CALCULATION OF PHONON

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DISPERSION CURVES IN METALS:

ALUMINUM

THE CALCULATION OF PHONON DISPERSION CURVES IN METALS WITH APPLICATION TO ALUMINUM

By

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SCOPE AND CONTENTS:

The purpose of this work is to calculate phonon dispersion curves in metals paying particular attention to the evaluation of a new electron-ion matrix element by use of orthogonalized plane waves (OPW). The dynamic role of the electrons in screening the electron-ion interaction has been studied. Our formalism makes use of recent developments in the theory of the many-body problem. Applications of our theory have been made to aluminum. The pseudopotential part of the OPW electron-ion matrix element produced an overscreening of the frequency modes. Comparison is made to the use of the Bardeen matrix element. Our results strongly suggest that this calculation applied to lead would explain the magnitude of Kohn kinks observed by Brockhouse et al. (B 62a).

(ii)

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CHAPTER 1: INTRODUCTION

1. BACKGROUND AND OBJECTIVE

In recent years phonon dispersion curves for metals have become available from the study of inelastic neutron scattering and diffuse scattering of monochromatic X-rays (B 62a; B 62b; W 56). Before that. the knowledge of the elastic constants determined only the slopes of the curves in the long wavelength limit. Since there are only three elastic constants in cubic metals very restrictive assumptions must be made about the nature of the interatomic forces (e.g. first and second neighbours). On the other hand, the complete dispersion curves specify the range of the interatomic forces. For example, the results of Brockhouse et al. (B 62a) on lead indicate that the forces may extend out as far as eight neighbours. The fact that these interatomic forces have such long range strongly suggests that simple Thomas-Fermi screening cannot describe the role of the electrons adequately. It has been recently shown that the redistribution of the conduction electrons gives rise to oscillating long range forces (LV 59). Thus it is not unexpected that the phonon dispersion curves contain information on the electronic structure of metals. It is the purpose of this research to make a detailed theoretical analysis of the effective ion-ion interaction due to the redistribution of electrons in their attempt to follow the ion motion.

The effective ion-ion interaction in a metal can be thought to consist of three parts. The first is the repulsive coulomb interaction of unscreened point ion charges. The second is the repulsive correction due to the finite ion cores which may be treated with a Born-Mayer potential (S 40). The third part of the effective ion-ion interaction and the one of primary interest to us arises from the strong screening effects of the conduction electrons. The recent observation of Kohn kinks (B 62a) has stressed the dynamic role of the electrons in the screening process: the screening depends on the phonon momentum q. One major reason for this research project is to investigate the magnitude of these observed anomalies.

The process by which the electrons screen the ion charge involves both the electron-ion interaction and the electron-electron interaction. Recent progress with the many-body problem has provided a method of treating the electron-electron interaction. This thesis is concerned with calculating a new electron-ion matrix element by use of orthogonalized plane waves (H 40) and applying the result to the problem of lattice vibrations.

The electron-ion interaction describes the scattering of an electron between single particle Bloch states by the unscreened perturbation caused when an ion is displaced from its equilibrium lattice position. The electron-ion interaction renormalized by the electron-electron coulomb interactions is called the electron-phonon interaction. The static part of the electron-ion interaction defines the Bloch electron states which are the basis eigenfunctions in our calculations.

Chester (C 61) has written a complete review discussing the present status of the theory of lattice vibrations in metals. Here we describe the background material relevant to our calculation.

The first fundamental paper on the electron-ion interaction was written by Bardeen (B 37). In a study of the conductivity of monovalent metals Bardeen calculated an electron-phonon interaction matrix element which gave results in satisfactory agreement with experiment. Using the Hartree approximation and a method due to Mott and Jones (MJ 36) the electron-ion matrix element was evaluated. Allowing this interaction to perturb the Fermi sea of Bloch electron states to first order, he found a self-consistent conduction electron distribution. The net effect was that the electron-ion interaction was screened by the conduction electrons. Bardeen stressed the fact that his approximations were valid only for monovalent metals. No calculation comparable to this has been published for polyvalent metals.

Nakajima (C 61) has given a field-theoretic treatment of this problem again in the Hartree approximation. He found that the electronelectron coulomb interactions screened the electron-ion matrix element with results identical to Bardeen's. When this effect is taken into consideration in calculating the lattice frequencies he discovered a large change from the frequencies obtained from the direct coulomb ionion interaction. This change is extremely important for the longitudinal mode since the coulomb lattice frequency does not go to zero in the long wavelength limit as it must to agree with the elastic properties of metals. Nakajima did not pursue this problem as he was primarily concerned

with understanding the effective electron-electron interaction arising through an exchange of virtual phonons suggested earlier by Fröhlich (F 50) as the mechanism in producing the superconducting state.

Toya (T 52; T 58) extended Bardeen's self consistent field method to include Hartree-Foch exchange via the Slater approximation and calculated the normal mode frequencies of the alkali metals. Brockhouse et al. (B 62b) has found agreement with Toya's (T 58) sodium calculations. Toya's expression for the frequency is similar to the one which we derive. However, we do not use his type of exchange or include any ion core overlap repulsion via some Born-Mayer potential.

Bardeen and Pines (BP 55) extended the Bohm-Pines collective coordinate description of an electron gas to take into account the electron-ion and electron-electron interactions in metals. Their phonondispersion relation is identical to that of Toya (T 52) and Nakajima (C 61). The elastic constants for sodium were calculated (without exchange) and were found to be in reasonable agreement with experiment.

Kohn (K 59) pointed out that in phonon dispersion curves for metals anomalies, often referred to as Kohn kinks, should appear for certain values of the phonon momentum corresponding to the scattering of electrons across the extremums of the Fermi surface. These anomalies reflect an image of the Fermi surface in metals. The only Kohn kinks that have been observed to date occur in lead (B 62a). Attempts to observe these anomalies in sodium (B 62b) and aluminum (YW 63) have been unsuccessful.

The magnitude of the Kohn kinks in lead cannot be explained on the basis of the Bardeen electron-ion matrix element (WK 62). For this

reason we decided to make a new calculation of the matrix element.

Recent success in other calculations with the method of orthogonalized plane waves (OPW) (H 57; KP 60; CH 61) has led us to use this approach in the calculation of a new electron-ion matrix element. This calculation is applied to aluminum for three reasons. First, Heine's extensive OPW work (H 57) on aluminum has provided the self consistent field potential and the knowledge that one OPW wave function is a good approximation except at points of symmetry. Further, this means that we can use spherical energy bands for aluminum. This has been corroborated by the more extensive work of Segall (Se 61). Secondly, the number of core states in aluminum simplifies our calculation to the barest essentials. In contrast a calculation for a complicated material like lead would be much more involved. Thirdly, lattice frequencies can be calculated with this new electron-ion matrix element and compared to the measured values of Walker (W 56).

Our calculation of lattice frequencies requires the use of the usual adiabatic approximation (BH 54; Z 60) and the fundamental assumption that the effective ion-ion interaction can be determined from a perturbation treatment. The fixed constants in our theory are the lattice constant a_{τ} and the ion valence Z'.

The magnitude of the screening process of the electrons varies strongly with the metal. In sodium (B 62b) the experimental values of the frequency squared at the Brillouin zone boundary are about 3/4 the value found using only the coulomb ion-ion interaction. In contrast, for lead (B 62a) and aluminum (W 56) these ratios are respectively 1/20 and 2/5.

In chapter 2, a reformulation of classical lattice vibrations in reciprocal lattice space is given. An expression for the normal mode frequencies is developed in terms of an effective ion-ion interaction. The rest of this chapter is concerned with establishing the general formalism of the calculation. The adiabatic approximation is made and the notion of the screening frequency introduced. Standard many-body theory is applied in chapter 3 to develop an expression for the effective ion-ion interaction energy which arises from the interaction of the electrons with the ions. This energy is calculated to second order in the electron-ion interaction and extended to all orders in the electronelectron interaction by use of the bubble approximation. The procedure for calculating frequencies from this perturbation energy is given after normal mode coordinates are introduced. Chapter 4 contains a general discussion on the evaluation of the electron-ion matrix element. The electron-ion matrix element is evaluated using orthogonalized plane waves (H 40) and compared with the Bardeen result (B 37). The description of our numerical procedure in treating the orthogonalized plane wave matrix element is given in chapter 6. The calculation is applied at this stage to aluminum. A discussion on the magnitude of the Kohn anomalies is given at this time. This chapter concludes with an analysis of the frequency curves calculated for aluminum using the Bardeen matrix element and the orthogonalized plane wave electron-ion matrix element. The results are not too similar. In the conclusions, chapter 6, we stress the possibility of our method being applied to lead to explain the size of the Kohn anomalies observed there (B 62a). Our conclusions are summarized here, and other ideas for further research are listed.

6, 7

Table 1



Lattice constant	aL	4.04 Å
Wigner-Seitz cell radius	ro	2.99 a
Fermi wave-vector	^k F	.927 $\frac{1}{a_0} = 1.127 \frac{2\pi}{a_L}$
Plasma Frequency	ω _p	$1.88 \times 10^{14} r.p.s.$

a is the Bohr radius

CHAPTER 2: FORMULATION OF PROBLEM

1. LATTICE VIBRATIONS FROM AN EFFECTIVE ION-ION INTERACTION

As pointed out in the introduction, an effective interaction between ions will be obtained by use of many-body perturbation theory. Since the results are most accurately expressed in momentum space, to have a basis of comparison with a classical treatment of ion vibrations, a reformulation of the classical theory is given in terms of reciprocal lattice space.

Consider a metal with one ion plus Z' conduction electrons per lattice point. The lattice vectors, \overrightarrow{L} , are the ionic positions at equilibrium. Small ionic displacements from equilibrium, $\overrightarrow{\delta R_L}$, will be treated.

Assume there exists an effective ion-ion interaction $V(\vec{L} + \delta \vec{R}_{L} - \vec{L'} - \delta \vec{R}_{L'})$ between the ions at points \vec{L} and $\vec{L'}$ depending only on their separation. This potential, V, includes the direct coulomb interaction between the ions, which throughout are assumed to be point charges, and effects due to the screening by the conduction electrons displaced by the small ionic motions.

For N ions, the total Hamiltonian is

$$H = \sum_{L=1}^{N} \frac{M}{2} \left[\frac{\bullet}{\delta R_{L}} \right]^{2} + \frac{1}{4} \sum_{L,L'}^{N} \left(\frac{\bullet}{\delta R_{L}} - \frac{\bullet}{\delta R_{L'}} \right) \cdot \frac{\partial^{2} V(\overline{L-L'})}{\partial (\overline{L-L'})^{2}} \cdot \left(\frac{\bullet}{\delta R_{L}} - \frac{\bullet}{\delta R_{L'}} \right)$$
(2-1)
(L+L')

The first term is the kinetic energy; M is the ion mass. The second term is the change in the potential energy for harmonic motion displacements. This Hamiltonian is invariant under an arbitrary linear translation of the lattice, that is, for all $\overrightarrow{\delta R}_{I}$ equal a constant.

To diagonalize the Hamiltonian H, one makes a transformation of coordinates. Define normal coordinates $Q(\vec{k},\sigma)$, where (\vec{k},σ) specify the coordinate which is time-dependent, by

$$\vec{\delta R}_{L} = (MN)^{-1/2} \sum_{\vec{k},\sigma} Q(\vec{k},\sigma) \vec{\epsilon}(\vec{k},\sigma) e^{i\vec{k}\cdot\vec{L}}$$
(2-2)

The sum on \overrightarrow{K} (N values) is over the first Brillouin zone; the polarization index σ has three values, which in symmetry directions are the longitudinal mode and two transverse modes; and $\overrightarrow{e}(\overrightarrow{K}, \sigma)$ are the eigenvectors of the normal frequencies problem and are orthonormal.

$$\vec{\epsilon}$$
 (\vec{x},σ) $\cdot \vec{\epsilon}(\vec{x},\sigma') = \delta_{\sigma'},\sigma$ (2-3)

Using the relationship,

$$\sum_{\vec{L}} e^{i \vec{q} \cdot \vec{L}} = N \delta_{\vec{q},\vec{d}}$$
(2-4)

where G is a reciprocal lattice vector,

$$Q(\vec{x},\sigma) = (M/N)^{\frac{1}{2}} \sum_{\vec{L}} \delta \vec{R}_{\vec{L}} \cdot \vec{\epsilon}(\vec{x},\sigma) e^{-i\vec{k}\cdot\vec{L}}$$
 (2-5)

We choose $\vec{\in}(\vec{x},\sigma)$ real and

$$\vec{\epsilon}$$
 $(\vec{k},\sigma) = \vec{\epsilon}(-\vec{k},\sigma)$

so that,

$$Q(\vec{x}, c) = Q^*(\vec{x}, c)$$
 (2-6)

Substituting (2) into (1) gives

$$H = \frac{1}{2} \sum_{\vec{k},\sigma,\sigma'} \left[\hat{q}(\vec{k},\sigma) \hat{q}^{*}(\vec{k},\sigma) + \frac{1}{M} \hat{q}(\vec{k},\sigma) \hat{q}^{*}(\vec{k},\sigma') \sum_{\vec{L}\neq 0} \vec{e}(\vec{k},\sigma) \right]$$

$$\cdot \frac{\partial^{2} V(\vec{L})}{\partial \vec{L}^{2}} \cdot \vec{e}(\vec{k},\sigma') \left\{ 1 - \cos \vec{k} \cdot \vec{L} \right\}$$
(2-7)

This ion Hamiltonian is now the sum of N uncoupled phonon Hamiltonians labelled by $\overrightarrow{\mathcal{R}}$. The sum over \overrightarrow{L} is extended to include $\overrightarrow{L} = 0$.

Introduce the Fourier transform of V(L), V(q), by

$$V(\vec{L}) = \frac{1}{N \Omega_0} \sum_{\vec{q}} V(\vec{q}) e^{i \vec{q} \cdot \vec{L}}$$
(2-8)

where $\Omega_{\vec{q}}$ is the volume of one unit cell. If $V(\vec{L}) = V(-\vec{L})$, we have that $V(\vec{q}) = V(-\vec{q})$ so that the sum over \vec{q} is symmetric with $-\vec{q}$.

Using (4), (7) and defining the $\tilde{\mathcal{R}}$ -phonon Hamiltonian $H(\tilde{\mathcal{R}})$ by

$$H = \sum_{\mathcal{R}} H(\mathcal{R}) \qquad (2-9)$$

one obtains

$$H(\hat{\mathcal{R}}) = \frac{1}{2} \sum_{\sigma,\sigma'} \left[\hat{\mathcal{Q}}(\hat{\mathcal{R}},\sigma) \, \hat{\mathcal{Q}}^{*}(\hat{\mathcal{R}},\sigma) + \frac{1}{M-\Gamma_{o}} \, \mathcal{Q}(\hat{\mathcal{R}},\sigma) \, \mathcal{Q}^{*}(\hat{\mathcal{R}},\sigma') \quad \sum_{\vec{q}} \, \mathcal{V}(\vec{q}) \left\{ \boldsymbol{\varepsilon}(\hat{\mathcal{R}},\sigma) \cdot \vec{q} \right\} \\ \left\{ \boldsymbol{\varepsilon} \, (\hat{\mathcal{R}},\sigma') \, \cdot \, \vec{q} \right\} \left\{ \delta_{\vec{q}}, \hat{\mathcal{R}} + \vec{g} - \delta_{\vec{q}}, \vec{g} \right\} \right]$$
(2-10)

Since we have chosen $Q(\vec{k}, c)$ to be the normal coordinates in (2), which satisfy

$$\vec{Q}(\vec{x},\sigma) + \omega^2 (\vec{x},\sigma) Q(\vec{x},\sigma) = 0$$
 (2-11)

where $\omega^2(\vec{R},\sigma)$ are the phonon frequencies, and $\vec{C}(\vec{R},\sigma)$ are the corresponding eigenvectors, $H(\vec{R})$ becomes diagonal in σ and σ' ,

$$H(\vec{\chi}) = \frac{1}{2} \sum_{\sigma} \left[\dot{q}(\vec{\chi},\sigma) \ \dot{q}^{*}(\vec{\chi},\sigma) + \frac{1}{M \Omega_{0}} \ Q(\vec{\chi},\sigma) \ Q^{*}(\vec{\chi},\sigma) \sum_{\vec{q}} V(\vec{q}) \right]$$

$$\left\{ \vec{\epsilon} \ (\vec{\chi},\sigma) \ \cdot \vec{q} \right\}^{2} \left\{ \delta_{\vec{q}}, \vec{\chi} + \vec{G} - \delta_{\vec{q}}, \vec{G} \right\}$$

$$(2-12)$$

and we have

$$\omega^{2}(\vec{x},\sigma) = \frac{1}{M \Omega_{0}} \sum_{\vec{c}} \left[\vec{c}(\vec{x},\sigma) \cdot \left[\vec{x},\vec{c}\right] \right]^{2} V(\vec{x},\vec{c}) - \left\{ \vec{c}(\vec{x},\sigma) \cdot \vec{c} \right\}^{2} V(\vec{c}) \right]$$

$$(2-13)$$

In symmetry directions the polarization vectors $\vec{\in}(\vec{k},\sigma)$ are known from inspection. Thus, from an expression of $V(\vec{q})$ we may calculate the phonon dispersion curves.

2. GENERAL FORMULATION: ADIABATIC APPROXIMATION

Consider a metal composed of N non-overlapping ions and Z' N conduction electrons in a volume $\Omega = N \Omega_0$, with one atom per lattice point.

The total Hamiltonian for this system is

$$H = \sum_{i=1}^{Z'N} \frac{(\vec{p}_{i})^{2}}{2m} + \sum_{L=1}^{N} \frac{(\vec{p}_{L})^{2}}{2M} + \sum_{i,L}^{V} v(\vec{x}_{i} - \vec{R}_{L}) + V_{I-I}(\vec{R}_{1}, ..., \vec{R}_{N}) + V_{e-e}(\vec{x}_{1}, ..., \vec{x}_{Z'N})$$
(2-14)

The first two terms are respectively electron and ion kinetic energies, the third term is the bare electron-ion interaction. The term V_{I-I} represents the bare coulomb interactions between the ions; and V_{e-e} , the electron-electron coulomb interactions. Since our system is neutral, we consistently neglect all $\dot{q}=0$ components of the Fourier Transforms of potentials. In other words, we add different uniform background charges which add to zero (BP 55).

