# LATTICE DYNAMICS OF SIMPLE METALS

S.H. Taole

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## ABSTRACT

This thesis addresses two problems. In the first problem the conventional theory of lattice dynamics is generalized to include the effect of volume forces on the phonon frequencies. This generalization provides a new way of tackling the compressibility problem in that it establishes the equivalence of the bulk modulus calculated by the method of long waves and that calculated by differentiation of the ground state energy without the need to include higher order perturbation terms in the dynamics. The effect of the volume forces on the phonon frequencies is studied for a number of simple metals using three local model pseudopotentials. Calculations are also presented for the polyvalent metals Al and Pb.

In the second problem the energies and lifetimes of phonons in Li between 110 and 424K are calculated using the self-consistent phonon theory. To describe Li the non-local ion-ion interaction potential described by Dagens, Rasolt and Taylor (DRT) was used. The results are compared with the neutron scattering measurements of Beg and Nielsen and these indicate that Li is less anharmonic than Na or K, and this is due to the strong Li ion-ion interaction potential which has a relatively soft core. There are also indications that in Li many body forces not included in the DRT potential have a more significant role than in Na or K.

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CONTENTS

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

Two problems are studied in this thesis; we study the compressibility or bulk modulus problem which has appeared in the literature from time to time but with no final solution.[1-3] We also study anharmonic properties of Li over the temperature range 110 to 424K using the self-consistent phonon theory.

In recent years the theory of metals has progressed to the point where the calculation of dynamical properties can be expected to yield reliable results. This is particularly so in simple metals like Na[4] and K[5] where interionic potentials have been calculated which describe the phonon spectra of these metals well over wide ranges of temperature. Much of the progress that has been made in the understanding of these metals can be attributed to the introduction of the pseudopotential concept which is used as a means of describing the interaction of a conduction electron and an ion in the metal. When the electron-ion interaction is known, then the effective ion-ion interaction can be calculated, and since the aim in solid state theory is to describe this interaction in such a way that a whole range of solid state properties can be calculated from it, a great deal of attention has in recent years been directed towards the calculation of reliable interionic potentials.

It has been known for many years that good qualitative calculations of some properties of metals could be obtained by applying the free-electron theory according to which the electrons in a metal move freely. What pseudopotential theory does is to give some justification for the nearly free-electron assumption and to provide a mathematical framework that can be used to calculate many properties of metals.[6]

### 1.2.1 Interionic Potentials Based on Pseudopotential Theory

An electron in the neighbourhood of an ion experiences a strong Coulomb attraction but is at the same time repelled by the core electrons. The cancellation between these two contributions results in a small net effective interaction, and it is this interaction which is represented by a pseudopotential. At the basis of pseudopotential theory is the fact that the conduction electrons are excluded from those regions of space occupied by the ions. This concept is represented mathematically by writing the wave function of a conduction electron in state $|k\rangle$ as a linear combination of OPW's which are plane waves that have been orthogonalized to the core states. Let $|\alpha>$ denote a core state, then an OPW is given by

$$\chi_k = |k> - \sum_{\alpha} <\alpha|k>|\alpha> \tag{1.1}$$

The conduction electron wave function is then given by

$$\psi_{\underline{k}} = \sum_{\underline{q}} a_q |\underline{k} + \underline{q}> \tag{1.2}$$

where q is a general vector reducing to a reciprocal lattice **vector for a crystal potential.** The Shroedinger equation for the energy eigenstates $\varepsilon_k$ of the conduction electrons is

$$\hat{H}\psi_k = \varepsilon_k \psi_k$$

and if we substitute (1.2) into this we end up with the equation

$$\{\hat{H} + (\varepsilon_k - \hat{H})\hat{P}\}\phi_k = \varepsilon_k \phi_k \tag{1.3}$$

This is equivalent to a Shroedinger equation in which the wave function $\psi_k$ is replaced by the pseudowave function $\phi_k$, and the potential energy V(r) is replaced by the pseudopotential

$$\hat{W} = V(r) + (\varepsilon_k - \hat{H})\hat{P} \tag{1.4}$$

where $\hat{P}$ is the projection operator

$$\hat{P} = \sum_{\alpha} |\alpha\rangle\langle\alpha| \tag{1.5}$$

In a rigorous theory $\hat{W}$ is an energy dependent non-hermitian operator[6], but in many cases it is convenient to make a local approximation and replace the second term in (1.4) by a non-operator term so that $\hat{W}$ then simply becomes a function of position.

The conduction electrons in a metal tend to move in such a way that they form a screening charge around the ions. The ions together with their screening charges then form the units of a metal and have been referred to as pseudoatoms[7]. As a result of the screening a conduction electron experiences not only the potential $w_B(r)$ of the bare ions, but also that of the screening charges. The screening is usually described by a dielectric function $\varepsilon(q)$ and in terms of this the form factors or matrix elements of $w_s(r)$ the screened ion potential and $w_B(r)$ are linearly related.

$$\langle k + q|w_s(r)|k\rangle = \langle k + q|w_B(r)|k\rangle/\varepsilon(q) \tag{1.6}$$

In the local approximation the equation takes the form

$$w_s(q) = w_B(q)/\varepsilon(q) \tag{1.7}$$

When the screening function $\varepsilon(q)$ and the bare ion potential $w_B(r)$ have been determined, the ion-ion interaction potential can be calculated. An essential approximation that is made towards this goal is the assumption that $\hat{W}$ is small compared to the kinetic energy and hence can be regarded as a perturbation with the free-electron gas as the zero order approximation. Application of perturbation theory to second order then gives for the total ground state energy of the electron gas

$$E_{gas} = E_o + E_{bs} \tag{1.8}$$

$E_o$ comes from the zeroeth and first order terms and is independent of the positions of the ions, depending only on the volume per ion. The band structure energy $E_{bs}$ is given by

$$\begin{aligned} E_{bs} &= \frac{1}{N^2} \sum_q{}' \sum_\ell F(q) e^{-iq.R_\ell} \\ &= \frac{1}{N} \sum_\ell{}' V'(r_\ell) + \frac{1}{N^2} \sum_q{}' F(q) \end{aligned} \tag{1.9}$$

where the prime on $\sum_q{}'$ means the q=o term is omitted.

Here F(q) is the energy wave number characteristic and it contains the pseudopotential to second order and the screening function. $V'(r)$ represents the interaction of two ions via the electron gas and is given by

$$V'(r) = \frac{\Omega_o}{\pi^2 r} \int_o^\infty F(q) q \sin(qr) dq \qquad (1.10)$$

In addition to this indirect interaction the ions also interact directly through a Coulomb force so that the total ion-ion interaction takes the form

$$V_{II}(r) = \frac{(Ze)^2}{r} + \frac{\Omega_o}{\pi^2 r} \int_o^\infty F(q) q \sin(qr) dq \qquad (1.11)$$

where Ze is the effective charge on the ion, and $\Omega_o$ the volume per ion. In general the pair potential $V_{II}(r)$ decreases from a strong repulsion at small values of r to an attractive minimum at about the nearest neighbour. At large r it has the oscillatory behaviour

$$V(r)_{asym} \propto \frac{\cos(2k_f r)}{(2k_f r)^3}$$

where $k_f$ is the Fermi wave vector.

The conditions for the pseudopotential formulation[6] namely that the metal should exhibit free-electron like behaviour, have spherical Fermi surface, and that the ion cores should be small and tightly bound so that they are not easily polarized, are best met in the alkali metals. As a result many calculations of pair potentials based on pseudopotential theory have been made for these metals. Some calculations have also been done for the polyvalent metals like Al.[8]

### 1.2.2 Empirical Pair Potentials Based on Pseudopotential Theory

In many cases a model potential representing the electron-ion interaction is assumed and its parameters are adjusted to reproduce some observed physical properties and in this way an empirical pair potential is determined. The most often quoted model is that of Heine and Abarenkov[9] in which the bare ion potential is given by

$$\begin{aligned} w_B(r<R_m) &= \sum_{\ell} A_{\ell}(E) P_{\ell} \\ w_B(r>R_m) &= -\frac{Ze^2}{r} \end{aligned} \qquad (1.12)$$

$A_{\ell}(E)$ is a parameter which varies slowly with E the energy of the incident conduction electron and with $R_m$ the radius of the core region, $P_\ell$ is a projection operator which selects from the wave function of the incident electron that component with angular momentum $\ell$. The constants of this model are fitted to spectroscopic data and hence it is an empirical model but one which follows the formal theory in having an energy dependent operator pseudopotential.

Shyu and Gaspari[10] have calculated pair potentials for the five alkali metals on the basis of the Heine-Abarenkov-Animalu[11] (HAA) form factors and they found that these potentials typically have asymptotic oscillations which decay rapidly after about the fifth neighbour except in Li where their range was longer. They also calculated the elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ by the method of long waves and found good agreement with experiment except in Li. These authors repeated their calculations using Ashcroft's[12] form factors which also have experimental input. The Ashcroft[13] model is a local form of the HA model in which $A_\ell(E)$ is identically zero. Their results showed that Li stands apart from the other four alkali metals in having long range oscillations in its potential. Again the experimental elastic constants were well reproduced except in Li.

It can be deduced from this that although Li has no significant core polarization, it nevertheless has its own special problems. These arise from the fact that the ionic core has only two electrons both of which are in the s state, and any p component in the wave function of the conduction electron is not shielded from the nuclear charge by the core electrons hence strong scattering phase shifts occur. The Fermi surface of this metal also shows pronounced deviations from sphericity and these are probably manifestations of this fact.[14] The weak shielding of the Li core results in an ion-ion potential which is relatively strong and this in turn means that straightforward application of perturbation theory to second order is highly questionable.

### 1.2.3 First Principles Pair Potentials Based on Pseudopotential Theory

When the form factors which are needed to calculate F(q) from which the indirect interaction of the ions is determined are calculated from first principles, a non-local energy dependent operator is required and the calculations become involved. Earlier first principles calculations of pair potentials include those calculated by Pick[15] on the basis of the Harrison form factors. When these were used to calculate the vibrational spectra of Na and Al, large variances with observed neutron scattering data were found. The HA form factors are generally regarded as being more reliable.

Until about a decade ago the most reliable interionic potentials were those which incorporated some experimental input. But more recently interionic potentials have been calculated by Dagens, Rasolt and Taylor, DRT,[16] which ~~do~~ not contain any parameters adjusted to any experimental data, hence the F(q) calculated by these authors represents a first principles calculation. The procedure followed by these authors is given in the literature,[17] in chapter IV a summary of their method is given, here we simply point out that by following their procedure all higher order terms representing multiple scattering events at a single ion site when the ion is placed in an electron gas are folded into the pseudopotential which can then be used in low order perturbation theory. Using a DRT pseudopotential to second order in perturbation theory provides an effective sum of all higher contributions to the two-body potential.

An interionic potential similar to the DRT pseudopotential has been used to calculate the phonon dispersion curves in the alkali metals Na and K with much success. In Na Glyde and Taylor[4] used it and the self-consistent phonon theory, to calculate the dispersion curves at 90K and 293K where anharmonic effects can be expected to be large. In both cases they found good agreement with experiment without prior fitting to experimental data. Subsequently calculations similar to those done for Na were made for K at various temperatures from 9 to 299K. Again good agreement with experiment for the dispersion curves was obtained indicating that these two metals can be adequately described by two-body interactions. The metals Rb and Cs on the other hand have large ionic cores which are loosely bound and therefore can have appreciable core polarizabilities. This effect has yet to be included in lattice dynamics, also the extension of the DRT method to these metals is still being done.

We now come to Li whose problems have already been mentioned. There are a number of calculations for Li but these have been in the harmonic approximation.[18-21] In view of the fact that the $Li^+$ ion is very light, the lightest of the alkali metals, it is conceivable that significant anharmonic effects are still present even at liquid nitrogen temperatures where neutron scattering experiments have been made, we have therefore calculated the anharmonic properties of Li using the self-consistent phonon theory partly to investigate this point. To describe the metal we used a DRT interionic potential and in view of the reasons mentioned above it is quite appropriate to use the DRT pseudopotential for the calculation of a Li pair potential. Furthermore, the recent neutron scattering measurements of Beg and Nielson[22] of the phonon dispersion curves up to 424K provide a challenging test of theory to see how well they can be reproduced from first principles calculations. In chapter IV we describe the potential used to describe Li and the techniques used to handle it. We calculate the energies and lifetimes of anharmonic phonons over the entire temperature range and compare these with experiment. There are no parameters adjusted to experiment and therefore the calculations can be regarded as being from first principles.

### 1.3.1. Calculations of Bulk Modulus by Static Method

The other problem to which we focus attention is the compressibility problem which arises from the observation that the bulk modulus calculated by static methods for an assumed model is not identical with that calculated by dynamical methods for the same model. This problem is closely related to another concerning the origin of the violation of the Cauchy relation $C_{12}=C_{44}$ which has been observed in cubic metals.

The starting point in the determination of the bulk modulus by the static method is the calculation of the total ground state energy which we equate to the internal energy or the free energy of the metal. To get the ground state energy we have to add to (1.8) the energy due to the direct Coulomb interaction of the ions. We can then write the total energy calculated to second order in the electron-ion pseudopotential in the form

$$\Phi = \Phi_o + \Phi_{Ew} + \Phi_{bs} \tag{1.13}$$

where the last two terms, the Ewald energy and the band structure energy, depend on the structure of the crystal and are together called the structural energy $\Phi_s = \Phi_{Ew} + \Phi_{bs}$. The first term depends parametrically on the positions of the ions in the adiabatic approximation but is primarily a function of the volume per ion. It can be regarded as being due to volume (dependent) forces. When the bulk modulus B is calculated by static methods, the total energy is differentiated twice with respect to volume so that

$$B = \frac{\Omega d^2\Phi}{d\Omega^2} \tag{1.14}$$

where $\Omega$ is the volume of the crystal. The compressibility $K = B^{-1}$ measures the response of the crystal volume to changes in pressure and since the application of pressure changes the elastic energy of a crystal the calculation of the bulk modulus from (1.14) means that we are equating changes in the ground state energy (1.13) brought about by a particular deformation of the crystal, namely a uniform dilation, to changes in the elastic energy. The static method is also sometimes referred to as the method of homogeneous deformations.[23] By considering other deformations of the crystal besides the uniform dilation, we can calculate the elastic constants by taking strain derivatives of the energy. In cubic metals three deformations are required to evaluate $C_{11}$, $C_{12}$, and $C_{44}$.

1.3.2 Calculation of Bulk Modulus by Dynamical Method

In the dynamical method of calculating the bulk modulus, we use the result from elasticity theory that the bulk modulus is given by

$$B = \frac{1}{3}(C_{11} + 2C_{12})$$

and then calculate the elastic constants by the method of long waves. The principle of the method is that in the limit of long wavelengths the frequencies of longitudinal and transverse acoustic phonons along symmetry directions are the same as those of elastic waves in the crystal. The longitudinal elastic constants $C_{11}$ and $C_{12}$ calculated from derivatives of the energy are not the same as those obtained from dynamics, but the transverse elastic constants $C_{44}$

and $(C_{11}-C_{12})$ are the same. The difference in each case is $\Delta_{bs}$ where the subscript indicates that this term which is not found in the dynamical method comes from the band structure energy. Since a fluid cannot support a shear wave, this difference is attributed to the presence of the electron gas.

To calculate the phonon frequencies only the structural energy is required because a lattice wave is a rearrangement of atoms at constant energy. At first sight it seems natural that there should be this difference in the longitudinal elastic constants calculated in two ways because in one method all terms in the ground state energy expression are used while in the other method only some of the terms are used. But then the total energy expression in (1.13) can be written as the sum of a volume term plus another term which is a summation in real space, or as a volume term plus a summation in Fourier space.

$$\Phi = U(\Omega) + \tfrac{1}{2}\sum_{\ell\ell'}{}' V_{II}(R_\ell) \tag{1.15}$$

When the energy is expressed as in (1.15) then it can be shown as Finnis[3] has done that even though the volume term $U(\Omega)$ accounts for most of the binding energy and that its second volume derivative is a substantial fraction of the bulk modulus, the term itself makes no contribution to the bulk modulus because it is cancelled by similar terms arising from the volume dependence of the pair potential $V_{II}(R)$, hence the problem still remains, there is this difference $\Delta_{bs}$ between values of the bulk modulus calculated by the two methods.

From the fact that $C_{11}$ and $C_{12}$ both involve $\Delta_{bs}$ whereas $C_{44}$ and $C_{11}-C_{12}$ do not, it follows that one of the reasons why the Cauchy relation is not satisfied in metals is the presence of the electron gas. The metallic solid is not in equilibrium under the operation of central forces only, which is a precondition for the validity of the Cauchy relation, but also under the operation of volume forces. The Cauchy relation will also not necessarily be satisfied if there are present in the metal many-body forces in addition to central forces. We can study the Cauchy relation and evaluate all contributions to $(C_{12}-C_{44})$ working entirely with static methods. This however, would still leave the compressibility problem. Therefore even though we calculate these quantities in chapter III, the main interest is in the extension of lattice dynamical theory in such a way that the bulk modulus obtained by the two methods is the same.

### 1.3.3 Previous Discussions of the Compressibility Problem

In his studies of lattice dynamics and elasticity of stressed crystals Wallace[24] showed that the dynamical matrices for a homogeneously strained crystal and for an ideal unstrained crystal are of the same form. He calculated the elastic constants by the method of homogeneous deformations and by the method of long waves and found that the two methods gave the same results if the same approximations were made in both treatments. Thus there exists a general derivation showing the equivalence of the bulk modulus calculated from the long wave limit of the harmonic phonon frequencies to that calculated by differentiation of the total energy. But as pointed out already the conventional theory of lattice dynamics using second order perturbation theory gives results which have the discrepancy $\Delta_{bs}$ in B. This discrepancy is attributed by Wallace to the use of finite order perturbation theory. In lattice dynamics the total energy is expanded in powers of the ion displacements and Wallace points out that there are contributions to the total energy which are of second order in the ion displacements but which appear in every order of the pseudopotential. If the ion displacements rather than the pseudopotential are treated as perturbations of the ground state energy, then in the dynamics terms of third and fourth order in the pseudopotential appear and when these are included the discrepancy will be removed.

In another study of the compressibility problem in metals, Brovman[1] et al wrote the energy of the metal in the form

$$\Phi = E_i + E^o + E^1 + E^2 + \qquad (1.16)$$

where $E_i$ is the energy of the ions, $E_q = E^o + E^1 + E^2 +$ is that of the electron gas and each $E^n$ involves the order parameter $(V_\tau/\varepsilon_F)$ to order n. $V_q$ is the Fourier transform of the pseudopotential and $\varepsilon_F$ the Fermi energy. For a static lattice and for $n \geq 2$ all the q's in $V_q$ are equal to reciprocal lattice vectors $\tau$. In dynamics each $E^n$ is expanded in powers of the ion displacements and the dynamical matrix for harmonic phonons can contain any order of $(V_\tau/\varepsilon_F)$. These authors then point out that the force constants involve Fourier transforms of the pseudopotential for arbitrary q not just $q=\tau$, as a result, although the contributions of $E^3$ and $E^4$ to the dynamical matrix are of order 3 and 4 in the pseudopotential, in some regions of phase space and in the limit of long waves the ordering parameter in these terms is $(V_\tau/\varepsilon_F)^2$. They then proceeded to show that when these terms are included in the dynamics the compressibilities calculated from statics and dynamics are the same.

Pethick[25] also studied the compressibility problem and made the point that the correct ordering parameter of terms which appear in the dynamical matrix is not the total number of electron-ion interactions but the total number of electron-ion umklapp processes. His conclusion is that in calculations of the dynamical matrix terms of third and fourth order in the electron-ion interaction must be included if results are to be the same as those based on the second order perturbation expression for the energy.

In a recent paper Upadhyaya[26] made the point based on Finnis' work that the use of central force models which are implied in a second order perturbation term of the electron-ion pseudopotential is not satisfactory for the calculation of phonon frequencies in metals because it leads to the discrepancy we have mentioned in the bulk modulus. On the basis of the work of Brovman et al and Wallace he proposed that unpaired forces introduced by third and fourth order terms in perturbation theory be taken into account.

### 1.3.4 Present Approach to the Compressibility Problem

In all previous discussions of the compressibility problem the approach has been to include higher order terms in the dynamics. The approach of Brovman et al, Wallace and Pethick leads to the conclusion that the phonon frequencies should be calculated not to second order in $V_q$ as $q \to o$, but to second order in $V_{q + \tau}$. In this thesis a different approach is followed. To begin, we note that the fundamental approximation made in the static method is that of equating the internal energy or the Helmholtz free energy which we represent by the total ground state energy to the elastic energy. The total energy can be expanded in powers of the strains, and the elastic constants are strain derivatives of the ground state energy. If the strains are now functions of time we get the equation for the propagation of elastic waves in the crystal, and this is exactly the same as the equation for the propagation of acoustic phonons along symmetry directions in the limit of long wavelengths. The elastic constants which appear as coefficients in the expansion of the ground state energy in powers of the strains are the same whether the strains are time dependent or time-independent. The conclusion from this is that the method of long waves leads to identical results for the elastic constants and bulk modulus as does the static method when the same approximations are made in both cases. It also follows from this that if we make the approximation that the ground state energy be given by

$$\Phi = E_i + E^o + E^1 + E^2$$

so that $E^n=0$ for all $n \geq 3$, then the elastic constants obtained from this as our starting point should be consistent whether calculated by the method of long waves or from derivatives of the energy. We have therefore extended lattice dynamics to satisfy this consistency criterion. In the Born-Oppenheimer approximation the total energy of the vibrating crystal is given by the kinetic energy of the ions plus the change in the energy of the static lattice introduced by the periodic distortions of the vibrating ions. When these two quantities are known we can construct the Lagrangian of the system and find the equations of motion of the ions. Now, the displacements of the ions change the total energy of the static lattice in two distinct ways. Firstly, they change the structure factor of the crystal and secondly they change the electron charge distribution. Conventional lattice dynamical theory does not take into account the second contribution to the total energy change. Our approach to the compressibility problem is to incorporate this contribution to the total energy change of the static lattice into lattice dynamics.

In chapter II the total ground state energy of a cubic lattice is calculated and differentiated twice with respect to volume to find the static method expression of the bulk modulus. This is followed by a discussion of lattice dynamics in the harmonic approximation and of self-consistent phonon theory. In chapter III lattice dynamics is extended to satisfy the consistency criterion stated above, we give numerical values of the elastic constants and of $\Delta_{bs}$ calculated for a number of simple metals using three models as well as some calculations of the polyvalent metals Al and Pb. We also show that lattice dynamics in real space and in Fourier space leads to the same frequencies at all phonon wave vectors. The need to show this arises because in the expressions for the total ground state energy the volume terms in the real space formulation and in the Fourier space formulation are of different magnitudes and have different volume dependences from which it follows that the structure dependent terms which go into the dynamics are also different in a similar way.

## REFERENCES


1. E.G. Brovman, Yu Kagan, A. Kholas, Soviet Phys. JETP, 30, 883 (1970).
2. D.C. Wallace, Phys. Rev. 182, 778 (1969).
3. M.W. Finnis, J. Phys. F 4, 1645 (1974).
4. H.R. Glyde, Roger Taylor, Phys. Rev. B 5, 1206 (1971).
5. M.S. Duesbery, Roger Taylor, H.R. Glyde, Phys. Rev. B 8, 1372 (1973).
6. W.A. Harrison, Pseudopotentials in the Theory of Metals (Benjamin, New York, 1966).
7. J.M. Ziman, Adv. Phys. 13, 89 (1964).
8. R.W. Shaw, V. Heine, Phys. Rev. B 5, 1646 (1972); M.S. Duesbery, R. Taylor, Phys. Rev. B 7, 2870 (1972).
9. I.V. Abarenkov, V. Heine, Phil. Mag. 12, 529 (1965).
10. Wei-Mei Shyu, G.D. Gaspari, Phys. Rev. 163, 667 (1967).
11. A.O.E. Animalu, V. Heine, Phil. Mag. 12, 1249 (1965).
12. Wei-Mei Shyu, G.D. Gaspari, Phys. Rev. 170, 687 (1968).
13. N.W. Ashcroft, Phys. Letters 23, 48 (1966).
14. J.J. Paciga, D.L. Williams, Can. J. Phys. 49, 3227 (1971).
15. R. Pick, CEA (France) Rep. No. CEA-R-2820 (1965).
16. L. Dagens, Mark Rasolt, Roger Taylor, Phys. Rev. B 11, 2726 (1975).
17. Mark Rasolt, Roger Taylor, Phys. Rev. B 11, 2717 (1975).
18. V. Bortolani, G. Pizzichini, Phys. Rev. Lett. 22, 840 (1969).
19. D.L. Price, K.S. Singwi, M.P. Tosi, Phys. Rev. B 8, 2983 (1970).
20. P.L. Srivastava, N. Mishra, Phys. Lett. A 46, 219 (1973).

21. P.L. Srivastava, N.R. Mitra, N. Mishra, J. Phys. F 3, 1388 (1973).

22. M.M. Beg, M. Nielsen, Phys. Rev. B 14, 4266 (1976).

23. D.C. Wallace, Thermodynamics of Crystal (Wiley, New York, 1972).

24. D.C. Wallace, Reviews Mod. Phys. 37, 57 (1965).

25. C.J. Pethick, Phys. Rev. B 2, 1789 (1970).

26. J.C. Upadhyaya, Proc. R. Soc. Lond. A 356, 345 (1977).

# CHAPTER 2

# BACKGROUND THEORY

## 2.1 Introduction

The main interests in this chapter are the calculation of the ground state energy of a static lattice from which the bulk modulus may be calculated by the method of homogeneous deformations, and the calculation of the frequencies of lattice vibrations from which the bulk modulus may be calculated by the method of long waves. To begin, an outline of the pseudopotential theory of simple metals in the local approximation is given, and the total ground state energy of a metallic crystal is calculated to second order in the electron-ion interaction pseudopotential. This ground state energy is differentiated twice with respect to volume to find the static method expression for the bulk modulus. The main points in the conventional lattice dynamical theory of Born and von Karman as well as the self-consistent concept are stated and the expressions for the frequencies of lattice vibrations both in the quasiharmonic and in the self-consistent harmonic approximation are given. This chapter concludes with a brief discussion of anharmonic phonons.

### 2.2.1 Theory of Metals

We consider a metallic solid of volume $\Omega$ containing N closed shell ions arranged in a primitive lattice in the electron subsystem formed by the ZN conduction electron, where Z is the valency of the material. More specifically we will be considering cubic materials. The conduction electrons are regarded as free to a first approximation, and the total interaction potential experienced by the conduction electrons at some point in the crystal in the potential field of all the electrons and that of the ions is represented by a pseudopotential which is regarded as a perturbation of the free electron gas.

In the adiabatic approximation the total crystal potential energy splits into an ion-ion potential $W_I$ and an electron gas potential $W_G$. The contributions to $W_G$ are the Coulomb interaction between the conduction electrons and $W_B(r)$ the potential energy due to all the ions in the system. We can write

$$W_B(r) = \sum_{\ell} w_B(|r - R_\ell|) \tag{2.1}$$

where $w_B(r)$ is the potential of a conduction electron at the point r due to a single bare ion placed at the origin. One of the major approximations of pseudopotential theory is the self-consistent field approximation.[1] In this approximation the Coulomb interaction between the electrons is replaced by a self-consistent or screening field $W_s(r)$ which is the same for each conduction electron. When this is done the total Hamiltonian for the conduction electrons is the sum of single particle Hamiltonians and we therefore have a single particle theory. A second major approximation made in the theory is the small core approximation. The electron states in the crystal are divided into conduction band states and core states. The ion cores are assumed to be small, do not overlap or touch and they interact directly through a central force potential the most important part of which is the Coulomb force. They also look essentially the same in the solid as in the free atom and hence they can be described by atomic wave functions. Herring[2] pointed out that $|\alpha\rangle$ the wave function of the core states and $\psi_k$ that of the conduction band states are orthogonal. This means that $\psi_k$ may be expanded in plane waves which are orthogonalized to the core states. When this is done we find that we can replace the wave equation of the single electron Hamiltonians by the pseudopotential equation

$$(\hat{T} + \hat{W})\phi_k = \varepsilon_k \phi_k \qquad (2.2)$$

In this equation $\phi_k$ is the pseudowavefunction which replaces the conduction electron wave function $\psi_k$, $\hat{W}$ the pseudopotential which replaces $W_G$, $\varepsilon_k$ is the exact single electron energy eigenvalue and $\hat{T}$ is the kinetic energy. The third major approximation of pseudopotential theory is to regard $\hat{W}$ as small compared to the kinetic energy $\hat{T}$ and this enables perturbation theory to be used.

The ground state energy of a conduction electron in state k calculated to second order in the pseudopotential is

$$\varepsilon_k = e_k + \underset{q \to o}{Lt} \langle k + q|\hat{W}(r)|k\rangle + \sum_q{}' \frac{\langle k + q|\hat{W}|k\rangle\langle k|\hat{W}|k + q\rangle}{e_k - e_{k+q}} \qquad (2.3)$$

where $e_k = \frac{\hbar^2 k^2}{2m}$ is the energy eigenvalue for a free particle in the state $|k\rangle$. The pseudowavefunction $\phi_k$ correct to first order in W is found to be

$$\phi_k = |k\rangle + \sum_q{}' C(q,k)|k + q\rangle \qquad (2.4)$$

where the expansion coefficients C(q,k) are given by

$$C(q,k) = \frac{\langle k + q|\hat{W}|k\rangle}{e_k - e_{k+q}} \qquad q \neq o \qquad (2.5)$$

$$= 1 \qquad q = o$$

The operator $\hat{W}$ has matrix elements $\langle k + q|W(r)|k\rangle$ which factorize into a structure factor and a form factor. The structure factor S(q) is defined by

$$S(q) = \frac{1}{N} \sum_{\ell} e^{-iq.R_{\ell}} \qquad (2.6)$$

and is a function which depends only on the detailed positions of the ions. The form factor $\langle k + q|w(r)|k\rangle$ depends only on the potential field of the individual ions and is independent of their positions. In the case of local pseudopotentials to which we confine ourselves here, W(r) is simply a function of position and the form factor becomes the Fourier transform of the simple ion potential.

$$\begin{aligned} W(q) &= \langle k + q|W(r)|k\rangle \\ &= S(q)w(q) \end{aligned} \qquad (2.7)$$

where the form factor is given by $w(q)=\frac{1}{\Omega_o}\int w(r)e^{-iq.r}dr$

and $\Omega_o=\Omega/N$ is the volume per atom.

