa'} C_{\alpha\beta}(\vec{q}_{\kappa\kappa'})] U_{\beta}(\kappa'|\vec{q}) \quad (2.28)$$

or in matrix form

$$(R + Z C Z) U = \omega^2 m U, \quad (2.29)$$

where Z and m are 3×3 s diagonal matrices containing the ionic charges and ionic masses, respectively.

The equations represented in (2.29) form the basis of the so-called point ion model of lattice dynamics. The model treats the ions as completely rigid point charges and thus neglects electronic polarizability. Kellerman [15] was the first to apply the model to calculate the lattice dynamics of NaCl. His results were in good agreement with the observed specific heat and the $\vec{q} = 0$ transverse optical frequency. Comparisons between measured and calculated dispersion curves based on the point ion model, however, have lead to large discrepancies. The most notable deviations occur in the longitudinal optical branches [16,17].

Presumably the point ion model is deficient because electronic polarizability has been ignored. In an attempt to remedy the situation Lyddane and Herzfeld [18] assumed polarizable ions, resulting in the addition of induced electronic dipoles to the problem. Surprisingly, this worsened the agreement. Lyddane and Herzfeld concluded that in addition to considering the electronic polarizability,

the effects of the repulsive forces on the polarization of the ions needed to be taken into account.

Shell Model

In attempting to explain the dielectric properties of alkali halide crystals, Dick and Overhauser [19] proposed a simple model of these solids which provides a mechanism for the short-range interaction polarization. Subsequently, Cochran [20-22] generalized the model, hereafter known as the shell model, to apply to the lattice dynamics of the alkali halides. The shell model has the following features: Each ion is assumed to consist of a central core of charge $X_n|e|$ containing the nucleus plus the inner electrons, and a shell of charge $Y_n|e|$ composed of the outermost cloud of electrons. The ionic charge is thus $Z_n|e| = (X_n + Y_n)|e|$, and in order to maintain electrical neutrality, the sum of ionic charges within a unit cell must add to zero, that is, $\sum_n Z_n = 0$. The shell and core of a particular ion are coupled through an isotropic force constant k_n . Neighboring shells and cores of different ions can interact through the overlap repulsion, represented by additional force constants. Furthermore, Coulomb forces can act between two ions, between a shell and an ion, and between two shells. The various short-ranged interactions are shown for nearest neighbors in Fig. 1.

During a lattice vibration the shell and core of an ion can undergo a relative displacement. This leads to a change in the electrical potential energy of the system which can be expressed in an electric multipole expansion. In the shell model, only dipole

Figure 1. Shell model short-range interaction.

moments are retained from the expansion, and these are assumed located at the positions of the cores. Interactions between these dipoles throughout the crystal are evaluated through the Coulomb coefficients, which have been previously defined.

Cochran [23] has given an expression for the energy of an ionic crystal which is assumed to be a quadratic function of the nuclear displacements and the electric dipole moments. From this expression he shows that the equations of motion are identical with those obtained from the shell model [24]. In matrix form these equations are

$$(R + ZCZ)U + (T + ZCY)W = \omega^2 m U \quad (2.30a)$$

$$(\tilde{T} + YCZ)U + (S + YCY)W = 0, \quad (2.30b)$$

where m , U , Z , and C have been previously defined; the $3s \times 3s$ matrices R , S , and T account for the short-ranged ion-ion, shell-shell, and ion-shell interactions, respectively; the $3s \times 3s$ diagonal matrix Y is constructed from shell charges; and the $3s \times 1$ column matrix W involves the relative displacement of shell and core of the ions. The significance of W is that the product YW gives the electronic dipole moments of the ions. The adiabatic approximation is introduced by setting the electron (shell) masses equal to zero in the second equation. The elimination of W yields the characteristic equation for the shell model,

$$\det\{[(R + ZCZ) - (T + ZCY)(S + YCY)^{-1}(\tilde{T} + YCZ)] - \omega^2 m\} = 0. \quad (2.31)$$

In order to reduce the number of independent parameters, it is usually assumed that the overlap forces act only between the shells of neighboring ions [16]. In this case, the shell-core and core-core short-ranged force constants are zero, and the matrices R and T become identical. Their form is thus

$$R_{\alpha\beta}(\vec{q}, \kappa\kappa') = T_{\alpha\beta}(\vec{q}, \kappa\kappa') = - \sum_{\ell\ell'} K_{\alpha\beta}^{(S)}(\ell\ell') \times \exp\{i\vec{q} \cdot [\vec{r}(\kappa') - \vec{r}(\kappa)]\}, \quad (2.32)$$

where the $K_{\alpha\beta}^{(S)}(\ell\ell')$'s are the shell-shell force constants. Furthermore, S becomes

$$S = R + k, \quad (2.33)$$

where k is a $3s \times 3s$ diagonal matrix containing the k_{κ} 's.

On the basis of the shell model, the two contributions to the polarizability of the ions can be easily visualized. Figure 2(a) shows the two ions in an unpolarized state at their equilibrium positions. Assume for the moment that the overlap repulsion between the shells is absent. Then during a lattice vibration, the shells and cores move to positions as shown in Fig. 2(b). In this case the polarized state is caused entirely by the electrical Coulomb field present at the ion sites. On the other hand, when the overlap repulsion is included, an additional displacement of the shells and cores results, so that the total shell-core displacement is as shown in Fig. 2(c).

(a) UNPOLARIZED

(b) POLARIZED WITHOUT OVERLAP

(c) POLARIZED WITH OVERLAP

Figure 2. The short-range interaction polarization. (a) Ions in unpolarized equilibrium state. (b) Ions polarized without overlap between shells. (c) Ions polarized with overlap between shells.

The short-ranged forces thus contribute to a polarizability which can be considered separately from the electrical polarizability. This short-range contribution is often called the mechanical polarizability and is a measure of the strength of the overlap forces.

The shell model approach provides a convenient link with the Born-von Karman theory by allowing the concept of the force constant to be retained. It is significant that a simple classical interpretation of the shell model is possible; however, in addition, the model has been given a quantum mechanical foundation by Cowley [25]. His treatment is based on the adiabatic, harmonic, and electrostatic approximations. By expanding the perturbed Hamiltonian of the crystal in multipole moments and retaining only the dipoles, Cowley shows that the resulting equations of motion are identical with those obtained from the shell model.

III. EXPERIMENTAL DETAILS

Neutron Scattering

When a beam of thermal neutrons impinges upon a system of nuclei, several different types of scattering may be distinguished. If all nuclei in the system scatter alike, then coherent scattering results. If, however, the scattering at each nucleus is not the same, due to different types of nuclei or different spin states between the neutron and a given nucleus, incoherent scattering will also result. For the nuclei held fixed, the scattering is totally elastic; but if the nuclei are allowed to recoil, the scattering can then be inelastic. Hence, in general, four types of scattering may be present: (1) elastic coherent, (2) elastic incoherent, (3) inelastic coherent, and (4) inelastic incoherent. Although the incoherent scattering can play an important role in the study of solids, the coherent scattering is usually of more interest.

The elastic coherent (Bragg) scattering of neutrons from a crystalline solid is governed by the equations

$$\vec{Q} = \vec{k} - \vec{k}' = \vec{G} \quad (3.1a)$$

$$E = E', \quad (3.1b)$$

where:

$\vec{Q}$ = wave vector transfer vector

$\vec{k}$ = incident neutron wave vector

$\vec{k}'$ = scattered neutron wave vector

$\vec{G}$ = reciprocal lattice vector

E = incident neutron energy

E' = scattered neutron energy.

In the general case of inelastic coherent scattering, the governing equations are

$$\vec{Q} = \vec{k} - \vec{k}' = \vec{G} + \sum_{i=1}^N (\pm \vec{q}_i) \quad (3.2a)$$

$$E - E' = \hbar \sum_{i=1}^N [\pm \omega(\vec{q}_i)] , \quad (3.2b)$$

where now N specifies the number of phonons created or annihilated in the crystal by the scattering process. For $N = 1$, the scattering involves one phonon; for $N = 2$, two phonons; etc. Most often one is interested in the one phonon process, and in this case Eqs. (3.2) become

$$\vec{Q} = \vec{k} - \vec{k}' = \vec{G} \pm \vec{q} \quad (3.3a)$$

$$E - E' = \pm \hbar \omega_j(\vec{q}). \quad (3.3b)$$

The one phonon processes give rise to sharp neutron groups in an inelastic neutron scattering experiment. The multiphonon processes, on the other hand, lead to a more or less uniform background which is essentially independent of the crystal orientation, angle of scattering, and neutron energy. This background can usually be minimized by maintaining the sample at a temperature much below that of its Debye temperature.

For neutron scattering from a crystal with more than one atom per unit cell, the partial differential cross section for the one phonon process [26] is given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{4\pi^2\hbar}{v} \left[N_j(\vec{q}) + \frac{1}{2} \pm \frac{1}{2} \right] \frac{k'}{k} g_j^2(\vec{q}, \vec{G}) \times \\ \delta(\vec{Q} - \vec{G} \mp \vec{q}) \delta(E - E' \mp \hbar\omega_j), \quad (3.4)$$

where v is the volume per primitive unit cell and the Bose-Einstein factor is defined as

$$N_j(\vec{q}) = \left[\exp(\hbar\omega_j(\vec{q})/k_B T) - 1 \right]^{-1}. \quad (3.5)$$

In Eq. (3.4) the upper signs are used for phonon creation and the lower signs for phonon annihilation. The delta functions express the conservation conditions of Eqs. (3.3). The quantity

$$S_j^2(\vec{q}, \vec{G}) = \left| \sum_{\kappa} \frac{b_{\kappa} \vec{Q} \cdot \vec{\xi}(\kappa | \vec{q})}{[m_{\kappa} \omega_j(\vec{q})]^{1/2}} \exp(-W_{\kappa}) \exp i[\vec{Q} \cdot \vec{r}(\kappa)] \right|^2 \quad (3.6)$$

is defined as the structure factor for inelastic scattering. Here b_{κ} is the bound scattering length, m_{κ} the mass, and $\exp(-W_{\kappa})$ the Debye-Waller factor for the κ th atom.

The structure factor can be useful in planning a neutron scattering experiment, by indicating in which zones in the reciprocal lattice one might find strong neutron groups for a particular phonon. Unfortunately, however, the structure factor is difficult to calculate accurately without considerable prior knowledge of the dynamics of the solid under question. As an example of this difficulty, Woods, Cochran, and Brockhouse [16] found substantial differences for the structure factors of NaI when calculated from two different models, the point ion model and the shell model.

Sample

The ^7LiD crystal used in this experiment was cylindrical in shape, $3 \frac{1}{4}$ inches long $\times$ 1 inch in diameter. The sample was grown by E. E. Thrasher of LASL, using techniques developed by F. E. Pretzel, et al. [27]. Because LiD reacts with atmospheric gases, the sample was removed from the growing chamber in a dry box containing an argon atmosphere. While in the dry box the sample was prepared for the present experiment by placing it in a thin-walled aluminum can and then sealing the can to maintain the crystal under argon.

