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Iowa State University, 1987
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UMI
Theoretical investigations of phonon anomalies in fcc La and W(001)

by

Xuewen Wang

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1987
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I. INTRODUCTION

People have known for a long time that sound travels at very different speeds in different materials. The reason that the sound speed, which is an important physical property of any material, is different in each material is the difference in the density and the elasticity of solids. And apart from this long wave length acoustic region, the physical properties of materials are even more diverse and have a more complicated dependence on the constituents of crystals and their micro-structures. Lattice dynamics (LD) is a classical field of solid state physics which investigates the atomic motion in crystalline solids. These atomic motions have strong influences on the thermodynamic properties of solids, they affect the interaction between solids and x-rays or neutrons, they can give rise to interaction between defects, and can even modify the electron-electron interaction so mysteriously as to make the electrons attract each other.

A piece of solid contains a large number of atoms and to actually solve the motion of each atom is not practically feasible. But because of the periodicity of the solid and the fact that under normal conditions the atoms are bound to their equilibrium positions, this problem simplifies a lot. In fact this becomes the classical small oscillation problem, and can be solved by classical mechanics. The early LD studies were all based on force constant models which were just the extension of Newtonian mechanics to systems of large degrees of
freedom. At that time useful concepts and techniques like normal modes and normal coordinate transformations were introduced. It is interesting to notice that the later discovered quantum mechanics did not complicate the problem. Besides the quantization of the normal modes and zero-point motion, most of the features of the force constants model remained. For those models the only information needed are the force constants (assumed to be constants since atoms only exercise small oscillation around their equilibrium positions) between all the atom pairs. Once those force constants are provided, one can solve the entire spectrum of atomic vibration in a straightforward manner. The first success of explaining the physical properties of solids by LD studies was marked by Einstein's paper in 1907, where he calculated the specific heat of a solid by treating the solid as a collection of uncoupled harmonic oscillators. Later, most of the fundamental problems of LD have been worked out in detail by M. Born and his colleagues between '10s and '30s. Until 1950, however, the field of LD remained relatively dormant owing to the fact that the forces between atoms are difficult to evaluate on the microscopic level (although the origin of them is the simple and the well-known Coulomb interaction) and experimentally, apart from long wavelength acoustic waves, all the other modes of atomic vibration were not directly measurable.

In 1955, the first neutron scattering experiment was done and soon the technique proved to be a powerful tool for phonon measurement, since then it has become a routine to measure the phonon dispersion curves by neutron scattering for any new material. The development of experiment
has inspired theoretical studies of LD. Many phonon models were proposed, developed, or discarded. For the last couple of years, people have witnessed the development of more sophisticated models and the realization of first-principles calculations, that is to obtain the inter-atomic interaction quantum mechanically free of any parameters. Nowadays one can numerically evaluate thermodynamic properties of the solid such as thermal expansion, specific heat, etc., from LD studies. The results of the LD studies, that is the phonon spectrum, have entered many other solid state physics field like phase transitions and the diffusion process, even the fascinating phenomena of superconductivity.

In the following chapters, we will first give a short review of some of the models used in LD studies, then introduce a semi-empirical scheme which has been applied with great successes in many cases of LD studies, especially in LD studies for transition metals and transition metal compounds, and then we will present results of our studies for two systems, one is lanthanum bulk and one is tungsten surface. There we will calculate the vibrational spectrum and demonstrate the relationship between the anomalous structures in the vibrational spectrum and the electronic structure of the system, and show how the LD properties are related to other physical properties of these systems like superconductivity and phase transition.
II. LATTICE DYNAMICS MODELS

Being the first model and most simple one, the force constant model (FCM) still deserves some attention because it sets the formalism for LD and is still used in a lot of cases under different variations. This model simply assumes the potential energy of a distorted lattice is a quadratic function of displacements:

\[ V_2 = \frac{1}{2} \sum_{L,L'} \Phi(L',L) u(L) u(L') \tag{1} \]

where \( L = (j, \kappa) \) denotes the \( \kappa \)th particle in the \( j \)th cell. \( u(L) \) denotes the displacement vector of the ion whose equilibrium position is at \( L \).

The equation of motion:

\[ M_{\kappa'} \frac{\partial^2 u(L')}{\partial t^2} = - \frac{\partial V_2}{\partial u(L')} = - \sum_L \Phi(L',L) u(L) \tag{2} \]

can be rewritten as:

\[ M_{\kappa'} \frac{\partial^2 u(L')}{\partial t^2} = - \sum_L \Phi(L',L)(u(L)-u(L')) \tag{3} \]

since sum of \( \Phi(L,L') \) over \( L \) must be zero to satisfy the translational invariance condition. Equation (3) gives \( -\Phi(L',L) \) a clear physical picture: It is the force matrix (3x3) between a pair of ions at \( L' \) and \( L \). To solve equation (3), one can exploit the translational invariance condition and enforce the \( u(L) \) and \( u(L') \) be equal within a phase factor, so we let \( u(j,\kappa) = u(0,\kappa) \exp(iq \cdot j) \), here we use the bold \( j \) to denote the position of \( j \)th cell. Substitute \( u(j,\kappa) \) in (3) and assume the motion is
periodic with frequency \( \omega \), we have equation of motion for the 0th cell as:

\[
\omega^2 \mathbf{K}' \mathbf{u}(0, \mathbf{K}') = \sum_j (\Phi(0, \mathbf{K}'; j, \mathbf{K}) (u(0, \mathbf{K}) e^{i \mathbf{q} \cdot \mathbf{j} + u(0, \mathbf{K}'))
\]

\[
= \sum_j (\Phi(0, \mathbf{K}'; j, \mathbf{K}) (u(0, \mathbf{K}) e^{i \mathbf{q} \cdot \mathbf{j}} + \sum_j \Phi(0, \mathbf{K}'; j, \mathbf{K}) u(0, \mathbf{K})
\]

\[
\sum_j \Phi(0, \mathbf{K}'; j, \mathbf{K}) e^{i \mathbf{q} \cdot \mathbf{j}} u(0, \mathbf{K})
\]

multiply \( (M_{\mathbf{K}'})^{-\frac{1}{2}} e^{-i \mathbf{q} \cdot \mathbf{K}'} \) to both side (here the bold \( \mathbf{K}' \) denotes the relative position of \( \mathbf{K}' \)th atom within a unit cell), then the final equation reads:

\[
\omega^2 \mathbf{v}(\mathbf{K}') = \frac{1}{M_{\mathbf{K}'}} \left( \sum_j (\Phi(0, \mathbf{K}'; j, \mathbf{K}) e^{i \mathbf{q} \cdot \mathbf{j}} - \sum_j \Phi(0, \mathbf{K}'; j, \mathbf{K}) u(0, \mathbf{K})
\]

\[
+ \frac{1}{(M_{\mathbf{K}'})^{\frac{1}{2}} \sum_j \Phi(0, \mathbf{K}'; j, \mathbf{K}) e^{i \mathbf{q} \cdot (j + \mathbf{K} - \mathbf{K}')} u(\mathbf{K})
\]

where \( \mathbf{v}(\mathbf{K}) = (M_{\mathbf{K}})^{-\frac{1}{2}} u(0, \mathbf{K}) e^{-i \mathbf{q} \cdot \mathbf{K}} \) is the normalized displacement vector. There are \( n \) (the number of particles in unit cell) such equations since \( \mathbf{K}' \) runs from 1 to \( n \). One can easily see that to solve for phonon spectrum is to solve the secular equation:

\[
(\omega^2(q, \lambda) I - \mathbf{D}) \mathbf{e}(q, \lambda) = 0
\]

and the all-important \( \mathbf{D} \) is the \((3n \times 3n)\) dynamical matrix.

This model is simple and can be solved exactly. But when applied to real systems people quickly found the simple FCM (usually central or axial symmetric) is inappropriate to describe the rich features in phonon dispersion curves. The number of force constants one has to use to reproduce phonon spectrum grows quickly and very soon those force
constants become just a set of parameters, which give little insight
into the real inter-atomic interactions. Nowadays this model is mainly
used as parameterization of phonon dispersion curves.

Let us take a general view of what are the inter-atomic forces. A
simple model to start with is a periodic array of ions embedded in the
valence electron sea. As an ion moves away from its equilibrium
position, it will feel a restoring force, the origin of this force is
the Coulomb forces from other ions but greatly modified by the response
of valence electrons (the dielectric response function). Even the
relaxation of outer shells of ion core electrons gives a large
modification, as in the case of the phonon dispersion of alkali halides.
So LD studies really require a full knowledge of electronic structure
which by itself is a major computational effort. That is why
microscopic LD studies began to flourish at about the same time when
high speed computers and efficient band structure calculation schemes
became available.

The first attempt to use real inter-atomic forces for LD studies is
the rigid ion model (RIM) for alkali halides. Since in certain sense
the valence electrons are absent here, one might take the inter-ion
Coulomb force as the only interaction. As for repulsive forces to
stabilize the crystal, RIM assumes short range potentials, for example
the Born-Mayer potential:

\[ V_{K, K'}(r) = A_{K, K'} \exp(-r/\rho_{K, K'}) \] (7)

Using the so called Ewald's method, the slowly converging Coulomb force
can be effectively summed up and the model gives good results for
acoustic and transverse optical phonon modes. The splitting of the transverse and longitudinal optical phonon frequencies as \( q \to 0 \), which is the evidence of lack of effective screening, is present, but the splitting comes out to be too big, because the macroscopic electric field generated by longitudinal distortion of ions is over estimated. This can be easily understood from the Lyddane-Sachs-Teller relation:

\[
\varepsilon_s \omega_T^2 = \varepsilon_0 \omega_L^2
\]

where \( \omega's \) are the long wave length optical phonon frequencies, \( \varepsilon_s \) is the static dielectric constant, and \( \varepsilon_0 \) is the optical dielectric constant which is the square of the index of refraction. For any material \( \varepsilon_0 \) should larger be than unity, but in the RIM because there is no screening effect at all, \( \varepsilon_0 = 1 \), so \( \omega_L \) becomes too high.

Realizing the necessity of including screening effects, people then proposed the shell model (SM) and its numerous improvements and variations, among those are deformable shell model (DSM) and double shell model (DSM). The basic ingredients of these models is to represent the valence electrons by a shell of negative charge and allow the shell to move relative to the nuclear cores. In this way, the models built in some screening effects and so give better results for phonon modes not only in alkali halides, but also for transition metal compounds where the screening effect is even stronger so that the splitting of transverse and longitudinal optical phonon vanishes as \( q \to 0 \). Although these models only use electronic structure in a global manner, their parameters are found to carry some physical properties of the system, sometimes one can assign physical quantities to the parameters.
like ionic polarizability and bond charge.

In 1977, C. Varma and W. Weber proposed a new approach for LD. Fully incorporating the electronic structure in a tight binding formalism, the scheme succeeded in explaining phonon anomalies for a large class of materials. In addition, the subsequent calculations on A-15 materials by W. Weber provided sensible electron-phonon interaction parameters and quantitatively confirmed BCS theory for superconductivity in those materials. We will give a detailed discussion for this scheme in the next chapter.