The total ground state energy of the ZN electrons is the sum over all occupied states of the one electron energies $\varepsilon_k$, minus a correction for double counting. This double counting is always present in self-consistent calculations. In this case it arises because the energy of each conduction electron is calculated in the potential field of the ions and all the electrons, so that the Coulomb interaction between any pair of electrons A and B say, is counted when the energy of electron A is calculated and again when calculating the energy of electron B. This means that an energy equal to the electron-electron Coulomb interaction energy has to be subtracted from the sum over occupied states to get $W_G$

$$W_G = \sum_{k<k_f} e_k + \mathop{\mathrm{Lt}}_{q\to o} \sum_{k<k_f} W(q) + \sum_{k<k_f} \sum_q{}' \frac{|W(q)|^2}{e_k - e_{k+q}} - \tfrac{1}{2}\int \rho(r) W_s(r)\,dr \qquad (2.8)$$

where $k_f$ is the Fermi wave vector and $\rho(r)$ is the electron density at the point r. The overcounting correction can also be written in the form [3]

$$\begin{aligned} \tfrac{1}{2}\int \rho(r) W_s(r)\,dr &= \frac{\Omega}{2}\sum_q \rho(q) W_s(q) \\ &= \frac{\Omega}{2}\rho(o) W_s(o) + \sum_q{}' \frac{\Omega}{2}\rho(q) W_s(q) \end{aligned} \qquad (2.9)$$

The first term in (2.8) gives the average kinetic energy of the NZ electrons in the system

$$\sum_{k<k_f} e_k = NZ\frac{3}{5}e_{k_f} \tag{2.10}$$

The second term in (2.8) is combined with the q=o part of the overcounting correction to give

$$NZ\{w(q=o) - \frac{\Omega_o}{2Z}\rho(q=o)w_s(q=o)\} \tag{2.11}$$

The third term in (2.8) is combined with the q≠o part of the overcounting correction to give the total second order contribution to the electron gas energy viz $\phi_{bs}$ the band structure energy. To combine these terms we first calculate $\rho(r)$ the electron gas density using equation (2.4) for the wavefunction of the conduction electron, and express this in terms of its Fourier components. We find that $\rho(o)=Z/\Omega_o$ and also that

$$-\frac{\Omega}{2}\sum_q{}' \rho(q)W_s(q) = -\sum_{k<k_f}\sum_q{}' \frac{W(q)W_s(-q)}{e_k - e_{k+q}} \tag{2.12}$$

From equations (2.8), (2.9) and (2.12) we can write the band structure energy in the form

$$\phi_{bs} = \sum_{k<k_f}\sum_q{}' \frac{W(q)\{W(-q) - W_s(-q)\}}{e_k - e_{k+q}} \tag{2.13}$$

$$\phi_{bs} = -N\sum_q{}' |S(q)|^2 \frac{\Omega_o q^2}{8\pi e^2} w_B(q)w(q)\{\varepsilon(q) - 1\}$$

where $\varepsilon(q)$ is the static dielectric function given by

$$\varepsilon(q) = 1 + \frac{2k_f me^2}{\pi\hbar^2 q^2}\{1 + \frac{4k_f^2 - q^2}{8k_f q}\ell n \left|\frac{2k_f + q}{2k_f - q}\right|\} \tag{2.15}$$

$$= 1 + \frac{4\pi e^2}{q^2}\Pi_o(q)$$

where $\hbar$ is Planck's constant, m the electron mass and e the electronic charge. This equation also defines the function $\Pi_o(q)$.

The total field seen by a conduction electron is the sum of that due to the bare ions $W_B(r)$ and the self-consistent field $W_s(r)$ whose effect is to screen the bare ion potential. In the Hartree approximation which neglects exchange and correlation in the gas, the Fourier transform of the screened interaction is linearly related to the total potential.

$$W(q) = W_B(q)/\varepsilon(q) \tag{2.16}$$

The use of this relation enables us to write the contribution of the electron gas to the total ground state energy in the form

$$W_G = N\{Z\frac{3}{5}e_{k_f} + Z[w(q=o) - \frac{w_s}{2}(q=o)] + \sum_q{}' |S(q)|^2 F(q)\} \qquad (2.17)$$

where the energy wave number characteristic F(q) is given by

$$F(q) = -\frac{\Omega_o q^2}{8\pi e^2}|W_B(q)|^2 \frac{(\varepsilon(q) - 1)}{\varepsilon(q)} \qquad (2.18)$$

The total Hartree wave function for the conduction electrons in the ground state is

$$\Psi = \hat{A}_k \Pi \phi_k \qquad (2.19)$$

where $\hat{A}$ is an antisymmetrization operator. This antisymmetrization of the wave function introduces exchange interactions into the electron system and these have to be taken into account. The above discussion has also not taken into account correlation effects in the system. Now, if all the effects of exchange and correlation are approximated by one electron potentials $W_x(r)$[3], then we can write the total potential experienced by a conduction electron at a given point in the form

$$
\begin{aligned}
W(q) &= W_B(q) + W_s(q) + W_x(q) \\
&= W_B(q) + W_s(q)(1 - Y(q)) \qquad (2.20) \\
&= W_B(q) + W_{sx}(q)
\end{aligned}
$$

The function $Y(q)$ takes into account the effects of exchange and correlation in the electron gas and is zero if they are neglected. $W_B(q)$ now includes exchange and correlation effects between the core electrons and the conduction electrons, and also $e_k$ in equation (2.8) includes the exchange and correlation energies of a uniform electron gas. This inclusion of exchange and correlation modifies (2.10) to

$$NZ\{\tfrac{3}{5}e_{k_f} + e_x + e_c\} \qquad (2.21)$$

where $e_x$ and $e_c$ are the exchange and correlation energies per electron for a uniform electron gas. Instead of (2.11) we now have

$$NZ\{w(q=o) - \tfrac{1}{2}w_{sx}(q=o)\} \qquad (2.22)$$

The energy wave number characteristic is still given by equation (2.18) except that the dielectric function $\varepsilon(q)$ now has to include exchange and correlation effects. Hubbard[4] has shown that these can be included by writing

$$\varepsilon(q) = 1 + \frac{4\pi e^2}{q^2}\Pi(q) \tag{2.23}$$

where
$$\Pi(q) = \frac{\Pi_o(q)}{1 - \frac{4\pi e^2}{q^2}Y(q)\Pi_o(q)} \tag{2.24}$$

Several versions of the function $\phi(q)=Y(q)/q^2$ have appeared in the literature.[5-7] In the original Hubbard approximation $\phi(q)$ was given by $(q^2 + k_f^2)/2$ but the most useful version is that of Geldart and Vosko[8] who wrote

$$\phi(q) = \frac{1}{2(q^2 + \xi k_f^2)} \tag{2.25}$$

where $\xi$ is chosen to satisfy the compressibility theorem. There have also appeared in the literature other calculations of the dielectric constant beyond the Hubbard approximation. These however, do not have analytic expressions which are valid for the entire range of q and as a result the

Geldart-Vosko formula is still extensively used. Another formula for $\phi(q)$ which is simpler than the Hubbard expression has been proposed by Taylor.[9] He treats $\phi(q)$ as a constant and determines its value by requiring it to satisfy the compressibility theorem. This approximation is equivalent to the Kohn and Sham approximation for exchange and correlation in the gradient expansion of the electron density.[10] He arrives at the expression

$$\phi(q) = (1 + 0.153)/4k_f^2 \tag{2.26}$$

where $\lambda = (\pi a_o k_f)^{-1}$, $a_o$ is the Bohr radius, and $k_f$ the Fermi wave vector.

### 2.2.2 Total Ground State Energy

To complete the calculation of the ground state energy of the crystal we have to add to $W_G$ the direct interaction energy of the ions. Since the ions are assumed to be small non-polarizable and non-overlapping, their direct interaction is a Coulombic interaction between sets of point charges at lattice points. It is convenient to write this energy in two parts and use the Ewald-Fuchs transformation.[11] We then have

$$W_I = \frac{2\pi Z^2 e^2}{\Omega} \sum_q \frac{e^{-q^2/4\eta^2}}{q^2} \sum_{\ell\ell'}' e^{iq.R_{\ell\ell'}} + \tag{2.27}$$

$$\frac{Z^2 e^2}{2} \sum_{\ell\ell'}' \frac{1}{R_{\ell\ell'}} \operatorname{erfc}(\eta R_{\ell\ell'})$$

where the complementary error function is defined by

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-y^2} dy$$

In the first term of (2.27) we add the $\ell=\ell'$ term and subtract it in the form $NZ^2e^2\eta/\sqrt{\pi}$, we also write the q=o term separately. Equation (2.27) becomes

$$W_I = \frac{2\pi Z^2 e^2}{\Omega} \sum_q' \frac{e^{-q^2/4\eta^2}}{q^2} \sum_{\ell\ell'} e^{iq.R_{\ell\ell'}} +$$

$$\frac{Z^2 e^2}{2} \sum_{\ell\ell'}' \frac{1}{R_{\ell\ell'}} \operatorname{erfc}(\eta R_{\ell\ell'}) - \frac{NZ^2e^2\eta}{\sqrt{\pi}} + \tag{2.28}$$

$$\underset{q\to o}{\mathrm{Lt}}\; 2\pi Z^2 e^2 \frac{e^{-q^2/4\eta^2}}{q^2} \sum_{\ell\ell'} \frac{e^{iq.R_{\ell\ell'}}}{\Omega}$$

we have

$$\frac{1}{\Omega}\sum_{\ell\ell'} e^{iq.R_{\ell\ell'}} = \frac{1}{N\Omega_o}\,\frac{N}{N}\sum_{\ell} e^{iq.R_{\ell}}\,\frac{N}{N}\sum_{\ell'} e^{-iq.R_{\ell'}} \tag{2.29}$$

$$= \frac{N}{\Omega_o} S(q)S(-q) \tag{2.30}$$

$$\operatorname*{Lt}_{q\to o} 2\pi Z^2 e^2 \frac{e^{-q^2/4\eta^2}}{q^2}\frac{N}{\Omega_o}|S(q)|^2 = \operatorname*{Lt}_{q\to o}\frac{2\pi Z^2 e^2}{q^2}\frac{N}{\Omega_o} - \frac{2\pi Z^2 e^2 N}{4\Omega_o \eta}$$

We now add the q=o terms from the electron gas energy and the ion-ion energy

$$NZ\{w(q=o) - \tfrac{1}{2}w_s(q=o)(1 - Y(q=o))\} + \operatorname*{Lt}_{q\to o}\frac{2\pi Z^2 e^2 N}{q^2\Omega_o}$$

$$= \operatorname*{Lt}_{q\to o} NZ\{[w_B(q) + w_{sx}(q) - \tfrac{1}{2}w_{sx}(q)] + \frac{2\pi Ze^2}{q^2\Omega_o}\} \tag{2.31}$$

$$= \operatorname*{Lt}_{q\to o} NZ\{w_B(q) + \frac{2\pi Ze^2}{q^2\Omega_o}\}$$

where equations (2.20), (2.25) and the Poisson equation $W_s(q)=\frac{4\pi e^2}{q^2}\rho(q)$ have been used to arrive at the last formula.

The bare ion potential $w_B(r)$ is a Coulomb interaction outside the small region of the ion core. It also has a contribution localized in the core region so that

$$w_B(q) = -\frac{4\pi Ze^2}{q^2\Omega_o} + w_c(q=o) \tag{2.32}$$

We can now write the total ground state energy for the metal in the form

$$= NZ[\tfrac{3}{5}e_{k_f} + e_x + e_c + w_c(q=o)] -$$

$$NZ^2e^2\{\frac{\eta}{\pi} + \frac{\pi}{2\eta^2\Omega_o}\} + N\sum_q{}' |S(q)|^2 F(q) +$$

$$N\sum_q{}' |S(q)|^2 \frac{e^{-q^2/4\eta^2}}{q^2}\frac{2\pi Z^2e^2}{\Omega_o} + \frac{NZ^2e^2}{2}\sum_\ell{}' \frac{1}{R_\ell}\operatorname{erfc}(\eta R_\ell) \tag{2.33}$$

$$= \Phi_o + \Phi_{Ew} + \Phi_{bs} \tag{2.34}$$

where $\Phi_o$ comes from the first two terms in (2.33) and is independent of structure, and $\Phi_{Ew}$ the Ewald energy is from the last two terms.

Equation (2.33) is convenient for calculation purposes because the Ewald convergence factor $\eta$ can be chosen to optimize the convergence of the real space and Fourier space sums in the Ewald energy. To work entirely in Q-space we write the ion-ion Coulomb interaction energy in the form

$$W_I = \tfrac{1}{2}\sum_{\ell\ell'}{}' \frac{Z^2e^2}{r_{\ell\ell'}} \tag{2.35}$$

$$= \frac{Z}{2}\sum_{\ell\ell'}{}' v(r)$$

$$W_I = \frac{Z}{2\Omega}\sum_{\ell\ell'}{}' \sum_q e^{iq\cdot r} v(q) \tag{2.36}$$

where $v(r) = \frac{1}{\Omega}\sum_q e^{iq\cdot r} v(q)$

In this way the ion-ion energy is written as a Fourier sum, and since the R-space sum in (2.33) comes from this contribution the total energy will then involve sums in Q-space only. This is equivalent to letting $\eta\to\infty$ in (2.33). It can be shown that

$$\underset{\eta\to\infty}{\mathrm{Lt}} \sum_{\ell}{}' \mathrm{erfc}(\eta R_\ell)/R_\ell = \underset{\eta\to\infty}{\mathrm{Lt}}\ \eta/2\sqrt{\pi} \tag{2.37}$$

hence

$$\underset{\eta\to\infty}{\mathrm{Lt}}\ \frac{NZ^2e^2}{2}\sum_{\ell}{}' \operatorname{erfc}(\eta R_\ell)/R_\ell \ -\ NZ^2e^2\{\frac{\eta}{\sqrt{\pi}} + \frac{\pi}{2\eta^2\Omega_o}\} = 0 \qquad (2.38)$$

The total energy becomes

$$\Phi = NZ\{\tfrac{3}{5}e_{k_f} + e_x + e_c + w_c(q{=}o)\} + N\sum_q{}' |S(q)|^2 G(q) \qquad (2.39)$$

where $G(q) = F(q) + \dfrac{2\pi Z^2 e^2}{\Omega_o q^2}$

In the real space formulation we retain (2.35) for the ion-ion energy and write the electron gas energy in the form

$$W_G = NZU_{eg} + \underset{q\to o}{\mathrm{Lt}}\ NZw_c(q) + N\sum_q{}' |S(q)|^2 F(q) \qquad (2.40)$$

$$= NZU_{eg} + \underset{q\to o}{\mathrm{Lt}}\ NZw_c(q) + \frac{N}{N^2}\sum_q{}' \sum_{\ell\ell'} e^{iq.R_{\ell\ell'}} F(q)$$

$$= NZU_{eg} + \underset{q\to o}{\mathrm{Lt}}\ NZw_c(q) + \tfrac{1}{2}\sum_{\ell\ell'}{}' \sum_q{}' e^{iq.R_{\ell\ell'}} \frac{2}{N}F(q) + \sum_q{}' F(q)$$

$$\Phi = \{NZU_{eg} + \sum_q{}' F(q) + \underset{q\to o}{Lt}\, NZw_c(q)\} +$$

$$\tfrac{1}{2}\sum_{\ell\ell}\{\frac{Z^2e^2}{R_{\ell\ell'}} + \frac{2}{N}\sum_q{}' e^{iq.R_{\ell\ell'}} F(q)\} \qquad (2.41)$$

where $U_{eg} = \frac{3}{5}e_{k_f} + e_x + e_c$

To conclude this section we note that in the band structure energy we have F(q) which has the explicit volume dependence $\Omega_o{}^{-1}$ because $w_B(q)$ is proportional to $\Omega_o{}^{-1}$, it also depends on volume through q and through the Fermi wave vector $k_f$ contained in the screening function.

## 2.3 Bulk Modulus by Differentiation of the Energy

The adiabatic bulk modulus $B^S$ is obtained as the second volume derivative of the thermodynamic state function U, the internal energy. That is

$$B^S = \Omega\frac{d^2U}{d\Omega^2} \qquad (2.42)$$

The isothermal bulk modulus $B^T$ is similarly defined but in terms of the Helmholtz free energy F. The bulk moduli are related to the isothermal and adiabatic elastic constants which appear as strain derivatives of the free energy and the internal energy respectively. The thermodynamic functions U and F are invariant under rotations and translations of the crystal. These invariance conditions together with the symmetry requirements of the crystal place restrictions on the elastic constants. In cubic materials there are three independent elastic constants viz $C_{11}$, $C_{12}$ and $C_{44}$, and in terms of these bulk moduli are given by

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{2.43}$$

At $T=0^{o}K$ there is no difference between the isothermal and adiabatic elastic constants and between the corresponding bulk moduli. In particular in the potential approximation when the free energy or the internal energy are approximated by the total ground state energy $\phi$, the elastic constants are obtained as strain derivatives of the crystal potential. The bulk modulus is given by

$$B = \Omega\frac{d^2\phi}{d\Omega^2} \tag{2.44}$$

The total volume derivative is written in the form

$$\frac{d}{d\Omega} = \{\frac{\partial}{\partial\Omega_o} + \frac{dk_f}{d\Omega_o}\frac{\partial}{\partial k_f} + \frac{dq^2}{d\Omega_o}\frac{\partial}{\partial q^2}\} \tag{2.45}$$

Then using the Pines Nozieres[12] formula for the exchange and correlation energy per electron for a uniform electron gas we find the contribution of the volume term $\phi_o$ in (2.34) to the bulk modulus per ion to be

$$B^o = \frac{Z}{\Omega_o}\{\frac{2}{3}e_{k_f} + \frac{4}{9}e_x - 0.01(Ry) + 2w_c(q=o)\} - \frac{Z^2e^2\pi}{\Omega_o^2\,\eta^2} \tag{2.46}$$

where $B^o\Omega_o$ is in Rydbergs. The contribution of the R-space part of the Ewald energy is

$$B^R = \frac{Z^2e^2}{\Omega_o}\{\frac{2}{9}\sum_\ell{}'\phi''(R_\ell)R_\ell{}^4 - \frac{1}{9}\sum_\ell{}'\phi'(R_\ell)R_\ell{}^2\} \tag{2.47}$$

where $\phi'(R) = \dfrac{d\phi(R)}{dR^2}$

$$\phi''(R) = \frac{d^2\phi(R)}{d(R^2)^2}$$

and $\phi(R) = \mathrm{erfc}(\eta R)/R$

The total contribution from the Fourier sums is found to be

$$B^Q = \frac{1}{\Omega_o} \sum_\tau{}' \{2G(\tau) + \frac{22}{9}\tau^2 G'(\tau) + \frac{4}{9}\tau^4 G''(\tau)\} + \Delta_{bs} \qquad (2.48)$$

where $G(q) = F(q) + \frac{2\pi Z^2 e^2}{\Omega_o} \frac{e^{-q^2/4\eta^2}}{q^2}$

and $$\Delta_{bs} = \frac{1}{\Omega_o} \sum_\tau \{\frac{10k_f}{9} \frac{\partial F(\tau)}{\partial k_f} + \frac{k_f^2}{9} \frac{\partial^2 F(\tau)}{\partial k_f^2} + \frac{2\tau k_f}{9} \frac{\partial^2 F(\tau)}{\partial \tau \partial k_f}\} \qquad (2.49)$$

The total bulk modulus is given by

$$B = B^O + B^R + B^Q \qquad (2.50)$$

Although equation (2.50) and (2.33) from which it is derived are convenient for purposes of numerical calculations they do not show the role of the volume terms $\phi_o$ and $B^O$. To clarify the role of the volume term in the bulk modulus we follow Finnis[13] who writes the total energy $\Phi$ in the real spaces formulation (2.41) in the form

$$\Phi = U(\Omega) + \frac{1}{2N} \sum_{\ell\ell'}{}' \phi(R_{\ell\ell'}, \rho) \qquad (2.51)$$

where the pair potential is written as $\Phi(R,\rho)$ to emphasize the fact that it depends on the average density $\rho$ of the electrons. The total volume derivations is written as

$$\frac{d}{d\Omega} = \frac{\partial}{\partial\Omega} + \frac{\partial}{\partial\Omega_{sc}}$$

where $\partial/\partial\Omega_{sc}$ operates on the implicit volume dependence of the screening function while $\partial/\partial\Omega$ operates on the remaining explicit volume dependence. The bulk modulus B is given by

$$B = \Delta_{bs} + \frac{\Omega\partial^2}{\partial\Omega^2}\{\frac{1}{2N}\sum_{\ell\ell'}{}' \Phi(R_{\ell\ell'}\rho)\} \tag{2.52}$$

This result which was obtained by Finnis shows that the contribution of the volume term $U(\Omega)$ to the bulk modulus is to a large extent cancelled by similar terms arising from the volume dependence of the pair interaction. There is however a term $\Delta_{bs}$ which is not cancelled, and it is this term which is omitted when the bulk modulus or the longitudinal elastic constants are calculated by the method of long waves.

## 2.4 Lattice Dynamics

In calculating the ground state energy of the crystal in section 2.2 the ions were assumed to be stationary. In a real crystal and at all temperatures, the atoms are always in a state of continual motion therefore the Hamiltonian of the system is the sum of the kinetic energy of the ions and the potential energy of the system. When the vibrational amplitudes of the ions are not large the crystal potential $\Phi$ can be expanded in a Taylor series in powers of the displacements $U_\alpha(\ell,t)$ of the ions from their equilibrium positions $R(\ell)$. In the Born Oppenheimer approximation the energy of the vibrating crystal is given at any time t by the energy of the static lattice structure in which the positions of the atoms are given by $\underline{R}(\ell,t)=\underline{R}(\ell)+\underline{U}(\ell,t)$ for that value of t plus the kinetic energy of the ions. The vibrational frequency of the lattice can then be calculated if the change in energy due to the static distortion of the lattice introduced by the ion displacements $\underline{U}(\ell,t)$ is known.

### 2.4.1 Quasiharmonic Approximation

In the harmonic approximation the series expansion of the crystal potential is terminated after terms of second order in the ion displacements, and the resulting quadratic Hamiltonian is solved for the normal vibrational modes.[14] When the temperature of the crystal is increased the lattice expands and the expansion of the crystal potential has to be made about a new equilibrium position, we then have a quasiharmonic treatment and it provides an account of the variation of the frequencies with volume.[15] The frequencies of the vibrational modes of the crystal or of the phonons which describe travelling waves through the crystal are calculated from the eigenvalue equation

$$\omega^2(kj) = \sum_{\alpha\beta} \varepsilon_\alpha(kj) D_{\alpha\beta}(k) \varepsilon_\beta(kj) \tag{2.53}$$

where the polarization vectors $\varepsilon_\alpha(kj)$ are usually chosen to be orthonormal. $\omega(kj)$ is the frequency of a phonon of wave vector k when it vibrates in mode $j(=1,2,3)$, and $\alpha$ and $\beta$ are Cartesian indices. The dynamical matrix $D_{\alpha\beta}(k)$ is given by

$$D_{\alpha\beta}(k) = \frac{1}{M}\sum_{\ell} \Phi_{\alpha\beta}(\ell,o)\, e^{-ik.R_\ell} \tag{2.54}$$

where M is the mass of each ion. The force constants $\Phi_{\alpha\beta}(\ell,o)$ describe the change in the total potential of the crystal $\Phi$ which results from the displacements $U_\alpha(\ell)$ and $U_\beta(o)$ while all the other ions are held stationary, and they satisfy the translational invariance condition.

$$\sum_{\ell} \Phi_{\alpha\beta}(\ell,o) = 0 \tag{2.55}$$

Using this expression in the case of a potential which can be written as a sum over pair interactions, we arrive at the following formula for the dynamical matrix

$$D_{\alpha\beta}(k) = \frac{1}{M}\sum_{\ell}{}' (e^{-ik.R_\ell} - 1)\nabla_\alpha(\ell)\nabla_\beta(o)V_{II}(r) \tag{2.56}$$

where $V_{II}(r)$ is the pair interaction potential.

For the purposes of lattice dynamics the only relevant part of the total ground state energy calculated in equation (2.33) is the structure dependent part, this is because a lattice wave is a rearrangement of the atoms while the macroscopic volume of the crystal remains unchanged. It is evident from equation (2.33) that the structure dependent part of the energy has a part which is simply a function of the positions of the ions and another which involves a Fourier sum. As a result the dynamical matrix can also be written as the sum of two parts one of which is conveniently evaluated in Q-space while the other is evaluated in R-space

$$D_{\alpha\beta}(k) = D^R_{\alpha\beta}(k) + D^Q_{\alpha\beta}(k) \tag{2.57}$$

where

$$D^R_{\alpha\beta}(k) = \frac{1}{M}\sum_{\ell}{}' (e^{-ik.R_\ell} - 1)\nabla_\alpha(\ell)\nabla_\beta(o)\frac{Z^2e^2}{R_\ell}\,\mathrm{erfc}(\eta R_\ell) \tag{2.58}$$

and

$$D^Q_{\alpha\beta}(k) = \frac{2}{M}\sum_{\tau} G(|\tau + k|)(\tau + k)_\alpha(\tau + k)_\beta - \frac{2}{M}\sum_{\tau}{}' \tau_\alpha \tau_\beta G(\tau) \quad (2.59)$$

is a reciprocal lattice vector and the function $G(q)$ was introduced in equation (2.48).

## 2.4.2 Self-Consistent Phonons

If a solid is only weakly anharmonic then its dynamics can be successfully treated using perturbation theory in which the harmonic term is treated exactly while the cubic and quartic terms in the expansion of the potential are treated as perturbations. But when the displacements of the atoms from their equilibrium positions are not small as would be the case in metals at high temperatures, then the treatment of the motion of the atoms in an approximation in which all the other equivalent atoms are held stationary is no longer a good approximation, and self-consistent methods have to be used. The self-consistent concept is that the forces on the atom of interest should rather be derived by regarding the other atoms as moving equivalently to the atom of interest.[16-18] This in turn means that the force constants $\Phi_{\alpha\beta}(\ell,o)$ have to be thermodynamically averaged over the vibrational distributions of the atoms.

The lowest order approximation in the self-consistent phonon theory is the self-consistent harmonic (SCH) approximation in which the idea is to find an effective harmonic Hamiltonian that best approximates the crystal Hamiltonian. Whereas in the QH approximation the frequencies are obtained by solving the harmonic Hamiltonian

$$H_h = \frac{1}{2M} \sum_{\ell} p^2(\ell,t) + \tfrac{1}{2} \sum_{\alpha\beta} U_\alpha \cdot \Phi_{\alpha\beta} \cdot U_\beta$$

in the SCH approximation the harmonic Hamiltonian is

$$H_s = \frac{1}{2M} \sum_{\ell} p^2(\ell,t) \quad \tfrac{1}{2} \sum_{\alpha\beta} U_\alpha \cdot \Pi_{\alpha\beta} \cdot U_\beta$$

and the force constants matrix $\Pi_{\alpha\beta}$ is determined variationally. It turns out that the best choice for the force constants is given by the thermal average of the equilibrium force constants $\Phi_{\alpha\beta}$ hence the effective Hamiltonian can be written in the form

$$H_s = \frac{1}{2M} \sum_{\ell} p^2(\ell,t) + \tfrac{1}{2} \sum_{\ell\ell'} \sum_{\alpha\beta} \langle \Phi_{\alpha\beta}(\ell\ell') \rangle U_\alpha(\ell,t) U_\beta(\ell',t)$$

The averaging of the force constants $\langle \Phi_{\alpha\beta}(\ell\ell') \rangle$ is taken with respect to the exact SCH frequencies $\Omega(kj)$ which are still obtained from the eigenvalue equation

$$\Omega^2(kj) = \sum_{\alpha\beta} \varepsilon(kj) D_{\alpha\beta}(k) \varepsilon_\beta(kj) \tag{2.60}$$

where the dynamical matrix is now given by

$$D_{\alpha\beta}(k) = \frac{1}{M} \sum_{\ell}{}' \left(e^{-ik.R_\ell} - 1\right) \langle \nabla_\alpha(\ell) \nabla_\beta(o) V_{II}(r) \rangle$$

Although the lowest order SCH theory equations which have to be solved by iteration are most easily derived by variational principles, when higher order terms are included the variational principle is lost. The most general method of calculating the self-consistent frequencies is via the use of many-body perturbation theory of the thermodynamic Green functions.[19-21]

The use of a harmonic Hamiltonian means that the vibrational distribution of the atoms is Gaussian. Hence the averaging can be effected by using Gaussian wavefunctions. The force constants are given by

$$\langle \nabla_\alpha(\ell) \nabla_\beta(\ell') V_{II}(r) \rangle = \{(2\pi)^2 \det\Lambda\}^{-\frac{1}{2}} \int d^3u \, \exp(-\tfrac{1}{2}u.\Lambda^{-1}u) \times$$

$$\nabla_\alpha(\ell) \nabla_\beta(\ell') V_{II}(r) \tag{2.61}$$

and the width of the Gaussian distribution is

$$\Lambda_{\alpha\beta}(\ell\ell') = \langle U_\alpha(\ell\ell')U_\beta(\ell\ell')\rangle$$

$$= \frac{\hbar}{MN}\sum_{kj}(1 - e^{-ik.R_{\ell\ell'}})\varepsilon_\alpha(kj)\varepsilon_\beta(kj) \times$$

$$\coth(\tfrac{1}{2}\beta\hbar\Omega(kj))/\Omega(kj) \qquad (2.62)$$

$U(\ell\ell')=U(\ell) - U(\ell)$ is the relative vibrational amplitude, $\hbar$ is Planck's constant and $\beta=(K_BT)^{-1}$ where T is the temperature and $K_B$ the Boltzmann's constant.