In the adiabatic approximation, we first suppose that the ions are in some fixed configuration, at positions $\vec{R}_L = \vec{L} + \delta \vec{R}_L$. We calculate the electron energy, $E(e, \vec{R})$, which depends on the ion coordinates.

$$H(e,\vec{R}) = \sum_{i=1}^{Z'N} \frac{(\vec{p}_i)^2}{2m} + \sum_{i,L} v(\vec{x}_i - \vec{R}_L) + V_{e-e} (\vec{x}_1, ..., \vec{x}_{Z'N}) \quad (2-15)$$

Assume the function $\mathscr{P}_{\mathsf{R}}(\vec{r})$ is a solution of

$$H(e,\vec{R}) \not \phi_{R}(\vec{r}) = E(e,\vec{R}) \not \phi_{R}(\vec{r})$$
(2-16)

Then, if we suppose

$$H\left[\Psi(\vec{R}) \ \phi_{R}(\vec{r})\right] = E\left[\Psi(\vec{R}) \ \phi_{R}(\vec{r})\right]$$
(2-17)

the adiabatic approximation (Z 60) results in $\Psi(\vec{R})$ satisfying

$$\sum_{L=1}^{N} \frac{(\vec{P}_{L})^{2}}{2M} + V_{I-I} (\vec{R}_{1}, ..., \vec{R}_{N}) + E(e, \vec{R}) \Psi(\vec{R}) = E \Psi(\vec{R})$$
(2-18)

The function $V(\vec{R}_1, \dots, \vec{R}_N) + E(e, \vec{R})$ is the total potential energy function for the ionic motion. It could possibly be equal to a sum of the two-body effective potentials discussed in section 1.

Since in symmetry directions the effective potential enters the calculation of ω^2 linearly, we can separate ω^2 into parts each corresponding to one term in the total ion potential energy.

We take V_{I-I} to be a sum of coulomb interactions and a uniform background of neutralizing charge. The potential V_{I-I} is expanded to second order in the $\delta \vec{R}_{L}$'s: the corresponding part of ω^2 we denote by $\omega^2_{coulomb} = \omega^2_{c}$. Because of the long range coulomb potential, the calculation of ω^2_{c} requires use of the Ewald construction method. For some symmetry directions, Clark (C 58) has published the coulomb frequencies for a BCC lattice and Vosko (unpublished, 1958) has calculated them for both FCC and BCC lattices. The results for the FCC lattice are shown on graphs 1 to 7.

The coulomb frequency, ω_c , is the phonon dispersion curve for a lattice of point ion charges immersed in a uniform fixed background of the opposite charge. This fixed background does not shift with the ionic motion, whereas real conduction electrons will very nearly follow the ionic motion (the adiabatic approximation: electron state is always just a function of the instantaneous ionic coordinates). Therefore, the conduction electrons will decrease the effective ion-ion interaction and so lower the phonon frequency curves from the coulomb frequency values. In other words, the contribution to the phonon frequencies from the electron energy $E(e, \vec{R})$ will be $-\omega_g^2$, the so-called screening contribution.

$$\omega^2 = \omega_c^2 - \omega_s^2 \qquad (2-19)$$

The main problem is the calculation of the electron energy $E(e, \vec{R})$. The energy $E(e, \vec{R})$ can be separated into two parts: the first, a constant E_B , which commutes with the ion conjugate momentum \vec{P}_L and hence does not affect lattice frequencies, and a second part, ΔE , which we shall calculate using many-body perturbation techniques.

Define

$$H(e, \vec{R}) = H_B + \Delta H$$
 (2-20)

$$H_{B} = \sum_{i=1}^{Z'N} \frac{(\overline{p}_{i})^{2}}{2m} + \sum_{i,L} \mathbf{v} (\overline{x}_{i} - \overline{L}) = \sum_{i=1}^{Z'N} h_{B}(i) \qquad (2-21)$$

$$\Delta H = V_{e-e} (\vec{x}_1, \dots, \vec{x}_{NZ}) - \sum_{i,L} \delta \vec{R}_L \cdot \frac{\partial v(\vec{x}_i - \vec{L})}{\partial (\vec{x}_i - \vec{L})}$$

+ electron-ion parts to be neglected (2-22) The potential function $\sum_{L} v(\vec{x}-\vec{L})$ is periodic in the lattice. Eigenfunctions of $h_{B}(i)$ are Bloch waves $B(\vec{k};\vec{x})$.

$$\left[\frac{p^2}{2m} + \sum_{\mathbf{L}} \mathbf{v}(\vec{\mathbf{x}} - \vec{\mathbf{L}})\right] \mathbf{B}(\vec{\mathbf{k}}; \vec{\mathbf{x}}) = \mathbf{E}(\vec{\mathbf{k}}) \mathbf{B}(\vec{\mathbf{k}}; \vec{\mathbf{x}})$$
(2-23)

We have used the extended zone scheme so that \vec{k} is not necessarily in the first Brillouin zone. With the usual periodic boundary conditions, there are N discrete values of \vec{k} per zone. These Bloch waves, $B(\vec{k};\vec{x})$, will form the basis set for the perturbation treatment of ΔH .

Write

$$\Delta H = V_{e-e} + V_{e-I} \qquad (2-24)$$

where

$$v_{e-e} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{(\vec{x}_i - \vec{x}_j)}$$
 (2-25)

and

$$\mathbf{v}_{e-\mathbf{I}} = -\sum_{\mathbf{i},\mathbf{L}} \delta \vec{\mathbf{R}}_{\mathbf{L}} \cdot \frac{\partial \mathbf{v}(\vec{\mathbf{x}}_{\mathbf{i}} - \vec{\mathbf{L}})}{\partial (\vec{\mathbf{x}}_{\mathbf{i}} - \vec{\mathbf{L}})}$$
(2-26)

CHAPTER 3: CALCULATION OF PERTURBATION ENERGY Δ E.

1. INTRODUCTION

We must calculate the shift in ground state energy of our electronion system to second order in the electron-ion interaction, that is, to second order in $\vec{\delta R}_{L}$. Thus, only harmonic terms are retained.

To use many-body perturbation techniques, the perturbation ΔH is first expressed in second quantized form. Bloch waves are our basis functions and we rewrite (2-23) in the notation

$$h_{R} |B\vec{k}\rangle = E(\vec{k}) |B\vec{k}\rangle \qquad (3-1)$$

The unperturbed Hamiltonian \hat{H}_B is

$$\hat{H}_{B} = \sum_{k} E(k) a_{k}^{\dagger} a_{k} \qquad (3-2)$$

The symbol $k \equiv (\vec{k}, s)$ where \vec{k} is the electron wave vector and s is the electron spin. The quantities a_k^+ and a_k are respectively the creation and annihilation operators for the Bloch electron $|B | k \rangle$ and obey the usual Fermion anti-commutation law.

$$\begin{bmatrix} a_{k'}, a_{k} \end{bmatrix}_{+} = \delta_{\vec{k}'}, \vec{k} \delta_{s,s'} \qquad (3-3)$$

Define the electron-ion interaction h(ep),

$$h(ep) = -\sum_{L} \vec{\delta R}_{L} \cdot \frac{\partial \mathbf{v}(\vec{\mathbf{x}} - \vec{\mathbf{L}})}{\partial(\vec{\mathbf{x}} - \vec{\mathbf{L}})}$$
(3-4)

In the Schrödinger picture, (2-25), (2-26) give

$$\hat{\mathbf{v}}_{\mathbf{e}-\mathbf{I}} = \sum_{\mathbf{k},\mathbf{k}'} \langle \mathbf{B} \mathbf{k}' | \mathbf{h}(\mathbf{e}\mathbf{p}) | \mathbf{B}\mathbf{k} \rangle \mathbf{a}_{\mathbf{k}'}^{\dagger} \mathbf{a}_{\mathbf{k}} \qquad (3-5)$$

$$\hat{\mathbf{v}}_{\mathbf{e}-\mathbf{e}} = \frac{1}{2} \sum_{\mathbf{k},\ell,\mathbf{m},\mathbf{n}} \langle \mathbf{B} \mathbf{k},\ell | \frac{\mathbf{e}^2}{|\overline{\mathbf{x}}-\overline{\mathbf{y}}|} | \mathbf{B} \mathbf{n},\mathbf{m} \rangle \stackrel{\mathbf{a}}{\mathbf{a}}_{\mathbf{k}} \stackrel{\mathbf{a}}{\mathbf{a}}_{\ell} \stackrel{\mathbf{a}}{\mathbf{m}}_{\mathbf{n}}$$
(3-6)

Since the wave functions of the electrons are plane waves over most of the crystal volume in which electron-electron interactions occur (not near the nucleus), we approximate

$$\langle B k, \ell | \frac{e^2}{|\overline{x}-\overline{y}|} | B n, m \rangle = \frac{1}{\Omega^2} \int dx \, dy \, e^{-i\overline{k}\cdot\overline{x}} e^{-i\overline{\ell}\cdot\overline{y}} \frac{e^2}{|\overline{x}-\overline{y}|} e^{i\overline{m}\cdot\overline{y}} e^{i\overline{n}\cdot\overline{x}}$$

$$= \delta_{\overline{\ell}+\overline{k}, \overline{m}+\overline{n}} \frac{4\pi e^2}{\Omega |\overline{k}-\overline{n}|^2}$$

Introduce the notation $k+q \equiv (\overline{k+q}, s)$. Then the expression for V_{e-e} is

$$\hat{\mathbf{v}}_{e-e} = \frac{1}{2} \sum_{k,k',\vec{q}} \frac{4\pi e^2}{\Omega_q^2} + + \frac{4\pi e^2}{\kappa_{+q}^2} + \frac{4\pi$$

However, for the electron-ion matrix element of (5) Bloch waves will be employed for it is more important near the nucleus.

The usual U-operator (Sch 61; H 57a) is now introduced.

$$U(t,t_{o}) = 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{n}\right)^{n} \int_{t_{o}}^{t} dt_{1} \int_{t_{o}}^{t_{1}} dt_{2} \cdots \int_{t_{o}}^{t_{n-1}} dt_{n}$$

$$\hat{v}(t_{1}) \hat{v}(t_{2}) \cdots \hat{v}(t_{n}) \qquad (3-8)$$

where

$$\hat{\mathbf{V}}(t) = e^{\frac{1}{H}H_{B}t} \begin{bmatrix} \hat{\mathbf{V}}_{e-e} + \hat{\mathbf{V}}_{e-I} \end{bmatrix} e^{-\frac{1}{H}H_{B}t}$$
(3-9)

The perturbation $\hat{V}(t)$ is in the interaction picture. Note that in the form of $U(t,t_0)$ chosen no time-ordering operators appear.

Define the frequency

$$w(k) = E(k)/K$$
 (3-10)

Expressions for \hat{V}_{e-I} (t) and \hat{V}_{e-e} (t), the interaction picture perturbations, are easily written down.

$$\widehat{V}_{e-I}(t) = \sum_{k,k'} \langle B k' | h(ep) | B k \rangle a_{k'}^{\dagger} a_{k} e^{i \left[w(k') - w(k) \right] t}$$
(3-11)

$$\hat{V}_{e-e}(t) = \frac{1}{2} \sum_{k,k',\vec{q}} \frac{4\pi e^2}{\Omega_q^2} a^{\dagger}_{k+q} a^{\dagger}_{k'-q} a^{\bullet}_{k'} a^{\bullet}_{k} a^{\bullet}_{k'} a^{\bullet}_$$

Let the ground state of H_B be $|\Psi_0\rangle$. Certain expectation values, called contractions, are needed.

$$\mathbf{a}_{\mathbf{k}}^{\dagger} \mathbf{a}_{\mathbf{k}}^{\dagger} = \langle \Psi_{\mathbf{0}} | \mathbf{a}_{\mathbf{k}}^{\dagger} \mathbf{a}_{\mathbf{k}}^{\dagger} | \Psi_{\mathbf{0}} \rangle = \delta_{\mathbf{k}, \mathbf{k}}^{\dagger} \delta_{\mathbf{s}, \mathbf{s}}^{\dagger} \theta \left[\mathbf{E}(\mathbf{k}_{\mathbf{F}}) - \mathbf{E}(\mathbf{k}) \right]$$
 (3-13a)

$$\overset{\bullet}{a_{k}} \overset{\bullet}{a_{k}} = \langle \Psi_{0} | \overset{\bullet}{a_{k}} \overset{\bullet}{a_{k}} | \Psi_{0} \rangle = \overset{\bullet}{b_{k}} \overset{\bullet}{k_{i}} \overset{\bullet}{s_{i}} \overset{\bullet}{s_{i}} \overset{\bullet}{s_{i}} \left[E(k) - E(k_{F}) \right] (3-13b)$$

The quantity $k_{\rm F}$ is the Fermi wave vector; all electron states k such that $E(k) \leq E(k_{\rm F})$ are occupied. $\theta(x)$ is the unit step function.

$$\theta(x) = 1 \quad x > 0$$

= 0 $x < 0$

The stage is set now for the decomposition of the U-operator and the calculation of contributions to ΔE_{\bullet}

2. SECOND ORDER DIAGRAM



The lowest order term in $U(t,t_o)$ which contributes an energy shift of order $(\delta R)^2$ is one part of $U^{(2)}(t,-\infty)$.

$$\mathbf{U}^{(2)}(\mathbf{t},-\infty) = \left(\frac{-\mathbf{i}}{4\mathbf{i}}\right)^2 \int_{-\infty}^{\mathbf{t}} d\mathbf{t}_1 \int_{-\infty}^{\mathbf{t}} d\mathbf{t}_2 \hat{\mathbf{v}}_{\mathbf{e}-\mathbf{I}}(\mathbf{t}_1) \hat{\mathbf{v}}_{\mathbf{e}-\mathbf{I}}(\mathbf{t}_2)$$

Inserting the expression (11) for \hat{V}_{e-I} gives as one factor in the integral the product

$$\begin{array}{c} + & + \\ \mathbf{a}_{k}, \mathbf{a}_{k} \mathbf{a}_{\ell}, \mathbf{a}_{\ell} \end{array}$$

To find the energy shift corresponding to the above Goldstone (or Feynman) diagram, use Wick's theorem (Sch 61) to pick out only the one direct linked vacuum term, $U_{LV}^{(2)}$.

$$U_{LV}^{(2)}(t,-\infty) = \sum_{k,k',\ell,\ell'} \left(\frac{-1}{n}\right)^2 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \langle B k' | h(ep) | B k \rangle$$

Employing (13) and Hubbard's rule (H 57a) of inserting in $\delta(t_1)$, the corresponding energy shift $\Delta E^{(2)}$ is

$$\Delta E^{(2)} = \sum_{\vec{k}, \vec{k}', \vec{\ell}, \vec{\ell}'} \langle B k' | h(ep) | B k \rangle \langle B \ell' | h(ep) | B \ell \rangle$$

s,s'

$$\left(\frac{-i}{\hbar}\right)^2 \int_{-\infty}^{t} i\hbar \delta(t_1) dt_1 \int_{-\infty}^{t_1} dt_2 e^{i\left[w(\ell') - w(\ell)\right]t_2}$$

$$\underbrace{i \left[w(k') - w(k) \right] t_{1}}_{k', \mathcal{L}} \delta_{s, s'} \theta \left[E(k_{F}) - E(k') \right]$$

$$\delta_{\vec{k},\vec{\ell}} \delta_{s,s} \theta \left[E(k) - E(k_{F}) \right]$$

$$\Delta E^{(2)} = -2 \sum_{\mathbf{E}(\vec{k}) \leq \mathbf{E}(\mathbf{k}_{\mathbf{F}})} \frac{\langle B\vec{k}|h(ep)|B\vec{k'}\rangle \langle B\vec{k'}|h(ep)|B\vec{k}\rangle}{\mathbf{E}(\vec{k'}) - \mathbf{E}(\vec{k})}$$
(3-14)
$$E(\vec{k'}) \geq E(\mathbf{k}_{\mathbf{F}})$$

Note that spin has been summed over to give the factor 2.

A very important simplication would take place if the restriction $E(\vec{k'}) > E(k_F)$ could be dropped and the integration over $\vec{k'}$ be free. This will now be proven.

Let $\vec{k'} = \vec{k+q}$ in analogy with the case of plane waves. Consider the quantity

$$\sum_{\vec{q}} \sum_{\vec{q}} \frac{\langle \underline{B} \, \vec{k} \, \underline{h} \, \underline{B} \, \overline{k+q} \rangle \langle \underline{B} \, \overline{k+q} \, \underline{h} \, \underline{B} \, \overline{k} \rangle}{E(\vec{k}+\vec{q}) - E(\vec{k})}$$

$$E(\vec{q}+\vec{k}) \langle E(k_{F}) = E(\vec{k}) \langle E(k_{F}) = E(\vec{k}) \rangle = E(\vec{k})$$

$$= \sum_{\vec{q}} \sum_{\vec{q}} \frac{\langle \underline{B} - \overline{k+q} \, \underline{l} \, \underline{h} \, \underline{B} - \overline{k} \rangle \langle \underline{B} - \overline{k} \, \underline{lh} | \underline{B} - \overline{k+q} \rangle}{E(-\vec{k}) - E(-\vec{k}+\vec{q})} \qquad (3-15)$$

$$E(-\vec{q}+\vec{k}) \langle E(k_{F}) = E(-\vec{k}) \langle E(k_{F}) \rangle$$

by putting $\vec{k} \Rightarrow -\vec{k+q}$; $\vec{k+q} \Rightarrow -\vec{k}$.

The Bloch wave function can be written as

$$B(\vec{k};\vec{x}) = e^{i\vec{k}\cdot\vec{x}} u(\vec{k};\vec{x})$$

 $u(\vec{k}; \vec{x}+\vec{L}) = u(\vec{k}; \vec{x})$.

where

We have that

$$B(-\vec{k};\vec{x}) = e^{-i\vec{k}\cdot\vec{x}} u(-\vec{k};\vec{x}) = e^{-i\vec{k}\cdot\vec{x}} u^*(\vec{k};\vec{x}) = B^*(\vec{k};\vec{x})$$

Therefore,

$$\langle B - \vec{k} | h | B - \vec{k} + \vec{q} \rangle = \int d^{3}x \ B(-\vec{k}; \vec{x}) \ h \ B(-\vec{k} + \vec{q}; \vec{x})$$

$$= \int d^{3}x \ e^{i\vec{k}\cdot\vec{x}} \ u(\vec{k}; \vec{x}) \ h \ e^{-i \ \vec{k} + \vec{q}} \cdot \vec{x} \ u^{*}(\vec{k} + \vec{q}; \vec{x})$$

$$= \langle B \ \vec{k} + \vec{q} | h^{+} | B \ \vec{k} \rangle = \langle B \ \vec{k} + \vec{q} | h | B \ \vec{k} \rangle$$

$$(3-16)$$

since h is hermitean.