Another approach for LD which appeared about same time is the inversion method. Where one starts from the bare Coulomb potential between ions and then evaluates the full response function utilizing the electronic structure information. Formally one has:

\[ \omega^2(q, \lambda) = \omega^2(q, \lambda) - M^{-1} e(-q, \lambda) \cdot g^0(-q, \lambda) \chi(q, \lambda) g^0(q, \lambda) \cdot e(q, \lambda) \]  (9)

here \( \omega^0 \) is the bare phonon frequency, \( g^0 \) is the bare electron phonon matrix element, \( e(q, \lambda) \) is the phonon polarization vector, and

\[ \chi(q, \lambda) = \varepsilon^{-1}(q, \lambda) \chi^0(q, \lambda) \]  (10)

is the full response function. To evaluate \( \chi \) one has to solve for the inverse of dielectric function \( \varepsilon \). One encounters the obstacle of an enormous computational task, so up to date relatively fewer LD studies were carried out along these lines. In the scheme put forward by Varma and Weber, part of the renormalization of the phonon frequency, the so-called D2 contribution, is calculated as:

\[ - M^{-1} e(-q, \lambda) \cdot g(-q, \lambda) \chi^0(q, \lambda) g(q, \lambda) \cdot e(q, \lambda) \]  (11)

here, one uses full electron-phonon interaction and bare susceptibility.
The similarities between (10) and (11) are easy to see, and it has been shown that the inversion method and the D$_2$ scheme are equivalent.

The first principles total energy calculation method, which has become more and more popular in solid state physics, uses the least amount of approximation, and gives highly accurate phonon frequencies free from any adjustable parameters. The only approximation used in electronic structure calculations is the local density functional approximation. The total hamiltonian of a crystal can be written as:

$$H = H_c\left(\frac{dR_j}{dt}, R_j\right) + H_e\left(\frac{dr_i}{dt}, r_i\right) + V(R_j, r_i)$$

(12)

here the $R_j$'s denote nuclear coordinates and $r_i$'s denote electronic coordinates. Because the electron is much lighter than the nucleus, the Born-Oppenheimer approximation is well justified. With this approximation the electronic wavefunction will change adiabatically following the instantaneous position of the nuclei, in other words, the electron only sees a 'frozen phonon'. Let $|G\rangle$ be the ground state for the electrons, we then have:

$$\frac{dr_i}{dt} (H_e\left(\frac{dr_i}{dt}, r_i\right) + V(R_j, r_i)) |G\rangle = E(R_j) |G\rangle$$

(13)

so we obtain a hamiltonian which is a function of nuclear coordinates only:

$$\langle G| H |G\rangle = H_c\left(\frac{dR_j}{dt}, R_j\right) + E(R_j)$$

$$= K_c + V_c(R_j) + E(R_j)$$

(14)

where $V_c$ is the Coulomb potential between nuclei and $K_c$ is kinetic
energy of nuclei. The procedure for a frozen phonon calculation is to solve equation (13) for each nuclear configuration using a highly accurate band structure calculation technique and then solve (14). Notice here one not only gets the phonon frequencies but anharmonic effects as well, which is essential for phonon-phonon interaction studies. In practice, to avoid a large computational task, the frozen phonon calculation is usually carried out only for high-symmetry phonons, where one knows from symmetry arguments the polarization vectors, so to solve (14) is trivial. However, with the development of large scale computers, there has been an increasing number of studies on surface phonon calculations using the frozen phonon approach, where the unit cell may contain a few tens of atoms. The success proves that first principles calculation is the most accurate scheme for LD studies.
III. NON-ORTHOGONAL TIGHT BINDING METHOD

In this chapter, we will first derive from perturbation theory the dynamical matrix, then we will see how this is realized in a non-orthogonal tight binding scheme.

A piece of crystal can always be viewed microscopically as a collection of ion cores and valence electrons (one can always re-define which electron to be considered as part of the ion core, to ensure that the core electrons are inert in the physical process). As said in the last chapter, the potential energy for the effective hamiltonian of the ionic system is:

\[ V_i(R) + E_b(R) - V_e(R) \] (15)

here \( R \) means a whole set of position vectors \( R \) for all the ionic cores. We have divided the electronic energy \( E \) in equation (14) of the last chapter into two terms, the band contribution \( E_b \), which is just the sum of eigenvalues of the single particle energy up to the Fermi level, and \( V_e \), the electron-electron Coulomb repulsion energy which is double counted in \( E_b \) and needs to be subtracted off. The advantage of writing the potential in this way is to re-group the terms. Because the effective screening in metals, it is easy to see that \( V_i \) and \( V_e \) will almost cancel each other, so we can write the potential as:

\[ V_n(R) + E_b(R) \] (16)

here \( V_n \) is the summation of \( V_i \) and \(-V_e\), as we just argued, it represents some kind of neutral body interaction and is smaller in magnitude than
$V_1$ or $V_e$. Another consequence of this re-grouping, which is more useful, is that the interaction range of $V_n$ becomes shorter, while the electrostatic nature of $V_1$ and $V_e$ makes their interaction range very long. The short range nature makes it easy to parameterize the $V_n$.

Using perturbation theory, the $E_b$, up to second order for small ionic distortions, can be written in four terms:

$$E_b(R) = E^0 + E_0 + E_1 + E_2$$

$$= E_b(R^0) + \sum_i \langle G | V_1 H | G \rangle \delta R_i + \sum_{i,j} \langle G | V_1 V_j H | G \rangle \delta R_i \delta R_j$$

$$+ \sum_{\Theta} \frac{|\langle \Theta | V_1 H | G \rangle \delta R_i |^2}{E_G - E_{\Theta}}$$

(17)

Here $|\Theta\rangle$ represents the excited states of the electronic system, and $|G\rangle$, the ground state. The $E_0$ and $E_1$ are the first order perturbation corrections for the band energy and $E_2$ is the second order perturbation energy. Let us assume for the moment that the electronic band structure can be described by a single-orbital tight binding hamiltonian, in usual notations we have:

$$H = \sum_{i,j} t(R_j, R_i) c^+(R_j) c(R_i)$$

(18)

From equation (18) it is easy to see that the terms contribute to the first order perturbation are like $V_1 t(R_j, R_i) \langle G | c^+(R_j) c(R_i) | G \rangle \delta R_i$, so the range of interaction represented in $E_1$ is just the same as the range of hopping integral $t$. If $t$ has a short range, so will $E_1$. But the situation is quite different for $E_2$, here the governing factor is the energy denominator. If there are low-lying excited states available and those states can couple with the ground state through $\mathcal{W}$, the
interaction $E_2$ carries can be of very long range.

For the neutral body interaction $V_n$ in (16) we can make the same expansion:

$$V_n(R) = V^o + V_0 + V_1$$

$$= V_n(R^o) + \sum_i V_i V(R^o) \delta R_i + \sum_{i,j} V_i V_j V_n(R^o) \delta R_i \delta R_j$$

(19)

The equilibrium condition requires $\delta(V_n + E_B) = 0$ up to the first order of $\delta R$, so $V_0 + E_0$ equals zero. Since $V^o$ and $E^o$ are constants, we can see from equations (17) and (19) that the effective potential energy for crystal is just $V_1 + E_1 + E_2$, and the second derivative of the potential will give the force matrix between $R_i$ and $R_j$. Following the procedures of FCM in Chapter One, we can easily get the dynamical matrix:

$$D(q) = D_0(q) + D_1(q) + D_2(q) = D_b(q) + D_2(q)$$

(20)

Here $D_0$, $D_1$ and $D_2$ is originated from the second derivatives of $V_1$, $E_1$ and $E_2$ respectively, and we have further combined $D_0$ and $D_1$ into $D_b$ for the 'bare' dynamical matrix. Here the $D_2$ accounts for the renormalization effect due to the electron-phonon interaction.

From now on, we will concentrate on transition metals and their compounds. Being metals, these materials have quite good screening effects, so the contribution to the dynamical matrix from $V_1$, that is the $D_0$, is of short range. The electronic structures of these materials have strong d-character, and a tight binding model with a few neighbor interactions describes the band structure well, which is another indication that $D_1$ is of short range. In fact, for the non-orthogonal tight binding scheme which we are going to use for our calculations, we
will show below that the longest interaction range in $D_1$ is just the sum of the interaction range for hopping and overlap matrix elements. In real space, the non-orthogonality means:

$$<0|c(R_i)c^+(R_j)|0> = S^{-1}(R_i,R_j) \neq \delta(R_i,R_j)$$  \hspace{1cm} (21)

here $|0>$ is the vacuum state and the $\delta$ is the Kronecker delta function. $S$ is a positive definite matrix. We can formally transform the non-orthogonal basis to orthogonal ones by defining a set of new operators as $\tilde{c} = S^{1/2}c$, and then the Hamiltonian can be rewritten accordingly:

$$H = \sum_{i,j} \varepsilon_i^+(R_i)S^{1/2}(R_i,R_j)S^{-1/2}(R_i,R_j)c(R_j)$$

$$= \sum_{i,j} \varepsilon_i^+(R_i)\varepsilon_i^+(R_i,R_j)\varepsilon_i^+(R_j)$$  \hspace{1cm} (22)

here we clearly see the range of $\varepsilon$ is the sum of that for the hopping and the overlap matrix elements. So at least for the systems we are concerning, the 'bare' dynamical matrix $D_b$ is of short range, so it can be well described by a force constant model with a few force parameters. We want to point out here that part of $D_b$, that is $D_1$, can be formulated in our tight binding scheme and would be easy to calculate, but for simplicity reasons we parameterize the whole $D_b$.

On the other hand, $D_2$ is calculated fully in this scheme. If we only take the single particle excitation states as $|\Theta>$ in equation (17), and make a Fourier transformation, we can write $D_2$ as:

$$D_2(\kappa\alpha, \kappa'\beta|q) = -\sum_{kmu'} \frac{f_{k'\mu'} - f_{k\mu}}{\varepsilon_{k'\mu'} - \varepsilon_{k\mu}} g^{\kappa\alpha}_{k\mu',k'\mu'} g^{\kappa'\beta}_{k'\mu',k\mu}$$  \hspace{1cm} (23)

the Fermi-Dirac function $f$ ensures the coupling is between occupied and
unoccupied states. $\varepsilon_{\mu k}$ is the eigenvalue of $\mu^{th}$ band at wave vector $k$. Here $g$ is the electron-phonon matrix element (for a detailed derivation see Section C in the Appendix). The so called bare susceptibility $\chi(q)$ can be calculated from equation (23) by setting the matrix element $g$ equal to unity and neglecting the minus sign in front of the summation.

From equation (23) we can see that there are two 'components' in $D_2$. One is the bare susceptibility, that is the density of the electronic states which are available for coupling to the phonons of wavevector $q$, it will be large when there are nesting features, that is when the wavevector $q$ connects two parallel pieces of Fermi surface. Another component is the matrix element, it takes into account the polarization of the phonon at wave vector $q$ as well as the geometry of the atomic wave functions used as the basis for tight binding wave functions. It is worth pointing out that because of the interference effects from different neighbors, the matrix element usually acquires maximum values at $q = 1/a$, where $a$ is the neighboring distance of the hopping matrix element. For a nearest neighbor tight binding model, $q$ will be at the Brillouin zone boundary. On the other hand, the bare susceptibility will have maxima at the nesting vector, which can appear at any position of the Brillouin zone. Another point one may notice from equation (23) is that $D_2$ is always negative, which means that the electron-phonon interaction always renormalizes the bare phonon frequency in such a way as to make it lower.