### 2.4.3 Anharmonic Phonons

In the self-consistent phonon theory the Hamiltonian is split into a harmonic and an anharmonic part. The total anharmonic part is usually broken up into terms which introduce interactions between a particular number of phonons, the harmonic part leads to noninteracting phonons and it includes all even anharmonic terms that would appear in a first order perturbation evaluation of the anharmonic shift to the QH frequencies. Of these the leading one is the quartic term representing a four-phonon process to first order. The leading correction to the SCH approximation in perturbation theory is the cubic anharmonic term which represents a three-phonon process to second order, and this can simply be added as a perturbation to the SCH frequencies. With the inclusion of the cubic anharmonic term the dynamical independence of the different lattice modes becomes destroyed and the phonon interactions lead to finite lifetimes.

Experimentally the phonon frequencies are determined by scattering thermal neutrons from a crystal. The incoming beam of neutrons excites mostly single phonons whose frequency is to be measured. When this is the case the scattering function $S(Q,\omega)$ for momentum transfer $\hbar Q$ has a maximum at energy transfer $\hbar\omega$ equal or near the energy of the phonon excited, hence the energies of the phonons are identified with the positions of the resonances in the scattering cross section or in the response function $A(Q\lambda,\omega)$ of the crystal which appears in the scattering function.

The total scattering function $S(Q,\omega)$ includes contributions from single and multiple phonons excited by the incoming neutron as well as interference effects between the phonons. Thus we can write

$$S(Q,\omega) = S_1 + S_2 + S_{12} + S_3 + \ldots \tag{2.63}$$

where $S_1$, $S_2$ and $S_3$ are the contributions of one, two and three phonons respectively and $S_{12}$ represents the interference between $S_1$ and $S_2$. The properties of interference between one and multiphonon contributions to the scattering function $S(Q,\omega)$ have been discussed by Glyde.[22] In this work only the first three terms in (2.63) are included in the calculation of $S(Q,\omega)$.

## REFERENCES


1. W.A. Harrison, Pseudopotentials in the Theory of Metals (Benjamin, New York, 1966).
2. C. Herring, Phys. Rev. 57, 1169 (1940).
3. D.C. Wallace, Thermodynamics of Crystals (Wiley, New York, 1972).
4. J. Hubbard, Proc. Roy. Soc. A 243, 336 (1957).
5. L.J. Sham, Proc. Roy. Soc. A 283, 33 (1965).
6. V. Heine, I.V. Abarenkov, Phil. Mag. 9, 451 (1964).
7. R.W. Shaw, R. Pynn, J. Phys. C 2, 2071 (1969).
8. D.J.W. Geldart, S.H. Vosko, Can. J. Phys. 44, 2137 (1966).
9. R. Taylor, J. Phys. F 8, 1699 (1978).
10. W. Kohn, L.J. Sham, Phys. Rev. 140, A1133 (1965).
11. K. Fuchs, Proc. Roy. Soc. A 151, 585 (1935); 157, 444 (1936); P.P. Ewald, Ann. Phys. (Leipz) 64, 243 (1921).
12. P. Nozieres, D. Pines, Phys. Rev. 111, 442 (1958).
13. M.W. Finnis, J. Phys. F 4, 1645 (1974).
14. A.A. Maradudin, E.W. Montroll, G.H. Weiss, I.P. Ipatova, Solid State Phys. Suppl. 3, (1971).
15. R.A. Cowley, Reports on Prog. in Phys. 31, 123 (1968).
16. N. Gillis, N.R. Werthamer, T.R. Koehler, Phys. Rev. 165, 951 (1968).
17. G. Baym, Phys. Rev. 121, 741 (1961).
18. D.J. Hooton, Phil. Mag. 3, 49 (1958).
19. A.A. Maradudin, A.E. Fein, Phys. Rev. 128, 2589 (1962).
20. R.A. Cowley, Adv. Phys. 12, 421 (1963).

21. P.F. Choquard, The Anharmonic Crystal (Benjamin, New York, 1967).

22. H.R. Glyde, Can. J. Phys. 52, 2281 (1974).

# CHAPTER 3

# VOLUME FORCES IN SIMPLE METALS

## 3.1 Introduction

In this chapter we outline the derivation of the equation of propagation of elastic waves in a solid whose solutions give the relations between the elastic constants and the frequencies of the waves. Using these relations we calculate the bulk modulus by the method of long waves and compare the result with that obtained by the static method in the previous chapter. We also show that the R-space and the Q-space formulations of dynamics are equivalent. We generalize lattice dynamics to take into account the effect of volume forces which are usually omitted in conventional lattice dynamical theory, and we also present numerical calculations of these effects on the dispersion curves and the Cauchy relation made for a number of simple metals using three model pseudopotentials. Some results are also presented for the polyvalent metals Al and Pb.

### 3.2.1 Dynamics without Volume Forces

An expression for the bulk modulus in the potential approximation was derived by differentiation of the total ground state energy. The bulk modulus can also be calculated from dynamical equations using the method of long waves. The essence of the method is that when the wavelengths of the phonons in a crystal are long compared to the range of the interatomic forces, then the system may be regarded as a continuous elastic medium. The frequencies of the phonons in the limit of long waves must therefore be the same as those obtained from the equations of propagation of elastic waves in an elastic medium.

Elastic vibrations in a medium are set up as a result of the interplay of inertial forces and elastic restoring forces developed between neighbouring particles when the medium is deformed. The deformation of a material comes about when it changes from one configuration to another and strain is one measure of such a deformation. It has to be defined in such a way that it excludes rigid rotations and translations. Let $\vec{dL}$ be the initial separation of two

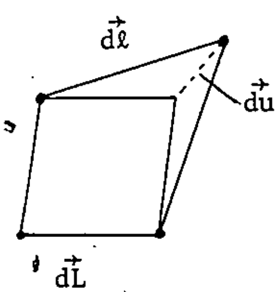



Fig. 1

particles in a solid, and $\vec{d\ell}$ be their separation after deformation, then the relative displacement

$$\vec{du} = \vec{d\ell} - \vec{dL}$$

is a measure of the deformations. In the linear approximation we can write in matrix notation

$$[d\vec{u}] = [D][dL] \tag{3.1}$$

where D is the displacement gradient matrix. This matrix can also be written as the sum of a symmetric strain matrix S which excludes rigid translations and rotations, and an antisymmetric matrix R which describes rotations in the crystal. The strain matrix can be written in the form[1]

$$[S] = \begin{bmatrix} \partial/\partial x & 0 & 0 \\ 0 & \partial/\partial y & 0 \\ 0 & 0 & \partial/\partial z \\ 0 & \partial/\partial z & \partial/\partial y \\ \partial/\partial z & 0 & \partial/\partial x \\ \partial/\partial y & \partial/\partial x & 0 \end{bmatrix} \begin{bmatrix} u_x \\ u_y \\ u_z \end{bmatrix}$$

$$S = \nabla_s \vec{u}$$

where $\nabla_s$ is the symmetric differential operator.

The energy of a crystal depends on its configuration, and if the crystal is strained, then its energy can be expanded in a Taylor series in powers of the strains. Starting with the expression for the change in the elastic energy of the crystal which has undergone a uniform dilation it can be shown that the bulk modulus defined by

$B = \dfrac{d^2\Phi}{d\Omega^2}$ is given by[2]

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{3.2}$$

The calculation of the bulk modulus by static methods thus leads to equation (3.2). In order to make connection with the bulk modulus calculated by dynamic methods we allow the displacements u in the crystal to be functions of time. This leads to the equation of propagation of elastic waves which in the limit to long wavelengths has the same solutions as the equations for harmonic phonons.

We now consider an element of volume $\delta v$ and surface area $\delta s$ within the crystal. The equation for translational motion is

$$\int_{\delta s} T\delta s = \int_{\delta v} \rho \frac{d^2 u}{dt^2}\, \delta v \tag{3.3}$$

where $\rho$ is the equilibrium density of the material within $\delta v$, T is the symmetric stress tensor. By using the divergence theorem we can write the equation of motion in the form

$$\nabla . T = \rho \frac{d^2 u}{dt^2} \tag{3.4}$$

We also use Hooke's law which states that for small deformations stress and strain are linearly related

$$T_{ij} = C_{ijk\ell}S_{k\ell}$$
$$T = C : S \tag{3.5}$$

We can now substitute for T in (3.5) in terms of the elastic constants $C_{ijk\ell}$ and the strain parameters $S_{k\ell}$, and also write the divergence operator in terms of the symmetric differential operator ($\tilde{\nabla}_s = \nabla.$) to get the equation of motion[1]

$$\tilde{\nabla}_s\{C:\nabla_s u\} = \rho\frac{d^2u}{dt^2} \tag{3.6}$$

This equation describes the propagation of a displacement wave in the crystal and it is the frequencies of such elastic waves which must be the same as those of phonons of long wavelengths. The latter are calculated from the dynamical matrix in (2.53). To find the relation between these frequencies and the elastic constants we assume plane wave solutions to (3.6) in the form $u=u_o \exp\{i(\omega t - k.r)\}$, where the wave vector k is along a symmetry direction. Substitution of this into the wave equation leads to expressions relating the density, elastic constants and frequencies for specified wave vectors. These expressions are[2]:

$$[qoo]\quad L\quad \omega^2\rho = C_{11}k^2$$

$$T\quad \omega^2\rho = C_{44}k^2$$

$$[qqo]\quad L\quad \omega^2\rho = \frac{k^2}{2}(C_{11} + C_{12} + 2C_{44})$$

$$T_1\quad \omega^2\rho = \frac{k^2}{2}(C_{11} - C_{12}) \qquad (3.7)$$

$$T_2\quad \omega^2\rho = k^2C_{44}$$

$$[qqq]\quad L\quad \omega^2\rho = \frac{k^2}{3}(C_{11} + 2C_{12} + 4C_{44})$$

$$T\quad \omega^2\rho = \frac{k^2}{3}(C_{11} + C_{44} - C_{12})$$

From these equations we find that a convenient expression for the bulk modulus is

$$B = (\omega^2_{L[qqq]} - \tfrac{4}{3}\omega^2_{T[qoo]}) \qquad (3.8)$$

<u>3.2.2 Bulk Modulus by Method of Longwaves</u>

In the method of long waves the dynamical matrix is expanded in powers of the phonon wave vector k up to second order and the frequencies are calculated from the eigenvalue equation (2.53). We write (2.59) in the form

$$D^{Q}_{\alpha\beta}(k) = \frac{2k_{\alpha}k_{\beta}}{M} G(|k|) + \frac{2}{M} \sum_{\tau}{}' \{G(|k + \tau|)(\tau + k)_{\alpha}(\tau + k)_{\beta} - \tau_{\alpha}\tau_{\beta}G(|\tau|)\} \tag{3.9}$$

A Taylor series expansion of $G(|\tau + k|)$ gives

$$G(|\tau + k|) = G(\tau) + G'(\tau) + G''(\tau)\frac{\Delta^{2}}{2} + \ldots$$

where $\Delta = 2\tau.k + k.k$. Hence up to order $k^2$

$$D^{Q}_{\alpha\beta}(k) = \frac{2k_{\alpha}k_{\beta}}{M}G(|k|) + \frac{2}{M} \sum_{\tau}{}' \{G(\tau)k_{\alpha}k_{\beta} + G'(\tau)[4(\tau.k)\tau_{\alpha}k_{\beta} + k^{2}\tau_{\alpha}\tau_{\beta}] + G''(\tau)2(\tau.k)^{2}\tau_{\alpha}\tau_{\beta}\} \tag{3.10}$$

By expanding the exponential in $D^{R}_{\alpha\beta}(k)$ we find that up to order $k^2$

$$D^{R}_{\alpha\beta}(k) = \frac{1}{M} \sum_{R}{}' \{2\phi'(R)\delta_{\alpha\beta} + 4\phi''(R)R_{\alpha}R_{\beta}\}\frac{(k.R)^{2}}{2} \tag{3.11}$$

The derivatives of $G(\tau)$ and $\phi(R)$ are defined as in (2.47).

The polarization vectors and phonon wave vectors for longitudinal and transverse waves along the [qoo] and [qqq] directions are:

$$T[qoo] \quad k_x = k, \quad k_y = k_z = 0$$

$$\varepsilon_x = \varepsilon_z = 0 = \varepsilon_y = 1$$

$$L[qqq] \quad k_x = k_y = k_z = \frac{\sqrt{k}}{\sqrt{3}}$$

$$\varepsilon_x = \varepsilon_y = \varepsilon_z = \frac{1}{\sqrt{3}}$$

To calculate the contributions of the different terms in the dynamical matrices (3.10) and (3.11) we use the following relations which are valid for primitive cubic lattices.[3]

$$\sum_{\ell}{}' \phi(R) R_\alpha R_\beta = \frac{\delta_{\alpha\beta}}{3} \sum_{\ell}{}' \phi(R) R^2$$

$$\sum_{\ell}{}' \phi(R) [3R_\alpha^4 + 6R_\alpha^2 R_\beta^2] = \sum_{\ell}{}' \phi(R) R^4$$

A. Contribution of $D^R_{\alpha\beta}(k)$ to Bulk Modulus

The contribution of $\phi'(R)$ is found from:

$$\omega^2_{L[qqq]} = \frac{2}{M} \sum_R{}' \sum_{\alpha\beta} \sum_{ij} \frac{\phi'(R)}{2} \delta_{\alpha\beta} \varepsilon_\alpha \varepsilon_\beta k_i R_i k_j R_j \tag{3.12}$$

$$= \frac{1}{M} \sum_R{}' \phi'(R) \frac{k^2}{3} (R_x^2 + R_y^2 + R_z^2 + \text{odd terms})$$

$$\omega^2_{L[qqq]} = \frac{1}{M} \sum_R{}' \phi'(R) \frac{k^2 R^2}{3} \tag{3.13}$$

Similarly we find that

$$\omega^2_{T[qoo]} = \frac{1}{M} \sum_R{}' \phi'(R) \frac{k^2 R^2}{3} \tag{3.14}$$

$$(\omega^2_{L[qqq]} - \tfrac{4}{3}\omega^2_{T[qoo]}) = - \frac{1}{\Omega_o} \sum_R{}' \phi'(R) \frac{R^2}{9} \tag{3.15}$$

The contribution of $\phi''(R)$ is

$$\omega^2 = \frac{2}{M} \sum_R{}' \sum_{\alpha\beta} (k.R)^2 R_\alpha R_\beta \phi''(R) \varepsilon_\alpha \varepsilon_\beta \tag{3.16}$$

For L[qqq] we have

$$\sum_{\alpha\beta} (k.R)^2 (R_x\varepsilon_x + R_y\varepsilon_y + R_z\varepsilon_z)^2 = \frac{(k.R)^2}{3} (R_x + R_y + R_z)^2 \tag{3.17}$$

$$\omega^2_{L[qqq]} = \frac{2}{9M} \Sigma' k^2 (R^2 + 2R_xR_y + 2R_yR_z + 2R_zR_x)^2 \phi''(R)$$

$$\omega^2_{L[qqq]} = \frac{2}{9M}\sum_R{}' \phi''(R)k^2\{R^4 + 4R_x^2R_y^2 + 4R_y^2R_z^2 + 4R_z^2R_x^2 + \text{odd terms}\}$$

$$= \frac{2}{9M}\sum_R{}' \phi''(R)k^2\{R^4 + 12R_x^2R_y^2\} \qquad (3.18)$$

For the T[qoo] direction we find that

$$\omega^2_{T[qoo]} = \frac{2}{M}\sum_R{}' \phi''(R)k^2R_y^2R_x^2$$

$$(\omega^2_{L[qqq]} - \tfrac{4}{3}\omega^2_{T[qoo]})\frac{\rho}{k^2} = \frac{2}{9\Omega_o}\sum_R{}' \phi''(R)R^4 \qquad (3.20)$$

The total contribution of the R-space dynamical matrix to the bulk modulus is

$$B^R = \frac{1}{9\Omega_o}\sum_R{}'\{2\phi''(R)R^4 - R^2\phi'(R)\} \qquad (3.21)$$

## B. Contribution of $D^Q_{\alpha\beta}(k)$ to Bulk Modulus

We calculate the contributions of the terms in the Q-space dynamical matrix to the bulk modulus in the same manner outlined above for $D^R_{\alpha\beta}(k)$, and find that the term

$G''(\tau)$ contributes

$$B^3 = \frac{4}{9\Omega_o} \sum_{\tau}{}' \tau^4 G''(\tau) \tag{3.22}$$

The contribution of $G'(\tau)$ is

$$B^2 = \frac{22}{9\Omega_o} \sum_{\tau}{}' \tau^2 G'(\tau) \tag{3.23}$$

and that of $G(\tau)$ is

$$B^1 = \frac{2}{\Omega_o} \sum_{\tau}{}' G(\tau) \tag{3.24}$$

From the $G(k)$ term in (3.10) we have

$$\omega^2_{L[qqq]} = \frac{2}{M} \sum_{\alpha\beta} k_\alpha \varepsilon_\alpha k_\beta \varepsilon_\beta G(|k|)$$

$$= \frac{2}{M} k^2 G(k) \tag{3.25}$$

and $\omega^2_{T[qoo]} = 0$

$$\left(\omega^2_{L[qqq]} - \frac{4}{3}\omega^2_{T[qoo]}\right)\frac{\rho}{k^2} = \underset{k\to o}{\mathrm{Lt}}\ \frac{2}{\Omega_o} G(k) \tag{3.26}$$

Evaluation of $\underset{k\to o}{\mathrm{Lt}}\ G(k)$

$$\underset{k\to o}{\mathrm{Lt}}\ G(k) = \underset{q\to o}{\mathrm{Lt}}\ \{F(q) + \frac{2\pi Z^2 e^2}{\Omega_o q^2}\, e^{-q^2/4\eta^2}\}$$

$$= \underset{q\to o}{\mathrm{Lt}}\ \{F(q) + \frac{2\pi Z^2 e^2}{\Omega_o q^2} - \frac{\pi Z^2 e^2}{2\Omega_o \eta^2} + Oq^2\} \qquad (3.27)$$

We combine equations (2.18), (2.23) and (2.32) to write the first term in the form

$$\underset{q\to o}{\mathrm{Lt}}\ 2F(q) = \underset{q}{\mathrm{Lt}} - \frac{2\Omega_o q^2}{8\pi e^2 \Omega_o^2} \left| - \frac{4\pi Z e^2}{q^2} + \Omega_o w_c(q=o) \right|^2 \frac{4\pi e^2 \Pi(q)}{q^2 + 4\pi e^2 \Pi(q)}$$

$$= - \frac{1}{\Omega_o} \left| v(q)^2 - 2\Omega_o w_c(q=o)\, v(q) + \right.$$

$$\left. (\Omega_o w_c(q=o))^2 \right| \frac{\Pi(q)}{1 + \frac{v(q)}{Z}\Pi(q)} \qquad (3.28)$$

where $v(q)=4\pi Ze^2/q^2$. We write the screening function in the form

$$\frac{\Pi(q)}{1 + \frac{v(q)}{Z}\Pi(q)} = \frac{1}{(q) \ + \Pi\frac{v(q)}{Z}}$$

$$\simeq \frac{Z}{v(q)} \{1 - \frac{Z}{v(q)\Pi(q)} + \ldots\}$$

$$= \frac{Z^2}{v(q)^2} \{\frac{v(q)}{Z} - \frac{1}{\Pi(q)}\} \qquad (3.29)$$

$$\operatorname*{Lt}_{q\to o} 2F(q) = \operatorname*{Lt}_{q\to o} -\frac{Z^2}{\Omega_o}\left[-\frac{2\Omega_o}{Z}w_c(q=o) + \frac{v(q)}{Z} - \frac{1}{\Pi(q)}\right] \qquad (3.30)$$

$$\operatorname*{Lt}_{k\to o} \frac{2}{\Omega_o}G(k) = \operatorname*{Lt}_{q\to o} \frac{1}{\Omega_o}\{2w_c(q)Z + \frac{Z^2}{\Omega_o\Pi(q)} - \frac{\pi^2 Z^2 e^2}{\Omega_o \eta^2}\} \qquad (3.31)$$

To evaluate the middle term we make use of the compressibility theorem which states that

$$\frac{\Pi_o(o)}{\Pi(o)} = \frac{K_o}{K}. \qquad (3.32)$$

where $K$ is the compressibility of the interacting electron gas. The subscript o refers to the non-interacting gas.

$$K_o^{-1} = \Omega_o \frac{d^2 U_o}{d\Omega_o^2} \qquad (3.33)$$

Using $U_o = \frac{3}{5}e_f$ and equation (2.15) from which $\Pi_o(q)$ can be determined we find that for the non-interacting electron gas

$$\frac{K_o}{\Pi_o(o)} = \Omega_o^2. \qquad (3.34)$$

$$\frac{1}{\Pi(o)} = \Omega_o^3 \frac{d^2 U_{eg}}{d\Omega_o^2} \qquad (3.35)$$

$U_{eg}$ is the energy per electron for the interacting electron gas and hence includes the exchange and correlation energies.

$$\underset{k\to o}{\mathrm{Lt}} \frac{2G(k)}{\Omega_o} = \frac{Z}{\Omega_o}\{\frac{2}{3}e_f + \frac{4}{9}e_x - 0.01(Ry) + 2w_c(q)\} - \frac{Z^2e^2\pi}{\Omega_o^2\eta^2} \tag{3.36}$$

The term $(2/\Omega_o)\underset{k\to o}{\mathrm{Lt}}\, G(k)$ coincides with $B^o$ of equation (2.46) hence when the method of long waves is used to calculate the bulk modulus every term obtained by differentiating the ground state energy to calculate the bulk modulus is recovered except the term $\Delta_{bs}$ written in (2.49).

### 3.2.3 Equivalence of Dynamics in R-space and Q-space

Whether the real space or the reciprocal space formulation is used the total ground state energy is still expressible as the sum of a volume dependent term and a structure dependent term. The volume terms in the two formulations are different in magnitude and they have different volume dependences[4]. It follows from this that the structure dependent terms have different magnitudes and volume dependences. In view of this it is necessary to show that in spite of this difference between the structure dependent terms which go into the dynamics, the phonon frequencies are the same at all phonon wave vectors.

The dynamical matrix in the real space formulation is given by

$$D_{\alpha\beta}(k) = \frac{1}{M}\sum_{\ell}{}'(e^{-ik.R(\ell)} - 1)\frac{\partial^2}{\partial r_\alpha(\ell)\partial r_\beta(o)}\phi(r) \qquad (3.37)$$

where $\phi(r)$ is a pair interaction potential. If we write $\phi(r)$ in terms of its Fourier components, then (3.37) takes the form

$$D_{\alpha\beta}(k) = \frac{1}{M}\sum_{\ell}{}'(e^{-ik.R(\ell)} - 1)\frac{\partial^2}{\partial r_\alpha(\ell)\partial r_\beta(o)}\cdot\frac{1}{\Omega}\sum_q e^{iq.r}\phi(q) \qquad (3.38)$$

$$D_{\alpha\beta}(k) = \frac{1}{M\Omega}\sum_{\ell}{}'\sum_q(e^{i(q-k).R(\ell)} - e^{iq.R(\ell)})(iq_\alpha)(-iq_\beta)\phi(q) \qquad (3.39)$$

$$D_{\alpha\beta}(k) = \frac{1}{M\Omega_o}\sum_\tau\{\phi(\tau+k)(\tau+k)_\alpha(\tau+k)_\beta - \tau_\alpha\tau_\beta\phi(\tau)\} \qquad (3.40)$$

Equations (3.37) and (3.40) lead to exactly the same frequencies for all phonon wave vectors k because the Fourier transformation is complete, and (3.40) differs from $D^Q_{\alpha\beta}(k)$ of (2.59) in having the $\tau=o$ included in the second term. We have to show that this extra term which is included in (3.40) but not in (2.59) is always zero whenever some screening is included in the theory. In a Coulomb lattice

$\phi(q) = \dfrac{4\pi Z^2 e^2}{q^2}$,

$$\mathop{\mathrm{Lt}}_{\tau\to o} \frac{\tau_\alpha \tau_\beta}{\Omega_o M}\phi(\tau) = \frac{4\pi Z^2 e^2}{3\Omega_o M} \tag{3.41}$$

$$= \frac{\omega_p^2}{3}$$

where $\omega_p$ is the ion plasma frequency. When the ions are screened the range of $\phi(r)$ is curtailed. At small q values Thomas-Fermi screening is valid[5] and we have

$$\phi(q) = \frac{4\pi Z^2 e^2}{q^2 + \lambda^2} \tag{3.42}$$

where $\lambda$ is the screening length.

$$\mathop{\mathrm{Lt}}_{\tau\to o} \frac{\tau_\alpha \tau_\beta}{\Omega_o M}\phi(\tau) = \mathop{\mathrm{Lt}}_{\tau\to o} \frac{\tau^2 4\pi Z^2 e^2}{3(\tau^2 + \lambda^2)\Omega_o M} \tag{3.43}$$

$$= 0 \text{ for finite } \lambda$$

It is evident from this that as long as the ions are screened the $\tau = o$ term can be added to $D^Q_{\alpha\beta}(k)$ or omitted and the frequencies will be identical to those obtained from its real space counterpart.

### 3.3.1 Volume Forces and Elastic Constants

The volume term $\Lambda_{bs}$ which appears as the difference between values of the bulk modulus calculated by differentiation of the total ground state energy and that calculated by the method of long waves is also the difference between values of the longitudinal elastic constants calculated by the two methods.

In materials with cubic symmetry where there are only three independent elastic constants, their values can be determined by considering changes in the ground state energy when the crystal undergoes three deformations. A uniform dilation of the material is one convenient deformation and this as pointed out in section 3.2 leads to the equation

$$\Omega\frac{d^2\phi}{d\Omega^2} = \frac{1}{3}(C_{11} + 2C_{12})$$

In addition to this particular deformation Fuchs[6] who was the first to make a satisfactory calculation of the elastic constants in cubic metals also considered an expansion of the crystal by the amount $\varepsilon_x$ along the x-axis and a contraction along the y-axis of such an amount that the volume remains constant to order $\varepsilon_x^2$. This leads to

$$\frac{1}{2\Omega}\frac{d^2\phi}{d\varepsilon_x^2} = C_{11} - C_{12} \qquad (3.44)$$

The third deformation considered was a shear by an amount $\gamma_{xy}$ in the xy plane such that the volume remains constant, from which we get

$$\frac{1}{\Omega}\frac{d^2\phi}{d\gamma_{xy}^2} = C_{44} \qquad (3.45)$$

The volume conserving deformations from which the transverse elastic constants $C_{44}$ and $C_{11}-C_{12}$ can be calculated via (3.44) and (3.45) do not involve $\Delta_{bs}$, on the other hand the calculation of $C_{11}$ and $C_{12}$ does involve $\Delta_{bs}$. It is evident from this that one of the reasons why the Cauchy relations according to which $C_{12}-C_{44}$ must vanish in a cubic material which is in equilibrium under the action of central forces only breaks down in metals is the presence of volume dependent forces giving rise to $\Delta_{bs}$. The Cauchy relation can also break down if in addition to central forces there are present many-body forces in the crystal.

The Cauchy difference $C_{12}-C_{44}$ can also be calculated from dynamics by making use of equations (3.7) which relate the phonon frequencies as $k \to o$ to the elastic constants. In terms of these

$$C_{12} - C_{44} = (\omega^2_{L[qoo]} - 3\omega^2_{T[qqq]})\frac{\rho}{k^2} \tag{3.46}$$

3.3.2 Volume Forces and Cauchy Relations

In this section we calculate the Cauchy difference $C_{12}-C_{44}$ and identify the various contributions to it such as those from the electron gas and the band structure energy.

This will show how well pseudopotential theory carried to second order accounts for the violation of the Cauchy relation and it will also give an indication of the importance of many-body forces in this respect.

The first volume derivative of the total energy of the crystal gives the pressure, and from equation (2.33) we obtain

$$P = -\frac{d\phi}{d\Omega}$$

$$= \frac{1}{\Omega_o}\sum_{\tau}{}'\{G(\tau) + \frac{2}{3}\tau^2 G'(\tau) + \frac{k_f}{3}\frac{\partial F(\tau)}{\partial k_f} - \frac{1}{3\Omega_o}\sum_{\ell}{}' R_\ell^2 \phi'(R_\ell) +$$

$$\frac{Z}{\Omega_o}\{\frac{2}{5}e_{k_f} + \frac{e_x}{3} - 0.01(Ry) + w_c(q=o)\} - \frac{Z^2 e^2 \pi}{2\Omega_o^2 \eta^2} \qquad (3.47)$$

By using the polarization vectors and phonon wave vectors for the [qqo] and [qoo] directions in (3.10) and (3.11) we can write (3.46) in the form

$$\Omega_o(C_{12} - C_{44}) = 2\sum_{\tau}{}' G(\tau) + \frac{4}{3}\sum_{\tau}{}'\tau^2 G'(\tau) - \frac{2}{3}\sum_{\ell}{}' R_\ell^2 \phi(R_\ell) +$$

$$Z\{\frac{2}{3}e_{k_f} + \frac{4}{9}e_x - 0.01(Ry) + 2w_c(q=o)\} -$$

$$\frac{Z^2 e^2 \pi}{\eta\Omega_o} \qquad (3.48)$$

This equation differs from one that is obtained from derivatives of the energy by $\Delta_{bs}$, and since $C_{12}$ includes $\Delta_{bs}$ we can simply add it to (3.48)

$$\Omega_o(C_{12} - C_{44}) = 2\sum_\tau{}' \{G(\tau) + \frac{4}{3}\,{}^2G'(\tau)\} - \frac{2}{3}\sum_\ell{}' R_\ell^2\phi'(R\ ) +$$

$$Z\{\frac{2}{3}e_{k_f} + \frac{4}{9}e_x - 0.01(Ry) + 2w_c(q=o)\} -$$

$$\frac{Z^2e^2\pi}{\eta\Omega_o} + \Delta_{bs}\Omega_o \qquad (3.49)$$

Combining (3.49) with (3.47) for the pressure we get

$$(C_{12} - C_{44}) = 2P + \Delta_{bs} - \frac{2}{3\Omega_o}k_f \sum_\tau{}' \frac{\partial F(\tau)}{\partial k_f} -$$

$$\frac{2Z}{3\Omega_o}(\frac{1}{5}e_{k_f} + \frac{1}{3}e_x) + \frac{(Z)0.01}{\Omega_o}(Ry) \qquad , (3.50)$$

From (3.50) we see that even if the pressure of the crystal was zero the Cauchy relation would still not be satisfied in a cubic metal because of the presence of the electron gas which gives rise to the last two terms, and also because of the variation of the screening function with volume from which we get the second and third terms.