From time-reversal invariance we know that

$$E(\vec{k}) = E(-\vec{k}) \qquad (3-17)$$

Therefore,

RHS (15) =
$$\sum_{\vec{q}} \sum_{E(\vec{+k}) < E(k_F)} \frac{\langle B \vec{k} | h | B \vec{k+q} \rangle \langle B \vec{k+q} | h | B \vec{k} \rangle}{E(\vec{k}) - E(\vec{k+q})}$$

 $E(\vec{q+k}) < E(k_F)$

= - LHS (15)

Hence, this quantity considered must be zero. We can thus write

$$\Delta E^{(2)} = -2 \sum_{\vec{q}} \sum_{E(\vec{k}) \leq E(k_{F})} \frac{\langle B \vec{k} \ln(ep) | B \vec{k} + \vec{q} \rangle \langle B \vec{k} + \vec{q} \ln(ep) | B \vec{k} \rangle}{E(\vec{k} + \vec{q}) - E(\vec{k})}$$
(3-18)

3. THIRD ORDER DIAGRAM



We consider now the term in the U-operator which contains \hat{V}_{e-I} to second order and \hat{V}_{e-e} to first order.

$$\mathbf{U}^{(3)}(\mathbf{t}, -\infty) = \left(\frac{-\mathbf{i}}{\mathbf{h}}\right)^{3} \int_{-\infty}^{\mathbf{t}} d\mathbf{t}_{1} \int_{-\infty}^{\mathbf{t}^{1}} d\mathbf{t}_{2} \int_{-\infty}^{\mathbf{t}^{2}} d\mathbf{t}_{3} \left[\hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{1}) \hat{\mathbf{v}}_{e-e}(\mathbf{t}_{2}) \hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{3}) + \hat{\mathbf{v}}_{e-e}(\mathbf{t}_{1}) \hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{2}) \hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{3}) \right]$$

$$+ \hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{1}) \hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{2}) \hat{\mathbf{v}}_{e-e}(\mathbf{t}_{3}) + \hat{\mathbf{v}}_{e-e}(\mathbf{t}_{1}) \hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{2}) \hat{\mathbf{v}}_{e-\mathbf{I}}(\mathbf{t}_{3}) \right]$$

$$(3-19)$$

Expressions for \hat{V}_{e-I} and \hat{V}_{e-e} are given by (11) and (12). Proceed as with $\Delta E^{(2)}$, picking out the direct linked vacuum contributions, using (13) and Hubbard's i H $\delta(t)$ rule. For example, for the first term of $U^{(3)}(t, -\infty)$ there are two sets of contractions.



It is straightforward to calculate the $\Delta E_{1}^{(3)}$ corresponding to the first term of (19).

$$\Delta E_{1}^{(3)} = 4 \sum_{\vec{k},\vec{k}',\vec{q}} \frac{4\pi e^{2}}{\Omega_{q}^{2}} \frac{\langle B \vec{k} | h | B \vec{k} + q \rangle \langle B \vec{k}' + q | h | B \vec{k}' \rangle}{\left[E(\vec{k} + q) - E(\vec{k})\right] \left[E(\vec{k}' + q) - E(\vec{k}')\right]} (3-20)$$

$$E(\vec{k}), E(\vec{k}') < E(k_{F})$$

$$E(\vec{k} + q), E(\vec{k}' + q) > E(k_{F})$$

Note that spins have been summed over to give the factor 4. Similarly for the second and third terms of (19),

$$\Delta \mathbf{E}_{2}^{(3)} = 4 \sum_{\vec{k},\vec{k}',\vec{q}} \frac{4\pi e^{2}}{\Omega q^{2}} \frac{\langle \mathbf{B} \vec{k} | \mathbf{h} | \mathbf{B} \vec{k} + \vec{q} \rangle \langle \mathbf{B} \vec{k}' | \mathbf{h} | \mathbf{B} \vec{k}' - \vec{q} \rangle}{\left[\mathbf{E}(\vec{k} + \vec{q}) + \mathbf{E}(\vec{k}' - \vec{q}) - \mathbf{E}(\vec{k}') - \mathbf{E}(\vec{k}) \right] \left[\mathbf{E}(\vec{k} + \vec{q}) - \mathbf{E}(\vec{k}) \right]}$$
(3-21)
$$\mathbf{E}(\vec{k}), \quad \mathbf{E}(\vec{k}') < \mathbf{E}(\mathbf{k}_{F})$$

$$\mathbf{E}(\vec{k} + \vec{q}), \quad \mathbf{E}(\vec{k}' - \vec{q}) > \mathbf{E}(\mathbf{k}_{F})$$

$$\Delta E_{3}^{(3)} = 4 \sum_{\vec{k},\vec{k}',\vec{q}} \frac{4\pi e^{2}}{\Box q^{2}} \frac{\langle B \ \vec{k}+\vec{q} \ | \ h \ | \ B \ \vec{k} \rangle \langle B \ \vec{k'-q} \ | \ h \ | \ B \ \vec{k'} \rangle}{\left[E(\vec{k}+\vec{q})+E(\vec{k'-q})-E(\vec{k'})\right] \left[E(\vec{k'-q})-E(\vec{k'})\right]} (3-22)$$

$$E(\vec{k}), E(\vec{k'}) \langle E(k_{F})$$

$$E(\vec{k+q}), E(\vec{k'-q}) > E(k_{F})$$

Since the sum, $\Delta E^{(3)} = \Delta E^{(3)}_1 + \Delta E^{(3)}_2 + \Delta E^{(3)}_3$ is real, we have

$$\Delta E^{(3)} = \Delta E^{(3)}_{1} + \frac{1}{2} \left[\Delta E^{(3)*}_{2} + \Delta E^{(3)}_{3} \right] + \frac{1}{2} \left[\Delta E^{(3)*}_{3} + \Delta E^{(3)}_{2} \right]$$
as $\Delta E^{(3)}_{1}$ is real. Now
$$\left[\Delta E^{(3)*}_{2} + \Delta E^{(3)}_{3} \right] = 4 \sum_{\vec{k}, \vec{k}', \vec{q}} \frac{4\pi e^{2}}{Lq^{2}} \frac{\langle B \vec{k} + \vec{q} | h | B \vec{k} \rangle \langle B \vec{k}' - \vec{q} | h | B \vec{k}' \rangle}{Lq^{2} \left[E(\vec{k} + \vec{q}) - E(\vec{k}) \right] \left[E(\vec{k}' - \vec{q}) - E(\vec{k}') \right]}$$

$$E(\vec{k}), E(\vec{k}') < E(k_{F})$$

$$E(\vec{k} + \vec{q}), E(\vec{k}' - \vec{q}) > E(k_{F})$$

Put $\vec{k}' \rightarrow -\vec{k}'$ and use (16), (17) and (20) to show that

$$\Delta E_{2}^{(3)*} + \Delta E_{3}^{(3)} = 4 \sum_{\vec{k},\vec{k}',\vec{q}} \frac{4\pi e^{2}}{\Omega q^{2}} \frac{\langle B \ \vec{k} + \vec{q} | h | B \ \vec{k} \rangle \langle B \ \vec{k}' | h | B \ \vec{k}' + \vec{q} \rangle}{\left[E(\vec{k} + \vec{q}) - E(\vec{k}) \right] \left[E(\vec{k}' + \vec{q}) - E(\vec{k}') \right]}$$

$$E(\vec{k}), E(\vec{k}') \langle E(k_{F})$$

$$E(\vec{k} + \vec{q}), E(\vec{k}' + \vec{q}) \rangle E(k_{F})$$

 $= \Delta E_{1}^{(3)} \qquad (3-24)$

The contribution to our perturbation energy for the third order diagram, $\Delta E^{(3)}$, is given by (20), (23) and (24). Again using the arguments of (14) to (18), the restriction $E(\overrightarrow{k+q}) > E(k_F)$ can be dropped from our sums.

The final expression for $\Delta E^{(3)}$ is

$$\Delta \mathbf{E}^{(3)} = 8 \sum_{\vec{q}} \frac{4\pi e^2}{\Omega q^2} \left[\sum_{\mathbf{E}(\vec{k}) < \mathbf{E}(\mathbf{k}_{\mathbf{F}})} \frac{\langle \mathbf{B} \vec{k} | \mathbf{h}(\mathbf{ep}) | \mathbf{B} \vec{k} \cdot \mathbf{q} \rangle}{\mathbf{E}(\vec{k} + \mathbf{q}) - \mathbf{E}(\vec{k})} \right]$$

$$\left[\sum_{\mathbf{E}(\vec{k}) < \mathbf{E}(\mathbf{k}_{\mathbf{F}})} \frac{\langle \mathbf{B} \vec{k} + \mathbf{q} | \mathbf{h}(\mathbf{ep}) | \mathbf{B} \vec{k} \rangle}{\mathbf{E}(\vec{k} + \mathbf{q}) - \mathbf{E}(\vec{k})} \right]$$
(3-25)

4. EXPRESSION FOR PERTURBATION ENERGY ΔE

So far in the perturbation treatment of ΔH we have calculated the energies $\Delta E^{(2)}$ and $\Delta E^{(3)}$ for the two lowest diagrams containing V_{ent} twice.

We shall take as the total value of ΔE without exchange the sum of the following diagrams.



The x⁻⁻⁻ line refers to a V_{e-I} factor, and --- refers to a V_{e-e} factor in the expansion of U.

In this "bubble approximation", the series of diagrams may be summed (L V 59) by replacing in the expression for $\Delta E^{(3)}$,

$$\frac{1}{q^2} \qquad by \qquad \frac{1}{q^2 + f_B(q)}$$

where

$$f_{B}(q) = \frac{2k_{F}}{\pi a_{o}} \left[1 + \left(\frac{k_{F}}{q} - \frac{q}{4k_{F}} \right) \ln \left| \frac{q + 2k_{F}}{q - 2k_{F}} \right| \right]$$
(3-27)

a is the Bohr radius.

If one associates the factor $-f_B(q)$ with each bubble, 0, and the factor $1/q^2$ with each photon line ---, a geometric series is formed.

An approximate way to include electron exchange has been given by Hubbard (H 57b). One replaces $f_B(q)$ by $f_H(q)$ where

$$f_{H}(q) = \frac{f_{B}(q)}{1 - \frac{f_{B}(q)}{2(q^{2} + k_{F}^{2})}}$$
(3-28)

The quantity $-f_{H}(q)$ is associated with the approximate sum of the diagrams



Then in the "bubble approximation", from (18), (25) and (4) the ΔE expression is

$$\Delta \mathbf{E} = \sum_{\mathbf{L},\mathbf{L}^{*}} \sum_{\vec{q}} \vec{\delta \mathbf{R}_{L}} \cdot \left[\Phi_{\mathbf{L}\,\mathbf{L}}^{(2)}(\vec{q}) + \Phi_{\mathbf{L}\,\mathbf{L}}^{(3)}, \overset{\infty}{(\mathbf{q})} \right] \cdot \vec{\delta \mathbf{R}_{L}}, \quad (3-29)$$

where

$$\Phi_{LL'}^{(2)}(\vec{q}) = -2 \sum_{E(\vec{k}) \leq E(k_F)} \frac{\langle \underline{B} \ \vec{k} | \nabla v(\vec{x} - \vec{L}) | \underline{B} \ \vec{k} + \vec{q} \rangle \langle \underline{B} \ \vec{k} + \vec{q} | \nabla v(\vec{x} - \vec{L'}) | \underline{B} \ \vec{k} \rangle}{E(\vec{k} + \vec{q}) - E(\vec{k})}$$
(3-30)

$$\Phi_{LL'}^{(3),\infty}(\vec{q}) = 8 \left[\frac{4\pi e^2}{\Omega \left[\bar{q}^2 + f_B(q) \right]} \right] \left[\sum_{E(\vec{k}) < E(k_F)} \frac{\langle B \ \vec{k} | \nabla v(\vec{x} - \vec{L}) | B \ \vec{k} + \bar{q} \rangle}{E(\vec{k} + \vec{q}) - E(\vec{k})} \right]$$

$$\left[\sum_{E(\vec{k}) < E(k_F)} \frac{\langle B \ \vec{k} + \bar{q} | \nabla v(\vec{x} - \vec{L}') | B \ \vec{k} \rangle}{E(\vec{k} + \vec{q}) - E(\vec{k})} \right] \quad (3-31)$$
and
$$\nabla v(\vec{x} - \vec{L}) = \frac{\partial v(\vec{x} - \vec{L})}{\partial (\vec{x} - \vec{L})} \quad (3-32)$$

and

This perturbation treatment has produced a ΔE value which is not zero when all the ions are displaced by an equal amount. Write (30) as

$$\Delta E = \sum_{L,L'} \vec{\delta R}_{L} \cdot \vec{\Phi}_{LL'} \cdot \vec{\delta R}_{L'}$$
(3-33)

where

$$\overline{\Psi}_{LL'} = \sum_{\vec{q}} \left[\overline{\Phi}_{LL'}^{(2)}(\vec{q}) + \overline{\Phi}_{LL'}^{(3), \infty}(\vec{q}) \right]$$
 (3-34)

To calculate this zero point energy, interpret first (33) noting that the sums are over all lattice positions $\vec{L}, \vec{L}'; \vec{L} = \vec{L}'$ included. The change in potential energy of the ion at position $\overrightarrow{L^{"}}$ when it is displaced $\delta \vec{R}_{L''}$ from equilibrium is

$$\delta \vec{R}_{L''} \cdot \left[\sum_{L'} \vec{\Phi}_{L'' L'} \cdot \vec{\delta R}_{L'} \right] + \left[\sum_{L} \vec{\delta R}_{L} \cdot \vec{\Phi}_{L L''} \right] \cdot \vec{\delta R}_{L''}$$

(3-32)

Therefore, the change in potential of all N ions for a <u>uniform</u> ion displacement is

$$\frac{1}{2} \sum_{\mathbf{L}''} \delta \vec{\mathbf{R}}_{\mathbf{L}''} \cdot \left[\sum_{\mathbf{L}'} \vec{\Phi}_{\mathbf{L}'' \mathbf{L}'} \cdot \delta \vec{\mathbf{R}}_{\mathbf{L}''} \right] + \frac{1}{2} \sum_{\mathbf{L}''} \left[\sum_{\mathbf{L}} \delta \vec{\mathbf{R}}_{\mathbf{L}''} \cdot \vec{\Phi}_{\mathbf{L}\mathbf{L}''} \right] \cdot \delta \vec{\mathbf{R}}_{\mathbf{L}''} \quad (3-35)$$

The factors $\frac{1}{2}$ are inserted since each potential change is counted twice in summing over the ions.

A normalized value of ΔE , one which is zero for a uniform ion displacement, is obtained by subtracting expression (35) from (33).

$$\Delta E = \frac{1}{2} \sum_{L,L'} (\delta \vec{R}_L - \delta \vec{R}_{L'}) \cdot \Phi_{LL'} \cdot (\delta \vec{R}_L - \delta \vec{R}_L) \qquad (3-36)$$

5. EXPRESSION FOR SCREENING FREQUENCY ω_g^2 FROM PERTURBATION ENERGY ΔE

Normal coordinates, $Q(\vec{x},\sigma)$, discussed in section (2-1), are now introduced into the ΔE expression. We proceed to find the screening contribution, ω_s^2 , to the phonon frequencies.

The ΔE value must be invariant under the translation group of the lattice, $\{\hat{T}_L\}$, which acts on functions of the electron coordinate \vec{x} . This will impose some selection rules on the electron-ion matrix elements in ΔE .

From basic Bloch wave function properties,

$$B(\vec{k}; \vec{x+L''}) \equiv \hat{T}_{L''} B(\vec{k}; \vec{x}) = e^{i\vec{k}\cdot\vec{L''}} B(\vec{k}; \vec{x})$$
(3-37)
Using expression (2-2) for $\delta \vec{R}_{L}$,

$$\hat{T}_{L''} \sum_{L} (\delta \vec{R}_{L} - \delta \vec{R}_{L'}) \cdot \nabla v(\vec{x} - \vec{L})$$

$$= (MN)^{-\frac{1}{2}} \sum_{L} \sum_{\vec{X}, \sigma} Q(\vec{x}, \sigma) \vec{\epsilon}(\vec{X}, \sigma') \cdot \nabla v(\vec{x} - \vec{L}) \left[e^{i \vec{X} \cdot (\vec{L} + \vec{L}'')} - e^{i \vec{X} \cdot L'} \right]$$

From (30) and (31), the quantity that must be independent of

$$\frac{1}{L''} is$$

$$\frac{\Lambda}{T_{L''}} \left[\sum_{L,L'} \langle B \vec{k} | (\delta \vec{R}_{L} - \delta \vec{R}_{L},) \cdot \nabla v(\vec{x} - \vec{L}) | B \vec{k} + q \right]$$

$$\langle B \vec{k} + q | (\delta \vec{R}_{L}, - \delta \vec{R}_{L}) \cdot \nabla v(\vec{x} - \vec{L}') | B \vec{k} \rangle \right]$$

$$= \frac{1}{MN} \sum_{L,L'} \sum_{\vec{n},\sigma} Q(\vec{n}', \sigma') Q(\vec{n},\sigma) \langle B \vec{k} | \vec{\epsilon} (\vec{n}', \sigma') \cdot \nabla v(\vec{x} - \vec{L}) | B \vec{k} + q \rangle$$

$$\langle B \vec{k} + q | \vec{\epsilon} (\vec{n}, \sigma) \cdot \nabla v(\vec{x} - \vec{L}') | B \vec{k} \rangle$$

$$\left[e^{i\vec{L}'} \cdot (\vec{n}' + \vec{n}) e^{i\vec{n}' \cdot \vec{L}'} + i\vec{n}' \cdot \vec{L} - e^{i\vec{L}} \cdot (\vec{n}' + \vec{n}) e^{i\vec{n}' \cdot \vec{L}''} \right]$$

$$(3-38)$$

For this expression to be independent of $\overrightarrow{L''}$ for all $\overrightarrow{\chi}$ and $\overrightarrow{\chi}'$ in the first Brillouin zone, the last factor becomes

$$\begin{bmatrix} e^{i\vec{x}\cdot(\vec{L}'-\vec{L})} & \delta_{\vec{x},-\vec{x}'} + e^{i\vec{x}\cdot\vec{L}} + i\vec{x}'\cdot\vec{L}' - e^{i\vec{x}\cdot\vec{L}} & \delta_{\vec{x}',0} \end{bmatrix}$$

$$= e^{i\vec{x}'\cdot\vec{L}'} \delta_{\vec{x},0}$$
(3-39)

In each of the matrix elements of (38), change the integration variable $\vec{x} - \vec{L} \rightarrow \vec{x}$. Using (38),

$$(B\vec{k}|\vec{e}(\vec{x}',\sigma') \cdot \nabla v(\vec{x}-\vec{L})|B\vec{k}+q) = e^{i\vec{q}\cdot\vec{L}} (B\vec{k}|\vec{e}(\vec{x}',\sigma') \cdot \nabla v(\vec{x})|B\vec{k}+q)$$
(3-40)

With (39) and (40), expression (38) becomes

$$\frac{1}{MN}\sum_{\vec{\chi},\vec{\chi}',\sigma,\sigma'} Q(\vec{\chi}',\sigma') Q(\vec{\chi},\sigma') \langle B \vec{k} | \vec{\epsilon}(\cdot_{\vec{\chi}'},\sigma') \cdot \nabla v(\vec{\chi}) | B \vec{k} + \vec{q} \rangle$$

$$\langle B \vec{k} + \vec{q} | \vec{\epsilon}(\vec{\chi},\sigma) \cdot \nabla v(\vec{\chi}) | B \vec{k} \rangle \sum_{L,L'} \left[e^{i(\vec{q}-\vec{\chi})} \cdot (\vec{L} - \vec{L}') \delta_{\vec{\chi}, -\vec{\chi}'} + e^{i(\vec{\chi} + \vec{q})} \cdot \vec{L} + i(\vec{\chi}' - \vec{q}) \cdot \vec{L}' - e^{i(\vec{\chi} + \vec{q})} \cdot \vec{L} - i \vec{q} \cdot \vec{L}' \right] \delta_{\vec{\chi}', 0}$$

$$= e^{i(\vec{\chi}' - \vec{q})} \cdot \vec{L}' + i \vec{q} \cdot \vec{L} \qquad (3-41)$$