Other important physical quantities which can be obtained from this tight binding scheme are the so called Eliashberg function $\alpha^2 F$ and
electron-phonon coupling parameter $\lambda$. The Eliashberg function is formulated as:

$$
\alpha^2(\omega)F(\omega) = \frac{1}{2N(\varepsilon_F)} \frac{1}{\langle \varepsilon \rangle} \int \frac{ds}{|\varepsilon_s|} \frac{ds'}{|\varepsilon_{s'}}| \sum_{\omega_q,j} \frac{1}{\delta(\omega-\omega_q,j)} \left[ e^{i\alpha(q,j)} \delta^{(q',j')} e^{i\beta(q,j)} \delta(\omega-\omega_q,j) \right] (24)
$$

Here the integrals are over Fermi surface and band indices $\mu$ and $\mu'$ in the summation are implied, $N(\varepsilon)$ is the density of states per spin, and $q = k' - k$ is the phonon wave vector, $j$ denotes the phonon polarization.

The electron-phonon coupling parameter $\lambda$ is given by:

$$
\lambda = 2 \int \frac{\alpha^2(\omega)F(\omega)}{\omega} d\omega (25)
$$

Now we outline the procedure for phonon calculations using this tight binding scheme. The first step is to derive the tight binding Hamiltonian, we use the tight binding model with the non-orthogonal Slater-Koster two center approximation and fit the tight binding parameters to first principles calculated band structure. The process is repeated for the slightly different band structures corresponding to small changes in the lattice parameters. With this not only reliable tight binding parameters are obtained, but also their derivatives with respect to the inter-atomic distances. The second step is to calculate $D_2$, which involves the evaluation of eigenvalues and eigenvectors of bands on a certain mesh in the first Brillouin zone, and then put into the $D_2$ formula for summation over $k$-points and bands. The third step is to decide a FCM to represent $D_b$. This is done either by fitting to the
experimental phonon spectrum or deriving these force constants from other relevant phonon calculations. An alternative way is to utilize the first principles frozen phonon calculation results to determine the force constants and in this way the whole calculation is free from any experimental inputs.

This scheme, since proposed in 1978, has been used in a variety of systems, especially in transition metals and their compounds like refractory and A-15 materials, and has shown great successes in explaining phonon anomalies and the origin of superconductivity in those materials. We have applied this scheme to calculate the fcc La anomalous phonon spectrum and had good results. Later we have extended this scheme to handle the more complicated system of crystal surfaces, and applied it to the W(001) and Mo(001) surface dynamics calculations to study the interesting surface reconstruction phenomena.
IV. BULK PHONON CALCULATIONS:
ANOMALOUS PHONON SPECTRUM IN FCC LA

With the development of larger scale computers and more accurate computational techniques, very detailed electronic structure can now be obtained from first-principles calculation. On the other hand, the empirical tight-binding scheme, when given few parameters, is able to provide the complete phonon dispersion curves. The combination of these two will certainly open new frontiers for theoretical studies of material properties. It was with such a motivation we started our theoretical investigation. The first system we studied was the fcc La.

A. Introduction

The unusual physical properties of La have drawn considerable attention. The main point of interest and speculation here is on the role of 4f electronic levels. Being the first member of rare-earth elements, La and its compounds are frequently compared with other rare-earth materials and help to interpret the physical properties associated with 4f levels. When compared with its isoelectronic elements Y and Sc, which are not superconductors at ambient pressure, La has a fairly high superconducting temperature $T_c$ of 6.05 K and relatively low Debye temperature. The most dramatic feature is the rapid rise of its $T_c$ with pressure. People have speculated that the superconducting properties
of La may be associated with the low-frequency phonon modes which couple strongly with the electronic excitation involving the empty low-lying 4f levels. Other interesting properties of this system are the unusual negative thermal expansion at low temperature and the soft-phonon phase transition near 50 kbar. These properties may again be associated with the anomalous behavior of certain phonon modes. La has the stable fcc structure at high temperature and below 660 K it undergoes a phase transformation to the dhcp structure, because of the metastability of its fcc phase, although there were measurements on polycrystalline samples which indicated lower phonon frequencies in fcc phase than dhcp phase, there were no low temperature fcc La phonon dispersion curves available before.

In 1982, a large single crystal of metastable fcc La was grown for the first time and neutron scattering experiments were successfully performed at 10 K. The most striking feature discovered was a sharp and strongly-temperature-dependent dip in the transverse [ξξξ] branch near ξ=0.42 (Fig. 1). These measurements strongly suggested that the low-lying [ξξξ] branch phonons play an important role in the phase transformation and prompted our theoretical investigations of this interesting phenomena.

There have been several electronic structure calculations of fcc La. The most extensive work (up to 200 kbar) was reported by Pickett et al., who used a highly accurate, first-principles, self-consistent linear-augmented-plane-wave (LAPW) band-structure method. By including the 4f levels, they were able to show that the 4f bands, which are about
Figure 1. Dispersion curves for fcc La along \((\xi, \xi, \xi)\). The triangles are neutron experimental data, solid curves are theoretical calculations, and dashed lines represent the results without the D₂ contribution.
1 eV wide and lying \( \sim 2.5 \) eV above the Fermi level, only have an average electronic occupation of \( \sim 0.05 \) for pressure up to 50 kbar. Thus they concluded that below 50 kbar, the increase of superconducting temperature \( T_c \) is the result of increased p-d excitations rather than excitations involving 4f bands. Those authors also presented in their paper the bare susceptibility \( \chi(q) \). As well known, the peaks displayed by \( \chi(q) \) are frequently good candidates for phonon anomalies originating from electron-phonon interactions. Their results, although showing a generally increasing electronic screening effect along the [111] direction, did not indicate any strong features near \( \xi = 0.42 \) (Fig. 9 of Ref. 9). So the electronic origin of phonon anomalies as discovered by Itassis et al. was still not clear.

B. The Electronic Band Structure

The band structure calculations were performed by utilizing a mixed-basis, first-principles, pseudo-potential method\(^{10}\), the norm-conserving scheme\(^{11}\) was used to construct the non-local ionic pseudo-potential which well reproduced the results of relativistic all-electron atomic calculations with spin-orbit coupling neglected\(^{12}\). The quality of the so-constructed pseudo-potential is summarized in Table 1. The 4f levels are removed from the calculations since we speculated the 4f levels, although being low-lying, are not responsible for the low-frequency phonons. To check this, we first performed frozen-phonon calculations at a few wave vectors for the high-temperature bcc phase as well as the
Table 1. La pseudo-potential quality for different excited configurations. The valence states are 6s, 5p, 5d and 4f. The atomic calculation was performed by solving the Dirac equation, then the eigenvalues, $E_{\text{atom}}$'s for the various levels were determined by J-weighted average. The Hedin-Lundqvist form of exchange-correlation was used. The $E_{\text{pseudo}}$'s were obtained from solving the Schroedinger's equation with the same form of exchange-correlation.

<table>
<thead>
<tr>
<th>Configuration (s-p-d-f)</th>
<th>s</th>
<th>d</th>
<th>f</th>
<th>$E_{\text{atom}} - E_{\text{pseudo}}$ (10⁻³ Hartree)</th>
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<tr>
<td>2.0-6.0-1.0-0.0</td>
<td>0.003</td>
<td>-0.17</td>
<td>0.61</td>
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<td>1.5-6.0-1.5-0.0</td>
<td>0.58</td>
<td>-1.1</td>
<td>-0.77</td>
<td>-4.8</td>
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<td>1.0-6.0-2.0-0.0</td>
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<td>-3.2</td>
<td>-0.92</td>
<td>-9.3</td>
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<td>1.3-5.5-2.2-0.0</td>
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<td>3.0</td>
<td>-0.16</td>
<td>1.5</td>
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<td>2.0-6.0-0.9-0.1</td>
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<td>-0.20</td>
<td>-0.58</td>
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<td>1.9-6.0-1.0-0.1</td>
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<td>-0.70</td>
<td>-0.73</td>
<td>6.3</td>
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<td>2.0-6.0-0.8-0.2</td>
<td>1.1</td>
<td>-2.2</td>
<td>-1.0</td>
<td>13.0</td>
</tr>
</tbody>
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Ground State Configuration (s-p-d-f) | Atomic Eigenvalues (Hartree)
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<td>2.0-6.0-1.0-0.0</td>
<td>-0.28671</td>
<td>-1.66203</td>
<td>-0.24168</td>
<td>-0.33970</td>
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fcc phase, all the results were in good agreement with the experiments (see Table 2). If the 4f levels play a significant role, we would anticipate the calculated phonon frequencies, especially the low-lying L-point for fcc La, should be much higher than the experimental values. The Hedin-Lundqvist\(^{13}\) form of the local exchange-correlation potential was used in the calculations. The pseudo-potential were constructed for 5d, 6p and 6s, with local orbital of Gaussian type for the d levels. Similar calculations were repeated for a pseudo-potential for 5d, 5p and 6s with local orbitals for d and p levels to check for the core-like 5p-level relaxation. Changes in the band structure and phonon frequencies were found to be negligible.

The calculated energy bands (Fig. 2) were found to be very similar to those of Ref. 9. Near the Fermi level, however, with the 4f levels missing, there is less compression of the bands, and this results in some changes in the Fermi surface topology. In particular, a small nesting feature develops in band 2 (the only band which crosses the Fermi level). The Fermi surface is shown in Fig. 3, the region enclosed by Fermi surface is the unoccupied states. The nesting vector crosses the 'neck' and is shown clearly in Fig. 4. This nesting gives a small but fairly sharp peak in \(\chi(q)\) along [111] direction. The \(\chi(q)\) from \(\Gamma\) to \(L\) is plotted in Fig. 5, similar to the results of Pickett et al.,\(^9\) the susceptibility increases by \(\approx 35\%\) for the zone boundary \(L\)-point from the zone-center \(\Gamma\)-point. The peak is at \(\xi=0.42\) which is just the position of the phonon anomaly.
Table 2. Phonon frequencies from frozen-phonon calculations. The q vector for bcc H-point is \((2\pi/a,0,0)\), and for fcc L-point is \((\pi/a,\pi/a,\pi/a)\), where \(a\) is the lattice constant of bcc and fcc respectively.

<table>
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<th>(v_{\text{exp}}) (Thz)</th>
<th>(v_{\text{th}}) (Thz)</th>
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<tr>
<td><strong>bcc H-point:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(v_{\text{exp}})</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td><strong>fcc L-point:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>longitudinal</td>
<td>(2.61 \pm 0.05)</td>
<td>(2.4)</td>
</tr>
<tr>
<td>transverse</td>
<td>(0.78 \pm 0.03)</td>
<td>(0.8)</td>
</tr>
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Energy Bands for fcc La

Figure 2. Energy bands for fcc La. The Fermi level is set at 0.0.
Figure 3. The Fermi surface of fcc La.
Figure 4. An off-symmetry plane in Brillouin zone showing the nesting, the coordinates are given in $\pi/a$ units.
Figure 5. Generalized susceptibility along the (\xi, \xi, \xi) direction for fcc La.
C. Electron-Phonon Interaction and Phonon Anomalies

Although the calculated $\chi(q)$ shows a peak at about the right wave vector, it was not clear whether such a tiny peak will actually induce a giant phonon anomaly. Another point of interest is that the big anomaly only occurs in the transverse branch, while the longitudinal branch shows little, if any, anomalous behavior. To better understand the situation, we used the tight binding scheme\textsuperscript{14} for the calculations of electron-phonon interactions.

The non-orthogonal tight-binding parameters were obtained via a fit to the band structure obtained from first-principles, pseudo-potential calculations. A s-p-d basis was used and the hopping and overlap matrix elements were taken up to the second nearest neighbor. The fit was done for 17 k-points with a total \approx 140 energy eigenvalues. With a small rms error ($<0.02\text{eV}$), the band structure and the $\chi(q)$ along $[\xi\xi\xi]$ were accurately reproduced. Similar fitting were performed for fcc La with 2% and 4% smaller unit cell volume, and a consistent trend for the tight binding parameters were observed. The derivative of those parameters with respect to the inter-atomic distance were then determined under the assumption that the parameters can be written as $f=f^0\exp(-\alpha r^2)$, where $f$ denotes any hopping or overlap matrix elements, and $f^0$, $\alpha$ are constants. The parameters and their exponent $\alpha$ are listed in Table 3.