If we write the electron gas energy per electron as

$$U_{eg} = \frac{3}{5}e_{k_f} + e_x + e_c$$

$$= \frac{2.21}{r_s^2} - \frac{.916}{r_s} - (.115 - 0.031\ln(r_s)) \tag{3.51}$$

Then we can show that

$$Z\left(2\frac{dU_{eg}}{d\Omega_o} + \Omega_o\frac{d^2U_{eg}}{d\Omega^2}\right) = -\frac{2Z}{3\Omega_o}\left(\frac{1}{5}e_{k_f} + \frac{1}{3}e_x\right) + \frac{0.031}{3\Omega_o}(Ry) \tag{3.52}$$

The Cauchy difference now becomes

$$(C_{12} - C_{44}) = 2P + \Delta_{bs} - \frac{2}{3\Omega_o}k_f \sum_{\tau}{}' \frac{\partial F(\tau)}{\partial k_f} +$$

$$Z\left(2\frac{dU_{eg}}{d\Omega_o} + \Omega_o\frac{d^2U_{eg}}{d\Omega_o^2}\right) \tag{3.53}$$

The last equation is the same as that found by Finnis working in the real space formulation, or that derived by Brovman[7] et al. In the next section the contributions of the various terms to the quantity $(C_{12}-C_{44})$ are calculated for a number of simple metals using three model pseudopotentials and the results are compared with experiment.

## 3.4 Volume Forces and Dynamics

The difference between values of the bulk modulus calculated by static method and dynamic method comes from variations of the screening parts of the energy wavenumber characteristic $F(\tau)$ for $\tau \neq o$ with volume. In this section we generalize lattice dynamics to include this term.

The general formula for the dynamical matrix is

$$D_{\alpha\beta}(k) = \frac{1}{M} \sum_{\ell} \Phi_{\alpha\beta}(\ell,o) e^{-ik.R_{\ell}} \tag{3.54}$$

These force constants $\Phi_{\alpha\beta}(\ell,o)$ describe the change in the total energy $\Phi$ resulting from the displacements $u_\alpha(\ell)$ and $u_\beta(o)$. These displacements change the energy of the crystal by changing the structure factor but also by changing the screening of the ions. We therefore have to take into account these two contributions when calculating the force constants. We denote the total change in energy resulting from the displacements $u_\alpha(\ell)$ of one atom by $d\Phi/du_\alpha(\ell)$, and this is made up of the term $\partial\Phi/\partial u_\alpha(\ell)$ describing the change in the structure factor, and another term $\partial\Phi/\partial u_\alpha(\ell)_{sc}$ which describes the change in the screening function. In our model of the metal this second factor will only be non-zero in the band structure energy.

The screening function depends on the Fermi wave vector $k_f$ so we can write

$$\frac{\partial}{\partial u_\alpha(\ell)_{sc}} = \frac{\partial}{\partial k_f}\frac{dk_f}{d\Omega_o}\frac{d\Omega_o}{du_\alpha(\ell)}$$

$$= \frac{d\Omega_o}{du_\alpha(\ell)}\frac{\partial}{\partial\Omega_{osc}} \tag{3.55}$$

$$\frac{d}{du_\alpha(\ell)} = \frac{\partial}{\partial u_\alpha(\ell)} + \frac{d\Omega_o}{du_\alpha(\ell)}\frac{\partial}{\partial\Omega_{osc}} \tag{3.56}$$

$$\frac{d^2}{du_\alpha(\ell)\partial u_\beta(o)} = \frac{\partial^2}{\partial u_\alpha(\ell)\partial u_\beta(o)} + \{2\frac{d\Omega_o}{du_\alpha(\ell)}\frac{\partial^2}{\partial u_\beta(o)\partial\Omega_{osc}} +$$

$$\frac{\Omega_o}{du_\alpha(\ell)}\frac{d\Omega_o}{du_\beta(o)}\frac{\partial^2}{\partial\Omega_{osc}}\} \tag{3.57}$$

From equation (3.56) we can see that by rewriting the partial derivatives in the force constants as total derivatives, we can write the dynamical matrix as the sum of two parts of each involving one of the two terms in (3.57).

$$D_{\alpha\beta}(k) = \frac{1}{M}\sum_{\ell} \frac{\partial^2\Phi(\ell,o)}{\partial u_\alpha(\ell)\partial u_\beta(o)} e^{-ik.R_\ell} + D^{sc}_{\alpha\beta}(k) \tag{3.58}$$

$$\text{where } D^{sc}_{\alpha\beta}(k) = \frac{1}{M}\sum_{\ell}\{2\frac{d\Omega_o}{du_\alpha(\ell)}\frac{\partial^2}{\partial u_\beta(o)\,d\Omega_{osc}} +$$

$$\frac{d\Omega_o}{du_\alpha(\ell)}\frac{d\Omega_o}{du_\beta(o)}\frac{\partial^2}{\partial\Omega^2_{osc}}\}\Phi(\ell,o)e^{-ik.R_\ell} \tag{3.59}$$

In the cross term in equation (3.59) we make use of the fact that the screening function depends on q to write

$$\frac{\partial}{\partial u_\beta(o)} = \frac{dq}{d\Omega_o}\frac{d\Omega_o}{du_\beta(o)}\frac{\partial}{\partial q} \tag{3.60}$$

The differential operator in equation (3.59) can now be written in the form

$$\frac{d\Omega_o}{du_\alpha(\ell)}\frac{d\Omega_o}{du_\beta(o)}\{2\frac{dq}{d\Omega_o}\frac{\partial^2}{\partial q\partial\Omega_{osc}} + \frac{\partial^2}{\partial\Omega^2_{osc}}\} \tag{3.61}$$

We use the relations $dq/d\Omega_o=-2q/3\Omega_o$ and $dk_f/d\Omega_o=-k_f/3\Omega_o$ to write (3.61) in the form

$$\frac{d\Omega_o}{du_\alpha(\ell)}\frac{d\Omega_o}{du_\beta(o)}\frac{\hat{\Delta}_{bs}}{\Omega_o^2} \tag{3.62}$$

where the operator $\hat{\Delta}_{bs}$ is given by

$$\hat{\Delta}_{bs} = \frac{10k_f}{9}\frac{\partial}{\partial k_f} + \frac{k_f^2}{9}\frac{\partial^2}{\partial k_f^2} + \frac{2}{9}qk_f\frac{\partial^2}{\partial q\partial k_f} \tag{3.63}$$

This expression is of the same form as that appearing in equation (2.49). The total dynamical matrix can now be written as

$$\begin{aligned} D_{\alpha\beta}(k) &= \frac{1}{M}\sum_{\ell}{}''(e^{-ik.R_\ell} - 1)\Phi_{\alpha\beta}(\ell,o) + \\ &\frac{1}{M}\sum_{\ell}\frac{d\Omega_o}{du_\alpha(\ell)}\frac{d\Omega_o}{du_\beta(o)}\frac{\Delta_{bs}}{\Omega_o}\Phi(\ell,o)e^{-ik.R_\ell} \end{aligned} \tag{3.64}$$

where the force constants $\Phi_{\alpha\beta}(\ell,o)=\partial^2\Phi/\partial u_\alpha(\ell)\partial u_\beta(o)$ are evaluated at the equilibrium points. The translational invariance condition has been used in the first part of $D_{\alpha\beta}(k)$.

The factors $d\Omega_o/du_\alpha(\ell)$ describe changes in the volume per atom when the $\ell^{th}$ atom is displaced in the $\alpha$-direction. These changes are local and we note also that they affect only the longitudinal vibrations of the lattice.

The displacements $u_\alpha(\ell)$ have been written by Heine and Weaire[8] in the form

$$u_\alpha(\ell) = u_\alpha \cos \omega t \cos k.R(\ell) \tag{3.65}$$

Since only longitudinal phonons are going to give a volume change we retain the $\alpha$-component only in k.R

$$u_\alpha(\ell) = u^o \cos \omega t \cos k_\alpha R_\alpha(\ell) \tag{3.66}$$

To find $d\Omega_o/du_\alpha(\ell)$ we determine the changes in the ionic positions induced by a lattice vibration frozen at t=o. With $u_\alpha(\ell)$ given by (3.66) the displacements are all equal. and maximum as $k \to$ zero and this corresponds to a uniform translation of the crystal. If we choose the phases in such a way that as $k \to o$, the displacements are zero then

$$\begin{aligned} u_\alpha(\ell) &= u^o \sin k_\alpha R_\alpha(\ell) \\ &= u^o \text{ Im } e^{ik_\alpha R_\alpha(\ell)} \end{aligned}$$

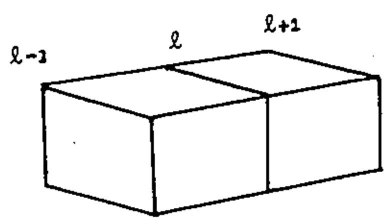



Fig. 2

We now consider a simple cubic lattice of a side $a_o$. Then $\Omega_o = a_o^3 = Aa_o$. The change in the atomic volume around atom $\ell$ is given by

$$d\Omega_o = \text{Im}\,\frac{Au^o}{2}\{e^{ik_\alpha R_\alpha(\ell + 1)} - e^{ik_\alpha R_\alpha(\ell - 1)}\}$$

$$= \text{Im}\,\frac{Au^o}{2}\,e^{ik_\alpha R_\alpha(\ell)}\{e^{ik_\alpha R_\alpha(1)} - e^{-k_\alpha R_\alpha(1)}\} \qquad (3.67)$$

$$\frac{d\Omega_o}{du_\alpha(\ell)} = A \sin k_\alpha R_\alpha(1) \qquad (3.68)$$

Substituting for $d\Omega_o/du_\alpha(\ell)$ and $d\Omega_o/du_\beta(o)$ from (3.68) and using $\Omega_o = Aa_o$ we can write the dynamical matrix $D^{sc}_{\alpha\beta}(k)$ in the form

$$D^{sc}_{\alpha\beta}(k) = \frac{1}{Ma_o^2}\sum_\ell \sin k_\alpha a_o \sin k_\beta a_o e^{-ik.R(\ell)}\Delta_{bs}\Phi(\ell,o) \qquad (3.69)$$

The only contribution to $D^{sc}_{\alpha\beta}(k)$ comes from the band structure energy

$$\Phi_{bs} = N\sum_q{}' S(q)S(-q)F(q) \qquad (3.70)$$

$$\Phi_{bs}(\ell,o) = \frac{1}{N}\sum_q{}' e^{iq.R(\ell)}F(q) \qquad (3.71)$$

$$D^{sc}_{\alpha\beta}(k) = \frac{1}{MNa_o^2} \sum_{\ell} \sum_{q}{}' \sin k_\alpha a_o \sin k_\beta a_o \hat{\Delta}_{bs} e^{i(q-k)R(\ell)} F(q)$$

(3.72)

$$= \frac{1}{Ma_o^2} \sum_{\tau}{}' \sin k_\alpha a_o \sin k_\beta a_o \hat{\Delta}_{bs} F(|\tau + k|)$$

where the relation $\sum_{\ell} e^{ik.R(\ell)} = N\Delta(k-\tau)$ has been used to arrive at the last equation.

## 3.5 Longwave Limit of $D^{sc}_{\alpha\beta}(k)$

In deriving this additional dynamical matrix we have been strongly guided by the fact that in the long wave limit we must get the contribution $\Delta_{bs}$ to the bulk modulus. For phonons of long wavelengths as $k \to o$, $\sin k_\alpha a_o \to k_\alpha a_o$ also

$$F(|\tau + k|) = F(|\tau|) + \frac{\partial F(\tau)}{\partial \tau^2}(2\tau.k + k.k) + \ldots$$

The dynamical matrix calculated to second order in k becomes

$$D^{sc}_{\alpha\beta}(k) = \frac{1}{Ma_o^2} \sum_{\tau}{}' k_\alpha k_\beta a_o^2 \hat{\Delta}_{bs} F(\tau) \qquad (3.73)$$

This makes no contribution to the transverse frequencies. The contribution to $\omega^2_{L[qqq]}$ is given by

$$\omega_L^2[qqq] = \frac{1}{M}\sum_{\tau}{}' \sum_{\alpha\beta} \varepsilon_\alpha k_\alpha k_\beta \varepsilon_\beta \hat{\Delta}_{bs} F(|\tau|)$$

$$= \sum_{\tau}{}' \frac{k^2}{M} \Delta_{bs} F(|\tau|) \tag{3.74}$$

$$B^{sc} = (\omega_{L[qqq]} - \frac{4}{3}\omega_{T[qoq]})\frac{\rho}{k^2}$$

$$= \frac{1}{\Omega_o}\sum_{\tau}{}' \hat{\Delta}_{bs} F(\tau) \tag{3.75}$$

$$= \Delta_{bs}$$

The new term $D^{sc}_{\alpha\beta}(k)$ which we add to the usual form of the dynamical matrix is thus seen to have the correct behaviour at long wavelengths. Its effect on phonon frequencies at finite wave vectors is investigated in the next section for three local pseudopotential models.

### 3.6.1 Numerical Calculations

The dynamical matrix $D^{sc}_{\alpha\beta}(k)$ introduced in the last section has been used to study the effects of volume forces on longitudinal phonon frequencies along symmetry directions in simple metals. Calculations of elastic constants have also been made on the polyvalent metals Al and Pb. Because the total dynamical matrix used gives results for the elastic constants which are exactly the same as those found by differentiating the total energy, these quantities need only be calculated by one method, and the method of long waves was used. The model pseudopotentials used for the simple metals are the modified point-ion model of Harrison[9] and the local models of Ho[10] and Taylor.[11]

### 3.6.2 Point-Ion Model

This model consists of a Coulomb interaction with a function of the form of a 1s electron density for the core region. The bare ion form factor is given by

$$w_B(q) = \frac{1}{\Omega_o}\left\{-\frac{4\pi Ze^2}{q^2} + \frac{V_o}{(1 + R_m^2 q^2)^2}\right\}$$

For q=o the ion core part is given by

$$w_c(q=o) = \frac{V_o}{\Omega_o}$$

where the constants $V_o$ and $R_m$ are treated as adjustable parameters. In his calculations for the alkali metals Na and K using this model Wallace included a Born-Mayer repulsion between ions in the ground state energy $\Phi$, and the three parameters $V_o$, $R_m$ and $\alpha_B$ were adjusted so that theory and experiment agreed for the crystal binding energy and its first two volume derivatives at zero temperature and pressure. The parameter $\alpha_B$ comes from the Born-Mayer energy $\sum_\ell{}' \alpha_B e^{-\gamma R_\ell}$, and $\gamma$ was chosen to be the same for all metals. For a primitive lattice $S(q)=\Delta(q-\tau)$ so that the band structure energy is given by

$$\Phi_{bs} = \sum_\tau{}' F(\tau)$$

The model is used in conjunction with RPA screening and the Hubbard-Sham[12] modification to take into account exchange and correlation in the electron gas. In accordance with the notation used in section 2.3 we write $F(q)$ in the form

$$F(q) = -\frac{\Omega_0 q^2}{8\pi e^2} \frac{|w_B(q)|^2 (\varepsilon(q) - 1)}{1 + (\varepsilon(q) - 1)(1 - \gamma(q))}$$

where $\varepsilon(q)$ is the static dielectric function, $\gamma(q)= q^2\phi(q)=q^2/(q^2+\xi k_f^2)2$, and $\xi$ is fixed by requiring agreement between the homogeneous deformation and the long waves calculation of the bulk modulus. This has been shown[9] to be equivalent to the Geldart-Vosko result which is obtained by using the compressibility theorem.

The parameters used in the calculations of the alkali metals Li, Na and K are given in Table 1, also included in this table are the constants for Al; these are quoted by Wallace.[13] In the case of Al the parameters were adjusted to give good graphical fit to the measured phonon frequencies along symmetry directions. Table 2 gives the elastic constants and energy calculated with the point-ion model for the metals listed. The values in brackets were calculated by the method of long waves with $D^{sc}_{\alpha\beta}(k)$ excluded, and the theoretical values of the bulk modulus B were calculated by numerical differentiation of the ground state energy. These agreed with those calculated by the method of long waves using the total dynamical matrix to within 0.3% in Li and K, and to within 3% in Na. The other theoretical values of the elastic constants were calculated by the method of long waves with the total dynamical matrix. The experimental values of the elastic constants are from 4.2K measurement of Marquardt[14] et al in the case of K, in Na they are from 78K data of Diederich and Trivisonno;[15] in Li they are from Nash[16] et al measurements at 78K and in Al from the measurements of Kamm and Alers.[17]

The values of the elastic constants calculated indicate that on the basis of this simple model the exclusion of $\Delta_{bs}$ can lead to large errors in the bulk modulus calculated from dynamics. The model can however, only give a good qualitative description of the dispersion curves. In the case of Al $\Delta_{bs}$ is about -170% of the experimental value for the bulk modulus, it is a smaller percentage in the alkali metals. The value of $\Delta_{bs}$ found for Al is much bigger than that predicted by Finnis and of a different sign. However, even in this case we still find that the bulk modulus calculated by the method of long waves and that calculated by differentiation of the energy are the same, whereas with $D^{sc}_{\alpha\beta}(k)$ excluded they are different. Because $\Delta_{bs}$ is so large in Al, calculation of the dispersion curves with $D^{sc}_{\alpha\beta}(k)$ included renders some of the frequencies imaginary and this is regarded as indication of the weakness of the model. It was found that in order to satisfy the symmetry requirements at the zone boundaries 100 shells had to be summed over in Q-space in the case of Al whereas only 20 shells were required to achieve the same accuracy in the alkali metals.

In Fig. 3 the dispersion curves for Li calculated with the full dynamical matrix are shown together with the 98K measurements of Smith et al.[18] The effects of the volume forces on the frequencies are shown in Table 3 where the frequencies calculated with and without $D^{sc}_{\alpha\beta}(k)$ in the dynamical matrix are compared. In Table 4 the contributions of the various terms in equation (3.53) to the quantity

$C_{12}-C_{44}$ are presented and compared with the experimental values taken from Table 2. In all metals except Al 30 shells in Q-space were summed over and the longitudinal and transverse frequencies at the zone boundary along the [100] and [111] directions were the same to within less than 0.001%.

Table 1 Values of the constants used in the point-ion model. $a_b$ is the Bohr radius.

| Material | $V_o(Ry a_b^3)$ | $R_m(a_b)$ | $\alpha_B(Ry)$ | $\Omega_o(a_b^3)$ |
|---|---|---|---|---|
| Li | 23 | .33 | 0 | 142.5 |
| Na | 37 | .50 | 10.5 | 255.5 |
| K | 66 | .69 | 124 | 485.3 |
| Al | 47.5 | .24 | 0 | 110.6 |

Table 2. Values of quantities calculated with the point-ion model. The bulk modulus B and elastic constants are in $10^{11}$ dynes/cm$^2$

| | $C_{11}$ | | $C_{12}$ | | $C_{44}$ | | B | | $\Delta_{bs}$ | % | $\Phi$(Ry) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Theory | Expt | Theory | Expt | Theory | Expt | Theory | Expt | | | Theory | Expt |
| Li | 1.388 | 1.48 | 1.173 | 1.248 | 1.106 | 1.08 | 1.248 | 1.325 | -.382 | -30.6% | -.555 | -.512 |
| | (1.77) | | (1.555) | | | | (1.626) | | | | | |
| Na | .786 | .85 | .696 | .704 | .539 | .588 | .728 | .741 | -.046 | -6.4% | -.475 | -.46 |
| | (.832) | | (.742) | | | | (.773) | | | | | |
| K | .394 | .416 | .350 | .341 | .263 | .286 | .366 | .367 | -.031 | -8.4% | -.394 | -.388 |
| | (.425) | | (.381) | | | | (.406) | | | | | |
| Al | | 11.425 | | 6.198 | 3.472 | 3.166 | -8.088 | 7.94 | -13.537 | -167% | -1.578 | -1.38 |
| | (7.885) | | (4.271) | | | | (5.476) | | | | | |

Table 3. Phonon frequencies $\nu$ in units of $10^{13}$ c/s for Li calculated with the point-ion model. $\nu^{sc}$ is calculated with $D^{sc}_{\alpha\beta}(k)$ included

| | [qoo] | | [qqq] | | [qqo] | |
|---|---|---|---|---|---|---|
| $q(2\pi/a)$ | $\nu$ | $\nu^{sc}$ | $\nu$ | $\nu^{sc}$ | $\nu$ | $\nu^{sc}$ |
| 1.0 | .843 | .843 | .845 | .845 | - | - |
| .7 | .805 | .803 | .384 | .341 | - | - |
| .5 | .690 | .690 | .710 | .710 | .981 | .981 |
| .3 | .465 | .457 | .843 | .831 | .777 | .768 |
| .1 | .163 | .147 | .365 | .347 | .287 | .271 |

Table 4. Values of terms contributing to $(C_{12} - C_{44})$ in equation (3.53) calculated with the point-ion model. All quantities in $10^{11}$ dynes/cm$^2$

| | 2P | $\Delta_{bs}$ | $-2\sum_{\tau}\frac{\partial F(\tau)}{\partial\Omega}_{osc}$ | Elec gas | Total | $(C_{12} - C_{44})_{exp}$ |
|---|---|---|---|---|---|---|
| Li | -.0896 | -.382 | .2695 | .272 | .0699 | .168 |
| Na | .0014 | -.046 | .0292 | .175 | .159 | .116 |
| K | .0096 | -.031 | .0139 | .095 | .088 | .055 |

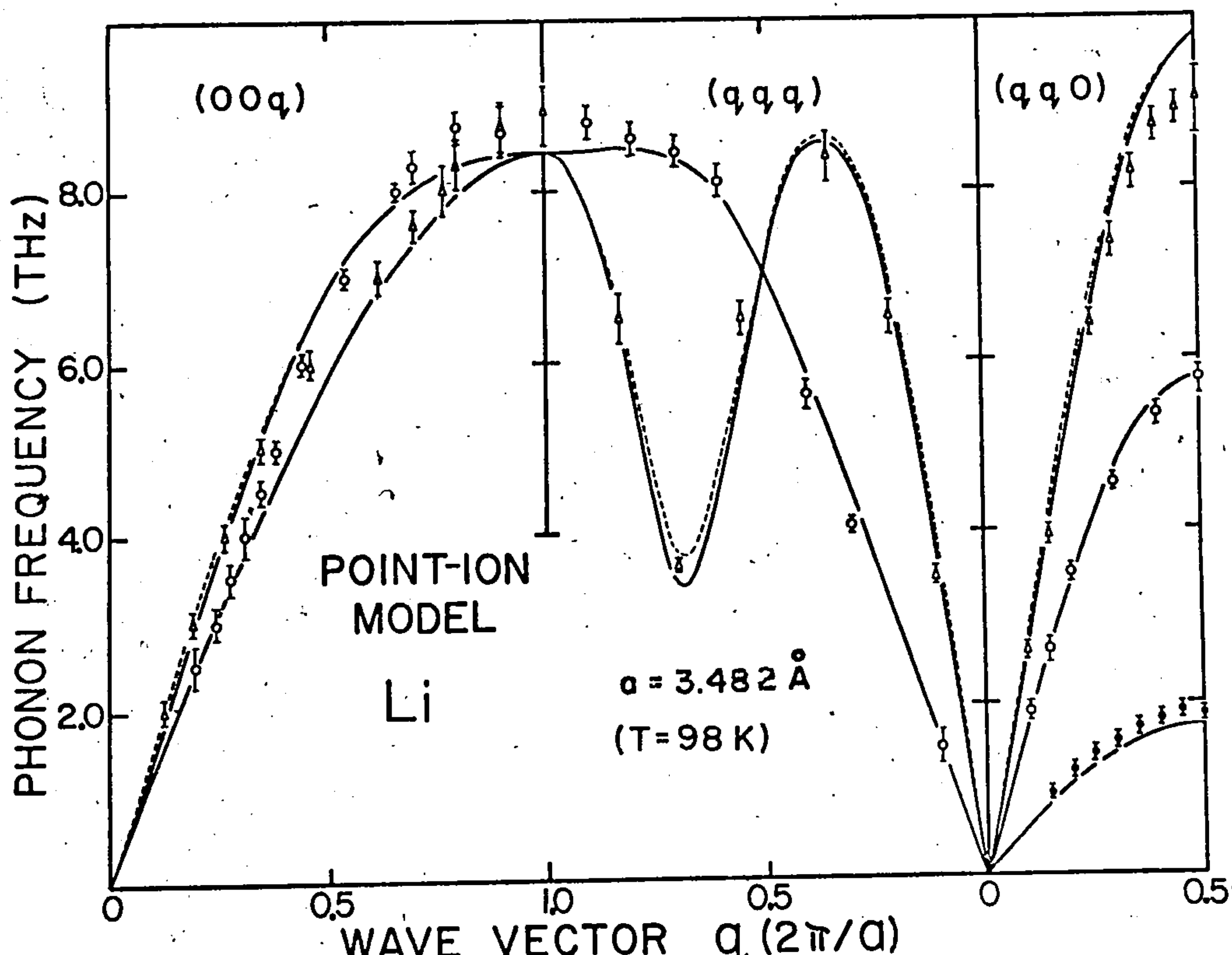



Fig. 3 Dispersion curves for Li. --- includes $D^{SC}_{\alpha\beta}(q)$

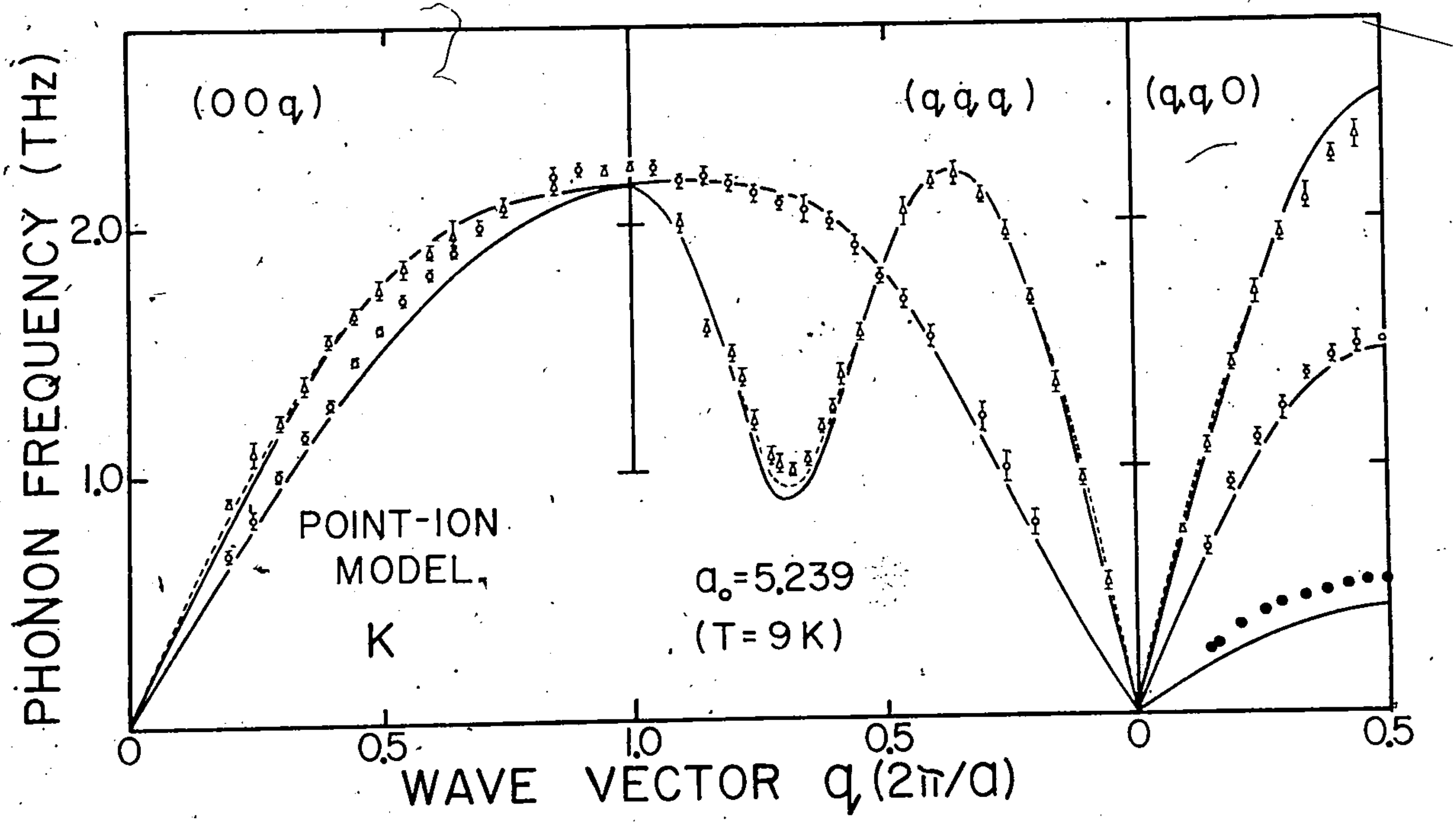



Fig. 4 Dispersion curves for K. Experimental data - Ref. 19. --- includes $D^{sc}_{\alpha\beta}(q)$

### 3.6.3 The Ho Local Model

The model used by Ho is essentially a local form of the Heine-Abarenkov model. It consists of a Coulomb interaction outside the core region and a square well of radius $R_m$ and depth $V_o$ inside the ion core. The form factor for the bare ion is given by

$$w_B(q) = -\frac{4\pi Ze^2}{q^2\Omega_o}\left(1-\frac{R_mV_o}{Ze^2}\right)\cos R_mq + \frac{R_mV_o}{Ze^2}\frac{\sin R_mq}{R_mq}$$

The core part is given by

$$w_c(q=o) = \frac{2\pi R_m^2}{\Omega_o}\left(Ze^2 - \frac{2}{3}V_oR_m\right)$$

The parameters $V_o$ and $R_m$ are adjusted to the experimental elastic constants using the method of long waves without $D^{sc}_{\alpha\beta}(k)$. The model is also used with the Geldart Vosko screening function $\gamma(q)=q^2/(q^2+\xi k_f^2)2$ which takes into account exchange and correlation in the electron gas. Calculations were done for the alkali metals and the values of the constants used are given in Table 5.