The sum over L and L' is now easily done using (2-4). The last factor of (41) becomes

$$N^{2} \begin{bmatrix} \delta_{\vec{q},\vec{\chi}+\vec{G}} & \delta_{\vec{\chi},\vec{v}} + \delta_{\vec{q},\vec{\chi}+\vec{G}} & \delta_{\vec{q},\vec{q}} & \delta_{\vec{q},\vec{q}} & \delta_{\vec{q},\vec{G}} & \delta_{\vec{q},\vec{G}} & \delta_{\vec{q},\vec{q}} & \delta_{\vec{q},\vec{$$

Since $\vec{\chi}$ and $\vec{\chi}'$ are restricted to the first Brillouin zone, and in (29) $\sum_{\vec{q}} = \sum_{-\vec{q}}, \text{ use of } (2-6) \text{ gives the result}$ $\frac{1}{2} \sum_{L,L'} \langle B \vec{k} | (\delta \vec{R}_L - \delta \vec{R}_{L'}) \cdot \nabla v(\vec{x}-\vec{L}) | B \vec{k}+\vec{q} \rangle \langle B \vec{k}+\vec{q} | (\delta \vec{R}_{L'} - \delta \vec{R}_{L}) \cdot \nabla v(\vec{x}-\vec{L'}) | B \vec{k} \rangle$ $= \frac{N}{M} \sum_{\vec{R},\sigma,\sigma'} Q^*(\vec{X},\sigma') Q(\vec{X},\sigma) \langle B \vec{k} | \vec{e} \langle \vec{X},\sigma' \rangle \cdot \nabla v(\vec{x}) | B \vec{k}+\vec{q} \rangle$

$$\langle \mathbf{B} \ \vec{\mathbf{k}} + \vec{\mathbf{q}} \ | \ \vec{\mathbf{c}} (\vec{\mathbf{x}}, \sigma) \cdot \nabla \mathbf{v}(\vec{\mathbf{x}}) \ | \ \mathbf{B} \ \vec{\mathbf{k}} \rangle \left[\delta_{\vec{\mathbf{q}}, \vec{\mathbf{x}} + \vec{\mathbf{d}}} - \delta_{\vec{\mathbf{q}}, \vec{\mathbf{d}}} \right]$$
(3-42)

Convenient expressions for $\Delta E^{(2)}$ and $\Delta E^{(3)}$, ∞ may now be written in the form (2-10). From (30), (31), (34), (36) and (42) these expressions are the following:

$$\Delta E^{(2)} = \frac{1}{2} \sum_{\vec{k}',\sigma,\sigma'} Q^{*}(\vec{k},\sigma') Q(\vec{k},\sigma) \sum_{\vec{q}} \frac{-4N}{M} \left[\delta_{\vec{q}'}, \vec{k}+\vec{G}' - \delta_{\vec{q}'}, \vec{G}' \right]$$

$$\sum_{\vec{k}',\sigma,\sigma'} \frac{\langle B \vec{k} | \vec{\epsilon} (\vec{k},\sigma') \cdot \nabla v(\vec{x}) | B \vec{k}+\vec{q} \rangle \langle B \vec{k}+\vec{q} | \vec{\epsilon} (\vec{k},\sigma) \cdot \nabla v(\vec{x}) | B \vec{k} \rangle}{\langle B \vec{k}+\vec{q} | \vec{\epsilon} (\vec{k},\sigma) \cdot \nabla v(\vec{x}) | B \vec{k} \rangle} (3-43)$$

$$E(\vec{k}) \langle E(\vec{k}_{p}) \qquad E(\vec{k}+\vec{q}) - E(\vec{k})$$

$$\Delta E^{(3)}, \approx = \frac{1}{2} \sum_{\vec{k}',\sigma',\sigma'} Q^{*}(\vec{k},\sigma') Q(\vec{k},\sigma') \sum_{\vec{q}'} \frac{16N}{M} \left[\delta_{\vec{q}'}, \vec{k}+\vec{G}' - \delta_{\vec{q}'}, \vec{G}' \right]$$

$$\frac{4\pi e^{2}}{\sqrt{q^{2} + f_{B}(q)}} \left[\sum_{\vec{k}(\vec{k}) \langle E(\vec{k}_{p})} \frac{\langle B \vec{k} | \vec{\epsilon} (\vec{k},\sigma') \cdot \nabla v(\vec{x}) | B \vec{k}+\vec{q} \rangle}{E(\vec{k}+\vec{q}) - E(\vec{k})} \right]$$

$$\sum_{\mathbf{E}(\vec{k}) \leq \mathbf{E}(\mathbf{k}_{\mathbf{F}})} \frac{\langle \mathbf{B} \ \vec{\mathbf{k}} + \vec{\mathbf{q}} \ \mathbf{I} \ \vec{\mathbf{e}}(\vec{\mathbf{k}}, \sigma) \cdot \nabla \mathbf{v}(\vec{\mathbf{x}}) \ \mathbf{I} \ \mathbf{B} \ \vec{\mathbf{k}} \rangle}{\mathbf{E}(\vec{\mathbf{k}} + \vec{\mathbf{q}}) - \mathbf{E}(\vec{\mathbf{k}})}$$
(3-44)

The arguments of (2-10, 11, 12) for normal coordinates require that ΔE be diagonal in σ and σ' . The expression for ΔE becomes

$$\Delta \mathbf{E} = \Delta \mathbf{E}^{(2)} + \Delta \mathbf{E}^{(3)}, \stackrel{\infty}{=} = \frac{1}{2} \sum_{\vec{\mathcal{R}}, \sigma} Q^*(\vec{\mathcal{R}}, \sigma) Q(\vec{\mathcal{R}}, \sigma) \omega_p^2 \sum_{\vec{\mathcal{G}}} \left[\mathbf{F}(\vec{\mathcal{G}}) - \mathbf{F}(\vec{\mathcal{R}} + \vec{\mathcal{G}}) \right] \qquad (3-45)$$

The plasma frequency ω_p is defined by

$$\omega_{p}^{2} = \frac{4\pi (Z' e)^{2}}{M - C_{0}}$$
(3-46)
The dimensionless function $F(\vec{q})$ is given by

$$F(\vec{q}) = I^{(2)} - I^{(3)*} \frac{1}{q^2 + f_B(q)} I^{(3)}$$
 (3-47)

where

$$I^{(2)} = \frac{-\Omega^2}{8\pi^4 (\mathbb{Z}'e)^2} \int_{\mathbf{E}(\vec{k}) \leq \mathbf{E}(\mathbf{k}_F)} \frac{|\langle \mathbf{B} \ \vec{k} + \vec{q} \ | \ \vec{e}(\vec{k}, \sigma) \cdot \nabla \mathbf{v}(\vec{x}) | \mathbf{B} \ \vec{k} \rangle|^2}{\mathbf{E}(\vec{k}, \sigma) \leq \mathbf{E}(\mathbf{k}_F)} (3-48)$$

$$I^{(3)} = \frac{-1}{2Z\pi^{3}} \int_{E(\vec{k}) < E(k_{F})} d^{3}k \frac{i\langle B \ \vec{k} + \vec{q} | \vec{\epsilon}(\vec{x}, \sigma) \cdot \nabla v(\vec{x}) | B \ \vec{k} \rangle}{E(\vec{k} + \vec{q}) - E(\vec{k})}$$
(3-49)

The screening contribution to the phonon frequency, ω_s^2 , follows from (45). Define

$$\omega_{g}^{2}(\vec{x},\sigma) = \omega_{p}^{2}\left[\sum_{\vec{d}} F(\vec{k}+\vec{d}) - \sum_{\vec{d}} F(\vec{d})\right]$$

To use the ω_c^2 values computed by Vosko (unpublished, 1958), we must omit the $\overline{G} = 0$ term from the second sum. Thus,

$$\omega_{g}^{2}(\vec{x},\sigma) = \omega_{p}^{2} \left[\sum_{\vec{d}} F(\vec{x}+\vec{d}) - \sum_{\vec{d}\neq 0} F(\vec{d}) \right]$$
(3-50)

and we have

 $\omega^2 = \omega_c^2 - \omega_s^2$ (3-51)

The terms $\vec{G} \neq 0$ in (50) are called the Umklapp contribution to

 ω_s^2 . If the effective ion-ion interaction is central, then the transverse frequency modes are screened only by the Umklapp processes.

CHAPTER 4: EVALUATION OF ELECTRON-ION MATRIX ELEMENT

1. INTRODUCTION

From the results of the previous chapter, it is evident that the important quantity is the electron-ion matrix element

$$i \langle B \overline{k+q} | \vec{\epsilon} \cdot \nabla v(\vec{r}) | B \vec{k} \rangle \qquad (4-1)$$

To proceed with the calculation, this matrix element is required as a reasonably simple function of \vec{k} , \vec{q} so that the integrations over \vec{k} in (3-48) and (3-49) can be carried out in closed form. This is difficult to calculate mainly because the Bloch states $|B\vec{k}\rangle$ are complicated functions of \vec{r} . The potential $v(\vec{r})$ can be calculated with some labour by the self-consistent field method.

From first principles we know $\mathbf{v}(\vec{\mathbf{r}})$ for two regions. For $\mathbf{r} \rightarrow 0$, $\mathbf{v}(\vec{\mathbf{r}}) = -Ze^2/r$ where Z is the atomic number of the nucleus. For the region outside the range of the atomic core states, $\mathbf{v}(\vec{\mathbf{r}}) = -Z' e^2/r$, where Z' is the ion valence. In principle, the potential $\mathbf{v}(\vec{\mathbf{r}})$ may be determined in the intermediate region from Poisson's equation and a knowledge of the atomic core wave functions. Note that this self-consistent calculation for $\mathbf{v}(\vec{\mathbf{r}})$ requires only the core-electron states.

A crude approximation is to use plane wave electron states and the unscreened coulomb electron-ion interaction which is good for most of the crystal volume.

$$\mathbf{v}(\mathbf{\dot{r}}) = \frac{-\mathbf{Z}'\mathbf{e}^2}{\mathbf{r}}$$
(4-2)

With these approximations the matrix element (1) is

$$\vec{\epsilon} \cdot \vec{q} \frac{4\pi Z' e^2}{\Omega q^2}$$
 (4-3)

This result is reasonable for small q, of order $q \lesssim (k_F/4)$. For larger q, q $\gtrsim k_F$, this result is invalid since plane waves are poor approximations to the Bloch wave functions near the nucleus and also the potential (2) is not correct in this vicinity. Conductivity results (B 37; Z 60) show that Umklapp contributions given by (3) are much too large.

To make a more accurate calculation, the first step is to improve the potential within the region of the Wigner-Seitz cell. It is necessary to assume that the core wave functions are negligible outside the central cell so that their screening effect is complete and (2) holds for $r > r_o$, where r_o is the radius of the Wigner-Seitz cell. A one-body selfconsistent electron-ion (unscreened) potential v(r) for $r < r_o$ may be determined as follows. The usual self-consistent potential calculated for metals is the actual potential U(r) observed by an electron within the central cell. This potential includes the interactions with conduction electrons. Although it is to be of Hartree form, it may include "averaged" core electron exchange and correlation effects. We shall exclude from the potential U(r) the exchange and correlation contributions due solely to the conduction electrons. Then, this "Hartree" potential U(r) is equal to the electron-ion potential, v(r), plus the potential of the conduction electron cloud within the cell.

If we assume the conduction electrons form a uniform background charge, we have

$$h_{B} = \frac{p^{2}}{2m} + \sum_{L} v(\vec{r}-\vec{L}) + background$$
$$= \frac{p^{2}}{2m} + \sum_{L} v(\vec{r}-\vec{L}) \qquad (4-4)$$

Within the central cell of radius r_0 , the potential of a uniform electron cloud is

$$\frac{3Z'e^2}{2r_0} - \frac{Z'e^2r^2}{2r_0^3}, r < r_0$$
(4-5)

If the potentials $U(\vec{r}-\vec{L})$ are non-overlapping, the potential of ions in neighbouring cells is cancelled by the potential of electrons within those cells. Thus, we shall take

$$\mathbf{v}(\mathbf{r}) = \mathbf{U}(\mathbf{r}) - \left[\frac{3\mathbf{Z}^{\dagger}\mathbf{e}^{2}}{2\mathbf{r}_{0}} - \frac{\mathbf{Z}^{\dagger}\mathbf{e}^{2}\mathbf{r}^{2}}{2\mathbf{r}_{0}^{3}}\right], \quad \mathbf{r} < \mathbf{r}_{0}$$

$$= -\frac{\mathbf{Z}^{\dagger}\mathbf{e}^{2}}{\mathbf{r}}, \quad \mathbf{r} > \mathbf{r}_{0}$$
(4-6)

This is defined so that $U(r_0) = 0$. For convenience define the quantity $v_a(r)$

$$\mathbf{v}_{a}(\mathbf{r}) = \frac{3\mathbf{Z}'e^{2}}{2\mathbf{r}_{o}} - \frac{\mathbf{Z}'e^{2}\mathbf{r}^{2}}{2\mathbf{r}_{o}^{3}}, \ \mathbf{r} < \mathbf{r}_{o}$$

$$= \frac{\mathbf{Z}'e^{2}}{\mathbf{r}} \qquad \mathbf{r} > \mathbf{r}_{o}$$
(4-7)

Then,

$$\mathbf{v}(\mathbf{r}) = \mathbf{U}(\mathbf{r}) - \mathbf{v}_{\mathbf{a}}(\mathbf{r}) \qquad (4-8)$$

The next section contains a short discussion of the Bardeen (B 37) matrix element. The rest of the chapter is concerned with the

calculation of the electron-ion matrix element by use of the orthogonalized plane wave representation of the Bloch functions. It is important in this treatment that U(r) enter the Schrodinger equation for Bloch states (cf. appendix B). For aluminum, Heine's U(r) (H 57; Se 61) (without Bohm-Pines exchange) is used in this work.

2. BARDEEN MATRIX ELEMENT

In the calculation on conductivity of monovalent metals, Bardeen (B 37) evaluated (1) with a potential of the form (8).

For the term involving v_a , Bardeen assumed plane waves for his Bloch states and by elementary methods found

$$-i \langle PW \overrightarrow{k+q} | \overrightarrow{e} \cdot \nabla v_{a} | PW \overrightarrow{k} \rangle = \overrightarrow{e} \cdot \overrightarrow{q} \frac{4\pi Z' e^{2}}{\Omega q^{2}} \mathcal{J}(qr_{o}) \qquad (4-9)$$

with the normalization

$$\langle PW \vec{k} | PW \vec{k} \rangle = 1$$
 (4-10)

The interference factor $\mathcal{H}(\mathbf{x})$ is

$$(x) = \int_{0}^{3} d^{3}r e^{i\vec{q}\cdot\vec{r}} = \frac{3(\sin x - x\cos x)}{x^{3}}$$
 (4-11)

Bardeen used the Mott and Jones identity (MJ 36) for evaluating the $\nabla U(\mathbf{r})$ term. The Bloch states were approximated by

$$B(\vec{k};\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u(0;\vec{r}) \qquad (4-12)$$

where $u(0; \vec{r})$ is the lowest eigenfunction of the conduction band. The function u(0; r) is spherically symmetric and $\nabla u(0, r_{s}) = 0$.

The Bardeen result is

$$i \langle B \overline{k+q} | \overline{\epsilon} \cdot \nabla U | B \overline{k} \rangle = \overline{\epsilon} \cdot \overline{q} \frac{U(r_0) - E_0}{N} \mathcal{H}(x)$$
 (4-13)

The quantity E_{o} is the energy of an electron in the lowest conduction state.

Expressions (1), (8), (9) and (13) give the Bardeen electron-ion matrix element.

$$i \langle B \overline{k+q} | \overline{\epsilon} \cdot \nabla v(\overline{r}) | B \overline{k} \rangle = \overline{\epsilon} \cdot \overline{q} \left[\frac{4\pi Z \cdot e^2}{-\Omega \cdot q^2} + \frac{U(r_o) - E_o}{N} \right] \mathscr{Y}(x) \quad (4-14)$$

3. ORTHOGONALIZED PLANE WAVES

Although many properties of metals indicate that conduction electrons behave like plane waves over most of the crystal volume, it is known that near the nucleus there is a strong peaking of the electron wave functions. It is in this region (perhaps, 1/10 of the crystal volume) where the conduction wave functions are peaked that the electronion interaction could be most important for large q values. The orthogonalized plane wave (OPW) method makes it possible to take advantage of the simplicity of plane waves while accounting for the peaking of the Bloch wave function in the vicinity of the ion.

Recent calculations using the OPW method have found it to be quite successful. Heine's OPW results (H 57) for the band structure of aluminum are in essential agreement with the later results of Segall (Se 61). In particular Heine's results for aluminum indicate that one OPW is a very good approximation, except at symmetry points where degeneracy must be included. Kleinman and Phillips (KP 60) have used the OPW procedure to generate a repulsive core potential. When added to the attractive nuclear potential, this gave an effective potential, a "pseudopotential", which was fairly constant and could be treated by perturbation theory. Their germanium and silicon band calculations using the pseudopotential give satisfactory results. Cohen and Heine (CH 61) and later Austin, Heine and Sham (AHS 62) have discussed the general theory of pseudopotentials and have indicated why OPW wave functions are good representation of Bloch wave functions.

However, for our purposes it is best to work directly with the OPW wave functions. This is due to the fact that we require matrix elements between states of different energy and the pseudopotential is defined in terms of the energy of the state in question.

An OPW wave function contains the ion core wave functions which are strongly peaked at the nucleus. Therefore, the use of one or a combination of OPW wave functions could be expected to give a reasonable electron-ion matrix element. For the case of aluminum, we expect one OPW to be sufficient (H 57; Se 61).

For completeness, we introduce some standard relations from Herring's classic paper (H 40) on the OPW method. Atomic units are used, M = m = e = 1, except that energies are measured in rydbergs, units of $(e^2/2a_n)$.

The "atomic" wave functions of the core electrons, $\mathscr{G}_{c}(\vec{r})$, $c \equiv (n, \ell, m)$, are eigenfunctions of the Schrodinger equation

$$\left[-\nabla^{2} + U(\mathbf{r})\right] \mathscr{G}_{\mathbf{c}}(\vec{\mathbf{r}}) = \mathbf{E}_{\mathbf{c}} \mathscr{G}_{\mathbf{c}}(\vec{\mathbf{r}}) \qquad (4-15)$$

The crystal wave functions for the core electrons by the tightbinding method are

These are eigenfunctions of the Bloch Hamiltonian h_{p}

$$h_{B} = -\nabla^{2} + \sum_{L} v(\vec{r} - \vec{L})$$
 (4-17)

with eigenvalues E.