For the numerical evaluation of $D_2$ as a function of $q$, the 1/48th irreducible wedge of the Brillouin zone were divided into 770 cubes, the
Table 3. NTB parameters and their derivatives for La fcc. The orbital energies, crystal-field parameters, and hopping matrix elements are in units of electron volt, and the derivatives are in units of (Bohr radius)$^{-1}$.

(a) orbital energies
\[
\begin{array}{ccc}
E_g & E_D & E_d \\
2.737897 & 6.372574 & 3.425320 \\
\end{array}
\]

(b) crystal-field parameters
\[
E_{dd} = -0.056966
\]

(c) hopping matrix elements
\[
\begin{array}{cccccc}
 & \langle ss\sigma \rangle & \langle sp\sigma \rangle & \langle sd\sigma \rangle & \langle pp\sigma \rangle & \langle pp\eta \rangle \\
1NN & -0.529878 & 0.041810 & -0.443870 & -1.051067 & -0.050493 \\
Der. & -0.061 & 16.026 & -0.589 & -0.446 & 1.548 \\
\end{array}
\]

\[
\begin{array}{cccccc}
 & \langle pd\sigma \rangle & \langle pd\eta \rangle & \langle dd\eta \rangle & \langle dd\delta \rangle & \\
1NN & 0.050500 & 0.136658 & -0.466648 & 0.410891 & -0.041309 \\
Der. & -1.836 & -0.541 & -0.432 & -0.327 & 0.279 \\
\end{array}
\]

\[
\begin{array}{cccccc}
 & \langle ss\sigma \rangle & \langle sp\sigma \rangle & \langle sd\sigma \rangle & \langle pp\sigma \rangle & \langle pp\eta \rangle \\
2NN & -0.101836 & 0.242695 & -0.145560 & 0.943966 & -0.168690 \\
Der. & -2.216 & 0.430 & 0.340 & -0.100 & 1.170 \\
\end{array}
\]

\[
\begin{array}{cccccc}
 & \langle pd\sigma \rangle & \langle pd\eta \rangle & \langle dd\eta \rangle & \langle dd\delta \rangle & \\
2NN & -0.416048 & -0.109085 & -0.199052 & -0.016591 & 0.003208 \\
Der. & -0.698 & -2.110 & -0.570 & -4.453 & -9.192 \\
\end{array}
\]

(d) overlap matrix elements
\[
\begin{array}{cccccc}
 & \langle ss\sigma \rangle & \langle sp\sigma \rangle & \langle sd\sigma \rangle & \langle pp\sigma \rangle & \langle pp\eta \rangle \\
1NN & 0.119485 & -0.216842 & 0.100381 & -0.324912 & 0.064742 \\
Der. & -0.712 & -0.339 & 0.237 & -0.057 & 0.015 \\
\end{array}
\]

\[
\begin{array}{cccccc}
 & \langle pd\sigma \rangle & \langle pd\eta \rangle & \langle dd\eta \rangle & \langle dd\delta \rangle & \\
1NN & 0.176771 & -0.090949 & 0.116746 & -0.078579 & 0.017571 \\
Der. & -0.095 & 0.066 & -0.174 & -0.375 & -0.507 \\
\end{array}
\]

\[
\begin{array}{cccccc}
 & \langle ss\sigma \rangle & \langle sp\sigma \rangle & \langle sd\sigma \rangle & \langle pp\sigma \rangle & \langle pp\eta \rangle \\
2NN & 0.005250 & -0.018432 & 0.011092 & -0.017843 & 0.004317 \\
Der. & -2.583 & -1.431 & -4.554 & 1.277 & -2.663 \\
\end{array}
\]

\[
\begin{array}{cccccc}
 & \langle pd\sigma \rangle & \langle pd\eta \rangle & \langle dd\eta \rangle & \langle dd\delta \rangle & \\
2NN & -0.006609 & -0.042307 & 0.007921 & -0.009546 & 0.000220 \\
Der. & -1.990 & -0.081 & 0.600 & -1.032 & -9.204 \\
\end{array}
\]
electronic wave functions were calculated for the k vectors at the center of each cube and stored, and later used to calculate the electron-phonon matrix element g. The susceptibility contributed from each cube was evaluated by the commonly practised tetrahedron method. To increase the resolution for those \( q \) vectors in the region of the anomaly, the mesh was later increased from 770 to 1638 k points. To further simplify the computation, the calculation was restricted to intraband contributions from band 2, since bands which cross the Fermi level yield the most important contributions causing strong anomalies, other inter-band contributions were believed to cause short range interactions and can be combined with \( D_b \) as the short-range part of the dynamical matrix. For the short-range FCM, we included the first- and second-nearest-neighbor force constants. Symmetry of the fcc structure only allows five independent force constants for the FCM, these adjustable parameters were determined by least-squares fitting to the experimental data at 19 different \( q \) vectors. The utilization of experimental data here is only for convenience. There are two points we would like to mention here: First, as our frozen-phonon calculations show, the first-principles, pseudo-potential method is able to produce reliable phonon frequencies, so should we calculate some more zone-boundary phonons we will be able to determine these five force constants and the entire phonon spectrum could be obtained totally from first principles. Second, the short-range part of the dynamical matrix contains little structure (the dashed line in Fig. 1), as it is always the case since forces with range \( r \) can only produce structure in
dynamical matrix at wave vector \( q = l/r \). The sharp anomaly only occurs when the strong \( D_2 \) contribution, which contains long range interactions, is included (the solid line in Fig. 1).

Analysis of the results showed that the strong electron-phonon interaction comes from two small nested regions of the Brillouin zone (roughly 0.8% of the total volume). The nesting gives \( \chi(q) \) a small peak. But in order to see how the electron-phonon matrix element \( g \) plays a role, especially how the matrix element differentiates transverse with longitudinal polarizations, let us concentrate on the d-like part of the wave functions relative to a coordinate system with the \( z \) axis pointing along the \([111]\) direction. In those regions, the wave function has a strong \( t_{2g} \) character, the \( d_{xz} \) component is dominant (~40%). The reason that the electron-phonon interaction only couples with transverse branch is the combined effect of wave function character and crystal structure geometry. Figure 6 is a schematic representation of this situation. The orbital lobe of the wave function at wave vector \( k \) extends between orbital lobes of the wave function at \( k + q \), since the two wave function are nested they couple strongly. However for a longitudinal displacement along \([111]\) direction, the cancellation in the matrix element due to phase differences maintained and the contribution to the dynamical matrix is zero, while on the other hand, a transverse displacement will upset the cancellation and result in a large change in the matrix element, and hence a large electron-phonon coupling. This mechanism is similar to the so-called 'dormant interaction' discussed by Weber.16
Figure 6. Schematic diagram showing the 'dormant interaction'. For longitudinal motion the electron-phonon matrix elements are zero due to the symmetry of orbitals, while for transverse motion a large coupling is obtained. The dashed orbital situates ~1.1Å above the plane of the other two.
With the same tight-binding scheme we also calculated the Eliashberg function $\alpha^2 F$, the electron-phonon mass enhancement $\lambda$, and superconducting transition temperature $T_C$. The phonon spectrum needed in the calculation was taken from a fit to the room-temperature experimental data. For the integral over the Fermi surface, a mesh of 140 k points on the section of the Fermi surface within the 1/48th irreducible wedge of the Brillouin zone was used. Figure 7 is a histogram of $\alpha^2 F$ together with the phonon density-of-states curve deduced from experiment. An almost constant $\alpha^2$ is evident and was also found in tunneling and neutron scattering experiments on polycrystalline samples. The position of two peaks (near 2.2 and 2.7 THz) and other general features of $\alpha^2 F$ are also comparable with the tunneling data (Fig. 6 of Ref. 5). $\lambda$ is found to be 1.10, when we employed a $\mu^*$ value of 0.13 (same as Ref. 9), and used the McMillan's formula as revised by Allen and Dynes, we found $T_C$ to be 5.93 K, which is in good agreement with the experimental value of 6.05 K.

D. Calculations for fcc La under High Pressure

To further investigate the electron-phonon interaction under higher pressure, we repeated all the calculations for fcc La at 14% smaller volume, which corresponds to ~50-kbar pressure. The 4f levels were excluded again since under this pressure their contribution is still negligible, also in this way the electron-phonon interaction in fcc La can be studied systematically. Similar to the results of Ref. 9, the
Figure 7. The phonon density of states (solid curve) and the calculated Eliashberg function $\alpha^2 F$ (histogram).
magnitude of $\chi(q)$ decreased with increasing pressure. Also, the peak at $\xi=0.42$ became weaker, this can be easily understood as the increase of the band dispersion. However, the electron-phonon matrix element increased dramatically because of a stronger 'dormant interaction', so the $D_2$ contribution to the transverse $[\xi\xi]$ branch became stronger.

Numerically, we found that the amount of $D_2$ increase was 28% near the anomaly ($\xi=0.42$) and 21% at the zone boundary L-point, so we predict the dip near $\xi=0.42$ will become stronger at higher pressure. To further investigate this prediction, we performed frozen-phonon calculations at 5% and 14% smaller volumes. The results showed that the transverse L-point phonon did decrease with increasing pressure, so the short range part of the dynamical matrix does not increase fast enough to compensate the increase of $D_2$ contribution. In fact, our calculation for 14% smaller volume showed an instability for transverse distortion. The possible 4f level influence was checked by comparing results for 5% and 14% smaller volumes. The consistent frequency decrease from normal volume to smaller volumes suggested that the 4f levels do not play any significant role, which was also the conclusion of Ref. 9.

Our results for higher pressure predict that at low temperature, the anomaly near $\xi=0.42$ should be the first to go soft assuming, of course, that the higher-order contributions (anharmonic effects) are not big enough to lock the system into a commensurate distortion.

The calculation for the Eliashberg function showed that the shape of $\alpha^2F$ did not change much but the values increased somewhat. As a result the $\lambda$ value increased to 1.69. When we used the same phonon spectrum
and $\mu^*$ this $\lambda$ value gave $T_c=10.3$ K, again in good agreement with experimental data of $T_c=10.0$ K.

E. Discussion

The calculations for phonon dispersion curves here successfully demonstrated the origin of the observed phonon anomaly in fcc La. The main part of the calculation is free from adjustable parameters. By employing the tight-binding scheme, reasonable electron-phonon coupling parameters were obtained at normal and 50 kbar pressure. The agreement with experimental phonon dispersion curves and superconducting transition temperatures demonstrated the accuracy of the tight-binding scheme for electron-phonon interaction calculations. The much-debated issue of the importance of the 4f levels was clarified to a certain extent by our calculations. Previous calculations concluded that the 4f levels do not play any important role for static properties of fcc La up to pressure of 50 kbar, our results further showed that the low-lying, almost empty 4f bands have very limited influences on lattice dynamics and superconductivity. The stronger electron-phonon coupling is due to a stronger d-d interaction, which may come from a stronger d-character in the wave function relative to the situation of Y and Sc. A small, yet fairly sharp nesting feature observed in our calculated band structure is crucial for the sharp anomaly along the $[\xi\xi\xi]$ direction. This nesting feature also helps to explain the strong temperature dependence of the anomaly, since at elevated temperatures the Fermi
surface is smeared out and consequently the nesting peak in $\chi(q)$ will decrease. This may also explain why in previous calculations$^8$ this Kohn anomaly peak was absent, since the nested region is very small and any modifications of the bands will destroy the nesting.