Neutron diffraction showed the sample to be very nearly single

crystal, but having a rather large mosaic spread. The rocking curves of the four $\{111\}$ planes investigated had full widths at half maximum averaging about 0.8° . Two of the four rocking curves showed two resolvable, misoriented regions separated by about 0.3° . Nevertheless, the sample was considered to be adequate for this experiment. As a final preparation, the $(01\bar{1})$ plane of the crystal was aligned in the plane of the experiment by neutron diffraction.

Apparatus

The experiments were carried out using the West Port triple axis neutron diffraction spectrometer located at the Omega West Reactor of the Los Alamos Scientific Laboratory. The West Port spectrometer, depicted schematically in Fig. 3, is a fixed incident energy instrument. Neutrons which Bragg scatter from the monochromator crystal thus have their energy E and wave vector $\vec{k}$ predetermined. This monoenergetic beam of neutrons is then made incident upon the sample crystal, and those neutrons which scatter inelastically from the sample are analyzed in energy and wave vector by Bragg scattering from the analyzer crystal. A neutron group will be detected when the conservation conditions expressed by Eqs. (3.3) are satisfied.

For the reactor at an operating power of five megawatts, the thermal neutron flux at the monochromator position was $1.2 \times 10^9/\text{cm}^2 \cdot \text{sec}$. The Bragg scattering angle 2θ of the monochromator was fixed at 37.8° . The incident neutron collimator consisted of Soller [28] slits and had an angular divergence of 0.60° full width at half maximum.

Because of the wide energy spread in the dispersion curves of

Figure 3. Schematic diagram of the triple axis spectrometer.

^7LiD , a total of three different incident neutron energies was used. These were obtained by using the (200), (220), and (311) planes of aluminum as monochromators. The respective incident neutron wavelengths and wave vectors were:

$$\begin{aligned}\text{Al (200): } \lambda &= 1.3076 \pm .0003 \text{ \AA} \\ |\vec{k}| &= 4.8052 \pm .0012 \text{ \AA}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Al (220): } \lambda &= 0.92655 \pm .00007 \text{ \AA} \\ |\vec{k}| &= 6.7813 \pm .0005 \text{ \AA}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Al (311): } \lambda &= 0.7900 \pm .0003 \text{ \AA} \\ |\vec{k}| &= 7.953 \pm .003 \text{ \AA}^{-1} .\end{aligned}$$

The values of the wavelengths were determined by least-squares fitting to powder diffraction patterns from NbO [29], for which the lattice space is accurately known.

The scattered neutron collimator also consisted of Soller slits and had an angular divergence of 0.90° full width at half maximum. The (111) planes of aluminum were used exclusively as an analyzer. The neutron detector consisted of a $^{10}\text{BF}_3$ proportional counter, Reuter-Stokes Model RSN-108S. In order to reduce the thermal and fast neutron background, extensive shielding surrounded the monochromator, analyzer, and detector.

Experimental Method

In the experiment the constant $\vec{Q}$ method [1] was used throughout. In this method the wave vector transfer vector $\vec{Q}$ is preselected

in magnitude and direction to correspond to a particular position in the reciprocal lattice, and the frequency is scanned over a pre-selected range. A phonon of wave vector $\vec{Q}$ is indicated by the detection of a neutron group centered at the phonon frequency. Because of the periodicity of the dispersion relation, the phonon wave vector can always be referred to the first Brillouin zone by subtracting the appropriate reciprocal lattice vector $\vec{G}$ from $\vec{Q}$ to yield the first-zone wave vector $\vec{q}$. For example, Fig. 4 shows a typical inelastic scattering process in the $(01\bar{1})$ plane of the reciprocal lattice. The vector construction can be seen to satisfy the wave vector conservation condition of Eq. (3.3a). The wave vector $\vec{q}$ of the phonon has been referred to the (044) zone and is propagating in the $[100]$ direction.

In the constant $\vec{Q}$ method it is required that the analyzer Bragg angle A, the scattering angle B, and the crystal orientation angle C all be varied as the frequency is scanned. The instrumentation of the West Port spectrometer allows these angles to be set automatically to precomputed values read from punched paper tape. The input program tapes were prepared for the constant $\vec{Q}$ mode using the Los Alamos MANIAC II digital computer. Angle A could be set to the nearest 0.001° , and angles B and C to the nearest 0.01° . The output data were recorded on an automatic electric typewriter. For a given neutron group, the number of counts versus the frequency were hand plotted, and from such a plot the frequency of the centroid was determined. A typical neutron group for ^7LiD corresponding to a transverse acoustic phonon propagating in the $[100]$ direction is shown in Fig. 5.

Figure 4. The $(01\bar{1})$ plane of the reciprocal lattice showing a typical inelastic scattering process.

Figure 5. A neutron group corresponding to a transverse acoustic phonon propagating in the [100] direction.

The dispersion curves of ^7LiD were measured at room temperature for phonons propagating along the three high symmetry directions of the crystal, the $[100]$, $[011]$, and $[111]$ directions. These symmetry directions in the NaCl (FCC) reciprocal lattice are labeled according to the group theoretical notation of Bouckaert, Smoluchowski, and Wigner [30] as Δ , Σ , and Λ , respectively.

By restricting consideration of the dispersion relation to the Δ , Σ , and Λ symmetry directions, the experimental procedures and theoretical interpretations can be greatly simplified. The symmetry of the NaCl structure requires that the polarization of phonons propagating in these directions be either longitudinal or transverse. The theoretical implication of this, as will be shown in the Appendix, is that the 6×6 dynamical matrix block diagonalizes into three 2×2 matrices. Each of the 2×2 blocks has two eigenvalues corresponding to acoustic and optical branches, respectively. For each direction, two of the three blocks correspond to pure transverse motion and the other block to pure longitudinal motion. Along the Δ and Λ directions the transverse vibrations are degenerate, but along Σ they are non-degenerate. By choosing the $(01\bar{1})$ mirror plane of the reciprocal lattice as the experimental plane, all vibrations except the transverse branches in the Σ direction whose polarizations are normal to this plane can be excited.

Performing the experiments along symmetry directions also greatly aids in the identification of the polarizations of the branches. The factor $\vec{Q} \cdot \vec{\xi}(\kappa | \frac{\vec{q}}{j})$ in the expression for the coherent one-phonon cross section makes this identification possible. In

most cases $\vec{Q}$ can be chosen to be nearly parallel to one of the polarization vectors and nearly perpendicular to the other two. Thus, scattering will be strongest in the former case. For example, when the polarization vector for the longitudinal mode is perpendicular to $\vec{Q}$ only the transverse mode, whose polarization is then parallel to $\vec{Q}$, will be excited. This approach can be visualized in a particular case by referring to Fig. 4. The phonon of wave vector $\vec{Q}$ is propagating in the [100] direction. Therefore, the transverse polarization vector lies in the [011] direction and the longitudinal polarization vector in the [100] direction. Because $\vec{Q}$ and $\vec{\xi}_T$ are nearly parallel for this case, one would expect the transverse mode to be the one predominately excited. By arranging the experimental conditions in this fashion, the polarizations of the branches can usually be identified unambiguously.

The structure factors for ^7LiD were not calculated in the present work. Rather, the published structure factors for NaI [16] based on a shell model calculation were used as a guide in choosing zones in the reciprocal lattice in which to make phonon scans. Care was taken in using these results, however, since the coherent scattering amplitude for ^7Li is negative. This has the effect of interchanging the two sets of curves given for NaI.

IV. RESULTS

Experimental Results

The observed normal mode frequencies and wave vectors for phonons propagating in the Δ , Σ , and Λ directions in ^7LiD are listed in Tables 1-3. The wave vector is expressed in terms of the dimensionless quantity ζ known as the reduced wave vector and defined by

Δ direction

$$\vec{q} = \frac{2\pi}{a_0} (\zeta, 0, 0) \quad 0 \leq \zeta \leq 1 \quad (4.1)$$

Σ direction

$$\vec{q} = \frac{2\pi}{a_0} (0, \zeta, \zeta) \quad 0 \leq \zeta \leq 1 \quad (4.2)$$

Λ direction

$$\vec{q} = \frac{2\pi}{a_0} (\zeta, \zeta, \zeta) \quad 0 \leq \zeta \leq 0.5 \quad (4.3)$$

where $a_0 = 4.0693 \text{ \AA}$ is the cubic lattice constant of ^7LiD . In Tables 1-3, each branch is labeled by the irreducible representation to which it belongs (see Appendix). In addition, the branches are designated as transverse acoustic (TA) or optical (TO) and longitudinal acoustic (LA) or optical (LO).

The dispersion curve data are plotted for the three directions in Figs. 6-9. Transverse branches are represented by closed circles and longitudinal branches by open circles. The curves drawn on the figures correspond to theoretical fits obtained from various force

TABLE 1. - Phonon frequencies for propagation in the Δ direction of ^7LiD at 300°K (units 10^{13} rad/sec).

ζ	$\Delta_5(\text{TA})$	$\Delta_1(\text{LA})$	$\Delta_5(\text{TO})$	$\Delta_1(\text{LO})$
0			8.60	
0.1			8.62	
0.2			8.79	
0.3	2.95		9.15	
0.4	3.75	5.03	9.48	
0.5	4.38	5.82	9.87	
0.6	4.84	6.52	10.20	
0.7	5.09	6.99	10.57	
0.8	5.25	7.29	10.92	
0.9	5.31		11.05	
1.0		7.50	11.04	

TABLE 2. - Phonon frequencies for propagation in the Σ direction of ^7LiD at 300°K (units 10^{13} rad/sec).

ζ	$\Sigma_4(\text{TA}_1)$	$\Sigma_3(\text{TA}_2)$	$\Sigma_1(\text{LA})$	$\Sigma_4(\text{TO}_1)$	$\Sigma_3(\text{TO}_2)$	$\Sigma_1(\text{LO})$
0					8.60	
0.1					8.80	
0.2					9.20	
0.3		4.10	5.76		9.60	
0.4		5.08	7.06		10.20	
0.5		5.90	7.59		10.60	
0.6		6.60				
0.7						12.10
0.8			6.80			11.40
0.9			5.90			11.20
1.0		7.50				11.04

TABLE 3. - Phonon frequencies for propagation in the Λ direction of ^7LiD at 300°K (units 10^{13} rad/sec).

ζ	$\Lambda_3(\text{TA})$	$\Lambda_1(\text{LA})$	$\Lambda_3(\text{TO})$	$\Lambda_1(\text{LO})$
0			8.60	
0.05			8.65	
0.10			8.60	
0.15			8.85	
0.20		5.40	9.20	
0.25	3.39	6.58	9.40	
0.30	3.80	7.50	9.60	
0.35	4.40	9.10	9.79	
0.40	4.80	10.00	10.00	
0.45	5.00	10.50	10.29	
0.50	5.20	10.60	10.49

Figure 6. Phonon dispersion curves of ${}^7\text{LiD}$ at 300°K , compared to calculated curves based on Model I.