In Table 6 the values of the quantities calculated with this model and their experimental values are given. As did the point-ion model this model also shows that $\Delta_{bs}$ is not negligible being of the order 20% in some cases.

For the description of the dispersion curves Fig. 5 and 6 show that the Ho model is not very different from the point-ion model (see Fig. 3 and 4) in that it too fails to show the dip near $(2\pi/a)q=.7$ on the longitudinal branches along the [100] direction. In Table 7 the values of the various quantities contributing to $C_{12}-C_{44}$ in (3.53) are given and compared with the experimental values in the last column.

Table 5. Parameters used in the Ho model for the alkali metals. $a_b$ is Bohr radius

| Material | $V_o$(eV) | $R_m$(A) | $\Omega_o(a_b^3)$ |
|---|---|---|---|
| Li | 9.38 | 0.89 | 142 |
| Na | 7.75 | 1.27 | 255.5 |
| K | 5.17 | 1.60 | 485.3 |

Table 6. Quantities calculated with the Ho model. The bulk modulus B and elastic constants are in units of $10^{11}$ dynes/cm$^2$

| | $C_{11}$ | | $C_{12}$ | | $C_{44}$ | | B | | $\Delta_{bs}$ | % | $\phi$(Ry) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Theory | Expt | Theory | Expt | Theory | Expt | Theory | Expt | | | Theory | Expt |
| Li | 1.472 | 1.48 | 1.283 | 1.248 | 1.053 | 1.08 | 1.349 | 1.325 | -.095 | -7% | -.555 | -.512 |
| | (1.567) | | (1.379) | | | | (1.442) | | | | | |
| Na | .816 | .85 | .693 | .704 | .558 | .558 | .736 | .741 | -.096 | -13% | -.466 | -.46 |
| | (.912) | | (.789) | | | | (.830) | | | | | |
| K | .395 | .416 | .324 | .341 | .276 | .286 | .349 | .367 | -.087 | -24.9% | -.390 | -.388 |
| | (.482) | | (.411) | | | | (.435) | | | | | |

Table 7. Values of terms contributing to $(C_{12} - C_{44})$ in equation (3.53) calculated with the Ho model. All quantities in $10^{11}$ dynes/cm$^2$

| | 2P | $\Delta_{bs}$ | $-2\sum_{\tau}{}' \frac{\partial F(\tau)}{\partial \Omega}_{osc}$ | Elec gas | Total | $(C_{12} - C_{44})_{exp}$ |
|---|---|---|---|---|---|---|
| Li | .0086 | -.0951 | .0483 | .272 | .234 | .168 |
| Na | .0229 | -.096 | .0352 | .175 | .137 | .116 |
| K | .0073 | -.08741 | .04823 | .095 | .049 | .55 |

-96a-

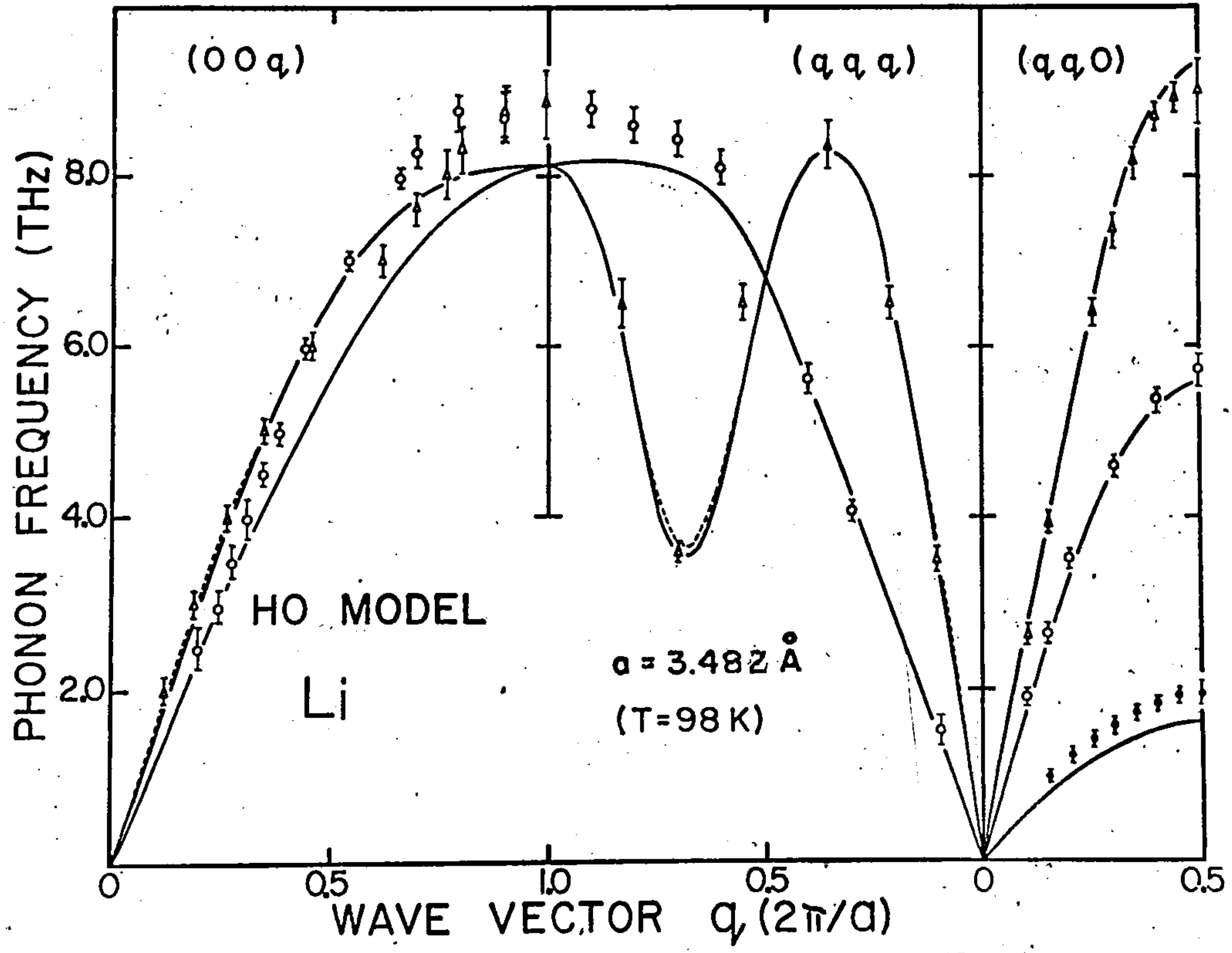



Fig. 5 Dispersion curves for Li. --- includes $D^{sc}_{\alpha\beta}(q)$

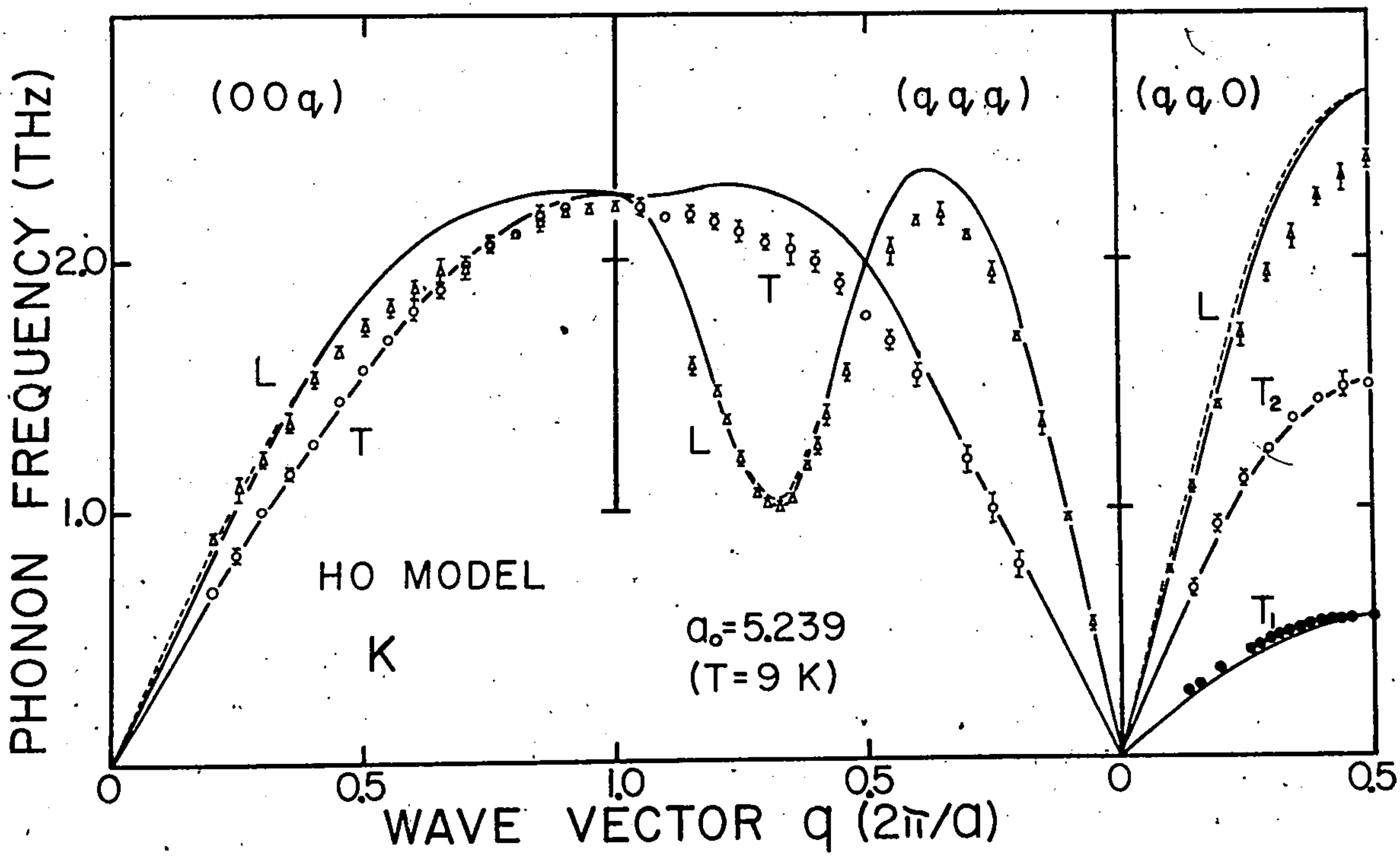



Fig. 6 Dispersion curves for K. Experimental data - Ref. 19. --- includes $D^{sc}_{\alpha\beta}(q)$

### 3.6.4 The Taylor Local Model

This model is similar to a local form of the Heine-Abarenkov type of pseudopotential in that it uses a square well to describe the ion core region and a Coulomb interaction outside the core. The model is used with the Taylor screening function described in section 2.2.1 This is similar to RPA screening with Hubbard-Sham modification for exchange and correlation. The difference is that the function $\phi(q)=Y(q)/q^2$ which accounts for exchange and correlation is a constant independent of $q$, and its value is chosen to satisfy the compressibility theorem. From equation (2.26) $\phi(q)=(1+.153\lambda)/4k_f^2$ , where $\lambda^{-1}=(\pi a_b k_f)$.
The bare ion form factor for the model is given by

$$w_B(q) = -\frac{4\pi Ze^2}{q^2\Omega_o}\left(1 - \frac{V_oR_m}{Ze^2}\right)\cos R_mq + \frac{V_oR_m}{Ze^2}\frac{\sin R_mq}{R_mq}$$

For the core region we have

$$w_c(q=o) = \frac{2\pi R_m^2}{\Omega_o}\left(Ze^2 - \frac{2}{3}V_oR_m\right)$$

where $V_o$ is the depth of the square well and $R_m$ the radius. The only experimental input required for doing calculations with the model is the lattice spacing since $V_o$ and $R_m$ are not fitted to any experimental data, instead they are adjusted so that the charge density calculated using the pseudopotential and linear response theory **gave a best fit to the non-linear calculations of Dagens et al.**[22]

The values of the constants of the Taylor model are given in Table 8 while the elastic constants and energy calculated are shown in Table 11. The effects of the additional dynamical matrix $D^{sc}_{\alpha\beta}(k)$ on the phonon frequencies of Na are shown in Table 10 where the frequencies calculated with and without $D^{sc}_{\alpha\beta}(k)$ are compared. The dispersion curves for Na and K are shown in Figs. 7 and 8 respectively and in Table 9 the contributions to the Cauchy relation $C_{12}-C_{44}$ are given. Fig. 9 shows the [qoo]L branch for Na.

Since the only experimental input required in this model is the lattice constant, calculations done with the Taylor model are a severer test of theory than those done with the point-ion or the Ho models. The results of the dispersion curves show that the Taylor model gives more detailed information in that the dip in the longitudinal branch along the [100] direction is now obtained whereas the other models did not show it. The frequencies for Na calculated with $D^{sc}_{\alpha\beta}(k)$ included are much lower around

$q(2\pi/a)=.7$ along the [111] direction than those calculated without the additional dynamical matrix or the experimental ones. The value of $\Delta_{bs}$ found using this model is again negative and this agrees with the calculations done using the other two models. In Al $\Delta_{bs}$ is neither large nor positive as predicted by Finnis, and in general it depends on the model pseudopotential used as well as on the volume per atom of the material studied.

Table 8. Values of the parameters used in the Taylor model. $a_b$ is the Bohr radius

| Material | $V_o$(RY) | $R_m(a_b)$ |
|---|---|---|
| Na | .32 | 1.94 |
| K | .42 | 2.94 |
| Al | 2.22 | 1.4 |

Table 9. Values of quantities contributing to $(C_{12} - C_{44})$ in (3.53). All quantities in units of $10^{11}$ dynes/cm$^2$

| | 2P | $\Delta_{bs}$ | $-2\sum_\tau \frac{\partial F(\tau)}{\partial\Omega}_{osc}$ | Elec gas | Total | $(C_{12} - C_{44})_{exp}$ |
|---|---|---|---|---|---|---|
| Na | -.206 | -.2675 | .1372 | .175 | -.162 | .116 |
| K | -.075 | -.0871 | .0395 | .095 | -.027 | .055 |
| Al | 1.1134 | -.8488 | 2.1404 | -.251 | 2.154 | 3.032 |

Table 10. Phonon frequencies $\nu$ in $10^{13}$ c/s for Na calculated with the Taylor model. $\nu^{sc}$ is calculated with $D_{\alpha\beta}(k)$ included

| | [qoo] | | [qqq] | | [qqo] | |
|---|---|---|---|---|---|---|
| $q(2\pi/a)$ | $\nu$ | $\nu^{sc}$ | $\nu$ | $\nu^{sc}$ | $\nu$ | $\nu^{sc}$ |
| 1.0 | .361 | .361 | .362 | .362 | - | - |
| .7 | .321 | .320 | .172 | .138 | - | - |
| .5 | .268 | .268 | .286 | .268 | .378 | .378 |
| .3 | .185 | .178 | .337 | .330 | .310 | .303 |
| .1 | .067 | .056 | .153 | .141 | .120 | .110 |

Table 11. Elastic constants and binding energy calculated with the Taylor model. The bulk modulus B and elastic constants in $10^{11}$ dynes/cm$^2$

| | $C_{11}$ | | $C_{12}$ | | $C_{44}$ | | B | | $\Delta_{bs}$ | % | $\Phi$(Ry) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Theory | Expt | Theory | Expt | Theory | Expt | Theory | Expt | | | Theory | Expt |
| Na | .546 | .85 | .420 | .704 | .587 | .588 | .474 | .741 | -.268 | 56.5% | -.48 | -.46 |
| | (.814) | | (.688) | | | | (.730) | | | | | |
| K | .304 | .416 | .240 | .341 | .269 | .286 | .263 | .367 | -.087 | 33.1% | -.40 | -.388 |
| | (.391) | | (.327) | | | | (.349) | | | | | |
| Al | 10.536 | 11.425 | 6.204 | 6.198 | 4.131 | 3.166 | 7.765 | 7.94 | -.849 | 10.9% | -1.41 | -1.38 |
| | (11.385) | | (7.053) | | | | (8.497) | | | | | |

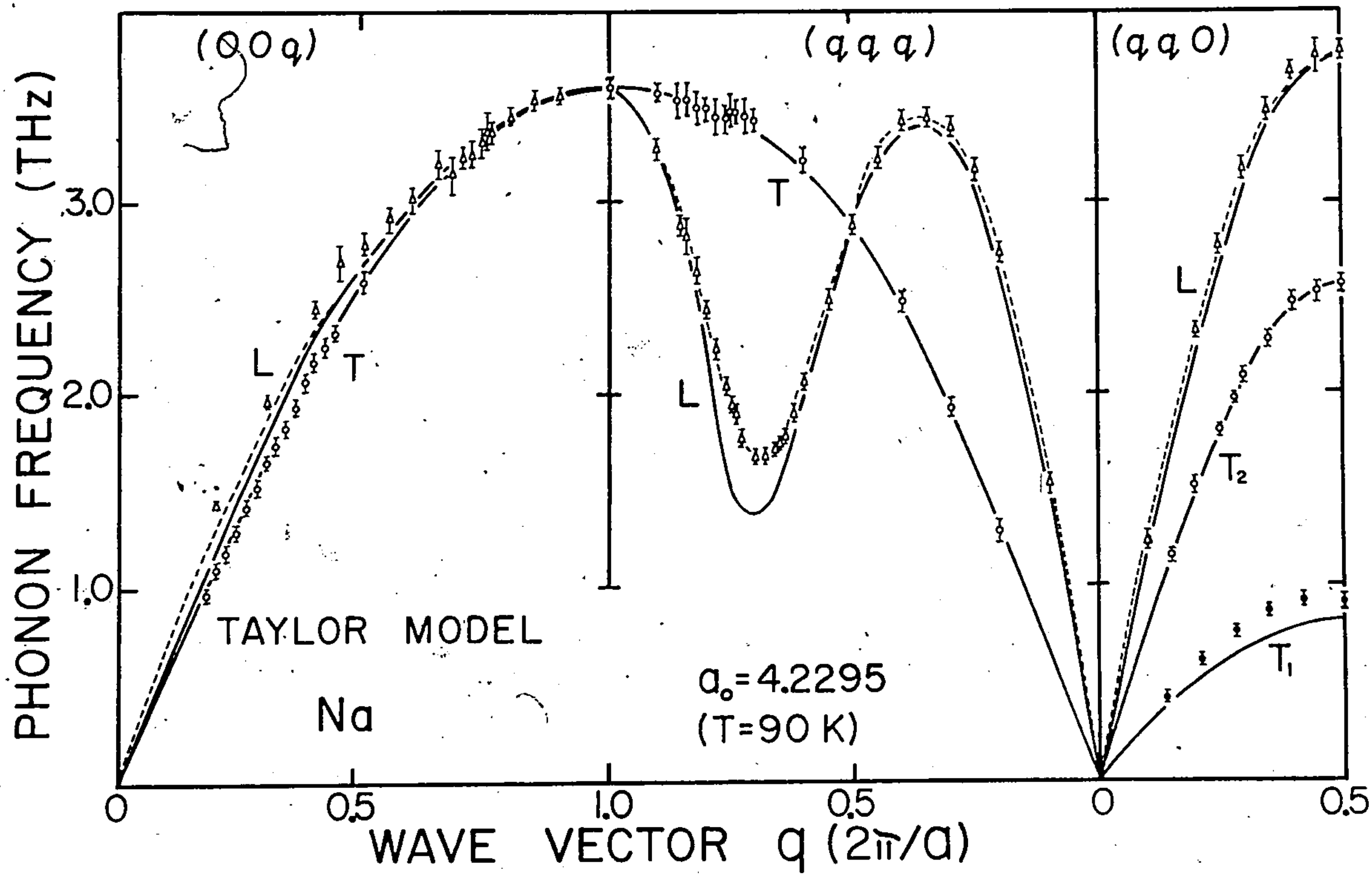



Fig. 7 Dispersion curves for Na. Experimental data - Ref. 20. --- includes $D^{sc}_{\alpha\beta}(q)$

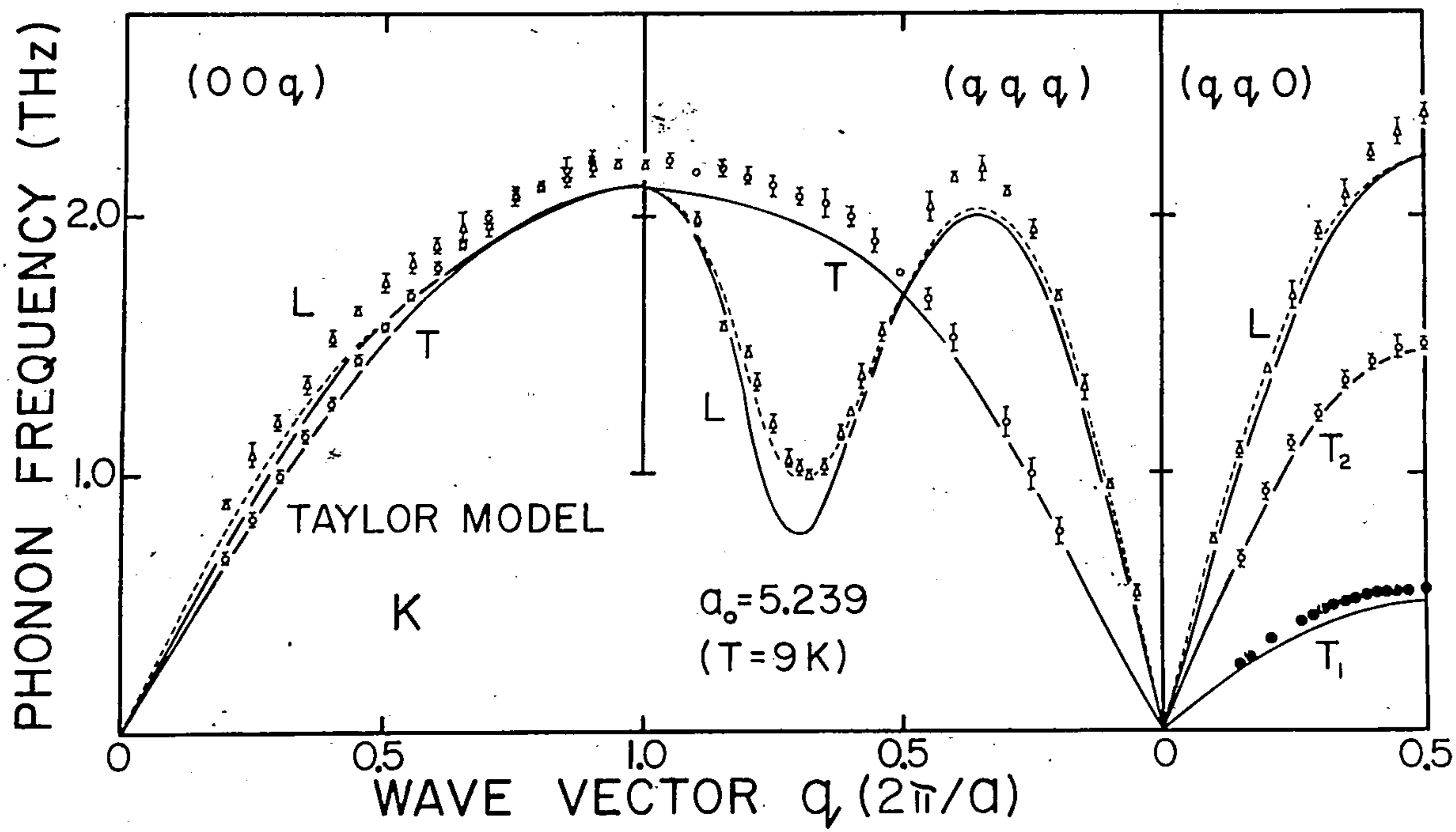



Fig. 8 Dispersion curves for K. Experimental data - Ref. 19. --- includes $D^{SC}_{\alpha\beta}(q)$

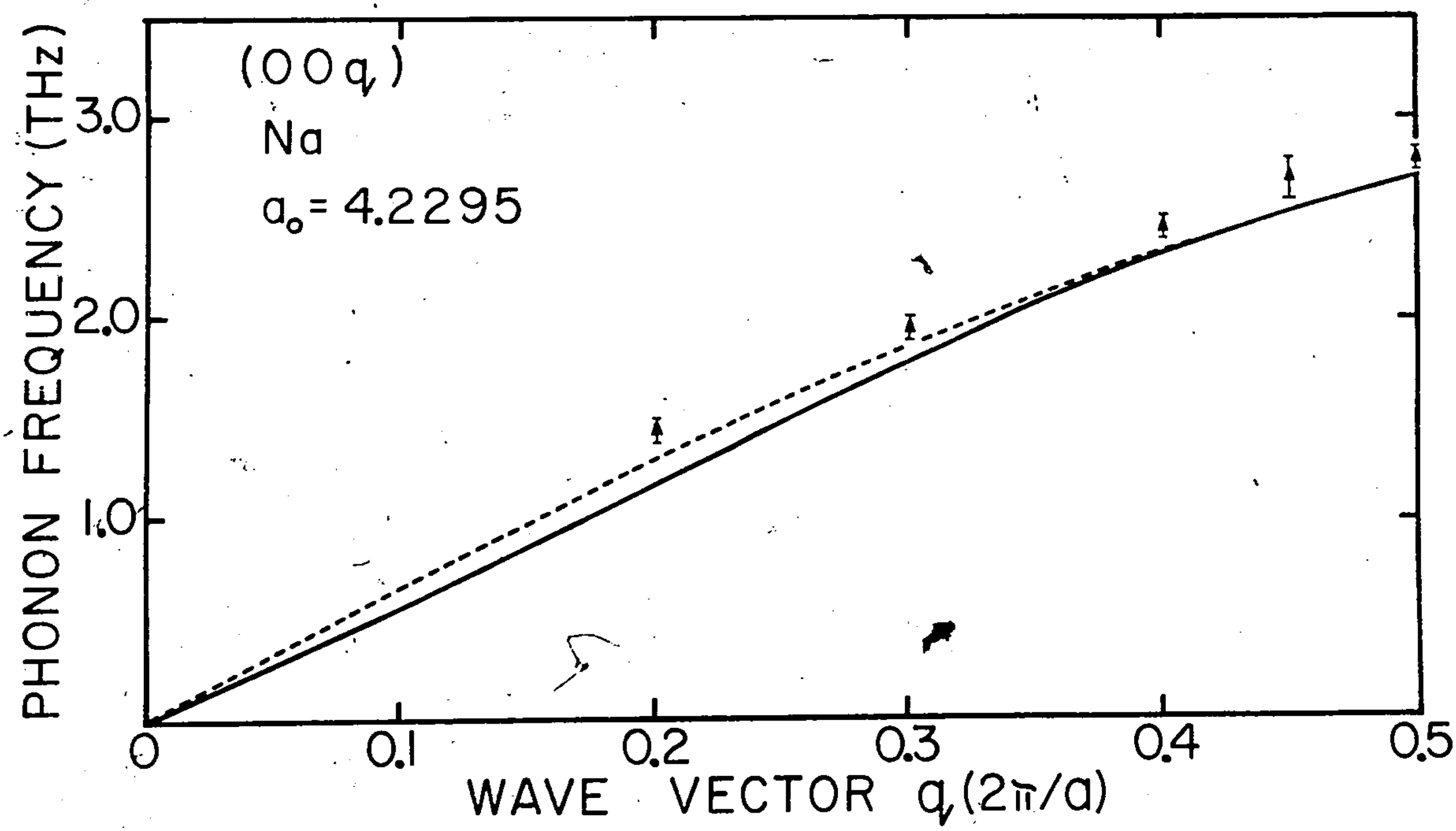



Fig. 9 L[100] Branch for Na calculated with the Taylor model. --- includes $D^{sc}_{\alpha\beta}(q)$

### 3.6.5 Localized Heine-Abarenkov Model

In view of the fact that the value of $\Delta_{bs}$ found with all the three local pseudopotential models described above was negative whereas Finnis specifically predicts that in the polyvalent materials such as Al and Pb $\Delta_{bs}$ should be positive and about 50% of the bulk modulus, further calculations for the metals Al and Pb as well as K were done, and for these the Heine-Abarenkov[23] model pseudopotential was adopted. In this model the bare ion potential is represented by

$$w_B(r<R_m) = A_\ell(E)P_\ell$$

$$w_B(r>R_m) = -\frac{Ze^2}{r}$$

where $A_\ell(E)$ is a parameter which varies slowly with E the energy of the incident conduction electron, $P_\ell$ is a projection operator which selects from the incident wavefunction a component with angular momentum $\ell$. The constants $A_\ell(E)$ are fitted to spectroscopically observed energy levels of a free ion. To simplify the calculations we adopted a local form of this model in which only the $\ell=0$ component was used, the assumption made being that only the magnitude of $\Delta_{bs}$ and not its sign would be affected by this approximation. This was confirmed by making calculations on K. With this approximation the bare ion form factor becomes the same as those of Ho and Taylor models, and the screening function used was that of Geldart and Vosko which was employed in the point-ion model and the Ho model.