Besides the anomaly near $\xi=0.42$, the whole transverse branch along $[\xi\xi\xi]$ couples with electronic states strongly, resulting in an anomalous low-energy phonon branch. At low temperatures the contribution to the specific heat from this branch will dominate. The specific heat due to lattice vibration is known to be:

$$c_V(q, \lambda) = \frac{\hbar \omega(q, \lambda)}{V} \frac{\partial n(q, \lambda)}{\partial T}$$  \hspace{1cm} (26)

where $n(q, \lambda) = [\exp(\hbar \omega(q, \lambda)/kT) - 1]^{-1}$ is the phonon occupation number, and $V$ is the volume of the crystal. According to our $D_2$ and frozen phonon calculations this low-lying branch has anomalous behavior under pressure: its frequencies decrease with increasing pressure. The Gruneisen parameter, which is defined for each normal mode as:

$$\gamma(q, \lambda) = -\frac{V}{\omega(q, \lambda)} \frac{\partial \omega(q, \lambda)}{\partial V} = -\frac{\partial (\ln \omega(q, \lambda))}{\partial (\ln V)}$$  \hspace{1cm} (27)

for this branch is negative. At low temperatures the overall Gruneisen parameter, which is defined as the weighted average of $\gamma(q, \lambda)$:

$$\gamma = \frac{\sum_{q, \lambda} \gamma(q, \lambda) c_V(q, \lambda)}{\sum_{q, \lambda} c_V(q, \lambda)}$$  \hspace{1cm} (28)

will be negative too since the average is dominated by the low-energy branch. It can be shown that the thermal expansion coefficient $\alpha$ is:

$$\alpha = \gamma c_V / 3B$$  \hspace{1cm} (29)
where $B$ is the bulk modulus. So, our argument suggests the possibility of a negative thermal expansion coefficient for fcc La at low temperatures, which was observed$^3$ and is unique to La among all the known nonmagnetic monatomic fcc crystals. The negative thermal expansion coefficient in the case of Si and Ge are known to be of the same origin.

The softening of the transverse [ξξξ] branch with increasing pressure may also be related to the low-temperature structural phase transition near 50 kbar. Grosshans et al.$^4$ using a diamond anvil cell, have reported superlattice reflections in fcc La beginning around 70 kbar (at room temperature) and identified the new structure as arising from the softening of the L-point phonon. Resistivity measurements$^1$ as a function of temperature and pressure have shown that this room-temperature transition at 70 kbar is related to the low-temperature transition near 50 kbar.$^1,18$ Our results suggested that at low temperatures pressure will induce the transverse mode near $ξ=0.42$ to go soft, resulting in a superlattice structure along [111] direction. As the temperature increases, the nesting gets weaker and the dip disappears at room temperature, then the pressure will induce the L-point to go soft. Neutron scattering experiments$^7$ did show that as the temperature rises, the dip in dispersion curve diminishes and at room temperature indeed a shallow minimum appears at the L-point. Another possibility is that the anharmonic terms cause phonon-phonon coupling and give an extra contribution to the free energy, and that may cause the lattice to lock into the commensurate wave vector (the L point) even
at lower temperatures.

Finally, the softening of $\xi=0.42$ transverse phonon at low temperature may help to explain the fcc-dhcp structural phase transition. In common notations, the fcc structure has the stacking sequence of ABCABC..., while the dhcp has ACABACAB.... It is easy to see that the simplest way to change from fcc to dhcp is the relative displacement of layers, which is exactly the transverse phonon distortion along $[111]$ direction. Since fcc structure has a three-layer pattern and dhcp structure has a four-layer pattern, the smallest unit can be involved in this displacive transition is a 12-layer slab, so the phonon wave vectors will be $q=(2n\pi/12a)[1,1,1]$, for $n$ from 1 to 6. Notice $q_5=0.417(2\pi/a)[1,1,1]$, so the anomaly could contribute substantially to the energetics of fcc to dhcp transition.
The success of our bulk phonon calculations prompted us to continue the studies on electron-phonon interactions. Surface phenomena, because of its close relationship with the catalytic properties of surfaces, have long been an active field in solid state physics. Due to the complexity of surfaces, however, theoretical investigations were limited to a few simple model calculations. Only recently, first-principles calculations for both structural properties and dynamic properties began to flourish. In our effort to investigate the surface phenomena via electronic structure and electron-phonon interaction calculations, we extended the tight-binding scheme for the application of this scheme for surface phonon calculations.

A. Introduction

The ideal W(001) surface has a relatively simple structure, where the surface atoms form a square lattice. Because of its high thermal stability, clean surfaces are easy to obtain and that is the primary reason that W was chosen as the testing case for new surface-sensitive experimental techniques. Since the first evidence of metallic surface states emerged on this surface twenty years ago, extensive studies, both theoretical and experimental, have been carried out and more and
more fascinating phenomena have been observed. Now, W(001) surface has become a prototype for a certain class of surface structural phase transitions. Early LEED studies\textsuperscript{20} showed that upon cooling from high temperatures the W(001) surface reconstructs from a p(1x1) into a c(2x2) structure. Further investigations\textsuperscript{21} determined that this reconstruction is intrinsic for this surface. About the same time, more evidence was collected\textsuperscript{22} and then it was established that the reconstruction pattern is a c(2x2) p2mg structure, which involves the lateral distortion of surface atoms along the diagonal (see Fig. 8). When hydrogen is absorbed, even at fairly low coverage, the symmetry of the reconstruction switches\textsuperscript{5} from p2mg to c2mm. At about coverage of $\Theta=0.5$ monolayer an incommensurate structure was observed\textsuperscript{23} with the periodicity wave vector close to the corner of the surface Brillouin zone (SBZ), the $\overline{\Gamma}$-point.

On the theory side, the need to understand the driving mechanism for the reconstruction has stimulated many studies. It has been previously proposed that two-dimensional Fermi-surface nesting, involving the so-called $\Sigma_2$ surface state, causes the c(2x2) reconstruction.\textsuperscript{24,25} Indeed, the first self-consistent, first-principles, band-structure calculations\textsuperscript{26} did discover that the $\Sigma_2$ surface states cross the Fermi level at half way between $\Gamma$ and $\overline{\Gamma}$, give rise a nesting vector of $\overline{\Gamma}$-point. Later, an independent calculation\textsuperscript{27} also confirmed this finding. Recent total-energy frozen-phonon calculations for the surface phonon\textsuperscript{28} concluded that the ideal (1x1) surface is unstable for $\overline{\Gamma}_5$ distortion (the basis for Debe-King distortion) and found that upon
Figure 8. (a) The Debe-King model for W(001) surface reconstruction, the open circles are the ideal (1x1) surface atoms and the filled circles are reconstructed surface. (b) The $\Sigma_1$ mode, where surface atoms move in or out of surface plane.
reconstruction the relatively high density-of-states on the surface layer for (1x1) surface is reduced dramatically, which again showed that a nesting induced charge-density-wave plays a crucial role in the c(2x2) reconstruction.

Angle-resolved photoemission spectroscopy, which is considered the most important technique to measure the surface electronic states, became available in the later '70s. The experiments performed on W(001) surfaces confirmed some of the theoretical findings, for example the surface state at just below the Fermi level, but detailed comparison for the dispersions showed that the measured surface band crosses $E_f$ at position rather close to $\bar{W}$ and there is very little nesting feature. These findings seriously questioned the nesting model and people turned to seek for other explanations and began to study the problem with phenomenological approaches.

The discrepancies between theoretical band structure and photoemission experiments required further investigation. Considering the fact that other properties agree so well, for example the measured work function value (4.63eV) agrees with the theoretical value (4.5±0.2 eV) remarkably, and further refinement of the calculations, like including spin-orbital interaction or incorporating surface relaxation into calculations does not change theoretical results substantially, we believe that the discrepancies are due to the misinterpretation of the high-temperature surface as the ordered (1x1) surface. Indeed, recent experimental evidence showed that the room-temperature surface, on which the photoemission measurements were
performed, is disordered. Also, early theoretical studies demonstrated that lateral displacement of surface atoms strongly influences the \( T_2 \) surface band.

Although we think the nesting model is valid, the simple susceptibility argument gives little insight into the problem, and a complete electron-phonon interaction calculation is required.

**B. Electronic Structure: The Surface Bands**

The band-structure calculations upon which our \( D_2 \) calculation was based on were performed by Mattheiss and Hamann, where both bcc W bulk and W(001) seven-layer slab band structures were calculated from a self-consistent scalar-relativistic linear-augmented-plane-wave (LAPW) method. The results were in good agreement with earlier calculations. The bulk energy-bands are shown in Fig. 9, and in Fig. 10a and 10b, the boundaries of the projected bulk bands onto (001) surface are shown as solid lines. Notice that along the \( T \)-line there is a wide symmetry gap for odd (\( T_2 \)) symmetry, while the even symmetry gap is less obvious. These authors then derived a non-orthogonal-tight-binding (NTB) hamiltonian for the seven-layer slab from their LAPW results. This NTB model allows further intercalation (that is, thicken the slab by adding more bulk-like layers at the center of slab), which is useful in sharpening the bulk-projected band edge and identifying the surface states and surface resonances.

The intercalated 13-layer slab band-structure is shown in Fig. 10a...
Figure 9. Energy bands for bcc W from Reference 27.
Figure 10a. Energy bands of odd symmetry for a 13-layer slab. The symmetry is labeled with respect to the two dimensional q-vectors. The solid lines denote the bulk continuum boundaries. Between X and M the even-odd symmetry distinction is meaningless.
Figure 10b. Energy bands of even symmetry for a 13-layer slab. The symmetry is labeled with respect to the two dimensional $q$-vectors. The solid lines denote the bulk continuum boundaries. Between $X$ and $M$ the even-odd symmetry distinction is meaningless.
and Fig. 10b, notice here the prominent $\Sigma_2$ surface band is lying in the middle of bulk-projected gap. The predominant character of this band is $d(x^2-y^2)$. We have analyzed the origin of this band by examining a pseudo-slab, that is a slab with bulk-like tight-binding interactions between the top and the bottom layers. The $d(x^2-y^2)$ orbitals on top and bottom layers form a unoccupied anti-bonding band and a occupied bonding band, as the interaction between top and bottom layers decreases to approach the situation of a real slab, these two bands collapse, and result in two surface bands (one for each surface). Since for metals charge-neutrality is achieved almost within the top layer, these surface bands have to be half-occupied, and $E_f$ has to be around mid-point from $\Gamma$ to $\overline{M}$.

The NTB model involves an s-p-d basis for each atom, and first- and second-nearest-neighbor hopping and overlap matrix elements. For the seven-layer slab the tight-binding parameters for surface and sub-surface layers were fitted to LAPW results and all the other parameters were kept at their bulk values. Extra crystal-field terms were employed for the two outmost layers to account for the symmetry breaking.

C. Electron-Phonon Interaction and Surface Phonons

The NTB parameters were taken from Ref. 27, as for the derivatives, we assumed that the parameters had a dependence on inter-atomic distance as $\exp(-\alpha r)$, and $\alpha$'s on the surface were the same as in the bulk. We obtained $\alpha$'s from Ref. 36 (in Table 4, all the NTB parameters and their
Table 4. NTB parameters and their derivatives for W(001) surface. The parameters were taken from Ref. 27, and the derivatives were taken from Ref. 36. The orbital energies, the crystal field terms, and the hopping matrix elements are in units of Rydberg. The overlap matrix elements are in units of (Bohr radius)$^{-1}$.