Figure 7. Phonon dispersion curves of ${}^7\text{LiD}$ at 300°K , compared to calculated curves based on Model II.

Figure 8. Phonon dispersion curves of ${}^7\text{LiD}$ at 300°K , compared to calculated curves based on Model III.

Figure 9. Phonon dispersion curves of ${}^7\text{LiD}$ at 300°K , compared to calculated curves based on Model IV.

models, and these will be discussed in detail later in this section.

The quality of the observed neutron groups depended strongly upon the particular branch of the dispersion relation under investigation. In general, the transverse phonons were more intense and better focused than the longitudinal ones, and are thus considered to be more accurate. The data for the Δ_5 transverse acoustic and optical branches were particularly strong and well defined compared with the data from the other branches. In some cases, however, the neutron groups were found to be asymmetric and of low intensity, having maxima which were only about twice background. The poor quality of the sample is undoubtedly responsible for much of the difficulty in these cases.

Uncertainties in the measured frequencies arise for several reasons. First, there is the difficulty in determining the center of a neutron peak in cases where the peak is poorly defined because of excessive width, lack of symmetry, or high background. It is estimated that the uncertainty from this source for any given frequency determination is no greater than 2-3 percent.

Other uncertainties arise from statistical fluctuations which affect the reproducibility of the data. These random errors are again estimated to be within the range 2-3 percent. This value of the error was obtained by scanning the same phonon several times and noting the deviations in the observed frequencies. The errors from these two sources can be combined to give an estimated random error of 3-4 percent.

In addition to the random errors, there may exist possible non-

random systematic errors. These are more difficult to estimate, but it is doubtful that they exceed 1-2 percent. Thus, the overall error in a given data point is estimated to be no greater than 3-5 percent.

No attempts were made to observe the Σ_4 transverse branches. These vibrations cannot be excited in the (011) plane, and no effort was made at reorienting the sample so that they could be observed.

The longitudinal optical branches in the Δ and Λ directions also went totally unobserved, but not for the same reasons. Numerous scans were made in various regions of the reciprocal lattice, with various incident energies, and over long (~48 hr) counting periods. All attempts to observe these branches so far have failed.

The (LO) frequency at the point Γ has, however, been determined from the Lyddane-Sachs-Teller (LST) relation [31]. This relation relates the (LO) and (TO) frequencies at Γ to the static and high frequency dielectric constants of the material. The expression is

$$\left(\frac{\omega_{LO}}{\omega_{TO}}\right)_{\Gamma} = \left(\frac{\epsilon_0}{\epsilon_{\infty}}\right)^{1/2}. \quad (4.4)$$

The value of the static dielectric constant $\epsilon_0 = 12.0$ was taken from Reference 27, and the high frequency dielectric constant was obtained from the measured value of the refractive index extrapolated to infinite wavelength [32], $\epsilon_{\infty} = (n_{\infty})^2 = (1.90)^2 = 3.61$. Using these values, together with the measured $\vec{q} = 0$ (TO) frequency from the present neutron experiment, the LST relation gives $(\omega_{LO})_{\Gamma} = 15.7 \times 10^{13}$ rad/sec. This value is plotted in Figs. 6-9 as an open square at the point Γ .

The (TO) reststrahlen frequency for ^7LiD has been determined

by Montgomery and Hardy [33] using infrared absorption techniques. The value they obtain is $(\omega_{TO})_{\Gamma} = 8.39 \times 10^{13}$ rad/sec, and this is shown plotted in Figs. 6-9 as a closed square at the point Γ . From the present neutron measurements the reststrahlen frequency is found to be $(\omega_{TO})_{\Gamma} = 8.60 \times 10^{13}$ rad/sec, and this is in good agreement with the infrared results.

Models

The models used in fitting the dispersion curves of ${}^7\text{LiD}$ have included two versions of the point ion model and two versions of the shell model. In all cases the short-ranged forces were assumed to extend no farther than second nearest neighbors. As is shown in the Appendix, two parameters occur in the symmetry reduced force constant matrices for first neighbors and three parameters for second neighbors. Thus, for general tensor forces, eight constants are required to specify these interactions: Two parameters for the Li-D interactions, three for the Li-Li interactions, and three for D-D interactions.

In applying the shell model, the short-ranged forces have been assumed to act entirely through the shells. This seems a particularly good assumption for LiH and LiD, since in these cases, the cores are composed of bare nuclei and the shells contain only two electrons. The nuclear wavefunctions obviously do not overlap, so that the core-core interactions are negligible; additionally, the nuclear-electronic overlaps of different ions are probably very small compared to the electronic overlaps.

The shell model has as additional parameters the isotropic force constants, k_1 and k_2 , linking the shell and core of a particular ion, and the shell charges of the ions, Y_1 and Y_2 . Also included as a parameter is the ionic charge Z , which is assumed equal in magnitude for both ions but of opposite sign. The shell model so far described involves a total of 13 parameters.

Because of their greater physical significance, it is more convenient to use as parameters the electrical and mechanical polarizabilities of the ions, α_+ , α_- , and d_+ , d_- , rather than the shell-core force constants and the shell charges. These can be defined in terms of the original quantities as

$$\alpha_+ = \frac{Y_1^2}{k_1 + (T_{11})_0}, \quad \alpha_- = \frac{Y_2^2}{k_2 + (T_{22})_0} \quad (4.5)$$

and

$$d_+ = \frac{-(T_{11})_0 Y_1}{k_1 + (T_{11})_0}, \quad d_- = \frac{-(T_{22})_0 Y_2}{k_2 + (T_{22})_0}, \quad (4.6)$$

where $(T_{\mu\mu})_0$ represents the value of the matrix element $T_{\alpha\alpha}(\mu\mu)$ at $\vec{q} = 0$.

Finally, it is assumed that the short-ranged interactions can be adequately described by axially-symmetric forces [34]. In this approach the short-ranged interionic potential V is assumed to depend only on the magnitude of the distance $\vec{r}$ between particles. When this potential is expanded for small displacements, it is possible

to specify the interaction between two particles in terms of two constants; one corresponds to a bond-bending constant describing the force along the line perpendicular to $\vec{r}$, and the other to a bond-stretching constant describing the force parallel to $\vec{r}$. For first nearest neighbors these constants are given by

$$\left(\frac{\partial^2 V_{12}}{\partial r^2}\right)_{\parallel} = \frac{e^2}{2v} A, \quad \left(\frac{\partial^2 V_{12}}{\partial r^2}\right)_{\perp} = \frac{e^2}{2v} B, \quad (4.7)$$

where e is the electronic charge and v is the volume of the primitive unit cell. For second nearest neighbors, four constants are involved.

For positive ions

$$\left(\frac{\partial^2 V_{11}}{\partial r^2}\right)_{\parallel} = \frac{e^2}{2v} A', \quad \left(\frac{\partial^2 V_{11}}{\partial r^2}\right)_{\perp} = \frac{e^2}{2v} B', \quad (4.8)$$

and for negative ions

$$\left(\frac{\partial^2 V_{22}}{\partial r^2}\right)_{\parallel} = \frac{e^2}{2v} A'', \quad \left(\frac{\partial^2 V_{22}}{\partial r^2}\right)_{\perp} = \frac{e^2}{2v} B''. \quad (4.9)$$

The number of parameters in the theory is now eleven: six short-range force parameters A , B , A' , B' , A'' , B'' , two electrical polarizabilities α_+ , α_- , two mechanical polarizabilities d_+ , d_- , and the ionic charge Z .

The four models which have been used are described as follows:

Model I - A four parameter point ion model assuming interactions between first neighbors and second neighbor negative

ions. The ionic charge is fixed at unity.

Model II - A seven parameter point ion model assuming interactions between first neighbors and second neighbor positive and negative ions. The ionic charge is allowed to vary.

Model III - A three parameter shell model allowing for bond-stretching forces between nearest neighbors. The negative ion is assumed polarizable, but the ionic charge is fixed at unity. Parameter B was fixed at the value determined from the equilibrium condition for ionic crystals [16].

Model IV - A seven parameter shell model allowing for first neighbor interactions and second neighbor negative interactions. The negative ion is polarizable and the ionic charge is varied.

Calculation of Theoretical Dispersion Curves

Based on the models described above, theoretical dispersion curves have been calculated and compared to the experimental data using non-linear least-squares fitting procedures. The least-squares computer code used in this work consisted of a modified version of the code described by Davidon [35]. Modifications to this original code were made by Dr. John L. Warren of LASL to permit the calculation of dispersion curves and to allow for compatibility with the LASL computers. The shell model subroutines were written by the author, using as a guide an existing shell model code obtained from Chalk River Nuclear Laboratories, Chalk River, Canada. All numerical computations were

made using the LASL CDC-6600 computer. Figures 6-9 show the comparison between the experimental data and the fitted dispersion curves based on the models previously described.

Among other investigators it has been customary to fix certain of the model parameters so as to give agreement with particular measured physical properties, such as the elastic constants and dielectric constants. In the present work this approach was not taken. Instead, a knowledge of the elastic constants C_{11} and C_{44} was used to determine small $\vec{q}$ values of the frequency for the Δ_5 , Δ_1 , and Σ_3 acoustic branches, and the dielectric constants were used to determine the (LO) frequency at Γ . These frequencies were then included as data points in the fitting. A consistent value for C_{12} is not yet available, and so was not used in the input.

In the fitting procedure the individual data points were weighted assuming a constant percentage error in frequency. The calculation then provides an estimate of this percentage error, assuming that the correct functions are being used in the fitting. The goodness of fit for a particular model is indicated by the value of this fitting error; thus, a good fit is obtained when the fitting error approaches the estimated error in the data. The values of the individual parameters obtained from fitting the various models are listed together with the corresponding fitting errors in Table 4.

From the parameters obtained from fitting, the values of certain physical quantities have been deduced. The derived quantities include the three elastic constants of the solid C_{11} , C_{12} , and C_{44} , the shell charges Y_1 and Y_2 , the shell-core force constants k_1 and k_2 ,

TABLE 4. - Model parameters. Parameters not followed by an error were held fixed during the fitting procedure at the values indicated.

Model	A ($e^2/2v$)	B ($e^2/2v$)	A' ($e^2/2v$)	B' ($e^2/2v$)
I	8.013±0.014	-1.362±0.007	0	0
II	2.286±0.032	0.126±0.010	0.881±0.017	-0.141±0.005
III	7.941±0.006	-1.165	0	0
IV	6.146±0.068	-0.748±0.017	0	0
Model	A'' ($e^2/2v$)	B'' ($e^2/2v$)	Z (e)	α_+ (10^{-24} cm^3)
I	-1.518±0.016	0.506±0.006	1.0	0
II	0.082±0.016	0.158±0.006	0.516±0.004	0
III	0	0	1.0	0
IV	-0.400±0.028	0.253±0.009	0.878±0.005	0
Model	d_+ (e)	α_- (10^{-24} cm^3)	d_- (e)	Fitting Error (percent)
I	0	0	0	21.3
II	0	0	0	5.7
III	0	0.1502±0.0006	0.6341±0.0016	8.8
IV	0	0.092±0.002	0.362±0.006	4.0

and the high frequency dielectric constant ϵ_{∞} . Table 5 lists the calculated values obtained from each model, together with the experimental values where known. The experimental values of C_{11} and C_{44} were determined by Dr. S. P. Marsh of LASL, and these are quoted from his unpublished work.