Tables 12 and 13 give the parameters used with this model and the values of the quantities calculated. Fig. 10 shows the dispersion curves for Pb and these are compared with the experimental data of Brockhouse[24] et al. Table 13 shows that the values of $\Delta_{bs}$ found in K and Al are still negative in agreement with previous results, in Pb however, it is positive. The calculated frequencies in Fig.10 are higher than the observed ones, it is expected however, that the inclusion of the $\ell \neq 0$ components in the bare ion potential would lead to improvements between experimental and theoretical values of the frequencies.

Table 12. Values of the constants used in the localized HA model

| | $V_o$(Ry) | $R_m(a_b)$ | a(Å) |
|---|---|---|---|
| K | .48 | 4.2 | 5.239 |
| Al | 2.76 | 2.0 | 4.0321 |
| Pb | 3.84 | 2.1 | 4.94 |

Table 13. Values of quantities calculated with the localized Heine-Abarenkov model. The bulk modulus B and elastic constants are in $10^{11}$ dynes/cm$^2$

| | $C_{11}$ | | $C_{12}$ | | $C_{44}$ | | B | | $\Delta_{bs}$ | % | $\Phi$(Ry) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Theory | Expt | Theory | Expt | Theory | Expt | Theory | Expt | | | Theory | Expt |
| K | .466 | .416 | .401 | .341 | .252 | .286 | .424 | .367 | -.029 | -6.7% | -.38 | -.388 |
| | (.495) | | (.429) | | | | (.451) | | | | | |
| Al | 22.99 | 11.425 | 17.84 | 6.198 | 9.28 | 3.166 | 19.55 | 7.94 | -.224 | 1% | -1.30 | -1.38 |
| | (23.21) | | (18.06) | | | | (19.78) | | | | | |
| Pb | 3.417 | 5.55 | 2.631 | 4.54 | 1.268 | 1.94 | 2.884 | 4.877 | 1.676 | 58% | -1.73 | -1.81 |
| | (1.741) | | (.955) | | | | (1.214) | | | | | |

# REFERENCES


1. B.A. Auld, Acoustic Fields and Waves in Solids, Vol. 1 (Wiley, New York, 1963).
2. C. Kittel, Introduction to Solid State Physics (Wiley, New York, 1971).
3. D.C. Wallace, Thermodynamics of Crystals (Wiley, New York, 1972).
4. M.W. Finnis, J. Phys. F 4, 1645 (1974).
5. J.M. Ziman, Principles of the Theory of Solids (U.P. Cambridge, 1965).
6. K. Fuchs, Proc. Roy. Soc. A 153, 622 (1936); A 157, 444, (1936).
7. E.G. Brovman, Yu Kagan, A. Kholas, Soviet Phys. (JETP) 30, 883 (1970).
8. V. Heine, D. Weaire, Solid State Phys. Vol. 24, 250 (1970).
9. W.A. Harrison, Pseudopotentials in the Theory of Metals (Benjamin, New York, 1966); D.C. Wallace, Phys. Rev. 182, 778 (1969).
10. P.S. Ho, Phys. Rev. 169, 523 (1968); I.M. Torrens, Interatomic Potentials (Academic, New York, 1972).
11. R. Taylor, Private Communication.
12. J. Hubbard, Proc. Roy. Soc. A 243, 336 (1957); L.M. Falicov, V. Heine, Adv. Phys. 10, 57 (1961).
13. D.C. Wallace, Phys. Rev. 178, 900 (1969); 187, 991 (1969); B 1, 3963 (1970).
14. W.R. Marquardt, J. Trivisonno, J. Phys. Chem. Solids 26, 273 (1965).
15. M.E. Diederich, J. Trivisonno, J. Chem. Solids 27, 637 (1966).
16. H.C. Nash, C.S. Smith, J. Phys. Chem. Solids 9, 113 (1959).

17. G.N. Kamm, G.A. Alers, J. Appl. Phys. 35, 237 (1964).

18. H.G. Smith, G. Dolling, R.M. Nicklow, P.R. Vijayaraghavan, M.K. Nilkinson, Neutron Inelastic Scattering, Vol. 1, 149 (Vienna, International Atomic Energy Authority); M.M. Beg, N. Nielsen, Phys. Rev. B 14, 4266 (1976).

19. R.A. Cowley, A.D.B. Woods, G. Dolling, Phys. Rev. 150, 487 (1966); G. Dolling, J. Meyer, J. Phys. F 7, 775 (1977).

20. A.D.B. Woods, B.N. Brockhouse, R.H. March, A.J. Stewart, R. Bowers, Phys. Rev. 128, 1112 (1962).

21. R. Taylor, J. Phys. F 8, 1699 (1978).

22. L. Dagens, M. Rasolt, R. Taylor, Phys. Rev. B 11, 2726 (1975).

23. A.E.O. Animalu, V. Heine, Phil. Mag. 12, 1249 (1965).

24. B.N. Brockhouse, T. Arase, G. Caglioti, K.R. Rao, A.D.B. Woods, Phys. Rev. 128, 1099 (1962).

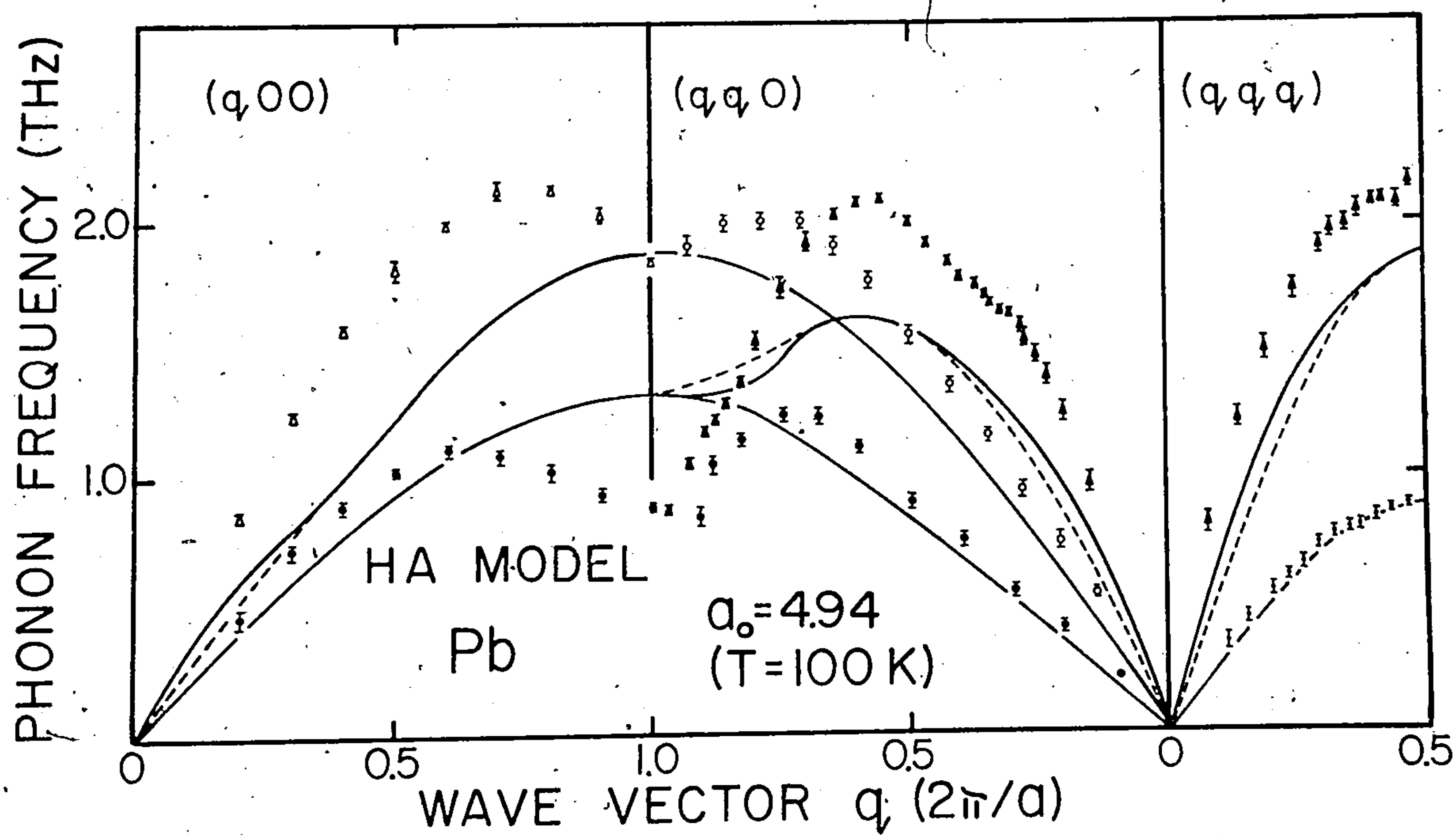



Fig. 10 Dispersion curve for Pb. --- includes $D^{sc}_{\alpha\beta}(q)$

# CHAPTER 4

## ANHARMONIC PROPERTIES OF Li

### 4.1 Introduction

This chapter deals with the calculation of anharmonic phonon energies and lifetimes in Li over the temperature range 110 to 424K which is .94 of the melting point. To describe Li we used the non-local ion-ion interaction potential described by Dagens, Rasolt and Taylor (DRT). This potential is strong and it exhibits asymptotic Friedel oscillations of large amplitude over a long range. As a result special techniques are required to handle it. The phonon energies and lifetimes were calculated using the self-consistent phonon theory, and the results are compared with the neutron scattering measurements of Beg and Nielsen.

### 4.2 Interionic Potential

In the DRT method of constructing interionic potentials, use is made of the fact that the charge density plays an important role in the calculation of properties. For example, if the charge density as a function of position is known, then the cohesive energy may be calculated.[1] The procedure is firstly to calculate the charge density induced by an isolated ion placed in an electron gas. This is carried out by solving the Hohenberg-Kohn-Sham[2] self-consistent equations. Next the full ionic potential is represented by an energy independent non-local pseudopotential of the type introduced by Heine and Abarenkov,[3] and then linear response theory is used to calculate the charge density induced in the electron gas by an isolated ion represented by this pseudopotential and placed in the gas. The parameters of the pseudopotential are adjusted to make this second calculation agree with the first for r values outside the ionic core. These authors point out that in this way the procedure is equivalent to summing the corresponding pseudopotential perturbation approach to all orders neglecting core effects, and as such takes into account multiple-scattering events at a single ion site. The interionic potential is used in conjunction with the Geldart-Taylor[4] dielectric function which includes both exchange and correlation in the electron gas.

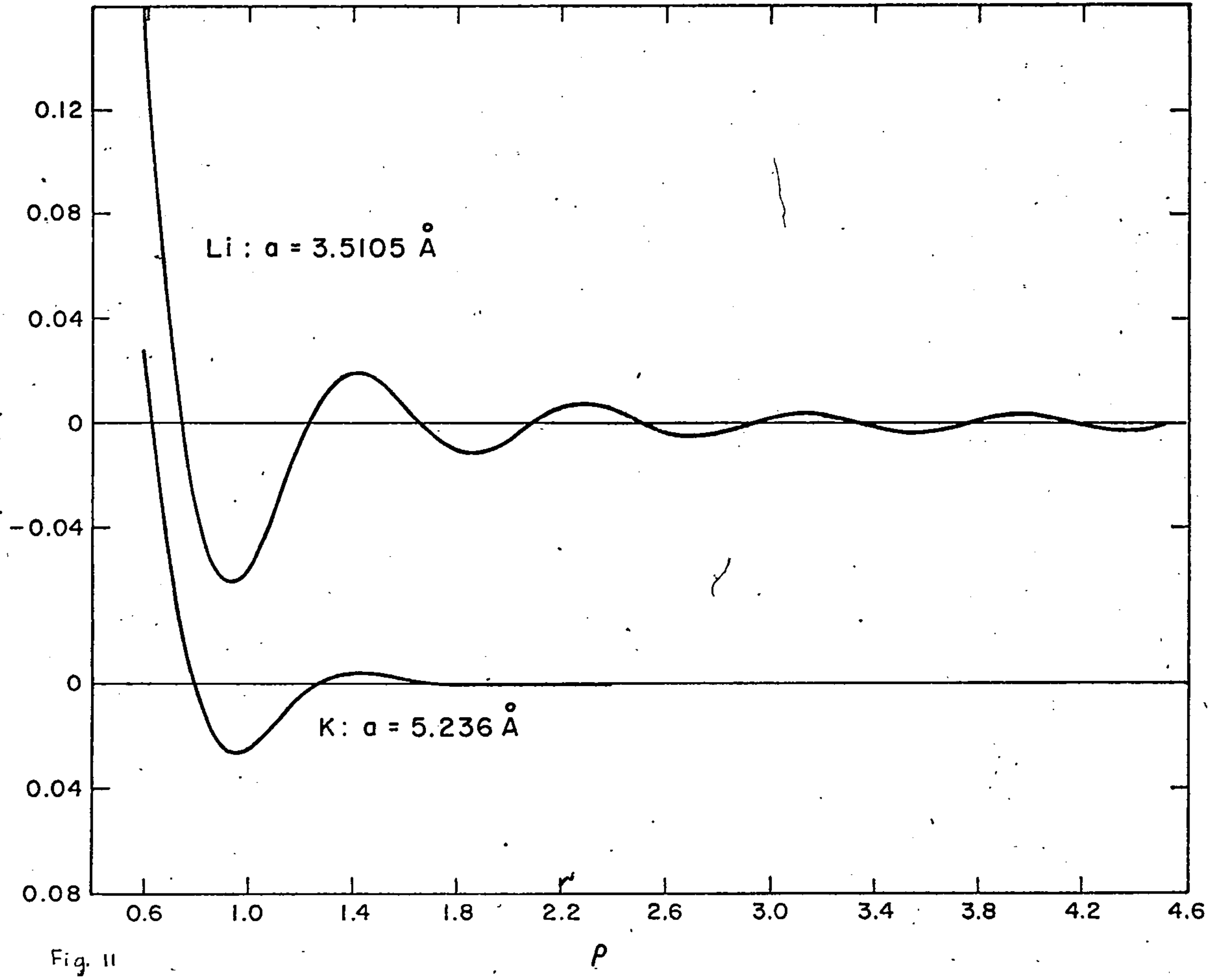
A characteristic of this interionic potential is that it has Friedel oscillations. Its asymptotic form is well described by

$$V_{as}(r) = 2k_f(Ze)^2\{A_3'\frac{\cos(2k_fr)}{(2k_fr)^3} + A_4'\frac{\sin(2k_fr)}{(2k_fr)^4} + \ldots\} \quad (4.1)$$

where the amplitude of the oscillations is large. Equation (4.1) gives the first two terms of an infinite series,[5] however its truncation at this point still gives a good description of Li in the range of interest and this was done in this work. The functional form of the potential gives rise to problems of convergence when sums over neighbours are performed, and this comes about because the number of neighbours summed over is proportional to $r^2$ and hence truncation of the sums at any finite distance can lead to large errors. In Fig. 11 we have plotted $r^2 V_{II}(r)$ where $V_{II}(r)$ is the ion-ion potential, and there it can be clearly seen that the long range oscillations of the Li potential are indeed large, particularly when compared with those of the K interionic potential derived according to the DRT prescription.

From the functional form of $V_{as}(r)$, we see that the problem of summing (4.1) over all neighbours is equivalent to that of summing functions of the form $e^{ik.r}/r^m$, and these can be handled with the Ewald-Fuchs construction. Following Duesbery and Taylor[5] we write the interionic potential in the form

$$V_{II}(r) = V_{sr}(r) + V_{as}(r) \tag{4.2}$$



$\rho^2 V_{II}(\rho)$ (eV)
0.12
0.08
0.04
0
-0.04
0
0.04
0.08
Li : a = 3.5105 Å
K: a = 5.236 Å
0.6
1.0
1.4
1.8
2.2
2.6
3.0
3.4
3.8
4.2
4.6
$\rho$


Fig. 11

where $V_{sr}(r)$ is that part of $V_{II}(r)$ that is left over when $V_{as}(r)$ is subtracted. The asymptotic part of the potential is evaluated by employing the identity

$$\frac{1}{x^m} = \frac{2}{\Gamma(m/2)} \int_o^\infty u^{m-1} e^{-(ux)^2} du$$

$$= \frac{2}{\Gamma(m/2)} \{\int_o^\alpha u^{m-1} e^{-(ux)^2} du + \int_\alpha^\infty u^{m-1} e^{-(ux)^2} du\} \qquad (4.3)$$

where $\Gamma(m/2)$ is the gamma function. From equations (4.1) and (4.3) we have

$$V_{as}(r) = \frac{2A_3}{\Gamma(3/2)} \cos\, x\int_\alpha^\infty u^2 e^{-u^2x^2} du +$$

$$\frac{2A_4}{\Gamma(2)} \sin\, x\int_\alpha^\infty u^3 e^{-u^2x^2} du + {}_o^\alpha V_{as}(r) \qquad (4.4)$$

where $x = 2k_f r$

$$\text{and } {}_o^\alpha V_{as}(r) = \frac{2A_3}{\Gamma(3/2)} \cos\, x\int_o^\alpha u^2 e^{-u^2x^2} du +$$

$$\frac{2A_4}{\Gamma(2)} \sin\, x\int_o^\alpha u^3 e^{-u^2x^2} du \qquad (4.5)$$

we evaluate ${}^{\alpha}_{o}V_{as}(r)$ in q-space and hence write

$$V_{as}(r) = V^{Q}_{as}(r) + V^{R}_{as}(r) \tag{4.6}$$

The short range part of the potential is given by

$$V_{sr}(r) = V_{II}(r) - A_3\frac{\cos x}{x^3} - A_4\frac{\sin x}{x^4} \tag{4.7}$$

The total interionic potential can now be written in terms of $V_{as}(r)$ and $V_{sr}(r)$ in the form

$$\begin{aligned} V_{II}(r) &= \{V_{sr}(r) + V_{as}(r)\} + V_{as}(r) \\ &= V_{eff}(r) + V_{as}(r) \end{aligned} \tag{4.8}$$

where

$$\begin{aligned} V_{eff}(r) = V_{II}(r) + A_3\cos x[\frac{2}{\Gamma(3/2)} J_3(x) - \frac{1}{x^3}] + \\ A_4\sin x[\frac{2}{\Gamma(2)} J_4(x) - \frac{1}{x^4}] \end{aligned} \tag{4.9}$$

$$\text{and } J_m(x) = \int_{\alpha}^{\infty} u^{m-1} e^{-u^2x^2} du \tag{4.10}$$

This representation of the potential raises the possibility of replacing $V_{II}(r)$ by $V_{eff}(r)$ ignoring $V_{as}^{Q}(r)$ and working entirely in the R-space formulation. To do this a suitable value of $\alpha$ would have to be chosen such that $V_{eff}(r)$ remains convergent in real space while at the same time leaving $V_{as}^{Q}(r)$ negligible. No such value was found and as a result calculations had to be done in both the real space formulation with $V_{eff}(r)$ and the reciprocal space formulation with $V_{as}^{Q}(r)$. The phonon frequencies were calculated from the dynamical matrix

$$D_{\alpha\beta}(k) = D_{\alpha\beta}^{R}(k) + D_{\alpha\beta}^{Q}(k) \tag{4.11}$$

The constants $A_3$ and $A_4$ were determined by joining $V_{II}(r)$ and $V_{as}(r)$ smoothly and at a point where their second derivatives were closest, that is at r such that

$$V_{II}(r) = V_{as}(r)$$

$$\frac{dV_{II}(r)}{dr} = \frac{dV_{as}(r)}{dr}$$

and $\left| \frac{d^2V_{II}(r)}{dr^2} - \frac{d^2V_{as}(r)}{dr^2} \right|$ is smallest.

Starting with the expression for ${}^{\alpha}_{o}V_{as}(r)$ we calculate $D_{\alpha\beta}(r)$ as follows

$$\text{Let } {}^{\alpha}_{o}V_{as}(r) = \frac{2A_3}{\Gamma(3/2)} \cos x\int_0^{\alpha} u^2 e^{-u^2x^2} du + \frac{2A_4}{\Gamma(2)} \sin x\int_0^{\alpha} u^3 e^{-u^2x^2} du = U_3(x) + U_4(x) \tag{4.12}$$

We can then write

$$F(q) = \int d^3r e^{-iq.r}\{U_3(x) + U_4(x)\} = F_3(q) + F_4(q) \tag{4.13}$$

The integrals $F_3(q)$ and $F_4(q)$ reduce to exponential and Dawson's integrals and are evaluated in the appendix. With $F(q)$ now determined, the dynamical matrix from the long range part of the potential contained in ${}^{\alpha}_{o}V_{as}(r)$ is evaluated from

$$D_{\alpha\beta}(k) = \frac{1}{M\Omega_o}\left(\frac{2\pi}{a_o}\right)^2 \sum_{\tau}\{(\tau + k)_{\alpha}(\tau + k)_{\beta}F(|\tau + k|) -$$

$$\tau_{\alpha}\tau_{\beta}F(|\tau|)\} \qquad (4.14)$$

By writing $D_{\alpha\beta}(k)$ as the sum of two parts as described above the dynamical matrix can be evaluated exactly in spite of the long range nature of $V_{II}(r)$.

## 4.3 Dynamics

### A. The Quasiharmonic Approximation

The phonon frequencies were calculated using the quasiharmonic approximation, the self-consistent harmonic approximation as well as the self-consistent harmonic approximation with the cubic anharmonic term included as a perturbation. The outlines of these various approximation were given in chapter 2. In the quasiharmonic approximation, QH, the frequency of a phonon having wave vector k and branch $\lambda$ is given by

$$\omega(q\lambda)^2 = \sum_{\alpha\beta} \varepsilon(q\lambda) D_{\alpha\beta}(k)\varepsilon_{\beta}(q\lambda) \qquad (4.15)$$

where $\varepsilon(q\lambda)$ is the phonon polarization vector. The derivatives of the effective potential $V_{eff}(r)$ which is contained in $D^R_{\alpha\beta}(k)$ and of $V^Q_{as}(r)$ contained in $D^Q_{\alpha\beta}(k)$ are evaluated at the equilibrium lattice spacing, and because the lattice spacing changes with temperature, the QH frequencies are dependent on temperature. That part of the potential which is contained in $D^Q_{\alpha\beta}(k)$ particularly affects the low frequency $T_1$ branch along the [110] direction. Calculation of the frequencies with $\alpha$ chosen to be zero showed that this branch is still unstable when $D^R_{\alpha\beta}(k)$ is summed to 19 shells ($V^Q_{as}(r)=0$). For a choice of $\alpha$=.17 $D^R_{\alpha\beta}(k)$ converges after about 20 shells and the energy of the QH phonon at the zone boundary ignoring $V^Q_{as}(r)$ is 0.54 meV, the complete value which includes the contribution of $V^Q_{as}(r)$ is 0.43 meV. Calculations were made with $\alpha$=0.23 and this made $D^R_{\alpha\beta}(k)$ to converge after 15 shells, and a sum over $\tau$ of three reciprocal lattice points was sufficient to obtain $D^Q_{\alpha\beta}(k)$.

B. The Self-Consistent Harmonic Approximation

It was pointed out in chapter 2 that the SCH approximation is of lowest order in the self-consistent phonon theory. In this approximation the frequencies are still given by (4.15), now however, the derivatives of the potential $V_{II}(r)$ are averaged over the vibrational amplitude of the ions. That part of the dynamical matrix that is evaluated in real space can be evaluated straightforwardly in the SCH approximation, but $D^{Q}_{\alpha\beta}(k)$ cannot be evaluated in the same way since the averaging introduces correlation between atomic motions and the reduction of $D^{Q}_{\alpha\beta}(k)$ to the reciprocal space expression requires no correlation between atoms.

Since $V_{eff}(r)$ continues to 15 shells and $V^{Q}_{as}(r)$ accounts for the remainder, we made the approximation that the averaging of $V^{Q}_{as}(r)$ would have a negligible effect on the phonon frequencies. Hence initial calculations using the self-consistent harmonic approximation were done without any averaging for atoms separated more than 15 shells. The QH values of $D^{Q}_{\alpha\beta}(k)$ were used. This approximation was found to work well for all the branches except the $T_1[110]$ branch where the frequencies showed unrealistic variations with wave vector. To improve this branch, the averaging of the outer shells in $D^{Q}_{\alpha\beta}(k)$ was approximated by using an uncorrelated Einstein model like Gaussian averaging of the same width as that in $D^{R}_{\alpha\beta}(k)$. This improved the frequencies in

$T_1$[110]but did not completely remove their unrealistic variation with wave vector. Fig. 12 shows dispersion curves for this branch calculated with no averaging of the outer shells SCH-N, and also with an independent Einstein model averaging using a Gaussian distribution SCH-G. The curve calculated using the quasiharmonic approximation is also shown as well as the experimental points of Beg and Nielsen[6] at 293K.

C. The SCH + Cubic Approximation

In the SCH approximation all even anharmonic terms such as $V_4$, $V_6$, ... that appear in a first order perturbation of the anharmonic shift to the phonon frequencies are included.[7] The leading connection to the SCH approximation in perturbation theory is the cubic anharmonic term. In the SCH+C approximation we add this term as a perturbation to the SCH frequencies. The inclusion of cubic anharmonic terms leads to interactions between the phonons which produce finite phonon lifetimes. The frequency of the phonon is now identified with the position of a resonance in the response function $A(q\lambda,\omega)$ of the crystal to an external probe when it is assumed that the probe creates or destroys a single phonon

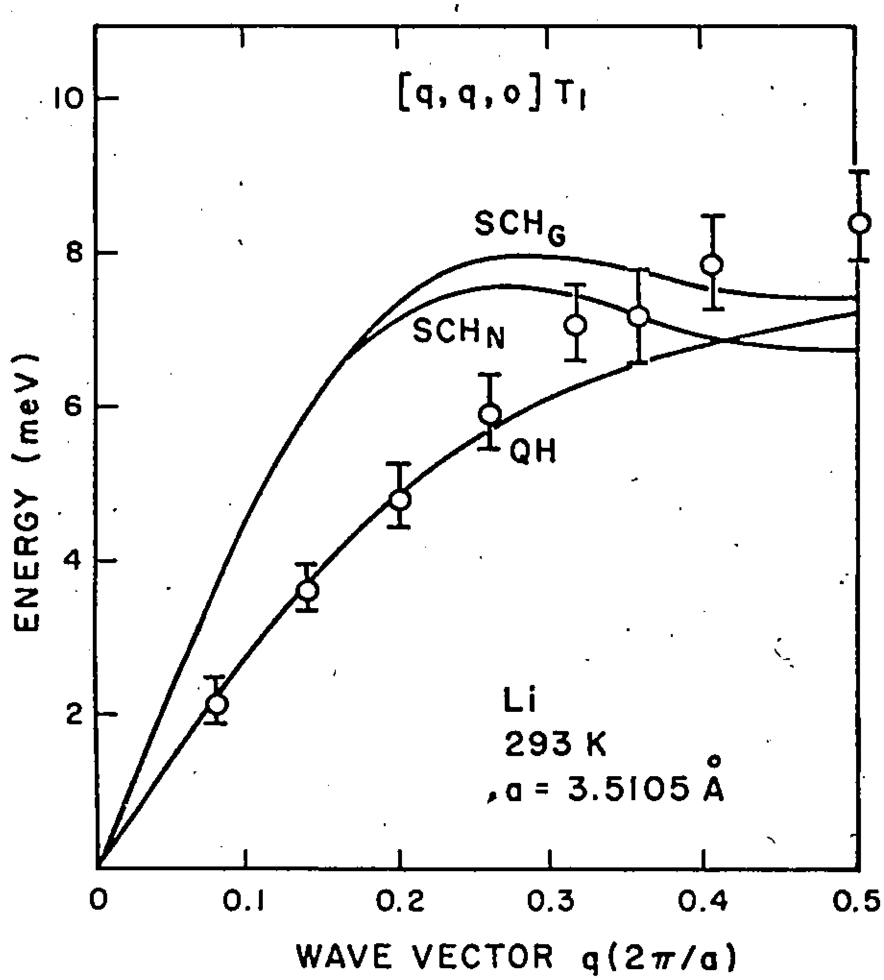



Fig. 12. $T_1$[110] Branch for Li

$$A(q\lambda,\omega) = \frac{8\omega^2(q\lambda)\Gamma(q\lambda,\omega)}{\{-\omega^2 + \omega^2(q\lambda) + 2\omega(q\lambda)\Delta(q\lambda,\omega)^2\} + \{2\omega(q\lambda)\Gamma(q\lambda,\omega)\}^2} \quad (4.16)$$

where $\Delta(q\lambda,\omega)$ is the shift in the SCH frequency resulting from the addition of the cubic term. $\Gamma(q\lambda,\omega)$ is the inverse lifetime of the phonons.[8]

In order to simplify the calculations we made the following approximation, the starting frequencies in the calculation of the frequency shifts introduced by the addition of the cubic anharmonic term were those calculated from $V_{eff}(r)$ and $D^R_{\alpha\beta}(k)$ only. Tests of the dependence of $\Delta$ and $\Gamma$ on $\omega(q\lambda)$ showed that this approximation of leaving out $D^Q_{\alpha\beta}(k)$ could lead to 10% error in $\Delta$ and $\Gamma$ or $\simeq$2% in the final SCH+C frequencies.