An orthogonalized plane wave is defined as

$$\langle \vec{r} | OPW \vec{k} \rangle = (N \Omega_0)^{-1/2} e^{i \vec{k} \cdot \vec{r}} - \sum_c b_{c;\vec{k}} \mathscr{G}_c(\vec{k};\vec{r})$$
 (4-18)

The quantity $b_{c;\vec{k}}$ is chosen so that the state $\langle \vec{r} \mid OPW \vec{k} \rangle$ is orthogonal to all the crystal core wave functions $\emptyset_c(\vec{k};\vec{r})$.



We have the usual expansion of a plane wave in terms of spherical harmonics and the addition theorem (CS 35)

$$e^{i\mathbf{k}\mathbf{r}\,\cos\omega} = \sum_{\ell=0}^{\infty} (2\ell+1) \,\mathbf{i}^{\ell} \,\mathbf{j}_{\ell}(\mathbf{k}\mathbf{r}) \,\mathbf{P}_{\ell}(\cos\omega) \qquad (4-20)$$

$$(\cos\omega) = \frac{4\pi}{2\ell+1} \sum_{\mathbf{m}} \mathbf{Y}_{\ell}^{\mathbf{m}}(\theta, \varphi) \mathbf{Y}_{\ell}^{\mathbf{m}}(\alpha, \beta) \qquad (4-21)$$

where

P_L

 $\cos \omega = \cos \theta \cos \alpha + \sin \theta \sin \alpha \cos (\varphi - \beta)$ Write the core orbitals as

where $R_{n\ell}$ is real. Then one finds

$$b_{c;\vec{k}} = \left[(4\pi)^{\frac{1}{2}} (2\ell+1)^{-\frac{1}{2}} Y_{\ell}^{m^{*}} (\alpha, \beta) \right] b_{n\ell}(k)$$
 (4-22)

$$b_{n\ell}(k) = \sqrt{\frac{4\pi(2\ell+1)}{\Omega_0}} i^{\ell} \int_{N_0}^{\infty} dr r^2 j_{\ell}(kr) R_{n\ell}(r)$$
 (4-23)

For a simple Bravais lattice,

$$\langle OPW \vec{k}' | OPW \vec{k} \rangle = \delta_{\vec{k},\vec{k}'} - \delta_{\vec{k},\vec{k}'+\vec{G}} \sum_{n,\ell} b_{n\ell}^*(k') b_{n\ell}(k) P_{\ell}(\cos \theta_{\vec{k},\vec{k}'})$$
(4-24)

$$\langle OPW \vec{k}' | h_{B} | OPW \vec{k} \rangle = k^{2} \delta_{\vec{k},\vec{k}'}$$

$$+ \delta_{\vec{k},\vec{k}'+\vec{G}} \left[U(\vec{G}) - \sum_{n\ell} E_{n\ell} b_{n\ell}^{*}(k^{*}) b_{n\ell}(k) P_{\ell}(\cos \theta_{\vec{k},\vec{k}'}) \right] \qquad (4-25)$$

The Fourier transform, $U(\vec{G})$, of the potential $U(\vec{F})$ is defined by

$$\mathbb{U}(\vec{G}) = \frac{1}{r_{0}} \int_{r_{0}} \mathbb{U}(\vec{r}) e^{-i\vec{G}\cdot\vec{r}} d^{3}\vec{r} \qquad (4-26)$$

Since U(r) = 0 for $r > r_0$

$$U(G) = \frac{4\pi}{\Omega_0} \frac{1}{G} \int_0^\infty dr r U(r) \sin Gr$$

4. OPW ELECTRON-ION MATRIX ELEMENT

The electron-ion matrix element (1) is now evaluated using OPW wave functions. The potential v(r) is given by (7) and (8).

For the Bloch state $|B \rightarrow k\rangle$, we take one OPW. As has been argued, this should work well for the case of aluminum.

$$|B\vec{k}\rangle = C_{\vec{k}} |OPW\vec{k}\rangle$$
 (4-27)

$$\langle \mathbf{B} \, \overline{\mathbf{k}} \, | \, \mathbf{B} \, \overline{\mathbf{k}} \rangle = 1 \qquad (4-28)$$

A rough calculation has indicated that for the $\nabla \mathbf{v}_a$ term the OPW wave functions may be approximated by plane waves. This $\nabla \mathbf{v}_a$ term is then identical with that given by Bardeen (B 37), expression (9), except for a factor $C_{\mathbf{k}+\mathbf{q}}^* - C_{\mathbf{k}}^*$.

However, since ∇U is large in the same region that the atomic core states are peaked, the complete OPW wave function must be used. Sham (Sh 61) has essentially made this calculation except that he has dropped terms which vanish for $E(\vec{k} + \vec{q}) = E(\vec{k})$. A summary of the calculation is given in appendix B for the general Bloch state

$$|B\vec{k}\rangle = \sum_{\vec{d}} c_{\vec{k},\vec{d}} |OPW\vec{k}+\vec{d}\rangle$$

The result for one OPW is

$$i \langle B\vec{k} + \vec{q} | \vec{\epsilon} \cdot \nabla U | B\vec{k} \rangle$$

$$= -\frac{C_{\vec{k}}^{*} + \vec{q}}{N} \left[\vec{\epsilon} \cdot \vec{q} \quad U(\vec{q}) + \vec{\epsilon} \cdot \vec{q} \quad \sum_{c} \left[\frac{E(\vec{k} + \vec{q}) + E(\vec{k})}{2} - E_{c} \right] b_{c,\vec{k}}^{*} + \vec{q} \quad b_{c,\vec{k}}$$

$$+ \vec{\epsilon} \cdot (2\vec{k} + \vec{q}) \frac{1}{2} \left[E(\vec{k} + \vec{q}) - E(\vec{k}) \right] \sum_{c} b_{c,\vec{k}}^{*} + \vec{q} \quad b_{c,\vec{k}}$$

$$+ \left[\mathbf{E}(\vec{k} + \vec{q}) - \mathbf{E}(\vec{k}) \right] \sum_{\mathbf{c},\mathbf{c}^{*}} b^{*}_{\mathbf{c}^{*},\vec{k} + \vec{q}} b_{\mathbf{c},\vec{k}} \int d\mathbf{c} \, \boldsymbol{\beta}^{*}_{\mathbf{c}^{*}} \, (\mathbf{i} \, \vec{\mathbf{e}} \cdot \nabla \boldsymbol{\beta}_{\mathbf{c}}) \right] \quad (4-29)$$

For convenience, we define the following quantities

$$U_{R}(\vec{k} + \vec{q}, \vec{k}) = \sum_{c} \left[\frac{E(\vec{k} + \vec{q}) + E(\vec{k})}{2} - E_{c} \right] b_{c', \vec{k} + \vec{q}}^{*} b_{c, \vec{k}}$$

=
$$\sum_{n, \ell} \left[\frac{E(\vec{k} + \vec{q}) + E(\vec{k})}{2} - E_{n\ell} \right] b_{n\ell}^{*}(|\vec{k} + \vec{q}|) b_{n\ell}(k) P_{\ell}(\cos \theta_{\vec{k}} + \vec{q}, \vec{k}) \quad (4-30)$$

which follows from (22); and

$$s = \vec{\epsilon} \cdot \vec{s}(\vec{k} + \vec{q}, \vec{k}) = \sum_{c,c'} b^*_{c',\vec{k}+\vec{q}} b_{c,\vec{k}} \int d\tau \, \phi^*_{c'}(i\vec{\epsilon} \cdot \nabla \phi_{c}) \quad (4-31)$$

Combining expressions (9) and (29) produces the complete electron-ion matrix element of (1).

$$i \langle B \vec{k} + \vec{q} | \vec{\epsilon} \cdot \nabla v | B \vec{k} \rangle$$

$$= C_{\vec{k}}^{*} + \vec{q} C_{\vec{k}} \left[\vec{\epsilon} \cdot \vec{q} \frac{4\pi Z' e^{2}}{\Omega q^{2}} \int (qr_{o}) - \frac{\vec{\epsilon} \cdot \vec{q}}{N} U(\vec{q}) - \frac{\vec{\epsilon} \cdot \vec{q}}{N} U_{R}(\vec{k} + \vec{q}, \vec{k}) - \frac{E(\vec{k})}{2N} \vec{\epsilon} \cdot (2\vec{k} + \vec{q}) \sum_{n\ell} b_{n\ell}^{*} (|\vec{k} + \vec{q}|) b_{n\ell}(k) P_{\ell}(\cos \theta_{\vec{k}} + \vec{q}, \vec{k})$$

$$- \frac{E(\vec{k} + \vec{q}) - E(\vec{k})}{N} \vec{\epsilon} \cdot \vec{s}(\vec{k} + \vec{q}, \vec{k}) \right] \qquad (4-32)$$

Note that $U(\hat{q})$ is negative so that the first two terms of (32) interfere constructively. U_R corresponds to the repulsive part of the pseudo-potential as discussed by many authors (KP 60, CH 61, Sh 61). The last two terms are peculiar to this problem since we require matrix elements between states of different energy in contrast to phonon-electron scattering where the electron energy is conserved (Sh 61).

The coefficient

$$C_{k} = \left[1 - \sum_{n\ell} |b_{n\ell}(k)|^{2}\right]^{-1/2}$$
 (4-33)

In aluminum, C_k is a monotonic decreasing function with $C_0 \simeq 1.09$, $C_{\infty} = 1$. In the following calculations, C_k is taken to be 1.

A more explicit form for the quantity S is developed in appendix C. In particular, the result for aluminum is given in (C-6).

CHAPTER 5: NUMERICAL PROCEDURE WITH RESULTS FOR ALUMINUM

1. INTERPOLATION FORMULA FOR ELECTRON-ION MATRIX ELEMENT

The screening contribution to the lattice frequencies, ω_s^2 , is evaluated by the sum in (3-50) involving $F(\bar{q})$. The function $F(\bar{q})$, defined by (3-47), involves the integrals $I^{(2)}$ and $I^{(3)}$ of (3-48, 49). These integrals require a knowledge of the electron-ion matrix element $i \langle B \bar{k} + \bar{q} \rangle \in \nabla \vee \langle B \bar{k} \rangle$ as a simple function of \bar{k} and \bar{q} so that the integrations over \bar{k} may be carried out. The parts which are functions only of \bar{q} are easily factored out.

Computational difficulties arise in evaluating the integrals $I^{(2)}$ and $I^{(3)}$ with the analytic expressions for the $b_{n\ell}(k)$ of (A-8, 9, 10) or for power series expansions of them. A reasonably simple yet accurate approach is needed.

As has been discussed in chapter 4, other OPW calculations have suggested the use of a repulsive core potential. Define the quantities

$$T_{2}(\vec{k} + \vec{q}, \vec{k}) = \frac{1}{2} \sum_{n\ell} b_{n\ell}^{*}(1\vec{k} + \vec{q}\,l) b_{n\ell}(k) P_{\ell}(\cos\theta_{\vec{k}} + \vec{q}, \vec{k}) + \frac{1}{2} \sum_{s=1s, 2s} \delta(s) \left[\frac{(-i)b_{2p}(1\vec{k} + \vec{q})}{1\vec{k} + \vec{q}\,l} b_{s}(k) + \frac{(-i)b_{2p}(k)}{k} b_{s}(l\vec{k} + \vec{q}\,l) \right] (5-1)$$

and

$$T_{3}(\vec{k} + \vec{q}, \vec{k}) = \frac{1}{2} \sum_{s=1s, 2s} \mathcal{J}(s) \left[-\frac{ib_{2p}(l\vec{k} + \vec{q}l)}{l\vec{k} + \vec{q}l} b_{s}(k) + \frac{ib_{2p}(k)}{k} b_{s}(l\vec{k} + \vec{q}l) \right]$$
(5-2)

The matrix element (4-32) for aluminum is now written as $\left[\text{using } (C-6)\right]$ $i\langle B \vec{k} + \vec{q} | \vec{\epsilon} \cdot \nabla v | B \vec{k} \rangle$ $= \vec{\epsilon} \cdot \vec{q} \left[\frac{4\pi Z' e^2}{\Omega q^2} \mathcal{D}(qr_0) - \frac{U(\vec{q})}{N} - \frac{U_R(\vec{k} + \vec{q}, \vec{k})}{N} - \frac{E(\vec{k} + \vec{q}) - E(\vec{k})}{N} T_3(\vec{k} + \vec{q}, \vec{k}) \right]$ $- \vec{\epsilon} \cdot (\vec{q} + 2\vec{k}) \frac{E(\vec{k} + \vec{q}) - E(\vec{k})}{N} T_2(\vec{k} + \vec{q}, \vec{k})$ (5-3)

The functions U_R , T_2 and T_3 are listed for selected \vec{q} and \vec{k} values in tables 2, 3 and 4. An inspection shows that they are not independent of \vec{k} for a fixed \vec{q} -value. We fit the functions by the following expressions.

$$U_{R}(\vec{k} + \vec{q}, \vec{k}) = A_{1}(q) + B_{1}(q) \frac{\vec{k} \cdot \vec{k} + q}{q^{2}}$$
 (5-4)

$$T_2(\vec{k} + \vec{q}, \vec{k}) = A_2(q) + B_2(q) \frac{\vec{k} \cdot \vec{k} + q}{q^2}$$
 (5-5)

$$T_{3}(\vec{k} + \vec{q}, \vec{k}) = A_{3}(q) \left[1 + \frac{2\vec{k} \cdot \vec{q}}{q^{2}} \right] + B_{3}(q) \left[1 + \frac{2\vec{k} \cdot \vec{q}}{q^{2}} \right]^{3}$$
(5-6)

Note that the form chosen for these functions satisfies relation (3-16) which is essential for the dropping of Pauli exclusion principle restriction in (3-14) (i.e. $E(\vec{k}^{*})$) $E(k_{\rm F})$. Values for the functions A_1 , B_1 , A_2 , B_2 , A_3 and B_3 are found in tables 2, 3 and 4. These values are weighted so that for each q-value the regions of integration in (3-48, 49) that are most important are represented best.

Expressions (4), (5), (6) inserted into (3) give an interpolation formula for the electron-ion matrix element.

2. THE FUNCTION F(q)

The electron-ion matrix element given by (3), (4), (5) and (6) is now substituted into the expressions (3-48, 49) for the integrals $I^{(2)}$ and $I^{(3)}$. The results are $I^{(2)} = (\vec{\epsilon} \cdot \vec{q})^{2} \left\{ \frac{\mathcal{Y}(qr_{0})}{q^{2}} - \mathcal{Y}\left\{ U(q) + A_{1}(q) \right\} \right]^{2} f_{B}(q)$ $-2 \left| \frac{\mathcal{G}(qr_0)}{q^2} - \mathcal{G}\left\{ U(q) + A_1(q) \right\} \right| \left[\mathcal{G}_{B_1}(q) j_1(q) \right]$ + 2 $\left\{A_2(q) + \frac{1}{5}\left(\frac{2k_F}{q}\right)^2 B_2(q)\right\} + 2 \left\{A_3(q) + \left[1 + \frac{3}{5}\left(\frac{2k_F}{q}\right)^2\right]B_3(q)\right\}\right\}$ + $\chi^2 B_1^2(q) j_2(q)$ + $\gamma B_1(q) \left(\left(\frac{2k_F}{q} \right)^2 A_2(q) + \left\{ \frac{1}{4} \left(\frac{2k_F}{q} \right)^4 + \frac{1}{5} \left(\frac{2k_F}{q} \right)^2 \right\} B_2(q)$ $+\left(\frac{2k_{\rm F}}{q}\right)^2 A_{\rm J}(q) + \int \frac{9}{5} \left(\frac{2k_{\rm F}}{q}\right)^2 + \frac{3}{5} \left(\frac{2k_{\rm F}}{q}\right)^4 \Big\} B_{\rm J}(q)$ + $\frac{9}{(a_{k_{F}})^{2}} = \frac{8}{2k_{E}} \left(\frac{q}{2k_{E}}\right)^{2} A_{2}^{2}(q) + \frac{36}{5} A_{2}(q) B_{2}(q)$ $+\frac{24}{5} A_{2}^{2}(q) + \frac{2}{5} B_{2}^{2}(q) + \left(\frac{2k_{F}}{q}\right)^{2} \int \frac{111}{70} B_{2}^{2}(q) + \frac{12}{7} A_{2}(q) B_{2}(q) \Big\}$ $+\frac{1}{5}\left(\frac{2k_F}{q}\right)^4 B_2^2(q)$

$$+ (a_{0}k_{F})^{2} \sqrt{\frac{8}{5}} \left\{ 6 A_{2}(q) A_{3}(q) + 20 A_{2}(q) B_{3}(q) \right. \\ + 8.5 B_{2}(q) A_{3}(q) + 5.3 B_{2}(q) B_{3}(q) + 32 \left(\frac{q}{2k_{F}}\right)^{2} A_{2}(q) \left\{ A_{3}(q) + B_{3}(q) \right\} \\ + \frac{166}{105} \left(\frac{2k_{F}}{q}\right)^{4} B_{2}(q) B_{3}(q) + \left(\frac{2k_{F}}{q}\right)^{2} \left\{ \frac{1104}{35} A_{2}(q) B_{3}(q) \right. \\ + \frac{204}{35} B_{2}(q) A_{3}(q) + \frac{440}{35} B_{2}(q) B_{3}(q) \right\} \right] \\ + \frac{204}{35} B_{2}(q) A_{3}(q) + \frac{440}{35} B_{2}(q) B_{3}(q) \right\} \right] \\ + \frac{1}{3} (a_{0}k_{F})^{2} \left[8 \left(\frac{q}{2k_{F}}\right)^{2} \left\{ A_{3}(q) + B_{3}(q) \right\}^{2} + \frac{8}{5} \left\{ 3 A_{3}^{2}(q) + 20 A_{3}(q) B_{3}(q) \right. \\ + 21 B_{3}^{2}(q) \right\} + 24 \left(\frac{2k_{F}}{q}\right)^{2} \left\{ \frac{2}{7} A_{3}(q) B_{3}(q) + B_{3}^{2}(q) \right\} + \frac{320}{14} \left(\frac{2k_{F}}{q}\right)^{4} B_{3}^{2}(q) \right\} \\ + (\vec{e} \times \vec{q})^{2} \left\{ \frac{1}{3} (a_{0}k_{F})^{2} \left[\frac{2}{5} A_{2}^{2}(q) + \left(\frac{2k_{F}}{q}\right)^{2} \left\{ \frac{4}{7} A_{2}(q) B_{2}(q) + \frac{9}{70} B_{2}^{2}(q) \right\} \right\} \\ + \frac{1}{18} \left(\frac{2k_{F}}{q} \right)^{4} B_{2}^{2}(q) \right\} \right\}$$

$$(5-7)$$

$$I^{(5)} = \vec{e} \cdot \vec{q} \left[\frac{2(qr_{0})}{q^{2}} f_{B}(q) - \frac{1}{3} \left\{ U(q) + A_{1}(q) \right\} f_{B}(q) - \frac{1}{3} \left\{ A_{3}(q) + \frac{1}{5} \left(\frac{2k_{F}}{q}\right)^{2} B_{2}(q) \right\} \right\}$$

$$(5-8)$$

The functions U(q), $A_1(q)$ and $B_1(q)$ are expressed in rydbergs in these formulae.