The dispersion curves of ^7LiH have been calculated under the assumption that the model parameters are the same as for ^7LiD . The results of the calculation based on Model IV are given in Fig. 10. The closed square plotted at Γ gives the reststrahlen frequency as determined by Montgomery and Hardy [33], and the open square gives $(\omega_{\text{LO}})_{\Gamma}$ as determined from the LST relation.

TABLE 5. - Calculated and observed properties of ${}^7\text{LiD}$.

	c_{11}	c_{12}	c_{44}	γ_1	γ_2	k_1	k_2	ϵ_∞
	$(10^{11} \text{ dynes/cm}^2)$			(e)		$(e^2/2v)$		
Model I	6.36	-1.47	4.02	0	0	∞	∞	1
Model II	6.41	1.25	4.42	0	0	∞	∞	1
Model III	9.52	4.68	4.68	0	-1.33	∞	6.15	6.09
Model IV	6.93	0.304	4.71	0	-1.19	∞	10.59	2.89
Experiment	6.26		4.19					3.61

Figure 10. Phonon dispersion curves of ${}^7\text{LiH}$ calculated using the parameter values of Model IV for ${}^7\text{LiD}$.

V. DISCUSSION OF RESULTS

Of the four models compared to the data, Model IV, the seven parameter shell model, gives the best fit, as indicated by a fitting error of 4.0%. This value of the fitting error agrees well with the 3-4% estimated random error in the data. In addition, the values of the parameters obtained from this model seem to be physically reasonable. For instance, the short-ranged bond-stretching force constant for second neighbor negative ions is about 7 % of the first neighbor forces. Considering the larger ionic radius of the negative ion, it is perhaps reasonable to expect that the positive ion overlaps can be neglected in comparison with the negative overlaps. It, furthermore, seems reasonable to neglect the positive ion polarizabilities, since it is well established for the alkali halides that the negative ion is generally the one more easily polarizable.

The value of the ionic charge obtained from the best fit model can be interpreted as giving the degree of ionicity in the ${}^7\text{Li-D}$ bond. Calder et al. [6] have estimated from their x-ray measurements that the bonding in LiH is between 80 and 100 percent ionic. From electronegativity considerations, Pretzel et al. [27] estimate the bond in LiH to be 12.5% covalent, and thus 87.5% ionic. The ionic charge from Model IV indicates an 87.8% ionic bond, and this is in excellent agreement with the above estimates.

Model II, the seven parameter point ion model, also fits

amazingly well. The same success in the use of this model for potassium iodide has been reported by Dolling et al. [36]. It is curious to note that the value of the ionic charge obtained from Model II, $Z_e = 0.516e$, is in excellent agreement with the Szigeti effective charge, $Z^*e = 0.52e$, reported for LiH by Filler and Burstein [37]. Using the expression for the effective charge given by Woods et al. [16],

$$Z^*e = (Z - d)e, \quad (5.1)$$

together with the "real" ionic charge obtained from Model IV, one finds $Z^*e = 0.516e$. This is again in good agreement with the Szigeti effective charge. Presumably the notion of effective charge can be used to account for the effects of polarization, in much the same way that the effective electron mass is used in band theory to account for unknown ionic potentials.

It has been pointed out by Calder et al. [6] that when large electronic overlaps exist in an ionic crystal, it may be impossible to assign a unique ionic charge to each of the ions. In such cases, the electronic charge density is distributed continuously throughout the unit cell, and under these conditions, it may also be difficult to define a unique ionic radius for each ion. For LiH, in fact, they find that the electronic charge density is never less than about $0.04 e \text{ \AA}^{-3}$ along the line joining nearest neighbors.

In view of these considerations, the success of Model II for ⁷LiD may be understood in the following way: The model seems to suggest that some of the electronic charge generally associated with

the negative ion is now to be associated with the positive ion. This results in a smaller effective charge for both ions, leads to an increase in the effective radius of the positive ion over its free ion radius, and allows for the possibility of positive ion overlap.

Model II, because of its neglect of ionic polarizabilities, is still physically less sophisticated than Model IV; nevertheless, Model II does give a relatively good fit to the data and can perhaps be considered as an alternative to the shell model description.

As expected, Model I seems to give large deviations for the (LO) branches. Obviously this simple point ion model is totally inadequate for these branches, although the fit to the other branches is fair. Contrary to what has been found for other alkali halides, Model III, the simple shell model, gives relatively poor agreement with the data. This perhaps indicates that for ^7LiD , the second neighbor negative ion overlaps are quite important.

In addition to the models described, attempts were made to fit an eleven parameter shell model to the data. This model considers short-ranged interactions between nearest neighbors, between second neighbor negative ions, and between second neighbor positive ions; both positive and negative ions are assumed polarizable; and the ionic charge is allowed to vary. Using this model, no improvement was found over the fit for Model IV. In fact, several fits were obtained from different sets of values of the model parameters, and all of these fits were about equally good. Probably the data are not sufficiently complete or accurate to allow the fitting code to uniquely determine the eleven parameters for this model.

The calculated dispersion curves of ${}^7\text{LiH}$, as shown in Fig. 10, reveal two interesting features. First, the acoustic branches are quite similar to those for ${}^7\text{LiD}$. The optical modes, however, are much higher in ${}^7\text{LiH}$. Secondly, a small forbidden band exists between the acoustic and optical branches for the three symmetry directions shown.

The calculated physical properties of ${}^7\text{LiD}$, as listed in Table 5, are less satisfactory than the calculated dispersion curves. The worse agreement is obtained in Model I, in which a negative value for C_{12} is calculated. Moreover, the elastic and dielectric constant agreement, in general, is only fair.

To conclude, the models given here should be considered as only approximations to the real system. The models are able to yield the gross features of the dynamics of the solid; however, some of the finer details seem to be lacking, as evidenced by the fact that the models are unable to give accurate values for the physical properties of the crystal. Undoubtedly, better agreement would require a more sophisticated theory. Considering the simplicity of the lithium hydride system, it is hoped that the experimental results given here will stimulate interest in a first principles calculation of the lattice dynamics for this solid.

SUMMARY

In an attempt to understand the lattice dynamics of the LiH-LiD systems, phonon dispersion curves have been measured along the three high symmetry directions in a single crystal of ^7LiD , using the techniques of coherent inelastic scattering of thermal neutrons. It has been estimated that the overall errors in the data do not exceed 5 percent. The value of the reststrahlen frequency as determined from the neutron data was found to be consistent with the value obtained from infrared measurements. Difficulties have been encountered in determining the (LO) branches in all directions. As has been pointed out by Woods et al. [17], this difficulty may be due to interaction between the (LO) vibrations and other modes. Such an interaction could possibly arise by virtue of the large electric field associated with the (LO) vibrations.

The data have been least-squares fitted to several versions of the point ion and shell models of lattice dynamics. A seven parameter shell model, which considers first neighbor and second neighbor negative ion short-range interactions, allows for the negative ion to be polarizable, and uses a variable ionic charge, gives the best fit. Based on this model, the dispersion curves of ^7LiH have been calculated. Again, good agreement is obtained with the infrared measurements. To simplify the application of the various models and to aid in classifying the dispersion curve branches, group theory has been applied to the

problem of lattice vibrations in the sodium chloride structure.

Although the models can accurately reproduce the dispersion curves, the values of physical properties of the crystal calculated from the models, when compared to experimental measurements, are somewhat disappointing. The models should, therefore, be considered as only approximations to the real system. Hopefully the results given here will, in some small measure, aid in future attempts to calculate the lattice dynamics of the alkali halides from first principles.

APPENDIX

GROUP THEORY AND LATTICE VIBRATIONS OF THE SODIUM CHLORIDE STRUCTURE

The symmetries possessed by crystalline lattices can be utilized through the powerful techniques of group theory to greatly simplify problems in lattice dynamics. In particular, group theory allows for the following: (1) reduction of the force constant matrices, (2) reduction of the dynamical matrix, (3) block diagonalization of the dynamical matrix, (4) determination of degeneracies, (5) determination of basis vectors of the irreducible representations, (6) labeling of dispersion curves according to their irreducible representations, and (7) use of compatibility to determine the connectivity of dispersion curve branches at symmetry points. In this appendix, group theory is applied to the sodium chloride structure to achieve these results.

General Considerations

The full symmetry of a lattice is specified by the space group operations which take the lattice into itself. In the Seitz notation [38] these operations are represented as $\{R|\vec{t}\}$, where R can be a proper or improper rotation and where $\vec{t}$ for symmorphic groups¹ involves only primitive translations. The set of operations $\{R\}$ defines the

¹The results given here are specialized to symmorphic groups. They may or may not apply directly to non-symmorphic groups.

point group of the lattice, and each such operation R_i can be represented by a 3×3 real orthogonal rotational matrix R_i of the form

$$R_i = \begin{bmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{bmatrix}. \quad (A.1)$$

The effect of a space group operator A_i^m on the equilibrium position vector of an atom is given by

$$A_i^m \vec{r}(\kappa) = \{R_i | \vec{t}_m\} \vec{r}(\kappa) = R_i \vec{r}(\kappa) + \vec{t}_m = \vec{r}(\kappa^{L+m}). \quad (A.2)$$

Thus, the operator A_i^m turns the lattice site (κ) into the equivalent site (κ^{L+m}) . Such an operation will be denoted by

$$A_i^m [\kappa] = [\kappa^{L+m}]. \quad (A.3)$$

It is frequently only necessary to consider elements of the space group which involve no translation. In this case, Eq. (A.2) becomes

$$A_i \vec{r}(\kappa) = \{R_i | 0\} \vec{r}(\kappa) = R_i \vec{r}(\kappa) = \vec{r}(\kappa^L), \quad (A.4)$$

where now this operation is denoted by

$$R_i [\kappa] = A_i [\kappa] = [\kappa^L]. \quad (A.5)$$

An important group which will be found useful in applying symmetry to the dynamical matrix can be formed from the operators which

leave invariant a vector $\vec{q}$ in wave vector space. This group $G(\vec{q})$ is called the point group of the wave vector and is a subgroup of the entire point group of the lattice. The elements R_1 of $G(\vec{q})$ have the property

$$R_1 \vec{q} = \vec{q} + \vec{G} . \quad (\text{A.6})$$

The reciprocal lattice vector $\vec{G}$ vanishes for $\vec{q}$ inside the first Brillouin zone, but if $\vec{q}$ lies on the zone boundary, $\vec{G}$ can then be non-zero.