In the calculation of the response function $A(q\lambda,\omega)$ we made the approximation of summing the cubic anharmonic coefficient

$$\left\langle \frac{\partial^3 V_{II}(|r_{\ell\ell'}|)}{\partial r_\alpha(\ell)\,\partial r_\beta(\ell')\,\partial r_\delta(\ell'')} \right\rangle$$

to five shells only. To test the validity of this approximation we compared phonon frequencies obtained when only 3 shells and when 5 shells were summed over in the cubic coefficient. The comparison showed that the frequencies were the same to within 2% for all $q \geqslant 0.1(2\pi/a)$.

The response function $A(q\lambda,\omega)$ appears in the calculation of the dynamic structure factor $S(Q,\omega)$ which is proportional to the cross-section for coherent inelastic scattering of neutrons. This $S(Q,\omega)$ is usually expanded in powers of scattering from single phonons, pairs of phonons and multiple phonons. That is

$$\begin{aligned} S(Q,\omega) &= S_1(Q,\omega) + S_2(Q,\omega) + S_{12}(Q,\omega) \\ &= S_p(Q,\omega) + S_2(Q,\omega) \end{aligned} \tag{4.17}$$

where $S_{12}(Q,\omega)$ represents the interference contribution between one and two phonon cases. Our calculations of $S_p(Q,\omega) + S_2(Q,\omega)$ revealed that the dominant contribution came from the one phonon part

$$S_1(Q,\omega) = n(\omega) + 1 \; |F(Q,q\lambda)|^2 A(q\lambda,\omega)\,\Delta(Q - q) \tag{4.18}$$

where $F(Q,q\lambda)$ is the structure factor and $n(\omega)$ the Bose function.[9]

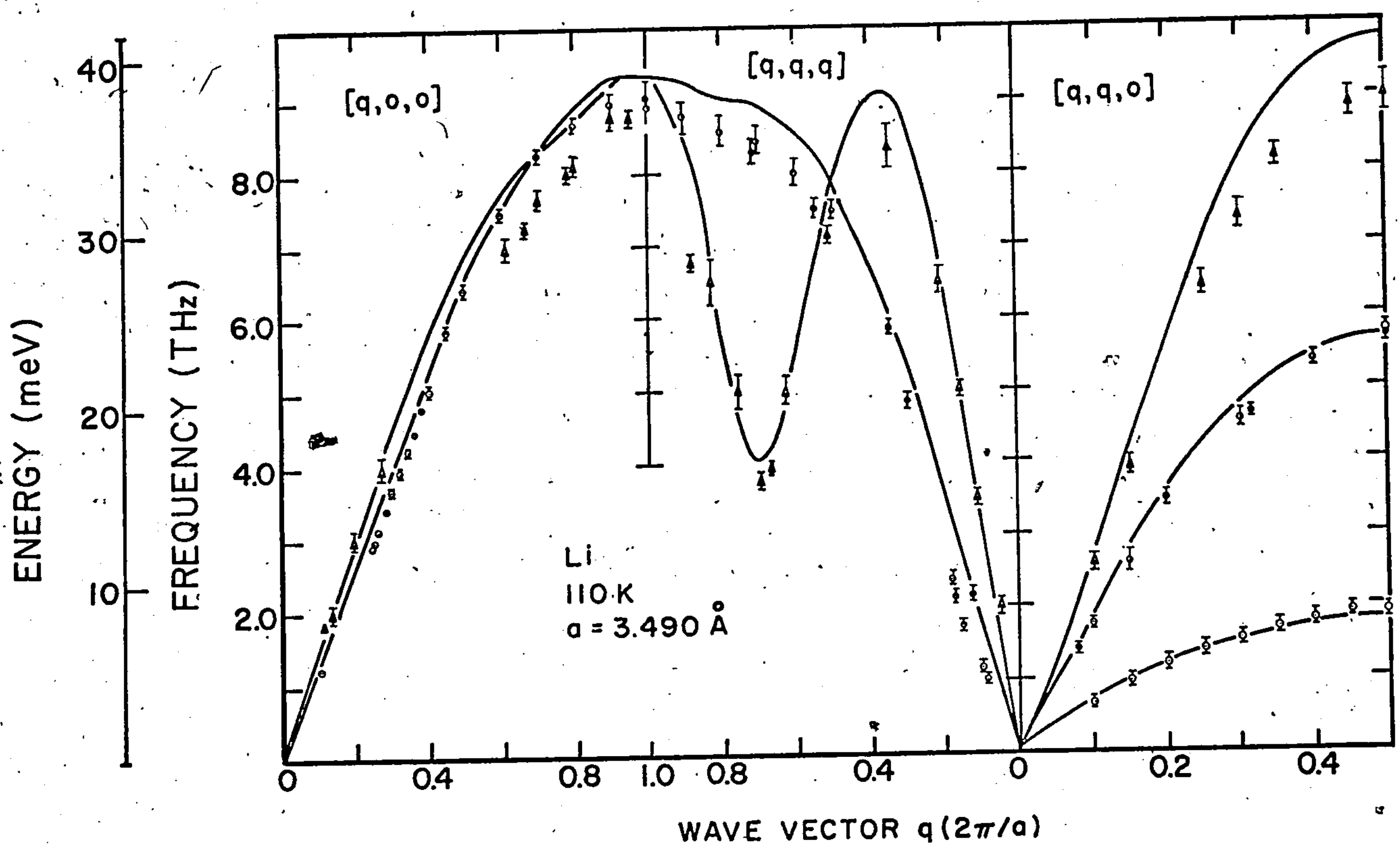



Fig. 13 Dispersion Curves for Li

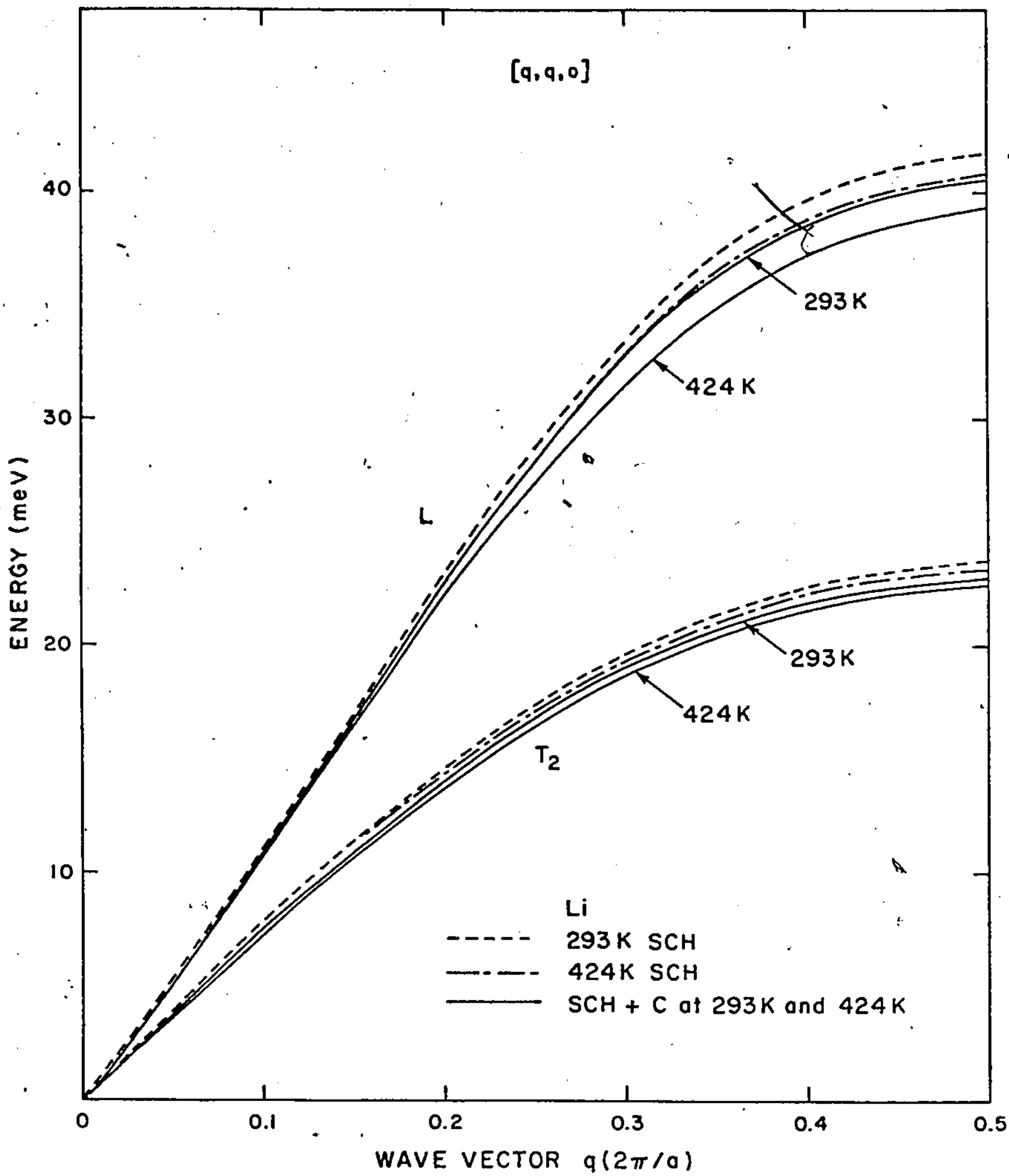

[q,q,o]
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
ENERGY (meV)
WAVE VECTOR q(2π/a)
L
T2
293K
424K
293K
424K
Li
293K SCH
424K SCH
SCH + C at 293K and 424K

Fig. 14

## 4.4 Results

### A. Low Temperature Phonon

The phonon dispersion curves for Li at 11OK calculated with the cubic term added (SCH + C) and using the DRT ion-ion interaction potential are shown in Fig. 13, and compared with the experimental data of Beg and Nielsen. The comparison shows that there is good overall agreement but there are also some discrepancies particularly around $q^{*} = (1,1,0) = (2\pi/a)q$, and at large wave vectors along the L[qqo] branch. In a previous calculation of the dispersion curves in Li using the DRT potential and the QH approximation, Dagens[10] et al found similar but somewhat larger discrepancies. It follows from this that the downward shifts in frequency introduced by the addition of the cubic anharmonic term is not large enough to make agreement with experiment better. It is possible that the discrepancy at this low temperature may be a reflection of the ion-ion potential used rather than the theory, however, we return to this point in chapter 5. In Fig. 14 which shows the longitudinal and transverse $T_2$ branches we can see that the addition of the cubic term does not greatly alter the frequencies calculated in the SCH approximation.

B. Temperature Shift

In Fig. 15 the dispersion curves calculated at 293K are shown and in this case we notice that the discrepancy along the L[qqo] branch is greater, also the $T_2$[qqo] branch now clearly lies above the experimental points. One of the reasons for this greater discrepancy could be that the theory does not predict a large enough downward shift in frequency with temperature, and from Fig. 14 we see that the downward shifts in frequencies from 293 to 424K is not large. It is also possible that since the potential used simulates the non linear electron screening only between pairs of ions, the discrepancy could be a reflection of the role of three- and four- body interactions in Li which are not represented in the present potential, or it could be that the pair potential is not sufficiently accurate. In chapter 5 we assess which of these three factors is the likeliest cause of the discrepancy.

With regard to the $T_2$[qqo] branch, we note that in Na and K it has been found that the shift in the energy of the phonons along the branch in going from QH to SCH approximations is negative, the shifts obtained when the cubic term is added to SCH is also negative in these materials.

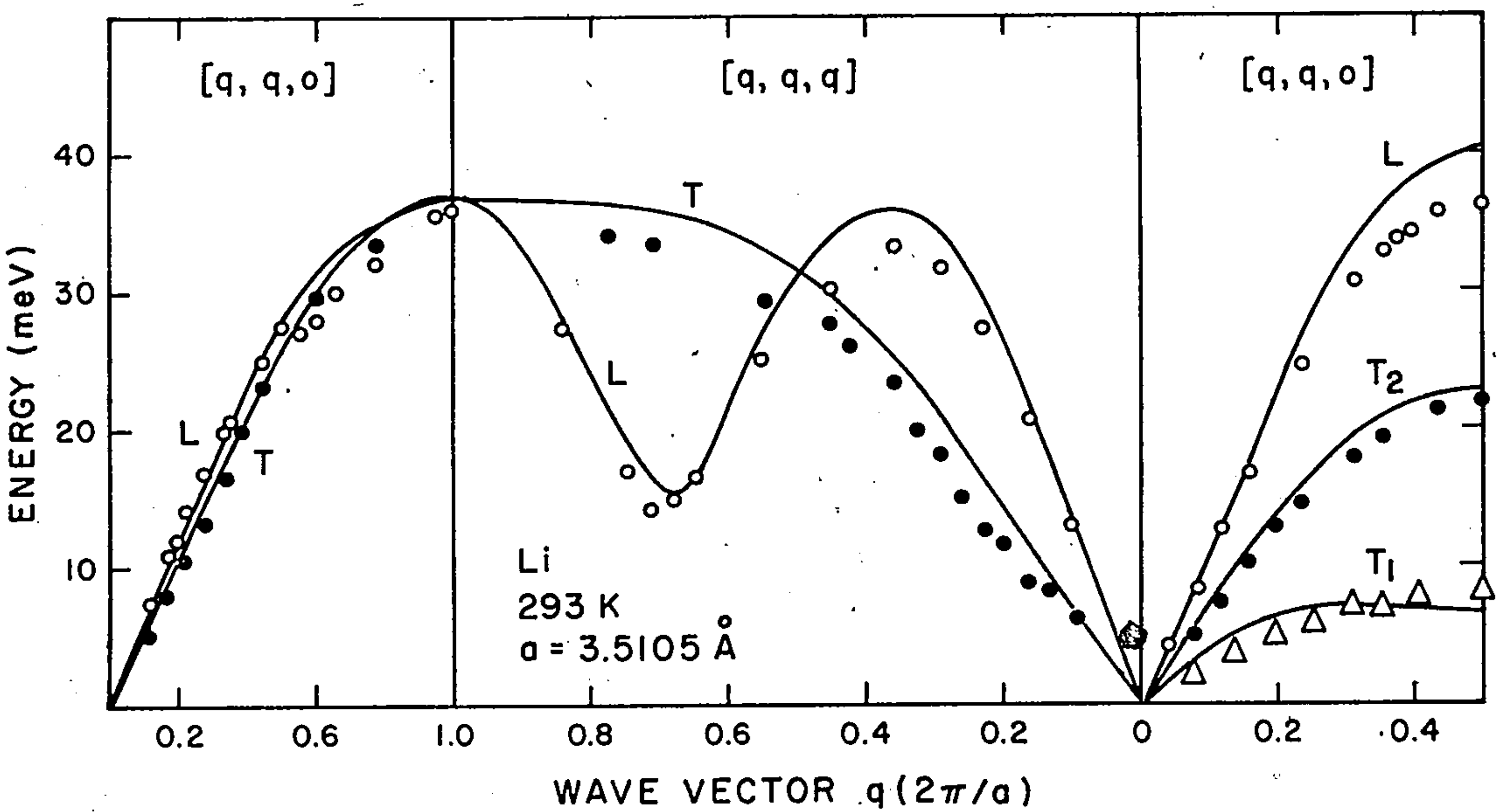



Fig. 15 Dispersion curves for Li

In the case of Li we have found similar results except that here the corresponding energy shifts are smaller. Table 14 shows the phonon energies obtained in different approximations for selected wave vectors. Generally the shifts in Li, (i.e. cubic shift and total shift) are a smaller percentage of the energy than in Na and K. For example there is a 5.5% shift in energy from 110 to 424K (.94 of the melting point) in Li at $q^*= (.5,.5,0)$ for the longitudinal phonons, the calculated shift is 3.9%. In K this phonon has an energy shift of 8% between 90K and 311K (.93 of the melting point), whereas the calculated shift is 9%. The corresponding calculated shifts for the $T_2$ phonon at $q^*= (.5,.5,0)$ between the same sets of temperatures are 3.4% in Li and 8.8% in K. While the observed shifts are 10.2% in Li and 9% in K. In Fig. 16 the observed and calculated energy shifts from 110K are shown.

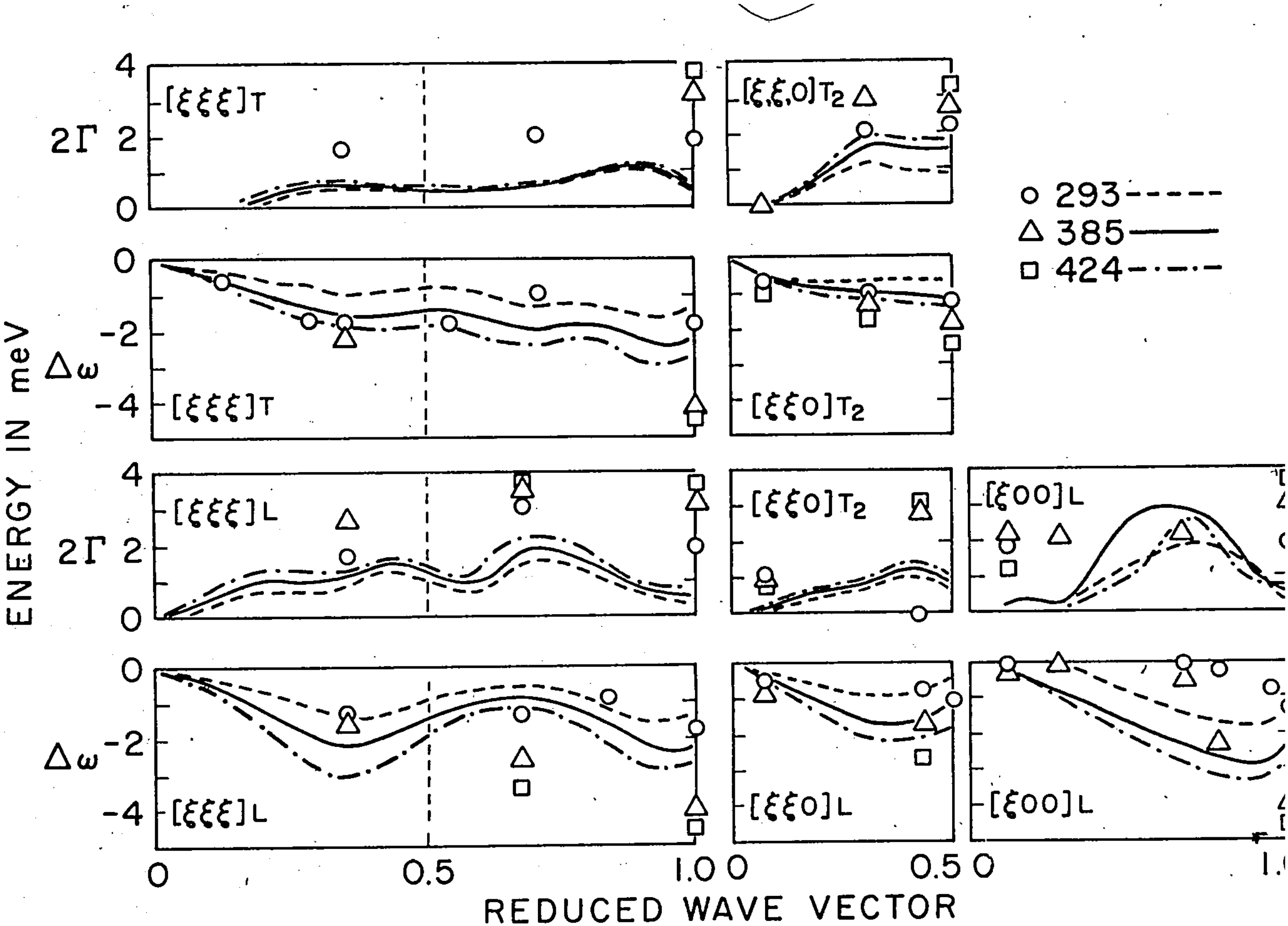
## C. Phonon Groups

We made calculations of the dynamic structure factor $S(Q,\omega)$ which included the one phonon scattering, the two phonon scattering, and the interference contribution between these two. The $S(Q,\omega)$ was also convoluted with a Gaussian function of full width at half maximum equal to the instrument resolution shown by the horizontal bars with the observed phonon groups, in this way comparison with experiment becomes more direct.

The $S(Q,\omega)$ calculated with the SCH+C theory for the longitudinal polarization at $q^*=(2-\xi,2-\xi,2-\xi)$ with $\xi=0.677$ and at the temperatures 110, 293, 385 and 424K are shown in Fig. 17, these are to be compared with the corresponding observed phonon groups shown in Fig. 18. The comparison shows that the shapes of the calculated phonon groups are similar to the observed ones, but that overall their widths are too low. For example, we found 2.5 meV at 424K as against 4meV for the observed phonon group.

In general the calculated phonon lifetimes are often three or four times as large as the observed ones. Some of this discrepancy can be attributed to the SCH+C theory rather than the interaction potential used because a comparison of the lifetimes calculated using SCH+C theory with those calculated using molecular dynamical theory in both cases using the same ion-ion interaction has been made in K, and it showed that a factor of two discrepancy arises from the use of SCH+C theory.[11]

The phonon groups shown in Fig. 17 do not have the large intensity on the low energy side of the observed groups. Such large intensities on the low frequency side of some phonon groups have been observed in K and these could be reproduced by including the interference terms.[12] We



ENERGY IN meV
2Γ
Δω
[ξξξ]T
[ξ,ξ,0]T2
[ξξ0]T2
[ξξξ]L
[ξ00]L
[ξξ0]L
○ 293
△ 385
□ 424
4
2
0
-2
-4
0
0.5
1.00
0.50
REDUCED WAVE VECTOR


Fig. 16

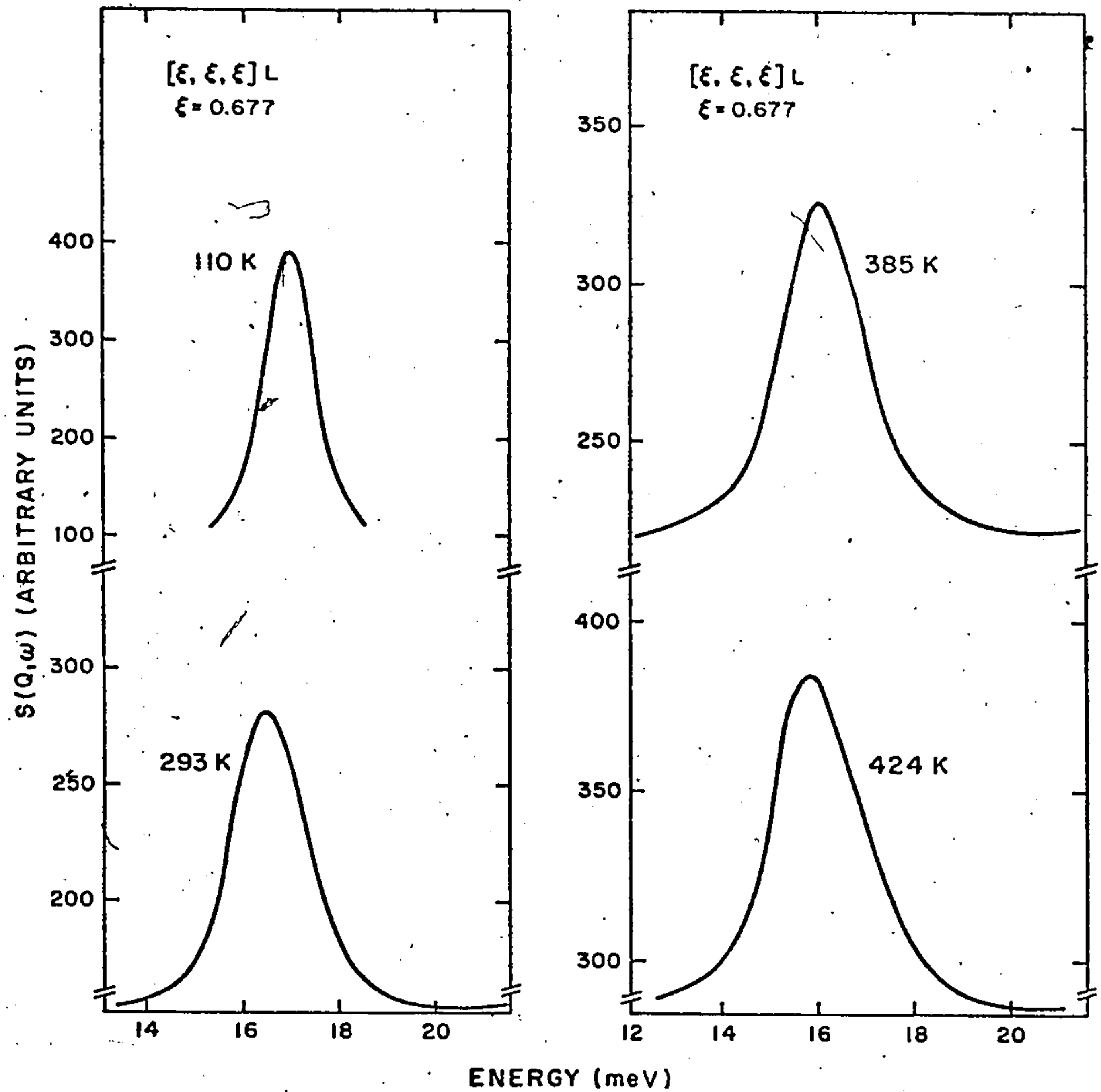



Fig. 17 Calculated Phonon Groups

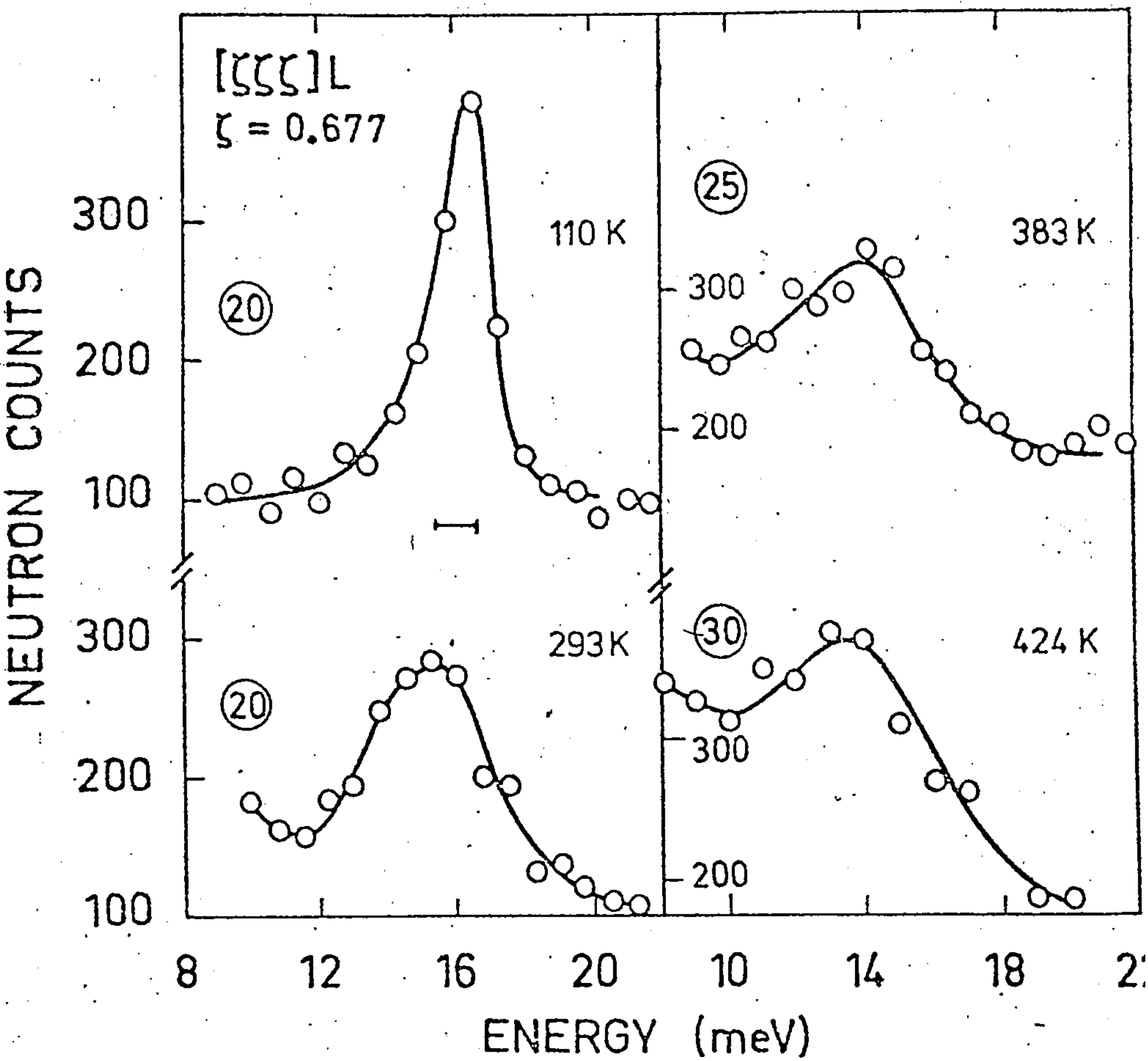



Fig. 18 Observed Phonon Groups

investigated this intensity by calculating $S(Q,\omega)$ for three phonons at three different wave vectors which had the same reduced wave vector. The results shown in Fig. 19 indicate that the interference does not contribute much scattering intensity at low energy. Therefore the observed intensity at low energy arises from scattering from three or more phonons. In the SCH+C theory, a single phonon can decay to two phonons via the coupling introduced by the cubic anharmonic term, the above discussion indicates that higher order processes are important.