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derivatives are listed). It is worthwhile to point out here that those derivatives were derived from first-principles calculations and were shown to work well for Nb and Mo bulk-phonon calculations. The calculations were performed on a 13-layer slab, and the same calculations were also performed on 5-layer and 7-layer slabs to check the numerical convergence. A sufficiently fine k-point mesh in the SBZ was used (78 k points in the 1/8th irreducible wedge), and all the inter-band summations (117 bands) were included. \( D_2 \) matrices of 36 q wave-vectors were calculated along symmetry line \( \overline{\Gamma} \), \( \overline{\Sigma} \) and \( \overline{T} \).

The \( D_2 \) here is a (39x39) matrix and in Fig. 11 we plotted one of the components \( D_2(1r,1r|q) \) as a function of \( \xi \) along \( \overline{T} \)-line, \( 1r \) here denotes the distortion of the first layer atoms in the directions parallel to the surface. The rapid increase in magnitude feature of this component as one approaches the \( \overline{M} \)-point indicates a strong electron-phonon interaction for phonons of large \( \xi \) value with their polarization parallel to surface (basic pattern for Debe-King type of reconstruction).

As for short-range \( D_b \), a first- and second-nearest-neighbor force-constant model was employed. To determine those force constants, we carried out parallel bulk phonon calculations using the same tight-binding scheme, after the \( D_2 \) for bcc W bulk were obtained, the force constants were determined by least-squares fitting to the experimental results. For the first step, all the short-range force-constants were kept at their bulk values, the resultant surface phonon dispersion curves are shown as solid line in Fig. 12. As the second step, in view
Figure 11. One component of $D_2$ (as explained in the text) is plotted as the function of $\xi$ from 0.0 (T-point) to 1.0 (H-point). Notice the dip at H-point.
of expected small charge redistribution at the surface,$^{26,27}$ we adjusted the surface to sub-surface inter-layer force constant utilizing the frozen-phonon calculations of Fu et al.,$^{28}$ and found a moderate 10% increase would bring our $\tilde{\omega}_1$ surface phonon frequency in a general agreement with the frozen-phonon results. The resultant surface phonon dispersion is shown as the dashed line in Fig. 12. The dispersion curves showed that we have obtained the usual sagittal-plane (SP) Rayleigh mode. In addition, there appear another SP mode and a shear-horizontal (SH) mode below the bulk continuum. The amplitude of both modes decay very rapidly into the bulk and their surface-layer displacement are mainly (in case of SH mode, exclusively) within the surface plane. Along the $\bar{\Gamma}$-line, the two modes stay quite close together and at the SBZ corner form the doubly-degenerate $\tilde{\omega}_5$ mode which is unstable from our calculations. A certain linear combination of the two degenerate $\tilde{\omega}_5$ modes corresponds to exactly the observed Debe-King $c(2\times2)$ surface reconstruction. Another feature in surface phonon dispersion is that the SP modes along line $\bar{\Gamma}$ are also unstable or have very low energies.

In order to assess the contribution of the electron-phonon interaction to the surface phonon softening, we also carried out a pure Born-von Karman (BvK) model fit to the bulk $W$ phonons, and calculated the surface phonons, also for a 13-layer slab, using a broken bond model (that is to keep all the force constant at their bulk value and cut off at the surface). The results, shown in Fig. 13, demonstrated that besides the Rayleigh mode, all the soft surface phonons are due to
Figure 12. Surface phonon dispersion curves for p(1x1) W(001). The bulk phonon continuum is indicated by the hatched areas, with different hatching for sagittal-plane (SP) and shear-horizontal (SH) modes. (This distinction is meaningless along $\bar{X}$ to $\bar{M}$).
Figure 13. Phonon curves for a 13-layer slab, calculated by broken bond model. All the force constants are taken from bulk phonon fittings.
surface electron-phonon coupling. The broken bond model almost gives the correct $\omega_1$ mode, because this mode, with its polarization perpendicular to the surface, does not couple with the surface electronic states. This observation is in agreement with the early first-principles calculations.\textsuperscript{28}

It will be instructive to examine first the susceptibility. Notice the surface $\Sigma_2$ band crosses the Fermi level in a very shallow way, so the contribution to $\chi(q)$ does not come solely from a limited region of SBZ (see Fig. 14), as a result, the classical nesting picture of diverging $\chi(q)$ does not appear. In fact the $k_f$ along $\Sigma$-line is not at exactly 0.5 but at 0.56, and calculated $\chi(q)$ only showed broad peak near $\bar{\Gamma}$ and $\bar{X}$. We found, however, that the matrix element strongly enhances and modifies the susceptibility effect. Sharp structures in $D_2$ (see Fig. 11) are really the results of a subtle interplay of the competing effects.

The analysis showed that although all possible interactions between surface states along $\Sigma$-line contribute markedly to the $D_2$, the biggest ones stem from the coupling of $\Sigma_2$-like states with wave vectors $k=(\pm 0.5, \pm 0.5)$. This coupling is the driving force for phonon softening both at $\bar{\Gamma}$ and $\bar{X}$. In Fig. 15-a, the phonon distortion patterns for lowest $\bar{\Sigma}$-point ($\bar{X}_2$) and $\bar{H}$-point ($\bar{H}_5$) are plotted, and the common features of dimerization along the $x$-axis are obvious. Look now at the $\Sigma_2$ surface states, the wave function is very concentrated on the surface-layer atoms and has a predominant $d(x^2-y^2)$ component. The $d(x^2-y^2)$ orbital has a planar character with its lobe pointing towards the
Figure 14. Reciprocal-space indication of which states in the surface Brillouin zone may couple strongly with surface phonons. The arrows indicate wave vectors for $\tilde{X}_2$, $\tilde{H}_5$, and $\tilde{Y}_2$ surface phonons.
Figure 15. Analysis of the electronic driving mechanism for soft surface phonons. (a) Displacive patterns for the $\overline{M}_5(x)$ and $X_2$ modes. The $\overline{M}_5(y)$ mode is obtained by a 90-degree rotation of $\overline{M}_5(x)$. (b) Real-space indication of the modulation of the most relevant $(dd\sigma)$ integrals involving $d(x^2-y^2)$ and $d(xy)$ orbitals. While the radial gradients are the same for $\overline{M}_5$ and $X_2$, the angular gradients are only effective for the $\overline{M}_5$ mode.
nearest-neighbor atom in the surface, so any modulation of the inter-atomic distance on the surface will have strong influences on the $\Sigma_2$ band. It is clear now that the $\Sigma_2$ mode, $\Sigma_5$ mode, and the whole branch of phonons along $Y$-line all have this dimer-formation character, so they all couple with $\Sigma_2$ surface bands through a strong radial gradient (Fig. 15-b) and result in a large renormalization effect on their vibrational frequencies. For the $\Sigma_5$ phonon (but not for $\Sigma_2$) there exists an additional coupling mechanism, that is between the $\Sigma_2$ band and the $\Sigma_1$ band, the $\Sigma_1$ band is a less prominent surface band with even symmetry. The $d(x^2-y^2)$ component of $\Sigma_2$ and $d(xy)$ component of $\Sigma_1$ couple because the change of overlap angle (see Fig. 15-b). This is a dormant interaction and this contribution to the matrix element ultimately leads to the bigger instability of $\Sigma_5$.

D. Discussion

The calculations of W(001) surface phonon dispersion curves was, for the first time, a successful application of tight-binding lattice-dynamics technique to the surface phonon studies. Our tight-binding calculations, which were based on first-principles energy-band calculations of W(001),\textsuperscript{27} revealed a whole region of soft surface phonons near the boundary of SBZ between $\bar{X}$ and $\bar{M}$. These modes exhibit primarily horizontal displacements of the surface atoms. The soft modes are caused by interactions with electronic surface states around $E_f$, especially those of $\Sigma_2$ symmetry.
The doubly degenerate \( H_5 \) phonon is the most unstable mode, caused by the combined effect of surface band nesting and neighboring atom d-orbital interaction. Thus our results demonstrated that the driving force for the c(2x2) reconstruction of clean W(001) is very much the classic Peierls instability, although the electron-phonon matrix element plays a very important role and the nesting at \( 2k_f \) is of less significance. The exclusion of surface relaxation effects in these calculations was justified by early theoretical findings that relaxation as large as 6% of the surface to sub-surface layer distance has a surprisingly small effect on surface electronic states,\(^3\) also there was theoretical evidence\(^2\) that the surface contraction reduces as reconstruction develops. Unlike the frozen-phonon calculations, where all the higher order terms can be obtained, our calculation employed the harmonic approximation, this prevents us from predicting the actual reconstruction pattern as well as the magnitude of the distortion. The doubly degenerate \( H_5 \) can form any polarization patterns in the surface, a particular pattern (for example, the Debe-King model) can only be stabilized by anharmonic effects.

The stable \( H_1 \) mode is due to the vanishing electron-phonon matrix elements for the out-of-plane distortion. In fact, our broken bond model calculation yielded almost same frequency for that mode. The two basic predictions of our calculations, that is the stable \( H_1 \) and the soft \( H_5 \), were later confirmed by helium scattering experiments.\(^4\) The surface phonon dispersion curves along the \( \Sigma \)-line measured at a temperature of 450K had a very good quantitative agreement with our
theoretical curves (see Fig. 16 and compare with Fig. 11).

The subtle interplay of Fermi surface nesting effect and real space orbital interactions may be the reason for the rich features of surface phase transformation when hydrogen is absorbed on W(001). Since any small changes in band structure may tip the balance of competing effects and give rise to a most-unstable surface phonon other than the \( \overline{\Gamma} \)-point. It was found with a very small coverage of H (\( \Theta < 0.1 \))\(^{41} \) the surface will switch from p2mg to c2mm structure (Fig. 17). This merely suggested that the angular anharmonic effect may be fairly small. At full coverage (\( \Theta = 2 \)) the surface returns to the (1x1) structure\(^{42} \) and it was found\(^{43} \) that the surface states were removed by hydrogen absorption. For coverage above \( \Theta = 1/3 \), however, incommensurate structures with wave vectors along the \( \overline{Y} \)-line but close to \( \overline{\Gamma} \) was observed.\(^{23} \) To see if this is due to the drifting of maximum electron-phonon interaction in \( \mathbf{q} \) space, we have investigated how much, in an ordered superstructure for \( \Theta = 0.5 \), the H atoms modify the W(001) electronic surface states. We added H s-orbital, used \( E_s(H) = -1.4 \text{eV} \), \( s\sigma(H) = 0 \), and \( s\delta(H-W) = -1.4 \text{eV} \) (the values were found by a rough estimate from results of Ref. 43). The c2mm(2x2) geometry was assumed with displacement of W atom \( \delta = 0.1 \text{Å} \), the surface W-W interaction was accordingly readjusted. The H's were placed on the bridge position on top of the shorter W-W bonds\(^{44} \) with a W-H-W bond angle \( 2\theta = 106^\circ \). Our results for the \( T_2 \) band show (see Fig. 18) a considerable splitting on the folded zone boundary, however, the surface states have not been removed. We concluded that the surface electron-phonon interaction is still important on the hydrogen covered W(001)
Figure 16. Dispersion curves of clean W(001) from $\Gamma$ to $\overline{M}$ as described in Ref. 40. The open circle is at 450 K and filled circle is at 280 K.
Figure 17. Schematic of the c2mm H/W(001) surface reconstruction. The crosses are the H atoms situating at the shorter bridge site.