Symmetry of Sodium Chloride

The sodium chloride (NaCl) structure consists of two interpenetrating face-centered cubic (FCC) sublattices, with sodium atoms on one sublattice and chlorine atoms on the other. The coordinate system of the FCC Bravais lattice is selected such that the position of an arbitrary "zeroth" atom defines the origin of the zeroth unit cell and the origin of the lattice coordinate system. This zeroth atom is chosen to be a Na ($\mu=1$) atom and is specified by the indices $(\frac{\mu}{1}) = (\{0, 0, 0\})$. The primitive unit cell, shown in Fig. A.1 is defined by the fundamental translation vectors

$$\vec{a}_1 = r_o(\vec{j} + \vec{k}) \quad (\text{A.7a})$$

$$\vec{a}_2 = r_o(\vec{i} + \vec{k}) \quad (\text{A.7b})$$

$$\vec{a}_3 = r_o(\vec{i} + \vec{j}) \quad (\text{A.7c})$$

and has a volume $v = 2r_o^3$. Here r_o is the distance between nearest

Figure A.1. Primitive unit cell for the sodium chloride crystal structure.

neighbors, and $\vec{i}$, $\vec{j}$, and $\vec{k}$ are unit vectors in Cartesian coordinates. The second atom in the unit cell is a Cl ($\kappa=2$) atom, and its position with respect to the cell origin is given by

$$\vec{r}(\kappa=2) = r_0(\vec{i} + \vec{j} + \vec{k}). \quad (\text{A.8})$$

A general vector of the real lattice in Cartesian coordinates is thus

$$\vec{r}(\kappa) = r_0[(l_2 + l_3)\vec{i} + (l_3 + l_1)\vec{j} + (l_1 + l_2)\vec{k}] + \vec{r}(\kappa), \quad (\text{A.9})$$

where l_1 , l_2 , and l_3 are integers.

The zeroth atom has as first nearest neighbors six Cl atoms. Each of these neighbors is labeled by an atom index which runs from 1 to 6. The 12 second nearest neighbors of the zeroth atom are Na atoms and are denoted by an atom index running from 7 through 18. For future reference, the positions of these first and second nearest neighbors are given in Table A.1. Also given are the space group operations which will take atom 1 into atoms 2-6 and atom 7 into atoms 8-18. The rotational matrices corresponding to each of the point group elements are listed in Table A.2 below.

Using the defining equations for the reciprocal lattice

$$\vec{a}_\alpha \cdot \vec{b}_\beta = 2\pi \delta_{\alpha,\beta} \quad \alpha, \beta = 1, 2, 3 \quad (\text{A.10})$$

$$\vec{b}_\alpha = \frac{2\pi (\vec{a}_\beta \times \vec{a}_\gamma)}{\vec{a}_\alpha \cdot (\vec{a}_\beta \times \vec{a}_\gamma)} \quad (\alpha, \beta, \gamma) = \begin{pmatrix} (1, 2, 3) \\ (2, 3, 1) \\ (3, 1, 2) \end{pmatrix} \quad (\text{A.11})$$

TABLE A.1 - Nearest neighbors to zeroth atom: $\ell = 0$, $\kappa = 1$.

Atom Index	Cell Indices				$\vec{r}(\ell'_i) - \vec{r}(\ell^0_1)$ (in units of r_0)	Space Group Element
	ℓ'_1	ℓ'_2	ℓ'_3	κ'		
First nearest neighbors						
1	-1	0	0	2	(1, 0, 0)	$\{R_1 0\}$
2	0	-1	0	2	(0, 1, 0)	$\{R'_{18} 0\}$
3	0	-1	-1	2	(-1, 0, 0)	$\{R_4 0\}$
4	-1	0	-1	2	(0, -1, 0)	$\{R'_{17} 0\}$
5	0	0	-1	2	(0, 0, 1)	$\{R'_{15} 0\}$
6	-1	-1	0	2	(0, 0, -1)	$\{R'_{16} 0\}$
Second nearest neighbors						
7	0	0	1	1	(1, 1, 0)	$\{R_1 0\}$
8	1	-1	0	1	(-1, 1, 0)	$\{R'_{18} 0\}$
9	0	0	-1	1	(-1, -1, 0)	$\{R_4 0\}$
10	-1	1	0	1	(1, -1, 0)	$\{R'_{17} 0\}$
11	0	1	-1	1	(0, -1, 1)	$\{R'_{22} 0\}$
12	0	1	0	1	(1, 0, 1)	$\{R'_{14} 0\}$
13	1	0	0	1	(0, 1, 1)	$\{R'_{15} 0\}$
14	1	0	-1	1	(-1, 0, 1)	$\{R'_{20} 0\}$
15	-1	0	0	1	(0, -1, -1)	$\{R_7 0\}$
16	-1	1	0	1	(1, 0, -1)	$\{R'_{13} 0\}$
17	0	-1	1	1	(0, 1, -1)	$\{R'_{16} 0\}$
18	0	-1	0	1	(-1, 0, -1)	$\{R_{14} 0\}$

the primitive translation vectors of the body-centered reciprocal lattice become

$$\vec{b}_1 = \frac{\pi}{r_0} (-\vec{i} + \vec{j} + \vec{k}) \quad (\text{A.12a})$$

$$\vec{b}_2 = \frac{\pi}{r_0} (\vec{i} - \vec{j} + \vec{k}) \quad (\text{A.12b})$$

$$\vec{b}_3 = \frac{\pi}{r_0} (\vec{i} + \vec{j} - \vec{k}). \quad (\text{A.12c})$$

If h_1 , h_2 , and h_3 are integers, a general reciprocal lattice vector in Cartesian coordinates is of the form

$$\vec{G} = \frac{\pi}{r_0} [(h_2 + h_3 - h_1)\vec{i} + (h_3 + h_1 - h_2)\vec{j} + (h_1 + h_2 - h_3)\vec{k}]. \quad (\text{A.13})$$

The space group of the NaCl structure is symmorphic and is identical with that of the FCC Bravais lattice. It is denoted by $O_h^5(\text{Fm}\overline{3}\text{m})$. The point group of NaCl consists of the 48 elements of the full octahedral group O_h . The O_h group can be formed from the direct product of the full tetrahedral group T_d and the inversion group C_i , that is,

$$O_h = C_i \times T_d. \quad (\text{A.14})$$

The inversion group C_i consists of two elements, the identity and the inversion operation I . The 24 rotational matrices associated with the T_d point group elements are listed in Table A.2. The remaining elements

of O_h are obtained through multiplication of the matrices listed by the inversion matrix

$$I = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad (\text{A.15})$$

and these are denoted as R_i' . Thus, for instance, $R_1' = I$, etc.

Each element in the point group can be thought of as an operator, which when applied to an arbitrary vector $\vec{r}$, changes it into a new vector $\vec{r}'$. The coordinates of both the original and transformed vectors are expressed in the same coordinates system. To obtain this transformed vector, the rotational matrices for the group are used. For example, if an arbitrary vector is written as

$$\vec{r} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \quad (\text{A.16})$$

then multiplying $\vec{r}$ by one of the rotational matrices R_1 of the group gives the coordinates of the new vector in the original system,

$$\vec{r}' = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = R_1 \begin{bmatrix} x \\ y \\ z \end{bmatrix}. \quad (\text{A.17})$$

This operation can easily be carried out for the group O_h to aid in visualizing the physical rotation (or improper rotation) corresponding to each element.

TABLE A.2. - Rotational matrices for point group T_d .

i	R_i	i	R_i	i	R_i
1	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	9	$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}$	17	$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
2	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	10	$\begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{bmatrix}$	18	$\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
3	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	11	$\begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{bmatrix}$	19	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$
4	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	12	$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{bmatrix}$	20	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}$
5	$\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$	13	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$	21	$\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}$
6	$\begin{bmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$	14	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}$	22	$\begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix}$
7	$\begin{bmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{bmatrix}$	15	$\begin{bmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{bmatrix}$	23	$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
8	$\begin{bmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{bmatrix}$	16	$\begin{bmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{bmatrix}$	24	$\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Transformation of Force Constant Matrices

The elements of the atomic force constant matrices transform as covariant tensors of rank two [39]. Their transformation law is thus

$$K_{\alpha\beta}(\overset{L-L'}{K} \overset{K'}{K'}) = \sum_{\lambda\mu} R_{\alpha\lambda} R_{\beta\mu} K_{\lambda\mu}(\overset{\ell-\ell'}{\kappa} \overset{\kappa'}{\kappa'}) \quad \lambda, \mu = 1, 2, 3 \quad (\text{A.18})$$

or in matrix notation

$$K(\overset{L-L'}{K} \overset{K'}{K'}) = R K(\overset{\ell-\ell'}{\kappa} \overset{\kappa'}{\kappa'}) R^{-1}. \quad (\text{A.19})$$

The matrix R takes $(\overset{\ell}{\kappa})$ into $(\overset{L}{K})$ and $(\overset{\ell'}{\kappa'})$ into $(\overset{L'}{K'})$. If one considers the case where R does not change either $(\overset{\ell}{\kappa})$ or $(\overset{\ell'}{\kappa'})$, Eq. (A.19) can be used to reduce the number of independent elements in the force constant matrices. This procedure will now be demonstrated for first nearest neighbors in NaCl.

Assume the force constant matrix for interaction between atom 1 and atom 0 is of the form

$$K(1) = \begin{bmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{bmatrix}. \quad (\text{A.20})$$

The point group operations which leave $(\overset{\ell}{\kappa}) = (\{0, 0, 0\})$ and $(\overset{\ell'}{\kappa'}) = (\{-1, 0, 0\})$ invariant are $R_1, R_2, R_{19}, R_{20}, R_3^i, R_4^i, R_{13}^i, R_{14}^i$. The identity element R_1 has no effect on $K(1)$. Applying R_2 ,

$$K(1) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad (\text{A.21})$$

which gives

$$\begin{bmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{bmatrix} = \begin{bmatrix} K_{11} & -K_{12} & -K_{13} \\ -K_{21} & K_{22} & K_{23} \\ -K_{31} & K_{32} & K_{33} \end{bmatrix}. \quad (\text{A.22})$$

Comparing the original $K(1)$ element-by-element with the transformed matrix, the following conditions are obtained: $K_{12} = K_{13} = K_{21} = K_{31} = 0$. The conditions obtained from applying the other matrices are as follows:

$$R_{19} \rightarrow K_{32} = K_{23}, \quad K_{22} = K_{33}$$

$$R_{20} \rightarrow \text{no additional conditions}$$

$$R_3^i \rightarrow K_{23} = 0$$

$$R_4^i, R_{13}^i, R_{14}^i \rightarrow \text{no additional conditions.}$$

The reduced form of $K(1)$ is thus

$$K(1) = \begin{bmatrix} K_{11} & 0 & 0 \\ 0 & K_{22} & 0 \\ 0 & 0 & K_{22} \end{bmatrix} = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{bmatrix}. \quad (\text{A.23})$$

Using the space group elements of Table A.1 which take atom 1 into the other five nearest neighbors, the corresponding force constant

matrices can be generated from Eq. (A.19). These, together with the force constant matrices for second nearest neighbors, are listed in Table A.3.