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(5-8)

The quantity

$$\begin{split} S &\equiv \frac{\Omega_{0}}{8\pi a_{0}Z^{*}} \end{split} \tag{5-9} \\ &= \left(\frac{a_{L}}{2\pi}\right)^{2} \left(\frac{a_{L}}{a_{0}} \frac{\pi}{8Z^{*}}\right) \text{ for FCC lattices} \\ &= \left(\frac{a_{L}}{2\pi}\right)^{2} \text{ for aluminum} \end{split}$$

The special functions introduced are

$$f_{B}(q) \equiv \frac{2e^{2}}{\pi^{2}} \int_{k < k_{F}} \frac{d^{3}\vec{k}}{E(\vec{k}+\vec{q}) - E(\vec{k})}$$

$$= \frac{2k_{F}}{\pi a_{o}} \left[1 + \frac{(2k_{F})^{2} - q^{2}}{2(2k_{F})q} \ln \left| \frac{q + 2k_{F}}{q - 2k_{F}} \right| \right]$$
(5-10)

$$j_{1}(q) = \frac{2e^{2}}{\pi^{2}} \frac{1}{q^{2}} \int_{k < k_{F}} d^{3}k \frac{\overline{k \cdot k + q}}{E(\overline{k + q}) - E(\overline{k})}$$

$$j_{1}(q) = \frac{2k_{F}}{\pi a_{o}} \left[\frac{1}{3} \left(\frac{2k_{F}}{q} \right)^{2} \right] - \frac{1}{2} f_{B}(q) + \frac{1}{8} f_{B1}(q)$$
(5-11)

where

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$$f_{B1}(q) = \left(\frac{2k_F}{\pi a_o}\right) \left\{ 1 + \frac{1}{3} \left(\frac{2k_F}{q}\right)^2 + \frac{(2k_F)^4 - q^4}{2(2k_F)q^3} \ln \left(\frac{q + 2k_F}{q - 2k_F}\right) \right\}$$
(5-12)

and

$$j_{2}(q) = \frac{2e^{2}}{\pi^{2}} \frac{1}{q} \int_{k < k_{F}} \frac{(\vec{k} \cdot \vec{k} + q)^{2}}{E(\vec{k} + q) - E(\vec{k})} d^{3}\vec{k}$$

$$= \frac{2k_{F}}{\pi a_{o}} \left\{ \frac{1}{10} \left(\frac{2k_{F}}{q} \right)^{4} - \frac{1}{6} \left(\frac{2k_{F}}{q} \right)^{2} \right\} + \frac{f_{B}(q)}{4}$$

$$- \frac{f_{B1}(q)}{8} + \frac{f_{B2}(q)}{48} \qquad (5-13)$$

where

$$f_{B2}(q) = \frac{2k_{F}}{\pi a_{o}} \left[1 + \frac{1}{3} \left(\frac{2k_{F}}{q} \right)^{2} + \frac{1}{5} \left(\frac{2k_{F}}{q} \right)^{4} + \frac{(2k_{F})^{6} - q^{6}}{2(2k_{F}) q^{5}} \left(\ln \left(\frac{q + 2k_{F}}{q - 2k_{F}} \right) \right) \right]$$
(5-14)

In these integrals we assumed a spherical energy band,

$$E(k) = E_0 + \frac{\pi^2}{2m} k^2$$
 (5-15)

The contribution from second order perturbation theory, $I^{(2)}$, is divergent for small q. This is characteristic of coulomb forces and is due to the long range part of v(r) which goes like $-\frac{Z'e^2}{r}$ outside the central cell. This divergence is eliminated by cancellation when summing all orders of perturbation theory due to the electron-electron interaction. Thus we see why the electron-electron interaction must be included. It gives the screening of the long range part of the coulomb potential and makes F(q), (3-47), finite for all values of q. The final result is

$$\begin{split} \mathbf{F}(\mathbf{q}) &= \frac{\left(\vec{\epsilon} \cdot \vec{q}\right)^{2} t_{\mathbf{B}}(\mathbf{q})}{q^{2} \left[q^{2} + t_{\mathbf{B}}(\mathbf{q})\right]} \left[\mathcal{G}(\mathbf{q}r_{\mathbf{q}}) - \mathcal{G}^{2} \left\{ \mathbf{U}(\mathbf{q}) + \mathbf{A}_{1}(\mathbf{q}) \right\} \right]^{2} \\ &= 2 \left[\frac{\left(\vec{\epsilon} + \vec{q}\right)^{2}}{q^{2} + t_{\mathbf{B}}(\mathbf{q})} \right] \left[\mathcal{G}(\mathbf{q}r_{\mathbf{q}}) - \mathcal{G}^{2} \left\{ \mathbf{U}(\mathbf{q}) + \mathbf{A}_{1}(\mathbf{q}) \right\} \right] \left[\mathcal{G}(\mathbf{q}r_{\mathbf{q}}) - \mathcal{G}^{2} \left\{ \mathbf{U}(\mathbf{q}) + \mathbf{A}_{1}(\mathbf{q}) \right\} \right] \left[\mathcal{G}(\mathbf{q}r_{\mathbf{q}}) - \mathcal{G}^{2} \left\{ \mathbf{U}(\mathbf{q}) + \mathbf{A}_{1}(\mathbf{q}) \right\} \right] \left[\mathcal{G}(\mathbf{q}r_{\mathbf{q}}) - \mathcal{G}^{2} \left\{ \mathbf{U}(\mathbf{q}) + \mathbf{A}_{1}(\mathbf{q}) \right\} \right] \left[\mathcal{G}(\mathbf{q}r_{\mathbf{q}}) - \mathcal{G}^{2} \left\{ \mathbf{U}(\mathbf{q}) + \mathbf{A}_{1}(\mathbf{q}) \right\} \right] \left[\mathcal{G}(\mathbf{q}r_{\mathbf{q}}) - \mathcal{G}^{2} \left\{ \mathbf{U}(\mathbf{q}) + \mathbf{U}(\mathbf{q}) + \mathbf{U}(\mathbf{q}) + \mathbf{U}(\mathbf{q}) - \mathbf{U}(\mathbf{q}) + \mathbf{U}(\mathbf$$

$$+ A_{j}(q) + \left\{ 1 + \frac{5}{2} \left(\frac{2k_{F}}{q} \right)^{2} \right\} B_{j}(q) \right]$$

$$- \frac{4(\vec{c} \cdot \vec{q})^{2}}{q^{2} + f_{B}(q)} \left[A_{j}(q) + \left\{ 1 + \frac{5}{2} \left(\frac{2k_{F}}{q} \right)^{2} \right\} B_{j}(q) \right]^{2}$$

$$- \frac{8(\vec{c} \cdot \vec{q})^{2}}{q^{2} + f_{B}(q)} \left[A_{2}(q) + \frac{1}{5} \left(\frac{2k_{F}}{q} \right)^{2} B_{j}(q) \right]$$

$$\left[A_{j}(q) + \left\{ 1 + \frac{5}{2} \left(\frac{2k_{F}}{q} \right)^{2} \right\} B_{j}(q) \right]$$

$$+ (\vec{c} \cdot \vec{q})^{2} \left[\gamma (a_{0}k_{F})^{2} \left[\frac{8}{5} \left\{ 6 A_{2}(q) A_{j}(q) + 20 A_{2}(q) B_{j}(q) \right] + 8.5 B_{2}(q) A_{j}(q) + 5.5 B_{2}(q) B_{j}(q) \right] + 52 \left(\frac{q}{2k_{F}} \right)^{2} A_{2}(q) \left\{ A_{j}(q) + B_{j}(q) \right\}$$

$$+ B_{j}(q) + \frac{166}{105} \left(\frac{2k_{F}}{q} \right)^{4} B_{2}(q) B_{j}(q) + \left(\frac{2k_{F}}{q} \right)^{2} \left\{ \frac{1104}{35} A_{2}(q) B_{j}(q) + \frac{204}{35} B_{2}(q) A_{j}(q) + \frac{440}{35} B_{2}(q) B_{j}(q) \right\}$$

$$+ \frac{204}{35} B_{2}(q) A_{j}(q) + \frac{440}{35} B_{2}(q) B_{j}(q) + \left(\frac{2k_{F}}{q} \right)^{2} \left\{ \frac{1104}{35} A_{2}(q) B_{j}(q) + \left(\vec{c} \cdot \vec{q} \right)^{2} \right\}$$

$$+ \left(\vec{c} \cdot \vec{q} \right)^{2} \left(a_{0}k_{F} \right)^{2} \left[8 \left(\frac{q}{2k_{F}} \right)^{2} \left\{ A_{j}(q) + B_{j}(q) \right\} \right]^{2}$$

$$+ \frac{8}{5} \left\{ 3 A_{j}^{2}(q) + 20 A_{j}(q) B_{j}(q) + 21 B_{j}^{2}(q) \right\}$$

$$+ 24 \left(\frac{2k_{F}}{q}\right)^{2} \left\{\frac{2}{7} A_{3}(q) B_{3}(q) + B_{3}^{2}(q)\right\} + \frac{339}{14} \left(\frac{2k_{F}}{q}\right)^{4} B_{3}^{2}(q) \right]$$

$$+ (\vec{\epsilon} \mathbf{x} \mathbf{q})^{2} \left(\mathbf{a}_{0} k_{F}\right)^{2} \left[\frac{2}{5} A_{2}^{2}(q) + \left(\frac{2k_{F}}{q}\right)^{2} \left\{\frac{4}{7} A_{2}(q) B_{2}(q) + \frac{9}{70} B_{2}^{2}(q)\right\} + \frac{1}{18} \left(\frac{2k_{F}}{q}\right)^{4} B_{2}^{2}(q) \right]$$
(5-16)

One feature of our calculation of the ion-ion interaction is the $(\vec{\epsilon} \times \vec{q})^2$ term which is due solely to the second order diagram. This result is general for an electron-ion matrix element of the form (4-32) in which the scalar product $\vec{\epsilon} \cdot \vec{k}$ occurs. Lehman et al (L 62) have used such a term in their axially symmetric model and obtained good agreement with Walker's (W 56) measurements of the phonon dispersion curves in Al. The force-constant parameters are obtained from the elastic constants and Walker's results. Also, their phenomenological model indicated that one only needed to include first and second nearest neighbour interactions.

For later convenience, define

$$F_{ps}(q) = \frac{(\vec{\epsilon} \cdot \vec{q})^2 f_B(q)}{q^2 [q^2 + f_B(q)]} \left[\mathcal{O}(qr_0) - \frac{1}{2} q^2 \{ U(q) + A_1(q) \} \right]^2 \qquad (5-17)$$

and

$$F_{WN}(q) = F(q) - F_{ps}(q)$$
 (5-18)

 $F_{ps}(q)$ would be the answer if one used a k-independent pseudopotential; $F_{WN}(q)$, the wave-number part, is what remains. The $(\vec{\epsilon} \cdot \vec{q})^2$ terms in (16) may be compared with the result that the Bardeen matrix element (4-14) gives

$$\mathbf{F}_{B}(q) = \frac{(\vec{\epsilon} \cdot \vec{q})^{2} \mathbf{f}_{B}(q)}{q^{2} \left[q^{2} + \mathbf{f}_{B}(q)\right]} \left[1 + \gamma q^{2} \left\{ \mathbf{U}(\mathbf{r}_{0}) - \mathbf{E}_{0} \right\}\right]^{2} \mathcal{A}^{2}(q\mathbf{r}_{0}) \quad (5-19)$$

where $U(r_0) - E_0$ is measured in rydbergs.

This comparison is made in figure 10 for the cases $U(r_0) - E_0 = 0$ and 3.7 ev. Further, we examine the change in magnitude of the Kohn kink amplitude in the next section.

3. THE MAGNITUDE OF KOHN KINKS

One of the main reasons this research project was started was to investigate the magnitude of Kohn kinks in metals. So far, the effect has been observed only in lead (B 62a). This calculation shows that the OPW electron-ion matrix element has the potential to explain the magnitude of such kinks in lead.

By the amplitude of a Kohn kink, D, we shall mean the coefficient of

$$\frac{1}{q^2 + f_B(q)} \left(\frac{2k_F}{\pi a_0}\right) \frac{2k_F^2 - q^2}{2k_F q} \ln \left(\frac{q + 2k_F}{q - 2k_F}\right)$$
(5-20)

in the expression for $\frac{q^2 F(q)}{(\vec{\epsilon} \cdot \vec{q})^2}$ evaluated at $q = 2k_F$. This definition

is used because it indicates the main strength of the anomaly.

For the Bardeen result (19), using (10) gives

$$D_{B} = \left[1 + \gamma q^{2} \{ U(r_{o}) - E_{o} \} \right]^{2} \Re^{2}(qr_{o})$$
(5-21)

For the expression (16) this amplitude is

$$D = \left[\mathcal{Y}(qr_{0}) - \mathcal{Y} q^{2} \left\{ U(q) + A_{1}(q) \right\} \right]^{2}$$

$$- 2 \mathcal{Y} q^{2} B_{1}(q) \left[\mathcal{Y}(qr_{0}) - \mathcal{Y} q^{2} \left\{ U(q) + A_{1}(q) \right\} \right] \left[\frac{1}{8} \left(\frac{2k_{F}}{q} \right)^{2} - \frac{3}{8} \right]$$

$$+ \mathcal{Y} q^{2} B_{1}^{2}(q) \left[\frac{\mathcal{Y} q^{2}}{48} \left\{ 7 - 5 \left(\frac{2k_{F}}{q} \right)^{2} + \left(\frac{2k_{F}}{q} \right)^{4} \right\}$$

$$+ \mathcal{Y} \frac{2k_{F}}{\pi a_{0}} \frac{1}{96} \left\{ 1 + \frac{20}{3} \left(\frac{2k_{F}}{q} \right)^{2} + 3 \left(\frac{2k_{F}}{q} \right)^{4} \right\}$$
(5-22)

For aluminum,

$$(2k_{\rm F})^2 = 2.2545$$
, $(2k_{\rm F})^2 = .8719$

From (21), for

 $U(r_0) - E_0 = 0;$ $D_B(2k_F) = .0069$ (5-23)

$$U(r_0) - E_0 = .272 \text{ ry}; D_B(2k_F) = .039$$
 (5-24)

From expression (22), the contributions are

$$D(2k_F) = .321 - .029 + .003 = .295$$
 (5-25)

The use of a pseudopotential alone would give D = .321; including the k-dependent terms in the electron-ion interaction makes about a 10% correction to this. This OPW result, (25), is about eight times as large as the Bardeen result (24).

In lead, one could expect the Kohn kink amplitude to be further amplified by the additional number of core states, somewhat in the ratio of the atomic numbers of the materials. These calculations strongly suggest that the Kohn kinks observed by Brockhouse et al. (B 62a) in lead can be explained by the OPW electron-ion matrix element.

4. DISCUSSION OF RESULTS

The results of our ω_s^2 calculations have been summarized in figures 1 to 7, and tables 5 to 7 for the symmetry directions (1,0,0), (1,1,1) and (1,1,0). In turn, we discuss the screening contribution to the frequencies ω_s^2 for the Bardeen matrix element (4-14) and the OPW matrix element (3,4,5,6).

The Bardeen screening contribution ω_s^2 (B) is the result of $F_B(q)$, expression (19), inserted into expression (3-50).

Define

$$\omega_{\rm B}^2 = \omega_{\rm c}^2 - \omega_{\rm g}^2({\rm B})$$
 (5-26)

Good convergence of the sum over G-vectors in (3-50) resulted from summing over six shells in reciprocal lattice space.

The value of $U(r_0) - E_0$ used in our calculations of ω_B^2 is .272 ry, obtained from (A-11) and Heine's potential (Se 61). Unfortunately the results are rather sensitive to this quantity. If the value $U(r_0) - E_0 = 0$ is used, the Umklapp contributions ($\vec{G} \neq 0$ parts of (3-50)) are smaller by factors of 2 to 4 and the normal term ($\vec{G} = 0$ for longitudinal mode) is decreased by roughly 30% at the Brillouin zone boundary. Using

this value of zero would increase ω_B^2 by about 50% for the transverse modes and by about 300% for the longitudinal modes, at the zone boundary. This would completely destroy the rough agreement indicated in figures 1 to 7.

It may be noted that in five of seven cases that the ω_B^2 values are higher than the experimental values of Walker (W 56). Some new experimental values have been obtained by Yarnell and Warren (YW 63) but are not yet available in sufficient detail to be used here. In general we may say that the screening contributions derived from $F_B(q)$, (19), are not quite large enough. Further, we have found that the Bardeen matrix element will not give Kohn kinks of the magnitude observed in lead by Brockhouse et al. (B 62a).

The screening function $f_B(q)$, (3-27), does not include any conduction electron exchange. Exchange may be included in an approximate way by using $f_H(q)$, expression (3-28), in place of $f_B(q)$ in (19). At the zone boundary this increases ω_g^2 longitudinal by about 15% and so decreases ω_B^2 longitudinal by about 80%; ω_g^2 transverse is increased by 10%, decreasing ω_B^2 transverse by about 5%. Although the adjustment improves the Bardeen results in general, we have not included these calculations in the figures, since this phase of the problem is not our major concern.

The calculation of the screening contribution using the OPW electron-ion matrix element was divided into two parts, a pseudopotential part which employed $F_{ps}(q)$, (17), and a "k-dependent" part which employed $F_{WN}(q)$, (18). The k-dependence refers to the electron-ion matrix element; of course, it is integrated out in calculating $F_{WN}(q)$.

The contribution coming from $F_{ps}(q)$ is called ω_{ps}^2 (on figures 1 to 7, ω^2).

$$\omega_{ps}^{2} = \omega_{c}^{2} - \omega_{s}^{2} (PS)$$
 (5-27)

To secure convergence of the G-sum in (3-50) it was necessary to sum over nine shells of reciprocal lattice space.

The pseudopotential produced $\omega_s^2(PS)$ which were too large and overscreened the ω_c^2 values. The agreement with experiment for ω^2 curves does not appear to be as good as the Bardeen result. However, both calculations have not included the Born-Mayer core repulsive term which would tend to increase the frequencies.

An attempt was made to calculate the screening $\omega_s^2(WN)$ using $F_{WN}(q)$ of (18). This is the part arising from the k-dependent parts in the electron-ion interaction. Unfortunately, the sum (3-50) did not converge after nine shells of G-vectors. It seems that further terms are needed in the expansions (4), (5) and (6) for U_R , T_2 and T_3 and the expansion coefficients A_i , B_i calculated for q-values out to about $a_q \leq 10$.