Figure 18. Changes of the $\Gamma_2$-type electronic surface band near $E_F$. The p(1x1) situation when folded into (2x2) Brillouin zone (solid lines), with the $\mathcal{H}_5$ type of reconstruction (dashed lines), and additional ordered H coverage of $\Theta=0.5$ (dotted lines).
surface and is likely to be the driving force for the incommensurate surface reconstruction. Another possible mechanism is based on a local picture,\textsuperscript{23} that is, at coverage $\Theta=0.5$ all the shorter-bridge sites are occupied by hydrogen, additional absorbed H has to go to the domain boundaries, thus creates incommensurate structures. According to this picture, the onset of incommensurate structure for $\Theta=0.3$ is due to the thermal migration of H on the W(001) surface.

Finally, the discrepancies between theoretical band structure and photoemission experiments are suspected to be unreal. Now both theoretical\textsuperscript{45} and experimental\textsuperscript{34} results have indicated the room-temperature surface is disordered. The Fermi surface nesting model, which was previously dismissed because of the photoemission experiments, seems still valid for ideal (1x1) surface. However, our early suggestions\textsuperscript{46} that at higher temperatures, the anharmonic terms (usually big for soft phonons) will come into effect and bring the $\mathcal{H}_5$ up to stable frequency so to retrieve the ideal (1x1) surface may not be applicable for this surface due to the large reconstruction energy.\textsuperscript{47} Also, there are theoretical results\textsuperscript{48} indicating that the $\mathcal{X}_2$ phonon is also unstable, for which our calculations could not give, apart from some qualitative predictions, very accurate quantitative agreement due to the lack of knowledge about the readjustment of the short-range force constants near the surface.
VI. CONCLUDING REMARKS

The results of our studies demonstrated that the electron-phonon interaction is the key for understanding many of the physical properties of materials, both for bulks and surfaces. The tight binding lattice dynamics scheme have been shown to work well in revealing the electronic driving mechanism for those interesting phenomena like superconductivity and phase transitions. Since all of the calculations were based upon realistic band structures, by that we mean that all of the NTB parameters and their derivatives were extracted from first principles electronic structure calculations, this scheme is able to get precise pictures of the underlying electronic processes in terms of Fermi surface geometry and local atomic wavefunction interactions. The tight binding lattice dynamics scheme is also computationally efficient, that allow us to use denser sampling points and check for convergence on numerical results.

The extension of this scheme to surface calculations is fairly successful. While other model calculations on W(001) were limited on either the r-space local bonding effect or the q-space nesting effect, our calculations contained both effects, and as a result, our calculations were able to explain in simple pictures the driving force for the W(001) surface reconstruction. Our results showed that although the energetics is basically controlled by the short range r-space orbital interactions, the ground state structure of W(001) is determined
by the subtle interplay between r-space and q-space interactions. Our subsequent calculations on Mo(O01) surface further established that this interplay is crucial for the geometry of the reconstructed Mo(O01) surface.

As the isoelectronic system of W(O01), Mo(O01) surface also reconstructs below room temperatures, yet the geometry of the reconstructed surface is different from the W(O01) case. The surface atoms of Mo(O01) form an incommensurate pattern with respect to the underlying bulk structure.49 Utilizing accurate band structure of Mo(O01) calculated from first principles,50 we have obtained the NTB hamiltonian for Mo(O01) and performed similar phonon spectrum calculations for Mo(O01) as for W(O01). The results showed that the ideal Mo(O01) p(1x1) is unstable and it should reconstruct with a planar dispalcive pattern very similar to W(O01), but the smaller relativistic corrections (molybdenum is much lighter than tungsten) to the electronic structures of Mo(O01) compared to W(O01) affect both the r-space and q-space electron-phonon interactions in such a way as to cause the Mo(O01) surface to acquire the most energetically favorable reconstruction pattern at incommensurate wave vector close to the \( \overline{M} \)-point. The wave vector \( q \) from our calculation is about 0.83 along the \( \overline{Z} \)-line, in good agreement with experimental results.49

Finally, some words about the limitation of this tight binding scheme are in order. The limitation of this scheme stems from the NTB hamiltonian. In order to take advantage of the efficiency of this scheme, one should avoid to have a large number of parameters in the NTB
hamiltonian, so one may not want to apply this scheme to free-electron systems like simple metals. Also, since in this scheme the NTB parameters have definite physical meanings as the overlap of neighboring atomic orbitals, cautions must be exercised to avoid those parameters to become unphysical, especially in the procedure of fitting the parameters to the first principles calculated energy bands, there the so-called local minima in the least-squares-fit are usually related to unphysical NTB parameters. For the same reason, the orthogonal tight binding scheme may not work well since there the atomic orbitals on neighboring sites are artificially forced to be orthogonal even under various lattice distortions. On the other side of the spectrum, the alkali halides are ionic, there the Coulomb force is the dominant part of the inter-ionic forces, so the tight binding lattice dynamics scheme, which concentrates mainly on the electron-phonon interactions, may not yield sensible results. Yet, for a large class of transition metals and transition metal compounds, this scheme is shown to work well and there are similar schemes which have been applied successfully for semiconductor materials.\textsuperscript{51}
VII. REFERENCES

48. H. Krakauer, Physics Department, College of William and Mary, private communication.
50. C.-T. Chan and K.-M. Ho, Physics Department and Ames Laboratory, Iowa State University, private communication.
A. Slater-Koster Two-Center Parameterized Hamiltonian

The full description of this method is given in a paper written by Slater and Koster more than thirty years ago. It was designed as an interpolation scheme to be used in connection with more accurate calculations made by other schemes.

The first step is the tight binding approximation, which assumes that the wave function can be written as:

$$\psi_{k,\mu}(r) = \sum_{l} C_{l}(k,\mu) \Phi_{l}\Phi^{*}(r)$$

(1)

where $k$ is the wave vector and $\mu$ is band index. $\Phi_{l}(r)$ is the Bloch sum of atomic orbitals:

$$\Phi_{l}(r) = \sum_{j} \psi_{l}(r-R_{j}-\tau_{l}) \exp(ik \cdot (R_{j}+\tau_{l}))$$

(2)

where $R_{j}$ denotes the position vector of $j$th cell and $\tau_{l}$ denotes the position of $l$th atom with respect to the position of the cell. $\psi_{l}$ denotes the atomic-like wave function. Here $l$ denotes the type of wave function as well as the member of atoms in the unit cell on which the wave function is centered. The coefficients $C's$ in equation (1) are the solution of secular equation $HA=SAE$. In this scheme the potential is also treated as a sum of atomic-like potentials.

$$V(r) = \sum_{i,j} v(r-R_{j}-\tau_{l})$$

(3)
The second approximation used in this scheme is the two-center approximation, that means the potential terms has the form:

\[
\int \psi^*(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_i') \psi (\mathbf{r} - \mathbf{r}_j' - \mathbf{r}_i) \, d^3r
\]

\[
= Q_{ij} \delta_{j, j'} \delta_{i, i'} + Q_{i'j'} \delta_{j', j} \delta_{i', i} + F_{ij} \delta_{j, j'} \delta_{i, i'}
\]

(4)

where \(Q\)'s and \(F\) are constants. Although this is a quite severe approximation, in most cases this scheme still describes the band structures (at least for those bands below the Fermi level) well, even for simple metals. However, the physical content of the hopping and overlap integral will be quickly lost, and those integrals will be reduced to merely parameters and has serious consequences for the phonon calculations.53

Let us look at an overlap matrix element \(\langle n, l, m | n', l', m' \rangle\), where the atomic-like wave function is situated at \(R_1\) and \(R_2\) respectively. The operator \(P_\phi\) which is the rotation around axis \(R_1 - R_2\) should leave this matrix element unchanged, so we have:

\[
P_\phi \langle n, l, m | n', l', m' \rangle = e^{i(m'-m)\phi} \langle n, l, m | n', l', m' \rangle = S \delta_{m', -m}
\]

(5)

and so among all the possible overlap matrix elements, only ten actually exist (for a s-p-d basis). People have adopted the molecular notation and called the overlap as \(\sigma\) state if \(m=0\), \(\pi\) state if \(m=\pm 1\), and \(\delta\) state if \(m=\pm 2\). In Table 5, we list all the overlap matrix elements when \(R_1 - R_2\) is along the z-axis. For arbitrary \(R_1\) and \(R_2\), there are simple relations can be followed to 'rotate' the overlap matrix element.1 Once all the pair-wise overlap matrix elements are known the overlap matrix \(S\) can be constructed:
\[ S_{l_1,l_2}(k) = \sum_{j} S_{l_1,l_2}(R_j + \tau - \tau_j) \exp(i k \cdot (R_j + \tau - \tau_j)) \] \hspace{1cm} (6)

The sum goes up to all the neighbor shells. The hopping matrix \( H \) can be constructed from hopping matrix element \( h \) in the same way. With this we get the secular equation \( H \alpha = \lambda \beta \).

Table 5. Overlap matrix element for a \( s-p-d \) basis. Here the direction connecting the two orbitals is along the \( z \)-axis. Also listed are the sign of these matrix elements.

<table>
<thead>
<tr>
<th>( s )</th>
<th>( s )</th>
<th>( p )</th>
<th>( p )</th>
<th>( d )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ss \sigma )</td>
<td>( &lt; s</td>
<td>s &gt; )</td>
<td>&gt;0</td>
<td>( sp \sigma )</td>
<td>( &lt; s</td>
</tr>
<tr>
<td>( sd \sigma )</td>
<td>( &lt; s</td>
<td>d(r^2-3z^2) )</td>
<td>&gt;0</td>
<td>( pp \sigma )</td>
<td>( &lt; p(z)</td>
</tr>
<tr>
<td>( pp \pi )</td>
<td>( &lt; p(x)</td>
<td>p(x) &gt; )</td>
<td>&gt;0</td>
<td>( pd \pi )</td>
<td>( &lt; p(z)</td>
</tr>
<tr>
<td>( pd \pi )</td>
<td>( &lt; p(x)</td>
<td>d(xz) &gt; )</td>
<td>&lt;0</td>
<td>( dd \sigma )</td>
<td>( &lt; d(r^2-3z^2)</td>
</tr>
<tr>
<td>( dd \pi )</td>
<td>( &lt; d(xz, yz)</td>
<td>d(xz, yz) &gt; )</td>
<td>&lt;0</td>
<td>( dd \delta )</td>
<td>( &lt; d(xy)</td>
</tr>
<tr>
<td>( dd \pi )</td>
<td>( &lt; d(yz)</td>
<td>d(yz) &gt; )</td>
<td>&lt;0</td>
<td>( dd \delta )</td>
<td>( &lt; d(x^2-y^2)</td>
</tr>
</tbody>
</table>
B. Tight-Binding Fit

We define a functional $L(C)$ as:

$$L(C) = \sum_i W_i (E_i - X_i)^2$$  \hspace{1cm} (7)

where $\{C\}$ denotes the whole set of Slater-Koster two-center non-orthogonal tight-binding parameters, and $X$'s are the eigenvalues to be fitted on all the k-points and all the bands. $W$'s are assigned weight for each eigenvalue to be fitted, so one can emphasize the accuracy of fitting in certain regions, for example near the Fermi level. The $E$'s are the eigenvalues generated by the tight-binding scheme with the parameter set $\{C\}$. The condition for minimization of $L(C)$ is:

$$\frac{\partial L}{\partial C_j} = 2 \sum_i W_i \frac{\partial E_i}{\partial C_j} (E_i - X_i) = 0$$  \hspace{1cm} (8)

for each $j$.