Transformation of the Dynamical Matrix

The effect of a space group operation A_1^m on the dynamical matrix is given by the matrix equation [40]

$$D(R_1 \vec{q}) = S(A_1^m, \vec{q}) \cdot D(\vec{q}) \cdot S(A_1^m, \vec{q})^{-1}, \quad (A.24)$$

where the elements of the 3×3 s matrices $S(A_1^m, \vec{q})$ are

$$S_{\alpha\beta}(A_1^m, \vec{q}) = \delta_{\kappa, A_1^m[\kappa']} \exp\{iR_1 \vec{q} \cdot [\vec{r}(\kappa) - A_1^m \vec{r}(\kappa')]\} (R_1)_{\alpha\beta}. \quad (A.25)$$

Any translation which results from applying the space group operation A_1^m to $\vec{r}(\kappa')$ will obviously cancel out when Eq. (A.24) is used; therefore, in Eq. (A.25) it is sufficient to consider only the point group elements of the space group. Furthermore, since for NaCl there exists no space group operation which will change sublattices and thus change κ' into κ , the operation $A_1^m[\kappa']$ gives just $[\kappa']$. Under these conditions, $S(A_1^m, \vec{q})$ becomes

$$S_{\alpha\beta}(R_1, \vec{q}) = \delta_{\kappa, \kappa'} \exp\{iR_1 \vec{q} \cdot [\vec{r}(\kappa) - R_1 \vec{r}(\kappa')]\} (R_1)_{\alpha\beta} \quad (A.26)$$

For all points in the interior of the Brillouin zone and at the point X, the S's can be written in block form as

$$S(R_1, \vec{q}) = \begin{bmatrix} R_1 & 0 \\ 0 & R_1 \end{bmatrix}. \quad (A.27a)$$

At the point L, however, the S's become

TABLE A.3. - Interatomic force constant matrices for interaction between the zeroth atom and its first and second nearest neighbors.

atom index 1	$K(1)$	atom index 1	$K(1)$	atom index 1	$K(1)$
1	$\begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{bmatrix}$	7	$\begin{bmatrix} \gamma & \epsilon & 0 \\ \epsilon & \gamma & 0 \\ 0 & 0 & \delta \end{bmatrix}$	13	$\begin{bmatrix} \delta & 0 & 0 \\ 0 & \gamma & -\epsilon \\ 0 & -\epsilon & \gamma \end{bmatrix}$
2	$\begin{bmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{bmatrix}$	8	$\begin{bmatrix} \gamma & -\epsilon & 0 \\ -\epsilon & \gamma & 0 \\ 0 & 0 & \delta \end{bmatrix}$	14	$\begin{bmatrix} \gamma & 0 & -\epsilon \\ 0 & \delta & 0 \\ -\epsilon & 0 & \gamma \end{bmatrix}$
3	$\begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{bmatrix}$	9	$\begin{bmatrix} \gamma & \epsilon & 0 \\ \epsilon & \gamma & 0 \\ 0 & 0 & \delta \end{bmatrix}$	15	$\begin{bmatrix} \delta & 0 & 0 \\ 0 & \gamma & \epsilon \\ 0 & \epsilon & \gamma \end{bmatrix}$
4	$\begin{bmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{bmatrix}$	10	$\begin{bmatrix} \gamma & -\epsilon & 0 \\ -\epsilon & \gamma & 0 \\ 0 & 0 & \delta \end{bmatrix}$	16	$\begin{bmatrix} \gamma & 0 & \epsilon \\ 0 & \delta & 0 \\ \epsilon & 0 & \gamma \end{bmatrix}$
5	$\begin{bmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{bmatrix}$	11	$\begin{bmatrix} \delta & 0 & 0 \\ 0 & \gamma & -\epsilon \\ 0 & -\epsilon & \gamma \end{bmatrix}$	17	$\begin{bmatrix} \delta & 0 & 0 \\ 0 & \gamma & \epsilon \\ 0 & \epsilon & \gamma \end{bmatrix}$
6	$\begin{bmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{bmatrix}$	12	$\begin{bmatrix} \gamma & 0 & -\epsilon \\ 0 & \delta & 0 \\ -\epsilon & 0 & \gamma \end{bmatrix}$	18	$\begin{bmatrix} \gamma & 0 & \epsilon \\ 0 & \delta & 0 \\ \epsilon & 0 & \gamma \end{bmatrix}$

$$s(R_1, \vec{q}) = \begin{bmatrix} R_1 & 0 \\ 0 & \theta R_1 \end{bmatrix}, \quad (\text{A.27b})$$

where $\theta = +1$ for $R_1 \in C_{3v}$ and $\theta = -1$ for $R_1 \in I \times C_{3v}$.

Suppose that in applying Eq. (A.24) one considers only point group elements R_1 of a particular group of the wave vector $G(\vec{q})$. Then, since R_1 leaves $\vec{q}$ invariant, Eq. (A.24) implies that the dynamical matrix is left invariant under the transformation involving the group $G(\vec{q})$. Therefore, for a particular $\vec{q}$, the group of the wave vector is in the symmetry group of $D(\vec{q})$.

For a given group of the wave vector $G(\vec{q})$, the following properties can be established [40]:

1. S and D commute.
2. Because of property (1), the eigenvectors of S are also eigenvectors of D .
3. The set of S 's forms a reducible representation of $G(\vec{q})$.
4. Each member of the set of S 's can be block diagonalized by a unitary transformation $VSV^\dagger$ to give the direct sum of the irreducible representation of $G(\vec{q})$.
5. If V block diagonalizes S , then V also block diagonalizes D .

Decomposition of the Representation $s(R, \vec{q})$

Suppose that the reducible representation $s(R, \vec{q})$ contains the irreducible representation $\Gamma^{(\alpha)}(R)$ a total of a_α times. Then the decomposition formula of group theory [41] gives

$$a_{\alpha} = g^{-1} \sum_R \chi^{(\alpha)}(R)^* \chi_S(R), \quad (\text{A.28})$$

where g is the order of $G(\vec{q})$, $\chi^{(\alpha)}(R)$ is the character of the $\Gamma^{(\alpha)}(R)$ representation, and $\chi_S(R)$ is the character of $S(R, \vec{q})$. Hence, knowing these characters, the number of times the various irreducible representations appear in S is uniquely determined. Having found the a_{α} 's from Eq. (A.28), the reduced form of S can then be written as the direct sum,

$$S = \sum_{\alpha} a_{\alpha} \Gamma^{(\alpha)}. \quad (\text{A.29})$$

Using this relation, it is possible to obtain specific information regarding the form of the block-diagonalized dynamical matrix. If n_{α} is the dimensionality of the α th irreducible representation, then Eq. (A.29) may be interpreted in the following way:

1. A block of dimensionality a_{α} will appear a total of n_{α} times in the block-diagonalized dynamical matrix.
2. There will be $a_{\alpha} \times n_{\alpha}$ branches of the dispersion relation which belong to the $\Gamma^{(\alpha)}$ irreducible representation, and these branches will be n_{α} -fold degenerate.

For NaCl the groups of the wave vector that are of interest are those corresponding to the special symmetry points and lines of the Brillouin zone as shown in Fig. A.2. Table A.4 lists and describes each of these points and lines, and also gives the principle axes and point groups corresponding to each. Along the $[100]$, $[011]$, and $[111]$

Figure A.2. Brillouin zone for the face-centered cubic lattice. The points and lines of symmetry are indicated.

TABLE A.4. - Symmetry points and lines in the NaCl (FCC) Brillouin zone

Point or Line	Description	Point Group	Principal Axes
Γ	Center of zone	O_h	$\langle 000 \rangle$
Δ	General point on k_y axis	C_{4v}	$\langle 100 \rangle$
Σ	General point along the bisector of the angle between k_x and k_y	C_{2v}	$\langle 110 \rangle$
Λ	General point along the body diagonal of the zone	C_{3v}	$\langle 111 \rangle$
Q	General point in the hexagonal face along the line extending from the center to one of the corners of this face	C_2	$\langle 110 \rangle$
S	General point on the line extending from the center of a square face to the midpoint of one of its edges	C_{2v}	$\langle 110 \rangle$
Z	General point on the line extending from the center of a square face to one of the corners of the square face	C_{2v}	$\langle 100 \rangle$
U	Midpoint of one of the sides of a square face	C_{2v}	$\langle 110 \rangle$
K	Midpoint of the edge of the zone which joins two hexagonal faces	C_{2v}	$\langle 110 \rangle$
W	Point which lies at one of the corners of the zone	D_{2d}	$\langle 100 \rangle$
L	Center of a hexagonal face	D_{3d}	$\langle 111 \rangle$
X	Center of a square face	D_{4h}	$\langle 100 \rangle$

directions, the following groups are encountered and are, therefore, of special interest: Γ , Δ , X , Σ , K , U , S , Λ , and L . The characters and irreducible representations for each of these groups have been tabulated by Slater [42], and for ease of reference, these are given² in Tables A.5 - A.9.

Projection Operators

The problem of finding the unitary matrix V which block diagonalizes S and D remains. Using the projection operator method one can in most cases construct V . The projection operator $P_{ij}^{(\alpha)}$ as defined³ by Chen [40] is

$$P_{ij}^{(\alpha)} = \sum_R \Gamma_{ij}^{(\alpha)}{}^*(R) s(R, \vec{q}), \quad (A.30)$$

where $\Gamma_{ij}^{(\alpha)}(R)$ is the i - j th matrix element of the α th irreducible representation belonging to the element R of $G(\vec{q})$. The summation is over all elements of the group.

The importance of the projection operator is that, when applied to an arbitrary vector

$$\vec{v} = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{bmatrix}, \quad (A.31)$$

²Because of its length, the table for Γ has been omitted. See Slater [42] for this table.

³This definition differs from the usual one. See for example, Tinkham [41].

TABLE A.5. - Matrix elements and characters for propagation along Δ .

	R_1	R_2	R_{19}	R_{20}	R'_3	R'_4	R'_{13}	R'_{14}
Δ_1	1	1	1	1	1	1	1	1
Δ'_2	1	1	1	1	-1	-1	-1	-1
Δ_2	1	1	-1	-1	1	1	-1	-1
Δ'_1	1	1	-1	-1	-1	-1	1	1
$(\Delta_5)_{11}$	1	-1	0	0	-1	1	0	0
$(\Delta_5)_{21}$	0	0	1	-1	0	0	-1	1
$(\Delta_5)_{12}$	0	0	1	-1	0	0	1	-1
$(\Delta_5)_{22}$	1	-1	0	0	1	-1	0	0
$\chi(\Delta_5)$	2	-2	0	0	0	0	0	0

TABLE A.6. - Matrix elements and characters for point X.