Even though the frequency curves are overscreened with the OPW electron-ion matrix, the previous section has indicated that it could be of the correct magnitude to explain Kohn kinks.

CHAPTER 6: CONCLUSIONS

As described in chapter 2, the calculation of phonon dispersion curves in metals divides naturally into two parts, the ion-ion coulomb contribution, and the electron screening contribution. In some metals such as lead and aluminum, but not in sodium, the screening contribution almost cancels the coulomb part. This work has demonstrated the importance of making a careful evaluation of the electron-ion matrix element for such metals.

The pseudopotential part of the OPW electron-ion matrix element appears to overscreen the frequencies too strongly. The results are quite different than those obtained using the Bardeen matrix element (4-14). This is not in agreement with comments made by Woll and Kohn (WK 62). Perhaps the correct inclusion of the k-dependent parts of the electronion matrix element will decrease the size of the screening contribution. However, our calculation strongly suggests that no further mechanism is necessary to explain the magnitude of Kohn kinks. The OPW electron-ion matrix element gives a Kohn kink amplitude about ten times what we could expect using the Bardeen matrix element with $U(r_0) - E_0 = .272$ ry. for aluminum. It is expected that this ratio would be even larger for a material like lead.

In evaluating the OPW electron-ion matrix element great care must be exercised because there are strong cancellations between various large terms. An earlier attempt went astray when cancellation effects were not

considered early enough in the calculation. The function F(q), figures 10 and 11, has more structure than might be anticipated. In particular the hump somewhat centered about $q \approx 2k_F$ reflects the fact that the socalled pseudopotential in real space $U_{ps}(r) \equiv U(r) + U_R(r)$ (KP 60; CH 61; Sh 61) is not constant within the central cell (for example see figure 1 of CH 61). Thus this behaviour can be explained in terms of a true pseudopotential. On the other hand $F_{WN}(q)$ which is not included in a pseudopotential treatment becomes important for $q > 3k_F$. The dominant term in this result is due to the terms with the $\left[E(\vec{k+q}) - E(\vec{k})\right]$ factor in (4-32), which goes like q^2 for large q. In the region considered in this work the b $(|\vec{k} + \vec{q}|)$'s have not started to fall off like $1/q^4$, and thus one obtains the increase of $F_{WN}(q)$ for $q > 3k_F$. The fall off in the b $(|\vec{k} + \vec{q}|)$ will cut this off for larger values of q. This point requires further investigation.

This calculation has produced a term involving $(\vec{\epsilon} \times \vec{q})^2$ in the expression for F(q), (5-16). When more reliable functions A₂ and B₂ are calculated it would be interesting to see how this term affects the frequencies, especially the transverse mode where now a normal process $(\vec{d} = 0)$ is possible. In general, an examination could be made of other metals with extra core electrons to see what other combinations of the polarization vectors enter and their relation to non-central forces and elastic constants in metals.

The calculation of the OPW matrix element for $\nabla \mathbf{v}_{a}$, \mathbf{v}_{a} defined by (4-7), has assumed that integrals involving the overlap between $\nabla \mathbf{v}_{a}$ and core states could be ignored. This would be a good approximation as long as there is not strong cancellation between other parts of the answer.

Further investigation should be made at this point. Also, it would be helpful if some estimate was made of the Born-Mayer ion core repulsive term. Toya (T 58) has included this in his sodium calculation and it gave a 10% correction. Percentage wise, this correction might be larger in aluminum because the experimental ω^2 are much smaller than ω_c^2 in contrast to sodium.

It should be emphasized that the single OPW approximation has been made, in all these calculations. In appendix B a general result is given including a complete set of OPW's. The correction to the single OPW would be important in metals which have a conduction band which is strongly non-spherical. These terms could give rise to large non-central effective ion-ion interactions.

The stage is now set for an interesting calculation in lead. This application to aluminum has indicated which steps in the OPW electron-ion calculation need to be treated with most care. It is hoped that the procedure used in our treatment of aluminum will when applied to lead give a satisfactory explanation of the Kohn kink amplitude observed by Brockhouse et al. (B 62a).

APPENDIX A: CORE WAVE FUNCTIONS FOR ALUMINUM AND OPW COEFFICIENTS

In an extensive OPW calculation, Heine (H 57) determined the crystal self-consistent potential of aluminum. He calculated various contributions to the potentials for angular momentum states $\ell = 0$ and 1. One minor correction was made later by Behringer (Be 58). We shall exclude the Bohm-Pines exchange energy, $V_{\rm BP}(k)$, since we require a Hartree form of potential.

With atomic units, M = m = e = 1, and energies in rydbergs, the potential U(r) in terms of an effective charge Z(r) is

$$U(\mathbf{r}) = -\frac{2Z(\mathbf{r})}{\mathbf{r}}$$
 (A-1)

Segall (Se 61) has tabulated the Heine values employed in this work. We used the same potential for s and p states, the differences being small. Note that Heine's U(r) becomes negligible at the Wigner-Seitz radius $r_o = 3a_o$.

The radial part of the core state \emptyset_c of (4-15) satisfies the equation

$$\left[\frac{d^2}{dr^2} + \left\{E_{n\ell} - U(r)\right\} - \frac{\ell(\ell+1)}{r^2}\right] r R_{n\ell}(r) = 0 \qquad (A-2)$$

with normalization

$$\int_{0}^{\infty} r^{2} R_{n\ell}(r) dr = 1$$
 (A-3)

The numerical integration employed the Runge-Kutta-Nystrom method. Our radial wave functions agree well with those calculated by Heine (H 62) although the $E_{n\ell}$ values are slightly different.

$$E_{1s} = -109.7 r_{y}$$

$$E_{2s} = -6.950 r_{y}$$

$$E_{2p} = -3.982 r_{y}$$
(A-4)

The following are normalized analytic fits to the wave functions (IA 56).

$$R_{1s} = 26.22 e^{-10.5r} + 64.608 e^{-13.931r}$$
 (A-5)

$$R_{2s} = (.16523-r) \left[10.952 e^{-3.3115r} + 67.471 e^{-5.1621r} + 60.597 e^{-9.2122r} \right]$$
(A-6)

$$R_{2p} = r \left[4.9235 e^{-2.7004r} + 32.591 e^{-4.6287r} + 28.413 e^{-9.0059r} \right] (A-7)$$

From (4-23), analytic forms for the $b_{n\ell}(k)$ are easy to calculate

$$b_{1s}^{(k)} = \frac{184.98}{[110.3 + k^2]^2} + \frac{604.73}{[193.8 + k^2]^2}$$

$$b_{2s} = 7.3584 \left[\frac{1.5471}{(k^2 + 10.97)^2} - \frac{43.864}{(k^2 + 10.97)^3} \right]$$

$$+ 45.332 \left[\frac{1.8529}{(k^2 + 26.65)^2} - \frac{106.59}{(k^2 + 26.65)^3} \right]$$

$$+ 40.714 \left[\frac{2.5221}{(k^2 + 84.86)^2} - \frac{339.46}{(k^2 + 84.86)^3} \right]$$
(A-8)
(A-9)
(A-8)
(A

$$-\mathbf{i} \ \mathbf{b}_{2p} = \frac{61.892 \ \mathbf{k}}{(\mathbf{k}^2 + 7.292)^3} + \frac{702.24 \ \mathbf{k}}{(\mathbf{k}^2 + 21.42)^3} + \frac{1191.2 \ \mathbf{k}}{(\mathbf{k}^2 + 81.106)^3}$$
(A-10)

The quantities b are dimensionless, k is in units $1/a_0$.

is

The energy of the lowest conduction state, E_0 , given by (4-24,25),

$$E_0 = -.394 ry$$
 (A-11)

APPENDIX B: EXTENSION OF SHAM'S OPW MATRIX ELEMENT

Sham (Sh 61) has considered the matrix element

$$1 \langle B \overline{k+q} | \in \nabla U(r) | B \overline{k} \rangle$$
 (B-1)

$$\langle B\vec{k} | B\vec{k} \rangle = 1$$
 (B-2)

The potential, U(r), discussed in chapter 4, satisfies the equation

$$\begin{bmatrix} -\nabla^2 + \sum_{\mathbf{L}} \mathbf{U}(\mathbf{\dot{\vec{r}}} - \mathbf{L}) \end{bmatrix} \mathbf{B}(\mathbf{\vec{k}}; \mathbf{\vec{r}}) = \mathbf{E}(\mathbf{\vec{k}}) \mathbf{B}(\mathbf{\vec{k}}; \mathbf{\vec{r}})$$
(B-3)

where $B(\vec{k};\vec{r}) = \langle \vec{r} | B \vec{k} \rangle$. Also, U(r) is chosen so that U(r) = 0, for $r > r_0$, where r_0 is the W-S cell radius.

The Bloch state $|B\bar{k}\rangle$ for the conduction electron can be expanded in terms of orthogonalized plane waves

$$|B\vec{k}\rangle = \sum_{\vec{G}} C_{\vec{k},\vec{G}} |OPW \vec{k+G}\rangle$$
 (B-4)

Then, we have

where

$$(B\vec{k}'|\vec{\epsilon} \cdot \nabla U|B\vec{k}) = \sum_{\vec{d},\vec{d}'} C^*_{\vec{k}',\vec{d}'} C_{\vec{k},\vec{d}'} (OPW \vec{k'+d'}|\vec{\epsilon} \cdot \nabla U|OPW \vec{k+d})$$
(B-5)

Each term in this double sum can be separated into four parts, if we write (4-18)

$$\langle \vec{r} | OPW \ \vec{k} + \vec{G} \rangle = (N \Omega_{o})^{-1/2} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

- $\sum_{c} b_{c, \vec{k} + \vec{G}} \phi_{c}(\vec{k} + \vec{G}; \vec{r})$ (B-6)

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$$I = \frac{1}{N C_{0}} \int_{N C_{0}} e^{-i(\vec{k'+G'}) \cdot \vec{r}} \left[\nabla U(r) \right] e^{i(\vec{k+G}) \cdot \vec{r}} d^{3}\vec{r}$$

Integrate by parts to get

$$I = \frac{i(\vec{k}' + \vec{G}' - \vec{k} - \vec{G})}{NC} \int d^{3}\vec{r} \ U(r) \ e^{i(\vec{k} + \vec{G} - \vec{k}' - \vec{G}') \cdot \vec{r}}$$

$$= \frac{i(\vec{k}' + \vec{G}' - \vec{k} - \vec{G})}{N} \quad U(\vec{k}' + \vec{G}' - \vec{k} - \vec{G}) \quad (B-7)$$

where $\overline{U(\vec{k})}$ is the Fourier transform as in (4-26).

$$-II = (N \cdot C_{c})^{-\frac{1}{2}} \int d^{3}\vec{r} e^{i(\vec{k} + \vec{d}) \cdot \vec{r}} (\nabla U) \left[\sum_{c'} b^{*}_{c'}, \vec{k'} + \vec{d}, \beta^{*}_{c'}(\vec{k'} + \vec{d'}; \vec{r}) \right]$$

Using the expression for $\mathscr{D}_{c}^{*}(\vec{k};\vec{r})$ from (4-16) and neglecting overlap terms like

$$\left[\nabla \mathbf{U}(\mathbf{r})\right] \phi_{c}(\vec{\mathbf{r}}-\vec{\mathbf{L}}), \vec{\mathbf{L}} \neq 0$$

gives

$$- II = \frac{1}{N \cdot Q_{o}^{\frac{1}{2}}} \sum_{c'} b_{c',\vec{k}'+\vec{G}'}^{*} \int_{Q_{o}} d^{3}\vec{r} e^{i(\vec{k}+\vec{G})\cdot\vec{r}} (\nabla U) g_{c'}^{*}(\vec{r})$$

From (4-15), we have

$$(-\nabla^2 + \mathbf{U}) \nabla \boldsymbol{\beta}^*_{\mathbf{c}} + (\nabla \mathbf{U}) \boldsymbol{\beta}^*_{\mathbf{c}} = \mathbf{E}_{\mathbf{c}} \nabla \boldsymbol{\beta}^*_{\mathbf{c}}, \qquad (B-8)$$

Inserting this, doing an integration by parts, and using (4-19), provides

$$-II = \frac{-i(\vec{k} + \vec{d})}{N} \sum_{c'} E_{c'} b^{*}_{c',\vec{k}'+\vec{d}'} b_{c',\vec{k}+\vec{d}'} b_{c',\vec{k}+\vec{d}'} d^{*}_{c',\vec{k}+\vec{d}'} d^{*}_{c',\vec{k}+\vec{d}'} d^{*}_{c',\vec{k}+\vec{d}'} d^{*}_{c',\vec{k}+\vec{d}'} d^{*}_{c'} d^{*}_{c',\vec{k}+\vec{d}'} d^{*}_{c'} d^{*}_{$$

$$= \frac{2 \operatorname{IR} (\nabla r)}{N} \sum_{c} E_{c} b_{c,\vec{k}}^{c} + \vec{G} b_{c,\vec{k}} + \vec{G}$$

$$+ \frac{1}{N \cdot \Omega_{o}^{\frac{1}{2}}} \sum_{c} b_{c,\vec{k}} + \vec{G} \int_{\Omega} d^{3}\vec{r} e^{-i(\vec{k}\cdot\vec{r}+\vec{G}\cdot)\cdot\vec{r}} (\nabla^{2}-\upsilon)\nabla \emptyset_{c}(\vec{r}) \quad (B-10)$$

$$IV = \int_{N \cdot \Omega_{o}} d^{3}\vec{r} \left[\sum_{c'} b_{c',\vec{k}} + \vec{G} \cdot \emptyset_{c'}^{*} (\vec{k}\cdot\vec{r}+\vec{G}\cdot\vec{r}) \right] \left[\nabla \upsilon(r) \right]$$

$$\left[\sum_{c} b_{c,\vec{k}} + \vec{G} \quad \emptyset_{c}(\vec{k}+\vec{G}\cdot\vec{r}) \right]$$

Using (4-16) and neglecting overlap terms as above with -II,

$$IV = (N)^{-1} \sum_{c,c} b_{c',\vec{k}'+\vec{G}'}^{*} b_{c,\vec{k}+\vec{G}} \int d^{3}\vec{r} \phi_{c}^{*} (\nabla U) \phi_{c}$$

Employing (8),

$$IV = (N)^{-1} \sum_{c,c'} b^{*}_{c'}, \vec{k'} + \vec{d'} b_{c,\vec{k}} + \vec{d} \int_{\Omega_{o}} d^{3}\vec{r} g^{*}_{c'}, (\nabla^{2} - \mathbf{E} + \mathbf{E}_{c}) \nabla g_{c}$$

Integrate the E_c term by parts and use (4-15) to find

$$IV = (N)^{-1} \sum_{c \ c} b^{*}_{c'}, \vec{k'} + \vec{q'} b_{c,\vec{k}} + \vec{q} \int_{-\Omega_{o}} d^{3}\vec{r} g^{*}_{c}, (\nabla^{2} - U)\nabla g_{c}$$

+ $\int_{\Omega_{o}} d^{3}\vec{r} (\nabla g^{*}_{c'}) (\nabla^{2} - U) g_{c}$ (B-11)

Combining the second terms of II and IV, we get from (6)

$$\frac{-1}{N \Omega_{0}^{\frac{1}{2}}} \sum_{c'} b_{c',\vec{k}'+\vec{d}'}^{*} \Omega_{0}^{\int} d^{3}\vec{r} \left[(\nabla^{2} - U) (\nabla \beta_{c'}^{*}) \right]$$

$$\left[e^{i(\vec{k} + \vec{d})} \cdot \vec{r} - \Omega_{0}^{\frac{1}{2}} \sum_{c} b_{c,\vec{k}+\vec{d}} \beta_{c}^{(\vec{r})} \right]$$

$$= - (N)^{-\frac{1}{2}} \sum_{c'} b_{c',\vec{k}'+\vec{d}'}^{*} \Omega_{0}^{\int} d^{3}\vec{r} (\nabla \beta_{c'}^{*}) (\nabla^{2} - U) \langle \vec{r} | OPW \vec{k} + \vec{d} \rangle$$

From (3) and the assumption of non-overlapping potentials U(r), the function $\langle \vec{r} | B | \vec{k} \rangle$ within the central cell satisfies

$$\left[-\nabla^2 + U(\mathbf{r})\right] B(\vec{k};\vec{r}) = E(\vec{k}) B(\vec{k};\vec{r})$$

From (4), (6), and (4-19), and an integration by parts,

$$II^{2nd} + IV^{2nd} = (N)^{-\frac{1}{2}} \sum_{c'} b^{*}_{c'}, \vec{k'} + \vec{d'} \int_{0}^{\infty} d^{3}\vec{r} [\nabla g^{*}_{c'}] E(\vec{k}) \langle \vec{r} | 0PW \vec{k} + \vec{d} \rangle$$

$$= \frac{-i(\vec{k} + \vec{d})}{N} \sum_{c} b^{*}_{c,\vec{k'}} + \vec{d'} b_{c,\vec{k}} + \vec{d}$$

$$- \frac{E(\vec{k})}{N} \sum_{c,c'} b^{*}_{c',\vec{k'}} + \vec{d'} b_{c,\vec{k}} + \vec{d} \int_{0}^{\infty} d^{3}\vec{r} g_{c} (\nabla g^{*}_{c'}) \qquad (B-12)$$
Similarly the second term of III and the first term of IV are combined

$$III^{2nd} + IV^{lst} = \frac{i(\vec{k}\cdot\vec{q}\cdot\vec{p}) \quad E(\vec{k}\cdot)}{N} \sum_{c} b^{*}_{c,\vec{k}}\cdot\vec{q}\cdot\vec{p} \quad b_{c,\vec{k}}\cdot\vec{q}}$$
$$- \frac{E(\vec{k}\cdot)}{N} \sum_{c,c} b^{*}_{c',\vec{k}}\cdot\vec{q}\cdot\vec{q} \quad b_{c,\vec{k}}\cdot\vec{q}} \int_{0}^{0} d^{3}\vec{r} \not g^{*}_{c'} \quad (\nabla \not g_{c}) \qquad (B-13)$$

From (9), (10), (12), (13) and the relation

$$\int d^{3}\vec{r} (\nabla \phi_{c}^{*}) \phi_{c} + \int d^{3}\vec{r} \phi_{c}^{*} (\nabla \phi_{c}) = 0$$

$$II + III + IV$$

$$= \frac{i}{N} (\vec{k}^{*} + \vec{G}^{*} - \vec{k} - \vec{G}) \sum_{c} \left[\frac{E(\vec{k}) + E(\vec{k}^{*})}{2} - E_{c} \right] b^{*}_{c,\vec{k}^{*} + \vec{G}^{*}} b_{c,\vec{k}^{*} + \vec{G}^{*}} (\nabla \phi_{c})$$
(B-14)