We start with a set of $(C^0_1, C^0_2, \cdots)$ which give a set of eigenvalues $(E^0_1, E^0_2, \cdots)$, and want to find a set of new parameters $(C_1, C_2, \cdots) = (C^0_1, C^0_2, \cdots) + (\delta_1, \delta_2, \cdots)$ so condition (8) holds. Expand $E$'s around $C^0$'s, we have:
\[
\frac{\delta L}{\delta C_j} = 2 \sum_i W_i \frac{\delta E_i}{\delta C_j} (E_i^0 + \sum_m E_i \frac{\delta E_i}{\delta C_m} - X_i) = 0 \quad (9)
\]

Solve for \( \delta_m \), we get:
\[
\delta_m = -\sum_j T^{-1}_{mj} (\sum_i W_i (E_i^0 - X_i) \frac{\delta E_i}{\delta C_j}) \quad (10)
\]
where the \( T \) matrix is defined as:
\[
T = \sum_i W_i \frac{\delta E_i}{\delta C_j} \frac{\delta E_i}{\delta C_m} \quad (11)
\]

To find the change of the eigenvalue \( E_i \) with changing of the tight binding parameter \( C_j \), we use first-order perturbation theory. So if \( C_j \) is a hopping parameter, we will have:
\[
\Delta E_i = \sum_{m,j} A^{*}_{m,i} (\Delta H)_{m,j} A_{j,i} \quad (12)
\]
and if \( C_1 \) is a overlap parameter, we will have:
\[
\Delta E_i = -E_i^0 \sum_{m,l} A^{*}_{m,i} (\Delta S)_{m,l} A_{l,i} \quad (13)
\]

For each step of finding \( \{ \delta \} \), we only need to solve the secular equation \( HA = SAE \) once and all the derivative of \( E \)'s with respect to \( C \)'s can be found by equations (12) and (13). Then the \( T \) matrix of equation (11) is formed and inverted, and \( \{ \delta \} \) is found by equation (10).

C. NTB Lattice Dynamics Formalism

The full description of this scheme can be found in Varma and Weber's original paper\textsuperscript{36} and their publications afterwards.\textsuperscript{54} Here we will present a somewhat condensed derivation. The basic approximation
used in the tight binding lattice dynamics scheme besides the usual tight-binding two-center approximation is that the atomic orbitals are assumed to move with the atom. Any relaxation of these orbitals upon distortion of the lattice is supposed to be accounted for by the derivative of the NTB matrix elements with respect to the lattice constant, and the derivatives are supposed to be independent of wave vectors and usually are derived from fittings to band structures of different lattice constant.

The NTB system is described by the secular equation $H\alpha = S\alpha \varepsilon$ with normalization condition $A^+S\alpha = I$. It is well known that this can be transformed into a normal secular equation $H'U = UE$ with $U = S^{1/2}A$ and $H' = S^{-1/2}HS^{-1/2}$. Upon lattice distortions, the hopping and overlap integrals will change and result in $H = H^0 + h$ and $S = S^0 + s$, and $H'$ now becomes:

$$H' = S^{-1/2}H S^{-1/2} = (S^0 + s)^{-1/2}(H^0 + h)(S^0 + s)^{-1/2} = (1 - \frac{s}{2S})S^0 - \frac{1}{2S}hS^0 - (1 - \frac{s}{2S^0})$$

(14)

here the higher order in the expansion of $(S^0 + s)^{-1/2}$ is omitted. If we only keep the terms up to linear in $s$ or $h$, we will have the secular equation:

$$(S^0 - \frac{1}{2}H^0 S^0 - \frac{1}{2} + S^0 - \frac{1}{2}hS^0 - \frac{1}{2} - \frac{s}{2}(S^0 - \frac{1}{2}H^0 S^0 - \frac{1}{2} + S^0 - \frac{1}{2}hS^0 - \frac{1}{2})) U = (H'^0 + \Delta H') U = U(E^0 + E^1 + E^2)$$

(15)

here the $E$'s are different orders of perturbation correction and the Hamiltonian is clearly separated into zeroth-order term and perturbational term. The first order perturbation term, $E^1 = U^+\Delta H'U$,
which will contribute to $D_1$, a short-range part of the dynamical matrix, will not be considered here. For the $D_2$ term, we will consider the $E^2$ term and because the harmonic approximation for lattice dynamics, we only need to consider $h$ and $s$ up to first order in lattice distortions.

With the neglect of three-center integrals, the hopping (or overlap) matrix in $k$-space is the sum of the pair-wise integrals:

$$H_{\nu,\nu'}(k',k) = N^{-1} \sum_{j,j'} \exp(i(k \cdot R_j - k' \cdot R_{j'})) H_{\nu,\nu'}(R_j - R_{j'})$$  \hspace{1cm} (16)

here $\nu$ denotes both the atomic species and the orbitals. For small distortions, we let $R = R^0 + u$ and expand equation (16) up to first order in $u$:

$$H_{\nu,\nu'}(k',k) = H_{\nu,\nu'}(k^0) + (u_j - u_{j'}) \cdot \nabla H_{\nu,\nu'}(R^0_j - R^0_{j'})$$  \hspace{1cm} (17)

notice $R^0_j - R^0_{j'} = R^0_{j'}$, we can rewrite (17) as:

$$H_{\nu,\nu'}(k',k) = H_{\nu,\nu'}(k^0) \delta_{k, k'} + N^{-1} \sum_{j} \exp(iR^0_j \cdot (k' - k)) u_j \cdot \sum_{j'} \left[ \exp(iR^0_{j'} \cdot k') - \exp(iR^0_{j'} \cdot k) \right] \nabla H_{\nu,\nu'}(R^0_{j'})$$  \hspace{1cm} (18)

notice $\sum_j \exp(iq \cdot R^0_j) u_j = u(q, \lambda)$ is the phonon mode $(q, \lambda)$, and define:

$$\gamma_{H,\nu,\nu'}^j(k) = \sum_{j \neq 0} \exp(ik \cdot R^0_j) \nabla H_{\nu,\nu'}(R^0_j)$$  \hspace{1cm} (19)

now, we can write $h$ linear in lattice distortion as:

$$h_{\nu,\nu'}(k + q, k) = u(q, \lambda) \cdot (\gamma_{H,\nu,\nu'}^j(k + q) - \gamma_{H,\nu,\nu'}^j(k))$$  \hspace{1cm} (20)

Similarly, the $s_{\nu,\nu'}(k', k)$ can be written in terms of $\gamma_{s,\nu,\nu'}^j$. Applying second order perturbation theory to equation (15), it is easy to show that the second order correction to eigenvalue $\varepsilon_{k,\mu}$ due to the coupling with phonon mode $(q, \lambda)$ is:
\[
\Delta \varepsilon_{k,\mu} = \sum_{\mu'} \frac{1 - f_{k',\mu'}}{\varepsilon_{k,\mu} - \varepsilon_{k',\mu'}} u(q,\lambda) \cdot g_{k',\mu';k,\mu} u(-q,\lambda) \cdot g_{k,\mu; k',\mu'}
\]  
(21)

here \( k' = k + q \), and factor \( 1 - f \) ensures that the excited state is not occupied. The electron-phonon matrix \( g \) is defined as:

\[
g_{k',\mu';k,\mu} = \sum_{\nu',\nu} A_{\nu',\nu}^{*}(k') [\gamma^{H}_{\nu',\nu}(k') - \gamma^{H}_{\nu',\nu}(k) - 0.5(\varepsilon_{k',\mu'} - \varepsilon_{k,\mu})(\gamma^{S}_{\nu',\nu}(k') - \gamma^{S}_{\nu',\nu}(k))] A_{\nu,\nu}(k)
\]  
(22)

And the total energy change due to electron-phonon coupling is \( f_{k,\mu} \Delta \varepsilon_{k,\mu} \) sum over \( k \) and \( \mu \).

To find \( D_{2} \), we first examine the potential term in the Hamiltonian for lattice dynamics, which can be written as:

\[
\mathcal{V} = \frac{1}{2} \sum_{q,\lambda} u(q,\lambda) D(q) u(-q,\lambda)
\]  
(23)

here the \( q \) is in the first Brillouin zone and \( D \) is the \((3n \times 3n)\) dynamical matrix, \( u(q,\lambda) = N^{-1/2} \sum_{j} u(R_{j}) \exp(-i q \cdot R_{j}) \) is a \( 3n \) column matrix.

Formally from equations (21) and (23) we would have:

\[
u(q,\lambda) D_{2}(q) u(-q,\lambda) = 2 \sum_{k,\mu} f_{k,\mu} \Delta \varepsilon_{k,\mu} (k' = k + q)
\]  
(24)

but to ensure the real space displacement \( u(R_{j}) \) to be real, the dynamical matrix \( D \) in (23) must have the property \( D(q) = D^{*}(-q) \). So, instead of (24), we should use:

\[
u(q,\lambda) D_{2}(q) u(-q,\lambda) = \sum_{k,\mu} f_{k,\mu} \Delta \varepsilon_{k,\mu} (k' = k + q) + \sum_{k,\mu} f_{k,\mu} \Delta \varepsilon_{k,\mu} (k' = k - q)
\]  
(25)

Notice here for crystals with inversion symmetry, the two terms on the right are equal. From equation (19) it is easy to verify the identity \( \gamma^{H}_{\nu,\nu'} = -[\gamma^{H}_{\nu',\nu}]^{*} \), then, equation (22) shows \( g_{k',\mu';k,\mu} = [\gamma^{H}_{\nu,\nu'}]^{*} \). Use this identity, also notice \( \sum_{k,\mu} f_{k,\mu} \Delta \varepsilon_{k,\mu} = \sum_{k+q,\mu} f_{k+q,\mu} \Delta \varepsilon_{k+q,\mu} \), we can combine
equations (21) and (25), and reach the expression for $D_2$:

$$D_2^{\alpha, \beta}(q) = \sum_{k, \mu} \frac{f_{k, \mu}^* f_{k', \mu'}}{\epsilon_{k, \mu} - \epsilon_{k', \mu'}} g^{\alpha, \beta}_{k', \mu'; k, \mu} g_{k, \mu; k', \mu'}$$  \hspace{1cm} (27)
IX. ACKNOWLEDGMENTS

I would like to express my deepest gratitude to Dr. Bruce N. Harmon, who, as my major professor, has guided me through the whole course of my graduate study. His support and encouragement have made my work and study in Iowa State University most fruitful and enjoyable.

I am most grateful to Dr. Kai-Ming Ho for his invaluable helps and important contributions in many projects I have worked on.

Dr. Werner Weber from KfK, West Germany deserves a special acknowledgment. Part of this thesis work was done in KfK under his supervision. I have benefited a lot from his deep insight on many field of physics, and his hospitality made my seven months stay in Karlsruhe most pleasant.

I sincerely thank the other members of my thesis committee: Dr. J. P. Vary, Dr. Marshall Luban, Dr. E. L. Wolf, Dr. B. C. Carlson, Dr. C. Stassis, Dr. B. L. Young, and Dr. John C. Hill. I also owe a special debt to Dr. C.-T. Chan for his helpful comments and suggestions.

I would like to acknowledge the indispensable support from the Physics Department and Ames Laboratory during the five years of my graduate career. I appreciate all the faculty and staff members of the Physics Department for their friendly helps.

This thesis is dedicated to my parents. They may not understand the subject, but they certainly understand me better than anyone else.