	R_1	R_2	R_3	R_4	R_{13}	R_{14}	R_{19}	R_{20}	R'_1	R'_2	R'_3	R'_4	R'_{13}	R'_{14}	R'_{19}	R'_{20}
x_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
x_2	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1
x_3	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1
x_4	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1
x'_1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
x'_2	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
x'_3	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1
x'_4	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1
$(x_5)_{11}$	1	-1	-1	1	0	0	0	0	1	-1	-1	1	0	0	0	0
$(x_5)_{21}$	0	0	0	0	-1	1	1	-1	0	0	0	0	-1	1	1	-1
$(x_5)_{12}$	0	0	0	0	1	-1	1	-1	0	0	0	0	1	-1	1	-1
$(x_5)_{22}$	1	-1	1	-1	0	0	0	0	1	-1	1	-1	0	0	0	0
$\chi(x_5)$	2	-2	0	0	0	0	0	0	2	-2	0	0	0	0	0	0
$(x'_5)_{11}$	1	-1	1	-1	0	0	0	0	-1	1	-1	1	0	0	0	0
$(x'_5)_{21}$	0	0	0	0	1	-1	1	-1	0	0	0	0	-1	1	-1	1
$(x'_5)_{12}$	0	0	0	0	-1	1	1	-1	0	0	0	0	1	-1	-1	1
$(x'_5)_{22}$	1	-1	-1	1	0	0	0	0	-1	1	1	-1	0	0	0	0
$\chi(x'_5)$	2	-2	0	0	0	0	0	0	-2	2	0	0	0	0	0	0

TABLE A.7. - Matrix elements and characters for Σ , K, U, and S.

	R_1	R_{23}	R'_4	R'_{24}
Σ_1, K_1, U_1, S_1	1	1	1	1
Σ_2, K_2, U_2, S_2	1	-1	-1	1
Σ_3, K_3, U_3, S_3	1	1	-1	-1
Σ_4, K_4, U_4, S_4	1	-1	1	-1

TABLE A.8. - Matrix elements and characters for propagation along Λ .

	R_1	R_5	R_9	R_{19}	R_{21}	R_{23}
Λ_1	1	1	1	1	1	1
Λ_2	1	1	1	-1	-1	-1
$(\Lambda_3)_{11}$	1	-1/2	-1/2	1	-1/2	-1/2
$(\Lambda_3)_{21}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$(\Lambda_3)_{12}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$(\Lambda_3)_{22}$	1	-1/2	-1/2	-1	1/2	1/2
$\chi(\Lambda_3)$	2	-1	-1	0	0	0

TABLE A.9. - Matrix elements and characters for point L .⁴

	R_1	R_5	R_9	R_{19}	R_{21}	R_{23}	R'_1	R'_5	R'_9	R'_{19}	R'_{21}	R'_{23}
L_1	1	1	1	1	1	1	1	1	1	1	1	1
L_2	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
L'_1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1
L'_2	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
$(L_3)_{11}$	1	-1/2	-1/2	1	-1/2	-1/2	1	-1/2	-1/2	1	-1/2	-1/2
$(L_3)_{21}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$(L_3)_{12}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$(L_3)_{22}$	1	-1/2	-1/2	-1	1/2	1/2	1	-1/2	-1/2	-1	1/2	1/2
$\chi(L_3)$	2	-1	-1	0	0	0	2	-1	-1	0	0	0
$(L'_3)_{11}$	1	-1/2	-1/2	1	-1/2	-1/2	-1	1/2	1/2	-1	1/2	1/2
$(L'_3)_{21}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$
$(L'_3)_{12}$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$-\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	0	$\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$
$(L'_3)_{22}$	1	-1/2	-1/2	-1	1/2	1/2	-1	1/2	1/2	1	-1/2	-1/2
$\chi(L'_3)$	2	-1	-1	0	0	0	-2	1	1	0	0	0

⁴Slater's representation L_4 has been called L'_3 to conform with the notation of Reference 30.

it projects out the basis vectors (or a linear combination of basis vectors) belonging to the j th row of $\Gamma^{(\alpha)}$. Useful information can be obtained from the basis vectors, depending upon the number of times $\Gamma^{(\alpha)}$ appears in the decomposition:

1. If $\Gamma^{(\alpha)}$ occurs only once in the decomposition, then the basis vectors uniquely determine the polarization vectors for that representation [40].
2. If $\Gamma^{(\alpha)}$ occurs twice, pure modes of vibration can be associated with the dispersion curve branches belonging to that representation. (Obviously the modes in case (1) are also pure.)
3. For representations occurring more than twice, pure modes, in general, will not exist.
4. In any case, one can decompose the basis vectors into a set of orthogonal vectors from which V can be constructed.

Compatibility

The notion of compatibility among the irreducible representations of two groups can often be useful in determining the connectivity of the dispersion curve branches which meet at certain symmetry points. To define compatibility one considers two groups, one of these being a subgroup of the other larger group. Then, a representation Γ_i of the subgroup is said to be compatible with the representation Γ_j of the larger group if the basis of Γ_i is included in the basis for Γ_j [41]. The compatibility relations for the O_h cubic group have been tabulated by Slater [42], and these are reproduced for the most

interesting symmetry points in Tables A.10 - A.12. To make use of compatibility in the study of lattice vibrations, one notes that the dispersion curve branches from two different directions, having a symmetry point in common, must connect continuously as dictated by the compatibility relations between the representations belonging to those branches.

Example for Propagation Along Σ

In order to illustrate the foregoing principles, an example will now be given for phonon propagation in the Σ direction. The group of the wave vector in this case is denoted by $G(\Sigma)$ and contains four elements: R_1 , R_{24}' , R_{23} , and R_4' . There are thus four S matrices for the group, and they can be written in the following block form:

$$S(R_1, \Sigma) = \begin{bmatrix} R_1 & 0 \\ 0 & R_1 \end{bmatrix} \quad (\text{A.32a})$$

$$S(R_{24}', \Sigma) = \begin{bmatrix} R_{24}' & 0 \\ 0 & R_{24}' \end{bmatrix} \quad (\text{A.32b})$$

$$S(R_{23}, \Sigma) = \begin{bmatrix} R_{23} & 0 \\ 0 & R_{23} \end{bmatrix} \quad (\text{A.32c})$$

$$S(R_4', \Sigma) = \begin{bmatrix} R_4' & 0 \\ 0 & R_4' \end{bmatrix} \quad (\text{A.32d})$$

TABLE A.10. - Compatibility relations at Γ .

Γ_1	Γ_2	Γ_1'	Γ_2'	Γ_{12}	Γ_{12}'	Γ_{15}	Γ_{15}'	Γ_{25}	Γ_{25}'
Δ_1	Δ_2	Δ_1'	Δ_2'	$\Delta_1\Delta_2$	$\Delta_1'\Delta_2'$	$\Delta_1\Delta_5$	$\Delta_1'\Delta_5'$	$\Delta_2\Delta_5$	$\Delta_2'\Delta_5'$
Λ_1	Λ_2	Λ_2	Λ_1	Λ_3	Λ_3	$\Lambda_1\Lambda_3$	$\Lambda_2\Lambda_3$	$\Lambda_2\Lambda_3$	$\Lambda_1\Lambda_3$
Σ_1	Σ_4	Σ_2	Σ_3	$\Sigma_1\Sigma_4$	$\Sigma_2\Sigma_3$	$\Sigma_1\Sigma_3\Sigma_4$	$\Sigma_2\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_3$

TABLE A.11. - Compatibility relations at X.

X_1	X_2	X_3	X_4	X_1'	X_2'	X_3'	X_4'	X_5	X_5'
Δ_1	Δ_2	Δ_2'	Δ_1'	Δ_1'	Δ_2'	Δ_2	Δ_1	Δ_5	Δ_5
Z_1	Z_1	Z_4	Z_4	Z_2	Z_2	Z_3	Z_3	Z_2Z_3	Z_1Z_4
S_1	S_4	S_1	S_4	S_2	S_3	S_2	S_3	S_2S_3	S_1S_4

TABLE A.12. - Compatibility relations at L.

L_1	L_2	L_1'	L_2'	L_3	L_3'
Λ_1	Λ_2	Λ_2	Λ_1	Λ_3	Λ_3
Q_1	Q_2	Q_1	Q_2	Q_1Q_2	Q_1Q_2

The characters of the S 's are obtained by summing the diagonal elements,

$$\chi_S(R_1) = 6 \quad (A.33a)$$

$$\chi_S(R_{24}') = -2 \quad (A.33b)$$

$$\chi_S(R_{23}) = 2 \quad (A.33c)$$

$$\chi_S(R_4') = 2 \quad (A.33d)$$

Using these, together with the characters of the Σ representations from Table A.7, the decomposition formula, Eq. (A.28), yields

$$a_1 = \frac{1}{4}[(1)(6) + (1)(-2) + (1)(2) + (1)(2)] = 2 \quad (A.34a)$$

$$a_2 = \frac{1}{4}[(1)(6) + (1)(-2) + (-1)(2) + (-1)(2)] = 0 \quad (A.34b)$$

$$a_3 = \frac{1}{4}[(1)(6) + (-1)(-2) + (1)(2) + (-1)(2)] = 2 \quad (A.34c)$$

$$a_4 = \frac{1}{4}[(1)(6) + (-1)(-2) + (-1)(2) + (1)(2)] = 2. \quad (A.34d)$$

The decomposition therefore gives S as a direct sum of the irreducible representations,

$$S(\Sigma) = 2\Sigma_1 + 2\Sigma_3 + 2\Sigma_4. \quad (A.35)$$

From the previous discussions, the following information can be obtained regarding the block-diagonal form of the dynamical matrix: Since the representations of Eq. (A.35) are one dimensional and appear twice, there will be one 2×2 block in the dynamical matrix corresponding

to each. For a given value of $\vec{q}$, each block will have two eigenfrequencies, corresponding to the acoustic and optical branches of the dispersion relation. Two of the blocks will yield pure transverse polarizations and the other, pure longitudinal. None of the representations is multidimensional; hence, there will be no degeneracy among the branches. It is of some interest to note that already a good deal of information has been obtained regarding the dispersion relation.