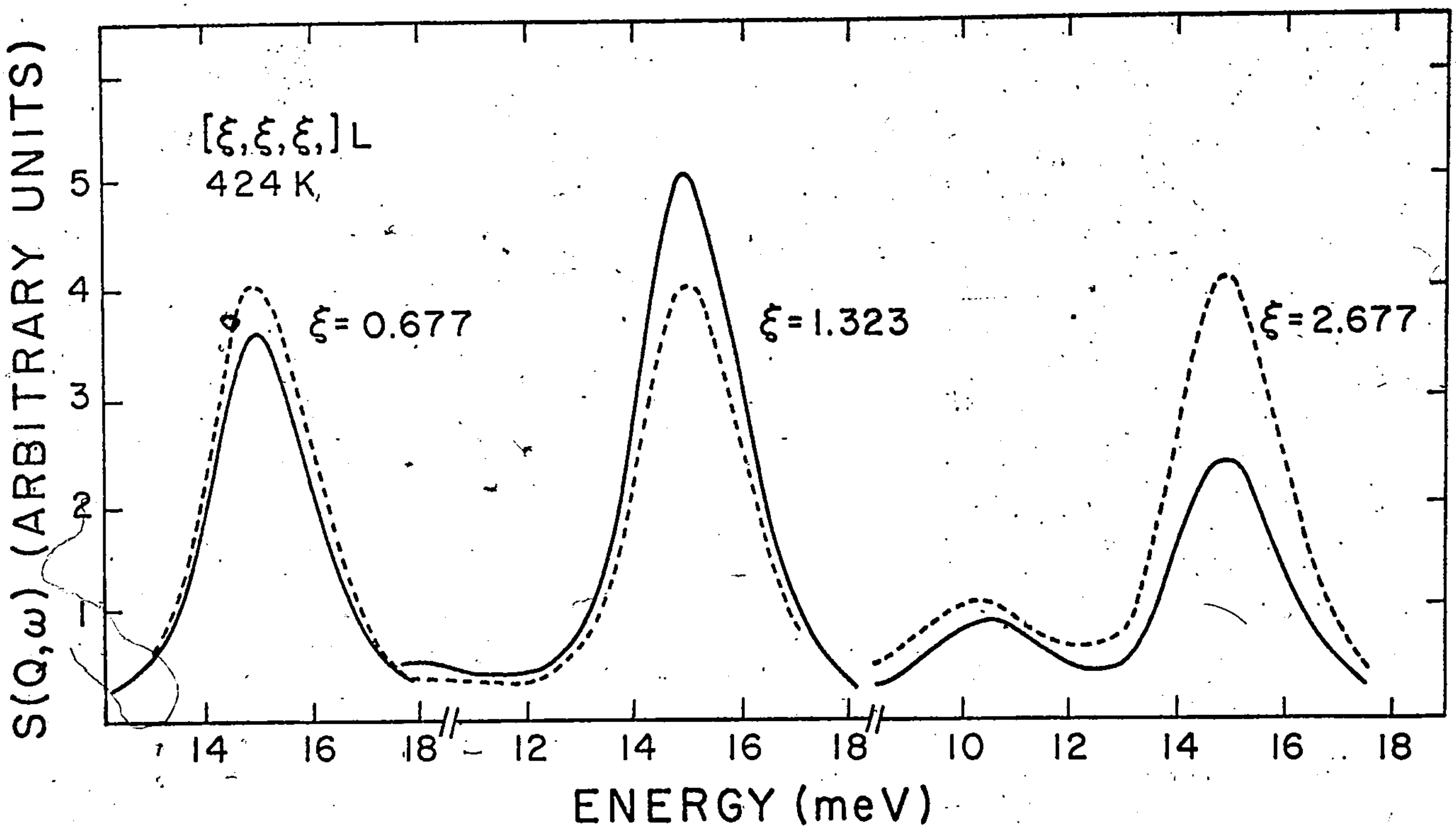



Fig. 19 Calculated $S(Q,\omega)$. --- excludes $S_{12}$

Table 14. Selected Phonon energies (meV) and intrinsic phonon group widths, $2\Gamma$ (meV) (phonon lifetime, $\gamma = \Gamma^{-1}$)

| Phonon | | Model | 110K | 293K | 424K |
|---|---|---|---|---|---|
| (1,0,0)L | | QH | 40.0 | 39.3 | 38.5 |
| | | SCH | 39.8 | 38.9 | 38.0 |
| | hω | SCH+C | 38.6 | 36.9 | 36.0 |
| | | OBS | 37.5±1.0 | 35.8±1.0 | 33.1±1.0 |
| | 2Γ | CAL. | 0.3 | 0.3 | 0.7 |
| | | OBS | - | 1.94±0.6 | 3.85±0.6 |
| (0.5,0.5,0)L | | QH | 41.2 | 40.2 | 39.0 |
| | | SCH | 42.3 | 41.7 | 40.8 |
| | hω | SCH+C | 41.0 | 40.6 | 39.4 |
| | | OBS | | 36.5±1.0 | |
| | 2Γ | CAL. | 0.6 | 0.8 | 1.0 |
| | | OBS.+ | - | 0.0±0.3 | 3.12±0.45 |
| $(0.5,0.5,0)T_2$ | | QH | 24.1 | 23.9 | 23.8 |
| | | SCH | 24.0 | 23.9 | 23.6 |
| | hω | SCH+C | 23.5 | 23.1 | 22.7 |
| | | OBS. | | | |
| | 2Γ | CAL. | 0.3 | 0.8 | 1.8 |
| | | OBS | - | 2.20±0.5 | 2.77±0.64 |
| $(0.5,0.5,0)T_1$ | | QH | 7.3 | 7.3 | 7.3 |
| | | SCH | (5.6) | (7.6) | (8.6) |
| | hω | SCH+C | (5.1) | (6.6) | (7.5) |
| | | OBS. | | 8.6±0.6 | |
| | 2Γ | CAL. | 0.3 | 1.6 | 2.8 |
| | | OBS. | - | | |

## REFERENCES


1. Mark Rasolt, Roger Taylor, Phys. Rev. B 11, 2717 (1975).
2. P. Hohenberg, W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn, L.J. Sham, Phys. Rev. 140, A1133 (1965).
3. I.V. Abarenkov, V. Heine, Phil. Mag. 12, 529 (1965).
4. D.J.W. Geldart, Roger Taylor, Can. J. Phys. 48, 167 (1970).
5. M.S. Duesbery, Roger Taylor, J. Phys. F 7, 47 (1977).
6. M.M. Beg, M. Nielsen, Phys. Rev. B 14, 4266 (1976).
7. H.R. Glyde, Can. J. Phys. 49, 761 (1971).
8. H.R. Glyde, Roger Taylor, Phys. Rev. B 5, 1206 (1972).
9. H.R. Glyde, Can. J. Phys. 52, 2281 (1974).
10. L. Dagens, M. Rasolt, R. Taylor, Phys. Rev. B 11, 2726 (1975).
11. H.R. Glyde, J.P. Hansen, M.L. Klein, Phys. Rev. B 16, 3476 (1977).
12. J. Meyer, G. Dolling, R. Scherm, H.R. Glyde, J. Phys. F 6, 943 (1976).

# CHAPTER 5

## Discussion and Conclusion

The two aims of this project have been firstly to study the compressibility problem with a view of extending the usual lattice dynamical theory so that the elastic constants and bulk modulus calculated by the method of long waves should be exactly the same as those calculated by the method of homogeneous deformations. Secondly to examine the anharmonic properties of Li both for its own interest as well as with the purpose of testing the effective ion-ion interaction potential used to describe it. We begin with the discussion of the compressibility problem.

In the pseudopotential theory of simple metals the assumption is always made that the pseudopotential which replaces the full electron-ion potential in the metal is a small perturbation of the free electron gas, and this justifies the use of perturbation theory usually to second order in the pseudopotential although some calculations have been made to third order[1]. To calculate the bulk modulus by static methods we first calculate the ground state energy and then differentiate it twice with respect to volume. In the dynamical method the bulk modulus is calculated from

$$B = \frac{1}{3}(C_{11} + 2C_{12})$$

Firstly, the total energy of the static lattice is expanded in a Taylor series in powers of the ion displacement then after taking the long wave limit of the dynamical matrix we can find expressions for the elastic constants which except for $\Delta_{bs}$ are the same as those obtained by taking strain derivatives of the total energy. By comparing these expressions it is easy to see what extra terms have to be added to the long wave harmonic dynamical matrix in order to bring the expressions for the elastic constants derived from it into coincidence with those from the static method. What has been done here is to extend this dynamical matrix to finite phonon wave vectors while working consistently to second order in the electron-ion interaction in both of the two methods.

In our extension of the long wave dynamical matrix to finite wave vectors great importance is attached to the fact that the force constants which enter the dynamical matrix describe changes in the total energy of the crystal brought about by the displacement of two ions. From the fact that $\Delta_{bs}$ which accounts for the difference between the elastic constants $C_{11}$ and $C_{12}$ and the bulk modulus obtained by the two methods comes from differentiation of the screening part of the total energy with respect to volume, we note that the results obtained from dynamics are different because no account is taken of the change in the total energy resulting from changes in the screening as the ions are displaced.[2] The dynamical matrix $D^{sc}_{\alpha\beta}(k)$ we have added now takes this into account. In terms of the picture of a metal as consisting of interacting pseudoatoms described by Ziman,[3] then we can state that as the pseudoatoms move in the crystal they not only change the structure factor of the solid but are themselves deformed somewhat. It is this deformation that has not been previously incorporated into lattice dynamical theory.

To take this deformation into account we write the total volume derivative in the form

$$\frac{d}{dv} = \frac{\partial}{\partial v} + \frac{\partial}{\partial v_{sc}}$$

where $\partial/\partial v$ operates on the explicit volume dependence of the function differentiated, and $\partial/\partial v_{sc}$ operates on the screening. In the reciprocal space formulation the corresponding expression is

$$\frac{d}{dv} = \frac{\partial}{\partial v} + \frac{dq}{dv}\frac{\partial}{\partial q} + \frac{dk_f}{dv}\frac{\partial}{\partial k_f}$$

This method of writing the total volume derivative has been used by Wallace,[4] Brovman[1] et al and by Finnis.[2] We use this as a guide and write the derivatives with respect to the ion displacements $U_\alpha(\ell)$ in the form

$$\frac{d}{dU_\alpha(\ell)} = \frac{\partial}{\partial U_\alpha(\ell)} + \frac{\partial}{\partial U_\alpha(\ell)_{sc}}$$

where the second term operates only on the screening function. By writing the derivatives with respect to the ion displacements in two parts as done above, we find that not only do we get the usual dynamical matrix but we also get the extra term $D^{sc}_{\alpha\beta}(k)$ which contains the operator $\hat{\Delta}_{bs}$ and the factors $d\Omega_o/dU_\alpha(\ell)$.

The fact that a lattice wave is regarded as a rearrangement of atoms at constant volume does not preclude local variations of the electron density as the ions move, it does however, mean that such local variations must add up to give a net zero volume change in a crystal of macroscopic size. Again in terms of pseudoatoms the local variations of electron density are equivalent to the deformations of the pseudoatoms which we now represent by changes in the volume per atom. To the extent that the net sum of such changes must be zero, and since in a primitive lattice there is an atom $R(\ell)$ for every one at $R(-\ell)=-R(\ell)$, these changes in volume per atom must be described by odd functions so that $\sum_{\ell}\frac{d\Omega}{dU_{\alpha}(\ell)}=0$. To meet this requirement we have used $\sin k_{\alpha}R_{\alpha}(\ell)$ to describe the displacements of the ions as against $\cos k_{\alpha}R_{\alpha}(\ell)$ as has been done by Heine and Weaire.[5] The total dynamical matrix thus derived still satisfies the ~~her~~miticity requirement $D_{\alpha\beta}(k)=D_{\alpha\beta}(-k)$.

An examination of the dispersion curves for all the metals studied with the new dynamical matrix shows that the contribution of $D^{sc}_{\alpha\beta}(k)$ to the phonon frequencies is not large at any wave vector except around $\overset{*}{q}=(.7,.7,.7)$ in the Taylor model. Here this additional dynamical matrix lowers the frequencies by rather large amounts. This effect comes about because at this wave vector all the atoms are vibrating in phase hence the change in density can be expected to be largest.

From Tables 2, 6 and 11 we see that the values of $\Delta_{bs}$ are dependent on the pseudopotential model adopted, hence this quantity is not only a function of the volume. The contribution of $\Delta_{bs}$ to the bulk modulus or the elastic constants calculated with the point ion model is negative in all metals considered, even in Al where the model does not yield as extensive information as in the alkali metals. We therefore find that our calculations do not bear out the prediction which has been made viz that $\Delta_{bs}$ should be $\sim 50\%$ of the bulk modulus in polyvalent metals. The constants of this model in the case of Na and K were chosen to give the observed crystal binding energy and its first two volume derivatives and so within the accuracy of the determination of these constants the dynamics should give the observed bulk modulus when $\Delta_{bs}$ is included.

In the model of Ho[6] the parameters of the pseudopotential were fitted to the elastic constants using the method of long waves when $D^{sc}_{\alpha\beta}(k)$ is not included. In the light of the above considerations it would be more appropriate to include $D^{sc}_{\alpha\beta}(k)$ in the determination of these parameters. No data were available for Al in this model and so calculations were made for the alkali metals only. The results obtained with this model agree with those found using the point ion model, namely that $\Delta_{bs}$ is negative and that $D^{sc}_{\alpha\beta}(k)$ overall makes a progressively small percentage change to the frequencies with increasing phonon wave vector.

The Taylor model is slightly similar to the Ho model in that it uses a square well to describe the ion core region and a Coulomb interaction outside it. The constants of the model are however, determined in a completely different manner, also the screening function used is different. Since no experimental data is required in determining the parameters of this model calculations made with the model provide a severer test of theory. An examination of the dispersion curves calculated with this model shows that the details in the dispersion curves calculated without $D^{sc}_{\alpha\beta}(k)$ are still produced when $D^{sc}_{\alpha\beta}(k)$ is added, but overall agreement with experiment is better when this extra term is excluded from the total dynamical matrix. On the other hand the value of $\Delta_{bs}$ is still found to be negative in agreement with the calculations done with the other two models.

We have found that all the three models give good descriptions of the ground state energies. The calculated values are all within 4% of the observed ones except in Al in the point ion model where the figure is 13%. In the case of the theoretical values of the bulk moduli which were calculated by numerical differentiation of the ground state energy the deviations from experiment can be large depending on the model under consideration. However, in all metals studied and for all models used the bulk modulus found from differentiation of the energy is the same as that found from the long wave limit of the total dynamical matrix.

The calculations made on Pb using a local Heine-Abarenkov model yielded a large and positive value for $\Delta_{bs}$, hence the possibility of obtaining large and positive values of $\Delta_{bs}$ in polyvalent metals is not ruled out, on the other hand generalization of this finding to all polyvalent metals seems unjustified in the light of our calculations on Al based on the point ion model and the Taylor model. We note finally on this point that Brovman et al have calculated the elastic moduli in Na and Al using a local Heine-Abarenkov type of model. They calculated the bulk modulus by differentiating the energy and by using the method of long waves in the usual form. Their findings were that the dynamic approach to the bulk modulus yields a value which is higher than that found by the static method. Since $\Delta_{bs}$ accounts for this difference this means that it is negative in both of these metals.

One of the conditions which have to be met in order for the Cauchy relation to be satisfied is that the pressure should be zero. In the first three models used we calculated the pressure by numerically differentiating the ground state energy with respect to volume and we found that although small in some cases the pressure is still not exactly zero. When the influence of the electron gas and the pressure are taken into account then the deviation of $(C_{12} - C_{44})$ from zero gives an indication of the importance of three-body forces. The results obtained indicate that when non-locality is neglected then of the three alkali metals Na, K and Li, the last is the one in which three-body forces are likely to play a more significant part.

To summarize the results we can state that this study has shown that it is possible to make a simple extension of conventional lattice dynamical theory by extrapolating to finite wave vectors the long wave dynamical matrix which gives the same results for the elastic moduli as those obtained by differentiation of the energy and still retain the smallness of the electron-ion pseudopotential as a consistency criterion in both types of calculation. The additional dynamical matrix does not appreciably alter the frequencies but it should be of interest to investigate its effect on other properties such as Gruneisen parameters. Also since non-locality can be important in some cases, for instance in Li, its incorporation into $D^{sc}_{\alpha\beta}(k)$ should be a useful extension of the theory described herein.

In the remainder of this chapter we discuss the anharmonic properties of Li. The most outstanding single result of the study is that Li is not very anharmonic. Compared to Na and K, Li is the least anharmonic of these alkali metals. This can be understood by looking at the maximum frequencies obtained as well as the interionic potential used to describe it.

The Li atom is the lightest of the alkali metals, and because $\omega \propto m^{-\frac{1}{2}}$, on the basis of the mass difference alone we would expect a ratio of 1.8 between the maximum phonon frequency in Li and that of Na, and a corresponding ratio of 2.4 for K. The ratios calculated are 2.5 for Na and 4.0 for K. If on the other hand the interionic potential in Li is strong, then it can counteract the effect of a small mass by providing strong restoring forces as the ions vibrate away from their lattice positions. The amplitude of the vibrations would then be reduced by these forces and the frequency would be increased. We have already pointed out that the potential in Li is strong on account of the fact that the p-wave component in the wave function of the conduction electrons is not shielded from the nucleus by the two s-state electrons in the core of the Li ion.

A traditional[7] measure of the importance of the anharmonic terms is the ratio $\delta$ of the RMS vibrational amplitude $<U^2>^{1/2}$ to the lattice spacing R. In Table 15 estimates of $\delta=<U^2>^{1/2}/R$ at the melting points of Li, Na and K are given. The values of $<U^2>^{1/2}$ are estimated from

$$<U^2> = \left(\frac{\hbar}{k}\right)^2 \left(\frac{9kT}{M\Theta_D}\right)$$

which is the harmonic result in the high temperature limit using a Debye approximation to the frequency spectrum. The table shows that the large Debye temperature $\Theta_D$ in Li has counteracted the effect of the small mass and that as a result the shifts in frequency due to the anharmonicity should be smaller in Li. In Table 16 we show the percentage anharmonic shifts $\Delta\omega/\omega$ in phonon frequency calculated using SCH + C theory for Li, Na and K. The values calculated for Li are smaller than those calculated for Na and K, and the observed values are also smaller. Since the SCH + C theory works well for Na and K, the large differences between the observed and calculated values in Li are a reflection of the potential.

The weak shielding of the ion core in Li gives rise to a soft repulsive part in the potential. This point can be made more precise by considering the expansion of the potential

Table 15. Estimates of the expansion parameter $\delta=\langle u^2\rangle^{\frac{1}{2}}/R$ at the melting temperature $T_m$

| | M | $T_m$ | $a_o(T_m)$ | $\Theta_D(T_m)$ | $\delta$ |
|---|---|---|---|---|---|
| | (amu) | (K) | | K | |
| Li | 7 | 453 | 3.54 | 430 | 12.7 |
| Na | 23 | 371 | 4.25 | 160 | 14.2 |
| K | 39 | 337 | 5.34 | 100 | 13.3 |

Table 16. Percentage anharmonic shift $\Delta\omega/\omega$ in phonon frequency calculated using SCH + C theory for Li (90 → 424K), for Na (5→361K), and for K (5 → 311K). The observed values in brackets are : Li Ref. 9 and K Ref. 10

| Phonon | Li | Na | K |
|---|---|---|---|
| (1.0,0,0) | -7.2% | -12.8% | -17.5% |
| | (-12±6%) | | (-14%) |
| (0.5,0.5,0)L | -4.0% | -10.0% | -11.5% |
| | (-6±3%) | | |
| $(0.5,0.5,0)T_2$ | 03.5% | -10.8% | -14.5% |
| | (-11±3%) | | |

as suggested by Horner.[8] Usually the potential is expanded powers of the displacement

$$\phi = \phi_o + \tfrac{1}{2}\phi_2 U^2 +$$

Horner pointed out that the expansion parameter should include a measure of the size of the derivatives of the potential. The size of these derivatives is largely fixed by the steepness of the repulsive part of the potential $\phi$ which can be approximated by

$$\phi(r) = \varepsilon\left(\frac{\sigma}{r}\right)^n$$

where the index n measures the steepness of $\phi(r)$. A more precise expansion parameter for $\phi$ is $\lambda = n\delta = n\langle U^2\rangle^{\frac{1}{2}}/R$, and if n and hence $\lambda$ is small, the Taylor series expansion converges rapidly. A comparison of the relative sizes of the cubic and quartic anharmonic terms gives an indication of how rapidly the Taylor series expansion converges and that in turn indicates how large n is and hence how steep the repulsive part of the potential.

In the rare gases the quartic shift in frequency $\Delta_4$ is large and is about twice the shift $\Delta_3$ introduced by adding the cubic anharmonic term to the SCH approximation.

The Taylor series does not converge rapidly and this is consistent with the large n ($n \simeq 12$) in these materials. This quartic shift $\Delta_4$ is approximately given by the difference between the QH and SCH frequencies. In the alkali halides, the quartic and cubic frequency shifts are comparable in size suggesting a more rapid convergence of the Taylor series here than in the rare gases, and consequently a smaller value of n. From the data given in Table 14 we see that in Li the difference between the QH and the SCH frequencies is quite small. This means that the shift $\Delta_4$ should also be quite small. The cubic anharmonic shift on the other hand is relatively larger and hence the Taylor series expansion of the Li potential in terms of the Horner parameter $\lambda$ should converge rapidly so that the core of the interionic potential is quite soft (n small). Finally on this point we note that a small $\Delta_4$ is what is required to get agreement with experiment. This is because $\Delta_4$ is generally positive and as can be seen in Fig. 15 lower frequencies are required to improve agreement with experiment at high temperatures.

The overall agreement of the calculated frequencies and anharmonic shifts with experiment in Li is not as good as in Na and K. To improve agreement with experiment, lower frequencies at high temperatures or larger negative shifts are required. Since the potential when expanded in a Taylor series in terms of the Horner parameter converges rapidly, the large negative shifts required cannot be obtained by including higher order anharmonic terms. If on the other hand three-body forces play a significant role in Li, these would introduce an additional class of cubic terms in $\Delta_3$ and these could substantially increase its size.

To conclude we note that the long range nature of the potential made the calculations difficult. It particularly affected the $T_1[qqo]$ branch which did not stabilize even when the force constants were summed to 30 shells of neighbours. However, by expressing $V_{II}(r)$ as the sum of a $V_{eff}(r)$ and an asymptotic part evaluated in reciprocal space the QH frequencies could be obtained exactly. The averaging of the force constants in the SCH approximation was found to be important for the $T_1[qqo]$ branch. This averaging could not be done exactly in reciprocal space. Since it is possible that the distant neighbour force constants affect other branches also a more accurate determination of the SCH frequencies as well as the SCH + C frequencies would be to fit a Born von Karman model to the QH dispersion curves. The force constants so derived could then be averaged exactly in r-space for the determination of the SCH frequencies.

## REFERENCES

1. E.G. Brovman, Yu M. Kagan, in Dynamical Properties of Solids edited by G.K. Horton and A.A. Maradudin.

2. M.W. Finnis, J. Phys. F 4, 1645 (1974).

3. J.M. Ziman, Adv. Phys. 13, 89 (1964).

4. D.C. Wallace, Thermodynamics of Crystals (Wiley, New York, 1972).

5. V. Heine, D. Weaire, in Solid State Physics 24, 249 (1970).

6. P.S. Ho, Phys. Rev. 169, 523 (1968) and in Ian M. Torrens Interatomic Potentials (Academic, N.Y. 1972).

7. R.E. Peierls, Quantum Theory of Solids (Oxford U.P., London 1955).

8. H. Horner, in Dynamical Properties of Solids edited by A.A. Maradudin and J.A. Venables (Academic, New York, 1976).

9. M.M. Beg, M. Nielsen, Phys. Rev. B 14, 4266 (1976).

10. W.J.L. Buyers, R.A. Cowley, Phys. Rev. 180, 755 (1969).

## APPENDIX

A. Evaluation of $F_3(q)$

From equations (4.12) and (4.13) $F_3(q)$ is given by

$$F_3(q) = \frac{2A_3}{\Gamma(3/2)}\, 2\pi\int_0^\pi \sin\theta d\theta \int_0^\infty \frac{x^2dx}{(2k_f)^3}\, \exp(-\frac{iqx}{2k_f}\cos\theta)\int_0^\infty u^2e^{-x^2u^2}\cos x du \qquad (1)$$

θ- integration:-

$$\text{Let } I = \int_0^\pi \sin\theta d\theta e^{-i\eta\cos\theta}$$

$$= \frac{e^{i\eta x'} - e^{-i\eta x}}{i\eta x}$$

where $\eta = q/2k_f$

$$\therefore\ \frac{\Gamma(3/2)}{2A_3}\frac{(2k_f)^3}{(2\pi)}\, F_3(q)i\eta = \int_0^\infty xdxe^{i\eta x}\int_0^\infty u^2e^{-x^2u^2}du\cos x -$$

$$\int_0^\infty xdxe^{-i\eta x}\int_0^\infty u^2e^{-x^2u^2}du\cos x$$

$$= \int_0^\infty u^2duI_1 - \int_0^\infty u^2duI_2 \qquad (2)$$

x- integration:-

$$I_1 = \int_0^\infty xdxe^{-u^2x^2} + i(1 + \eta)x$$

$$I_1 = \exp\left[-\frac{(1+n)^2}{4u^2}\right]\int_0^\infty x\,\exp\{-u^2[x - \frac{i(1+n)}{2u^2}]^2\}dx \tag{3}$$

By making the substitutions

$$x = y + \frac{i(1+n)}{2u^2}$$

$$\beta = \frac{1+n}{2u^2}$$

we find that

$$I_1 = \frac{1}{2u^2} + i\beta e^{-\left(\frac{1+n}{2u}\right)^2}\int_{-i\beta}^{\infty} e^{-u^2y^2}dy$$

$$= \frac{1}{2u^2} + \frac{i\beta}{u}\,e^{-\left(\frac{1+n}{2u}\right)^2}\,\frac{\sqrt{\pi}}{2}[1 + \mathrm{erf}(-i\beta u)]$$

$$\therefore \quad I_1 = \frac{1}{2u^2} + \frac{i(1+n)}{4u^3}\sqrt{\pi}\,e^{-\left(\frac{1+n}{2u}\right)^2} - \frac{(1+n)}{2u^3}D\left(\frac{1+n}{2u}\right) \tag{4}$$

where D(x) is Dawson's integral.

From equation (2) we have :-

$$I_2 = \frac{1}{2u^2} + \frac{i(1-\eta)}{4u^3}\sqrt{\pi}\, e^{-\left(\frac{1-\eta}{2u}\right)^2} - \frac{(1-\eta)}{2u^3} D\left(\frac{1-\eta}{2u}\right)$$

$$\therefore\ \frac{\Gamma(3/2)}{2A_3}\left(\frac{2k_f}{(2\pi)}\right)^3 F_3(q)\ i\eta = \int_0^{\infty} u^2 du[I_1 - I_2] \qquad (5)$$

From equation (5) we find an expression for $F_3(q)$, and since $F_3(q)$ is real, we retain its real part which is given by

$$F_3(q) = \frac{A_3\pi^{3/2}}{\Gamma(3/2)(2k_f)^3}\left\{\int_0^{\infty}\left(\frac{1+\eta}{\eta}\right) e^{-\left(\frac{1+\eta}{2u}\right)^2}\frac{du}{u} - \left(\frac{1-\eta}{\eta}\right) \times \int_0^{\infty} e^{-\left(\frac{1-\eta}{2u}\right)^2}\frac{du}{u}\right\} \qquad (6)$$

The integrals appearing in equation (6) were evaluated numerically.

B Evaluation of $F_4(q)$

The $\theta$- and $x$- integrations in $F_4(q)$ are the same as those in $F_3(q)$, and these give

$$\frac{\Gamma(2)}{2A_4}\left(\frac{2k_f}{(2\pi)}\right)^3 F_4(q) i\eta = \int_0^{\infty} u^3 du[I_1 - I_2] \qquad (7)$$

$$= \text{RHS}$$

Where $I_1$ and $I_2$ are the same as those in (5)

$$\text{RHS} = \int_0^{\alpha} u^3 du \Big[ \frac{i(1+n)}{4u^3} \sqrt{\pi}\, e^{-\left(\frac{1+n}{2u}\right)^2} - \frac{i(1-n)}{4u^3} \sqrt{\pi}\, e^{-\left(\frac{1-n}{2u}\right)^2} -$$

$$\frac{(1+n)}{2u^3} D\left(\frac{1+n}{2u}\right) + \frac{(1-n)}{2u^3} D\left(\frac{1-n}{2u}\right) \Big] \tag{8}$$

By taking the imaginary part of (8) we find that

$$F_4(q) = \frac{2A_4}{\Gamma(2)} \frac{(2\pi)}{(2k_f)^3} \tfrac{1}{2} \left\{ \frac{(1+n)}{n} P - \frac{(1-n)}{n} N \right\} \tag{9}$$

where $P = \int_0^{\alpha} du\, e^{-\left(\frac{1+n}{2u}\right)^2} \int_0^{\left(\frac{1+n}{2u}\right)} e^{t^2}\, dt$

and $N = \int_0^{\alpha} du\, e^{-\left(\frac{1-n}{2u}\right)^2} \int_0^{\left(\frac{1-n}{2u}\right)} e^{t^2}\, dt$

The integrals appearing in (9) were evaluated numerically.