From (5), (7) and (14) the final result is $i \langle B \vec{k}' | \vec{\epsilon} \cdot \nabla U(r) B \vec{k} \rangle$ $= - \sum_{\vec{d}, \vec{d}'} \frac{C^* \vec{k} \cdot \vec{d}' \cdot C_{\vec{k}, \vec{d}}}{N} \left[\vec{\epsilon} \cdot (\vec{k}' + \vec{d}' - \vec{k} - \vec{d}) \left\{ U(\vec{k}' + \vec{d}' - \vec{k} - \vec{d}) + \sum_{\vec{c}} \left[\frac{E(\vec{k}) + E(\vec{k}')}{2} - E_{\vec{c}} \right] b^*_{\vec{c}, \vec{k}' + \vec{d}'} b_{\vec{c}, \vec{k} + \vec{d}} \right] \right\}$ $+ \vec{\epsilon} \cdot (\vec{k}' + \vec{d}' + \vec{k} + \vec{d}) \frac{1}{2} \left[E(\vec{k}') - E(\vec{k}) \right] \sum_{\vec{c}} b^*_{\vec{c}, \vec{k}' + \vec{d}'} b_{\vec{c}, \vec{k} + \vec{d}} + \left[E(\vec{k}') - E(\vec{k}) \right] \sum_{\vec{c}, \vec{c}'} b^*_{\vec{c}, \vec{k}' + \vec{d}'} b_{\vec{c}, \vec{k} + \vec{d}} \int d^{\vec{2}}\vec{r} g^*_{\vec{c}}, (\vec{i} \cdot \nabla g_{\vec{c}}) \right]$ (B-15)

APPENDIX C: CALCULATION OF S

$$S = \sum_{c} b_{c,\vec{k}}^{*}, b_{c,\vec{k}} \int d\tau \, g_{c}^{*}, \, i \vec{\epsilon} \cdot \nabla g_{c} \qquad (C-1)$$

The symbol c denotes the atomic quantum numbers n, ℓ , m. The ∇ -operator is a dipole type operator. The best way to treat this integral is to use the identity

$$\vec{P}/m = \frac{i}{\pi} \left[H, \vec{r} \right]$$

and the relation $\overrightarrow{P} = -i A \nabla$. Combining these we have

$$\mathbf{i} \nabla = \frac{\mathbf{i} \mathbf{m}}{\mathbf{n}^2} \begin{bmatrix} \mathbf{r} \\ \mathbf{r} \\ \mathbf{\theta} \end{bmatrix}$$

In atomic units M = m = e = 1, with energies in rydbergs, units of $e^2/2a_o$, this becomes

$$i\nabla = \frac{1}{2}\left[\vec{r}, \theta\right]$$

and we have

$$\int d\tau \ \varphi_{c}^{*}, \ i \vec{\epsilon} \cdot \nabla \varphi_{c} = \frac{1}{2} \left(E_{c} - E_{c}, \right) \int d\tau \ \varphi_{c}^{*}, \ \vec{\epsilon} \cdot \vec{r} \ \varphi_{c} \qquad (C-2)$$

and

$$\vec{\epsilon} \cdot \vec{r} = r \left[\cos \theta \cos \theta_{\epsilon} + \sin \theta \sin \theta_{\epsilon} \cos \varphi \right]$$
$$= \left(\frac{2\pi}{3} \right)^{\frac{1}{2}} r \left[\sqrt{2} \cos \theta_{\epsilon} Y_{1}^{0}(\theta) + \sin \theta_{\epsilon} \left\{ Y_{1}^{-1}(\theta, \varphi) - Y_{1}^{1}(\theta, \varphi) \right\} \right]$$

We employ Condon and Shortley spherical harmonics and Gaunt's formula

$$\langle \mathbf{Y}_{\mathrm{L}}^{\mathrm{M}}, \mathbf{Y}_{\ell_{1}}^{\mathrm{m_{1}}}, \mathbf{Y}_{\ell_{2}}^{\mathrm{m_{2}}} \rangle = \sqrt{\frac{(2\ell_{1}+1)(2\ell_{2}+1)}{4\pi(2\mathrm{L}+1)}}$$

$$(\ell_{1}, \ell_{2}, \mathrm{m_{1}}, \mathrm{m_{2}}/\mathrm{LM}) (\ell_{1}, \ell_{2}, 0.0/\mathrm{L}, 0)$$

The latter two factors are the usual Clebsch-Gordan coefficients.

It is straight forward to find that

$$\int d\tau \, \mathscr{P}_{n',\ell'm'}^{*} \vec{\epsilon} \cdot \vec{r} \, \mathscr{P}_{n,\ell m} = \int_{0}^{\infty} dr \, r^{3} \, R_{n',\ell'} \, R_{n\ell}$$

$$\left[\delta_{m\,m'} \cos \theta_{\epsilon} \left\{ \delta_{\ell',\ell+1} \sqrt{\frac{(\ell-m+1)(\ell+m+1)'}{(2\ell+3)(2\ell+1)}} + \delta_{\ell',\ell-1} \sqrt{\frac{(\ell-m)(\ell+m)}{(2\ell-1)(2\ell+1)}} \right\} + \delta_{m',m-1} \sin \theta_{\epsilon} \left\{ \delta_{\ell',\ell+1} \sqrt{\frac{(\ell-m+1)(\ell-m+2)}{4(2\ell+1)(2\ell+3)}} - \delta_{\ell',\ell-1} \sqrt{\frac{(\ell+m)(\ell+m-1)}{4(2\ell+1)(2\ell-1)}} \right\} + \delta_{m',m+1} \sin \theta_{\epsilon} \left\{ -\delta_{\ell',\ell+1} \sqrt{\frac{(\ell+m+1)(\ell+m+2)}{4(2\ell+1)(2\ell+3)}} + \delta_{\ell',\ell-1} \sqrt{\frac{(\ell-m)(\ell-m-1)}{4(2\ell+1)(2\ell-1)}} \right\} \right] (C-3)$$

The quantities $b_{c,k}$ are given by (4-22) and (4-23). From (1), (2) and (3) is obtained a general expression for S.

In particular, we write down the answer for the case when (n, l) takes on values 1s, 2s and 2p. Define the constant

$$S(s) = \frac{E_{s} - E_{2p}}{2\sqrt{3}!} \int_{0}^{\infty} dr r^{3} R_{g}(r) R_{2p}(r) \qquad (C-4)$$

$$S = \sum_{s = 1s, 2s} \mathcal{J}(s) \left[-i \ b_{2p} (|\overline{k+q}|) \ b_{g}(k) \ \overline{\frac{k+q}{k+q}} \right]$$

$$- i \ b_{2p}(k) \ b_{g}(|\overline{k+q}|) \ \overline{\frac{\epsilon}{k}} \left[\frac{1}{k} \right]$$
(C-5)

The quantity S will be real. For aluminum, the wave functions of appendix A give the values $\mathcal{S}(1s) = -2.314$, $\mathcal{S}(2s) = 0.5253$.

In chapter 5, it was convenient to use the following symmetric form of S

$$S = \sum_{B=1s,2s} \mathcal{J}(s) \left\{ -\frac{i \ b_{2p}(1\vec{k} + \vec{q}1)}{|\vec{k} + \vec{q}|} \ b_{s}(k) - \frac{i \ b_{2p}(k)}{k} \ b_{s}(1\vec{k} + \vec{q}1) \right\}$$

$$\frac{(2\vec{k} + \vec{q})\cdot\vec{\epsilon}}{2} + \left\{ -\frac{i \ b_{2p}(|\vec{k} + \vec{q}|)}{|\vec{k} + \vec{q}|} \ b_{s}(k) + \frac{i \ b_{2p}(k)}{k} \ b_{s}(|\vec{k} + \vec{q}1|) \right\} \frac{\vec{\epsilon} \cdot \vec{q}}{2} \quad (C-6)$$

CAPTIONS

Figures 1 to 7

Various ω^2 are plotted in units of the plasma frequency, ω_p^2 , defined in (3-46), as a function of the phonon reduced wave vector \vec{q} . ZB refers to the Brillouin zone boundary, in the (1,0,0) direction at (1,0,0), in the (1,1,1) direction at (.5,.5,.5) and in the (1,1,0) direction at (.75,.75,0). ω_c^2 is the coulomb frequency (cf. (2-19)). ω_B^2 is the Bardeen frequency, defined by (5-26). $\omega_{exp.}^2$ are Walker's measured values (W 56). The curve for $\omega^2 (\omega_{ps}^2 \text{ of } (5-27))$ illustrates our present results for a pseudopotential.

Figure 8

U(q) is the Fourier transform of U(r), defined by (4-26). $A_1(q)$ is the function in expression (5-4). Both quantities are in rydbergs. Note that the sum $U(q) + A_1(q)$ forms the pseudopotential for one of our calculations.

Figure 9

The radial core wave functions for aluminum are shown. Note that they are essentially zero for $r > r_0$ where r_0 is the Wigner-Seitz cell radius.

Figures 10 and 11

Curves 1 and 2 illustrate the structure of $\frac{q^2 F_B(q)}{(\vec{\epsilon} \cdot \vec{q})^2}$, (5-19), plotted respectively for the values $U(r_0) = E_0 = 0$ and .272 ry. Curve 3 is the function $\frac{q^2 F_{ps}(q)}{(\vec{\epsilon} \cdot \vec{q})^2}$, (5-17), and curve 4 is the function minus $\frac{q^2 F_{WN}(q)}{(\vec{\epsilon} \cdot \vec{q})^2}$ of (5-18) except that the $(\vec{\epsilon} \times \vec{q})^2$ is neglected.

Tables 2, 3 and 4

A sample calculation for A_i and B_j proceeded as follows (for example A_1 and B_1). A fixed q value was chosen. Then the function U_R of (4-30) was evaluated for different k-vectors within the Fermi sea $(a_0k_F = .927)$. The value for k = 0 is in the second column. The next three columns give U_R for $a_0k = .75$ and k parallel, perpendicular, and anti-parallel to the fixed value of q. The values A_1 and B_1 are chosen to satisfy best the expression (4-30).

Tables 5. 6 and 7

The phonon reduced wave vector is in units of $\frac{2\pi}{a_L}$. The ω_c^2 values are the coulomb frequencies squared. The Bardeen column refers to frequencies calculated using $F_B(q)$, (5-19), the pseudopotential column uses $F_{sp}(q)$, (5-17), and the k-dependent column has employed $F_{WN}(q)$, (5-18). $\omega_s^2(N)$ is the normal term ($\vec{G} = 0$) of the sum (3-50), $\omega_s^2(U)$ is the Umklapp contribution, the $\vec{G} \neq 0$ terms.



Figure 1

Figure 2









ZB







Figure 8





Normalized Radial Wave Functions



Figure 10

Figure 11



Table 2

 $U_{R}(\vec{k},\vec{q}) = A_{l}(q) + B_{l}(q) \frac{\vec{k} \cdot (\vec{k} + \vec{q})}{q^{2}} ry$

q	ण _R (दे)	ण _R (वे); <u>k</u> =	.75	A ₁ (q)	B ₁ (q)
(atomic units)	$\dot{\vec{k}} = 0$	वे॥ह	d T K	₫ _k		
0,00		0.662			0.662	0,000
0.60		0.634	0.644		0.639	0.000
1.00	0.596	0,586	0.593	0.591	0.590	0.000
1.20	0,566	0,559	0.539	0.555	0.545	0.000
1.40	0,525	0.532	0.529	0.515	0.527	0.0075
1.50	0.517	0.518	0.518	0.495	0.509	0.018
1.75	0.474	0.482	0.476	0.468	0.473	0.014
2.00	0.433	0.449	0.436	0.390	0.418	0.077
2,50	0.356	0.420	0.349	0.294	0.330	0,208
3.00	0,287	0.331	0,293	0.224	0.271	0,218
4.00	0,180	0.242	0.191	0.091	0.154	0.387

Table 3

$$T_2(\vec{k},\vec{q}) = A_2(q) + B_2(q) \frac{\vec{k} \cdot (\vec{k} + \vec{q})}{q^2}$$

q	т ₂ (す)	$T_2(\vec{q})$; k = .75			A ₂ (q)	B ₂ (q)
(atomic units)	k = 0	я <mark>1</mark> 1р	dTr dTr	1 -k		
0.00		0.00752		·		
0.60		0.00839	0.00372			
1.00	-0.00722	0.00842	0,00310	-0.0114	0042	.010
1.20	-0.00644	0.00794	0,00188	-0.0144	0053	.013
1,40	-0.00678	0.00721	0.00124	-0.0163	0064	.016
1.50	-0.00642	0.00677	0.00104	-0.0174	0074	.018
1.75	-0.00627	0.00567	80000,0	-0,0188	0050	.019
2.00	-0.00625	0.00452	-0.00086	-0.0193	0063	.024
2,50	-0.00646	0.00240	-0.00239	-0.0188	0061	.027
3.00	-0.00674	0.00067	-0.00356	-0.0172	0071	.030
4.00	-0.00693	-0.00157	-0.00474	-0.0138	0048	.029

Table 4

$$T_{\mathcal{J}}(\vec{k},\vec{q}) = A_{\mathcal{J}}(q) \left[1 + \frac{2\vec{k} \cdot \vec{q}}{q^2} \right] + B_{\mathcal{J}}(q) \left[1 + \frac{2\vec{k} \cdot \vec{q}}{q^2} \right]^3$$

q	т ₃ (q)	т _д (ф); k=	A ₃ (q)	B ₃ (q)	
(atomic units)	k = 0	-q k	<u>व</u> े 1 म्	₫ <u> _</u> ҟ		
0 , 00		0				
0.60		0.00263	0.00115			
1.00	0.00313	0.00381	0.00170	-0.00170	0.0020	-0.0003
1.20	0.00432	0.00425	0.00284	-0.00103	0.0025	-0.0005
1.40	0.00452	0.00456	0.00339	-0.00016	0.0032	-0.0007
1.50	0.00500	0.00467	0.00369	-0.00001	0.0040	-0.0010
1.75	0.00561	0.00485	0.00415	0.00114	0.0056	-0.0011
2.00	0.00606	0.00497	0.00458	0.00220	0.00650	-0.00133
2.50	0.00643	0.00497	0.00492	0.00381	0.00660	-0.0015
3.00	0.00638	0.00483	0.00499	0.00466	0.00685	-0.00175
4.00	0.00587	0.00443	0.00471	0.00497	0.00715	-0.00225

Table	5
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с.		Bardeen		Pseudopotential		k-Dependent		
q	ω ² _c	ω ² (N)	ω <mark>²</mark> (ΰ)	ω <mark>²</mark> (Ν)	ω <mark>2</mark> (υ)	$\omega_s^2(N)$	ω ² (υ)	ω ² exp.
Longitudinal	$\vec{e}_{L} = \frac{1}{\sqrt{3}} (1, 1)$	1,1)	· · ·	<u></u>		• • • • • • • • • • • • • • • • • • •		
(.1,.1,.1)	.99112	.96361	.01516	.97020	.03887	00216	01333	.0077
(.2,.2,.2)	.96813	.86168	.06144	.88621	.13755	00864	04154	.0313
(.3,.3,.3)	.93 988	.71334	.14013	.76089	.25362	01763	07434	.0625
(.4,.4,.4)	.91712	•54377	.25393	.60401	.39952	01431	12224	. 0859
(.5,.5,.5)	. 90837	.37769	•3993 ⁸	.44243	.56255	01081	16686	.0955
Transverse,	$\dot{\bar{z}}_{T_1} = \frac{1}{\sqrt{2}} (1, -1)$	$\vec{\epsilon}_{T_2}$	 = <u>∫</u> [1,1,-2)			l . 		
(.1,.1,.1)	.00436		.00173		.00735		00262	.0017
(.2,.2,.2)	.01583		.00614		.01765		00615	.0070
(.3,.3,.3)	.02992		.01128		. 02788		00086	.0120
(.4,.4,.4)	.04123		.01581		.04228		.00376	.0170
(.5,.5,.5)	.04549		.01772		.04842		.01725	.0193

	Ta	ble	6
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		Bardeen		Pseudopotential		k-Dependent		
q	ω ² c	$\omega_{s}^{2}(N)$	ພ <mark>ຂ</mark> (ຫ)	$\omega_{s}^{2}(N)$	ພ <mark>ະ</mark> (ຫ)	ພ ² (N) ຮ	ω ² (υ)	ω ² exp.
Longitudins	al, $\vec{\epsilon}_{L} = (1,0,$	0)						
(.2,0,0)	.97093	.95178	.00602	.96047	.02481	00288	02466	.010
(.4,0,0)	.89328	.81963	.02697	.85138	.07018	01152	04809	.036
(.6,0,0)	.79382	.63570	.07343	.68968	.17601	01611	08115	.058
(.8,0,0)	.71035	.43919	.15602	.50366	.28765	01216	12856	.073
(1,0,0)	.67752	.26421	. 28682	.32249	.43492	00595	17971	.078
Transverse,	$\vec{e}_{T_1} = (0,1,0)$	$(0,0), \vec{e}_{T_2} = (0,0)$,1)	1				
(.2,0,0)	.01444		.00930		.02123		.00158	.0032
(.4,0,0)	.05322		.03434		.07873		.00158	.0120
(.6,0,0)	.10289		.06668		.15339		.00424	.0223
(.8,0,0)	.14451		.09352		.20350		.01488	.0318
(1,0,0)	.16071		.10414		.22255		.03208	.0360

Table 7

		Bardeen		Pseudopotential		k-Dependent		
q	ω ² _c	ω ² (N)	ω ² (υ)	$\omega_s^2(N)$	ພ ² (ຫ)	ω ₈ ² (Ν)	ω <mark>2</mark> (υ)	ω ² exp.
Longitudinal		(1,1,0)						
(.15,.15,0)	.98055	.94590	.01754	.95565	.04590	00324	02208	.012
(.30,.30,0)	.91408	.79930	.05795	.83436	.13868	01296	05210	.040
(.45,.45,0)	.78437	.59975	.09340	.65639	.16061	01541	09544	.066
(.60,.60,0)	.58924	.39369	.09537	.45856	.17530	01117	13724	.075
(.75,.75,0)	.36588	.21905	.06348	.26993	.11902	00669	16449	.061
Transverse,		(1,-1,0)						l .
(.15,.15,0)	.002141		00096		.00207	- -	00755	.0036
(.30,.30,0)	.01192		00026		.00064		01622	.014
(.45,.45,0)	.03556		.01125		.02162		08878	.032
(.60,.60,0)	.07458		.03731		.07139		.00586	.053
(.75,.75,0)	.11978		.07134		.14023		.02795	.071
Transverse,	= = (0,0	0,1)						
(.15,.15,0)	.01716		.01125		.02512		000262	.0025
(.30,.30,0)	.07378		.05069		.10471		00369	.0081
(.45,.45,0)	.17970		.13059		.22737		00263	.014
(.60,.60,0)	•33556		.25675		.39740		00722	.023
(.75,.75,0	.51329		.40720		.58951		01250	.030

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