Since the dynamical matrix is left invariant under the transformation involving the group of the wave vector, Eq. (A.24) can be used to reduce the number of independent elements occurring in D . The procedure to be followed is similar to that used in reducing the force constant matrices. When the S 's for the group $G(\Sigma)$ are applied to a general Hermitian dynamical matrix of the form

$$D = \begin{bmatrix} D_{11} & D_{12} & D_{13} & D_{14} & D_{15} & D_{16} \\ D_{12}^* & D_{22} & D_{23} & D_{24} & D_{25} & D_{26} \\ D_{13}^* & D_{23}^* & D_{33} & D_{34} & D_{35} & D_{36} \\ D_{14}^* & D_{24}^* & D_{34}^* & D_{44} & D_{45} & D_{46} \\ D_{15}^* & D_{25}^* & D_{35}^* & D_{45}^* & D_{55} & D_{56} \\ D_{16}^* & D_{26}^* & D_{36}^* & D_{46}^* & D_{56}^* & D_{66} \end{bmatrix}, \quad (\text{A.36})$$

the following reduced form is obtained,

$$D(\Sigma) = \begin{bmatrix} D_{11} & D_{12} & 0 & D_{14} & D_{15} & 0 \\ D_{12} & D_{11} & 0 & D_{15} & D_{14} & 0 \\ 0 & 0 & D_{33} & 0 & 0 & D_{36} \\ D_{14}^* & D_{15}^* & 0 & D_{44} & D_{45} & 0 \\ D_{15}^* & D_{14}^* & 0 & D_{45} & D_{44} & 0 \\ 0 & 0 & D_{36}^* & 0 & 0 & D_{66} \end{bmatrix} \quad (A.37)$$

To construct the unitary matrix V which block diagonalizes the 6×6 dynamical matrix, one makes use of the basis vectors obtained from the projection operator method. Using the definition of the projection operator, Eq. (A.30), together with the character table for Σ , the following results are obtained:

$$P_{11}^{(1)} = s(R_1) + s(R_{24}') + s(R_{23}) + s(R_4') \quad (A.38a)$$

$$P_{11}^{(2)} = s(R_1) + s(R_{24}') - s(R_{23}) - s(R_4') \quad (A.38b)$$

$$P_{11}^{(3)} = s(R_1) - s(R_{24}') + s(R_{23}) - s(R_4') \quad (A.38c)$$

$$P_{11}^{(4)} = s(R_1) - s(R_{24}') - s(R_{23}) + s(R_4') \quad (A.38d)$$

Applying each of the P 's to an arbitrary 6×1 vector of the form given by Eq. (A.31), one obtains

$$P_{11}^{(1)} \vec{v} = \begin{bmatrix} 2(v_1+v_2) \\ 2(v_1+v_2) \\ 0 \\ 2(v_4+v_5) \\ 2(v_4+v_5) \\ 0 \end{bmatrix} \quad (A.39a)$$

$$P_{11}^{(2)\rightarrow} \vec{v} = 0 \quad (\text{A.39b})$$

$$P_{11}^{(3)\rightarrow} \vec{v} = \begin{bmatrix} 0 \\ 0 \\ 4v_3 \\ 0 \\ 0 \\ 4v_6 \end{bmatrix} \quad (\text{A.39c})$$

$$P_{11}^{(4)\rightarrow} \vec{v} = \begin{bmatrix} 2(v_1-v_2) \\ -2(v_1-v_2) \\ 0 \\ 2(v_4-v_5) \\ -2(v_4-v_5) \\ 0 \end{bmatrix} \quad (\text{A.39d})$$

These results can be further simplified by decomposing each of the vectors of Eqs. (A.39) into two independent orthonormal vectors,

$$P_{11}^{(1)\rightarrow} \vec{v} = 2\sqrt{2} (v_1+v_2) \begin{bmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + 2\sqrt{2} (v_4+v_5) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{bmatrix} \quad (\text{A.40a})$$

$$P_{11}^{(3)\rightarrow} \vec{v} = 4v_3 \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} + 4v_6 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \quad (\text{A.40b})$$

$$P_{11}^{(4)+} v = \frac{2}{\sqrt{2}} (v_1 - v_2) \begin{bmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + \frac{2}{\sqrt{2}} (v_4 - v_5) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \end{bmatrix}. \quad (\text{A.40c})$$

The column vectors of Eqs. (A.40) can then be arranged row-wise to give V ,

$$V = \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 \end{bmatrix}, \quad (\text{A.41a})$$

$$V^\dagger = \begin{bmatrix} 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}. \quad (\text{A.41b})$$

Applying the unitary transformation, the block-diagonal form of D is

$$D(\Sigma) = \begin{bmatrix} D_{11} + D_{12} & D_{14} + D_{15} & 0 & 0 & 0 & 0 \\ D_{14}^* + D_{15}^* & D_{44} + D_{45} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{33} & D_{36} & 0 & 0 \\ 0 & 0 & D_{36}^* & D_{66} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{11} - D_{12} & D_{14} - D_{15} \\ 0 & 0 & 0 & 0 & D_{14}^* - D_{15}^* & D_{44} - D_{45} \end{bmatrix}. \quad (\text{A.42})$$

The problem of solving for the eigenfrequencies of D , thus reduces to the smaller problem of diagonalizing each of the 2×2 blocks in Eq. (A.42).

The decomposition and block-diagonal form of the dynamical matrix for each of the other interesting symmetry lines and points are given below:

$$s(\Delta) = 2\Delta_1 + 2\Delta_5 \quad (\text{A.43a})$$

$$D(\Delta) = \begin{bmatrix} D_{11} & D_{14} & 0 & 0 & 0 & 0 \\ D_{14}^* & D_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{22} & D_{25} & 0 & 0 \\ 0 & 0 & D_{25}^* & D_{55} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{22} & D_{25} \\ 0 & 0 & 0 & 0 & D_{25}^* & D_{55} \end{bmatrix} \quad (\text{A.43b})$$

$$s(\Lambda) = 2\Lambda_1 + 2\Lambda_3 \quad (\text{A.44a})$$

$$D(\Lambda) = \begin{bmatrix} D_{11}+2D_{12} & D_{14}+2D_{15} & 0 & 0 & 0 & 0 \\ D_{14}^*+2D_{15}^* & D_{44}+2D_{45} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{11}-D_{12} & D_{14}-D_{15} & 0 & 0 \\ 0 & 0 & D_{14}^*-D_{15}^* & D_{44}-D_{45} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{11}-D_{12} & D_{14}-D_{15} \\ 0 & 0 & 0 & 0 & D_{14}^*-D_{15}^* & D_{44}-D_{45} \end{bmatrix} \quad (\text{A.44b})$$

$$s(X) = 2X_4 + 2X_5 \quad (\text{A.45a})$$

$$D(X) = \begin{bmatrix} D_{11} & D_{14} & 0 & 0 & 0 & 0 \\ D_{14}^* & D_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{22} & D_{25} & 0 & 0 \\ 0 & 0 & D_{25}^* & D_{55} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{22} & D_{25} \\ 0 & 0 & 0 & 0 & D_{25}^* & D_{55} \end{bmatrix} \quad (A.45b)$$

$$s(L) = L_2' + L_1 + L_3' + L_3 \quad (A.46a)$$

$$D(L) = \begin{bmatrix} D_{11} + 2D_{12} & 0 & 0 & 0 & 0 & 0 \\ 0 & D_{44} + 2D_{45} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{11} - D_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & D_{44} - D_{45} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{11} - D_{12} & 0 \\ 0 & 0 & 0 & 0 & 0 & D_{44} - D_{45} \end{bmatrix} \quad (A.46b)$$

Using the decompositions, together with the compatibility table for the point X, the connectivity at X of the branches from the Δ and Σ directions can be established as shown in Figs. 6-10. Recall that the representations S in Table A.11 can be considered as continuations of the Σ representations along the line Γ -K-X.

LIST OF REFERENCES

1. B. N. Brockhouse, Inelastic Scattering of Neutrons in Solids and Liquids (International Atomic Energy Agency, Vienna, 1961) p. 113.
2. D. H. Ewing and F. Seitz, Phys. Rev. 50, 760 (1936).
3. For references, see P. O. Löwdin, Advances in Phys. 5, 1 (1956).
4. A. Morita and K. Takahashi, Progr. Theoret. Phys. 19, 257 (1958).
5. M. H. Brodsky and E. Burstein, in Lattice Dynamics, edited by R. F. Wallis (Pergamon Press, Inc., Oxford, 1965) p. 175.
6. R. S. Calder, W. Cochran, D. Griffiths, and R. D. Lowde, J. Phys. Chem. Solids 23, 621 (1962).
7. A. D. B. Woods, B. N. Brockhouse, M. Sakamoto, and R. N. Sinclair, Inelastic Scattering of Neutrons in Solids and Liquids (International Atomic Energy Agency, Vienna, 1961) p. 487.
8. M. G. Zemlianov, E. G. Brovman, N. A. Chernoplekov, and Iu. L. Shitikov, Inelastic Scattering of Neutrons (International Atomic Energy Agency, Vienna, 1965) Vol. II, p. 431 (English translation, LA-TR-65-35).
9. A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1963) Suppl. 3.
10. G. Dolling and A. D. B. Woods, in Thermal Neutron Scattering, edited by P. A. Egelstaff (Academic Press, Inc., New York, 1965) p. 193.

11. W. Cochran, Rep. Progr. Phys. 26, 1 (1963).
12. M. Dresden, Revs. Modern Phys. 33, 265 (1961).
13. R. E. Peierls, Quantum Theory of Solids (Clarendon Press, Oxford, 1955) p. 4.
14. P. P. Ewald, Ann. Phys., Lpz., (4) 64, 253 (1921).
15. E. W. Kellermann, Phil. Trans. Roy. Soc. A238, 513 (1940).
16. A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. 119, 980 (1960).
17. A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. 131, 1025 (1963).
18. R. H. Lyddane and K. F. Herzfeld, Phys. Rev. 54, 846 (1938).
19. B. G. Dick and A. W. Overhauser, Phys. Rev. 112, 90 (1958).
20. W. Cochran, Phys. Rev. Letters 2, 495 (1959).
21. W. Cochran, Proc. Roy. Soc. A253, 260 (1959).
22. W. Cochran, Phil. Mag. 4, 1082 (1959).
23. W. Cochran, Advances in Phys. 10, 401 (1961).
24. R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, Phys. Rev. 131, 1030 (1963).
25. R. A. Cowley, Proc. Roy. Soc. A268, 109 (1962).
26. B. N. Brockhouse, L. N. Becka, K. R. Rao, and A. D. B. Woods, Inelastic Scattering of Neutrons in Solids and Liquids (International Atomic Energy Agency, Vienna, 1963) Vol. II, p. 23.
27. F. E. Pretzel, G. N. Rupert, C. L. Mader, E. K. Storms, G. V. Gritton, and C. C. Rushing, J. Phys. Chem. Solids 16, 10 (1960).
28. W. Soller, Phys. Rev. 24, 158 (1924).

29. A. L. Bowman, T. C. Wallace, J. L. Yarnell, and R. G. Wenzel, Acta Cryst. 21, 843 (1966).
30. L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).
31. R. Lyddane, R. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).
32. E. Staritzky, Los Alamos Sci. Lab. Rep. LA-1559 (1953).
33. D. J. Montgomery and J. R. Hardy, in Lattice Dynamics, edited by R. F. Wallis (Pergamon Press Inc., Oxford, 1965) p. 491
34. G. W. Lehman, T. Wolfram, and R. E. DeWames, Phys. Rev. 128, 1593 (1962).
35. W. C. Davidon, Argonne Nat'l. Lab. Rep. ANL-5990(Rev.) (1959).
36. G. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson, Phys. Rev. 147, 577 (1966).
37. A. S. Filler and E. Burstein, Bull. Am. Phys. Soc. 5, 198 (1960).
38. F. Seitz, Annals of Mathematics 37, 17 (1936).
39. G. H. Begbie and M. Born, Proc. Roy. Soc. A188, 179 (1947).
40. S. H. Chen, "Neutron Scattering Studies of Lattice Vibrations in Metals". Unpublished Ph. D. thesis, Physics Department, McMaster University, Hamilton, Canada (Sept., 1964).
41. M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill, New York, 1964).
42. J. C. Slater, Quantum Theory of Molecules and Solids (McGraw-Hill, New York, 1965) Vol. 2.