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Crystal Dynamics of Lithium Based on the Pseudopotential Technique

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The lattice dynamics of bcc lithium have been studied on the basis of a two-parameter model potential proposed by Krasko and Gurskii. A calculation of phonon frequencies, specific heat, and Debye temperature gives a reasonably good agreement with the experimental results.

I. INTRODUCTION

The lattice dynamics of metals have received remarkable theoretical and experimental attention in present years. The neutron diffraction techniques have produced a wealth of data on the vibration spectra of solids, requiring a serious confrontation between theory and experiment. Out of these solids Li, an alkali metal, is the simplest from the theoretical point of view. The ionic size is very small compared with the interionic separations. The conduction electrons can be considered almost free. The Fermi surface is believed on both theoretical and experimental grounds not to be far from spherical. The metal undergoes a Martensitic type[1] of phase transformation into a hexagonal-closed-packed form. This transformation produces a lot of difficulties to the experimental and theoretical investigators. This is one of the reasons for the lack of literature on this metal.

For the first time, Toya[2] calculated the phonon frequencies of Na using the Hartree-Fock method. Dayal and Srivastava[3] made a significant improvement on his results by introducing a slight modification. Several calculations on the pseudopotential approach[4-9] have added considerably to the physical understanding of the crystal dynamics of metals. Recently Wallace[10-12] has calculated the phonon frequencies, binding energies, and Grüneisen parameters for Na, K, and Li using Harrison's modified pseudopotential with considerable success. Gupta and Tripathi[13,14] introduced an exponential term in the Harrison pseudopotential and calculated the phonon frequencies and binding energies with good agreement. Introduction of an exponential term in their potential makes convergence of their series more rapid than those of Wallace. However, these calculations have either given results in slight disagreement with the experiment, or involved extensive fitting of parameters to the measured frequencies. Also these model potentials need an extra exponential term[13-15] to cause the series to converge rapidly.

To overcome these difficulties a model potential was proposed by Krasko and Gurskii,[16] which was used to calculate the crystal stability of some simple metals.[17] It was, therefore, thought worthwhile to treat lithium metal on this model. The values of model parameters are taken from the paper of Gurskii and Krasko.[18] It is seen that our theoretical results are quite reasonable, which confirms the realistic nature of the proposed model potential.

II. GENERAL FORMULATION

The equations of motion for the atoms in a monatomic bcc crystal and the reduction of these equations to a dynamical matrix whose eigenvalues are proportional to the squares of the normal-mode frequencies lead to a 3×3 determinantal equation of the form

$$\left|D_{\alpha\beta}(q) - M\omega^2 I\right| = 0 , \tag{1}$$

where M is the mass of the atom and I is the 3×3 unit matrix. The elements of the dynamical matrix $D_{\alpha\beta}$ are usually represented as a sum of three

TABLE I. Data used in the calculations (a.u.) along with the values of ξ calculated from Nozières-Pines (NP) and Geldart-Vosko (GV) expressions.

Metal	Ω_0	a	r_c	z	r_s	k_F	ξ	ξ_{NP}	ξ_{GV}
Li	143.6	5.95	0.36	1	3.192	0.596	1.901	1.871	1.733

terms $[xy]^C$, $[xy]^R$, and $[xy]^E$. The first two terms represent the contributions from Coulomb and non-Coulomb ion-ion interactions, while the third term is due to the conduction electrons.

The expressions for electrostatic coupling coefficient $[xy]^C$ have been derived by Kellermann.[19] The numerical values for bcc crystals have been taken from the paper of Srivastava and Srivastava.[20] The Born-Mayer-exchange repulsive coupling coefficient $[xy]^R$ may be calculated on the usual lines.[2,3] However, the contribution due to this term is small and has been assumed to be negligible here. The most important term $[xy]^E$ arises from the screening of the ionic vibrations by the conduction electrons and is given by

$$[xy]^E = \frac{2z}{nM}\left[\sum_h (q_x+h_x)(q_y+h_y)F(|\vec{q}+\vec{h}|) - \sum_{h\neq 0} h_x h_y F(|\vec{h}|)\right], \quad (2)$$

where n denotes the number of ions in the primitive cell, M is the mass of the ion, z is the valence of the ion, $\vec{h}$ is a reciprocal-lattice vector, and the function F is called the energy–wave-number characteristic.

Following Krasko and Gurskii, we write the model pseudopotential in the form

$$W_0(r) = z\left(\frac{e^{-r/r_c}-1}{r} + \frac{a}{r_c}e^{-r/r_c}\right). \quad (3)$$

Its Fourier transform is written as

$$W_0(\vec{q}) = \frac{4\pi z}{\Omega_0 q^2}\,\frac{(2a-1)(qr_c)^2-1}{[(qr_c)^2+1]^2}, \quad (4)$$

where Ω_0 represents the atomic volume, and a and r_c denote the model parameter. The energy–wave-number characteristic may be written as

$$F(\vec{q}) = -\frac{\Omega_0 q^2}{8\pi e^2}\,|W_0(q)^2|\,\frac{\epsilon^*(\vec{q})-1}{\epsilon^*(\vec{q})[1+f(q)]}, \quad (5)$$

where $\epsilon^*(\vec{q})$ is the modified Hartree dielectric function which also takes into account the contributions from the exchange and correlation effects of conduction electron as suggested by Hubbard[21] and by Sham.[6] $\epsilon^*(\vec{q})$ is then defined by

$$\epsilon^*(\vec{q}) = 1 + \frac{1}{\pi q^2}\left(2k_F + \frac{(2k_F)^2-q^2}{2q}\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right) \times\left(1-\frac{1}{2}\,\frac{q^2}{q^2+\xi k_F^2}\right), \quad (6)$$

where k_F is the Fermi wave vector and ξ represents the exchange and correlation parameter. In some recent calculations,[22] ξ was computed from the compressibility of an electron gas. This leads to

$$\xi_{GV} = 2/[1+0.153\,(\pi a_0 k_F)^{-1}], \quad (7)$$

where a_0 is the Bohr radius.

According to Nozières and Pines,[23] the parameter takes the form

$$\xi_{NP} = 0.916/(0.458+0.012 r_s), \quad (8)$$

where r_s is the radius of the Wigner-Seitz sphere in the unit of a_0.

Since the real form of such correction is unknown at present, and there is much difference between the values of ξ calculated by the above two procedures, we have taken ξ as a variable parameter. (See Table I.)

III. NUMERICAL COMPUTATION OF PHONON FREQUENCIES, SPECIFIC HEAT, AND DEBYE TEMPERATURES

In order to keep the computation within limits, the Brillouin zone has been divided into a mesh of only 1000 equal parts. Owing to Born's cyclic boundary condition and the symmetry consideration of the lattice, the 1000 points reduce to only 47, including the origin, lying within $\frac{1}{47}$ part of the Brillouin zone. The 3000 frequencies corresponding to 1000 points in the zone are obtained by solving the secular determinant for 47 wave vectors lying within an irreducible element of the Brillouin zone.

The specific heats have been calculated by Blackman's sampling technique.[24] For this pur-

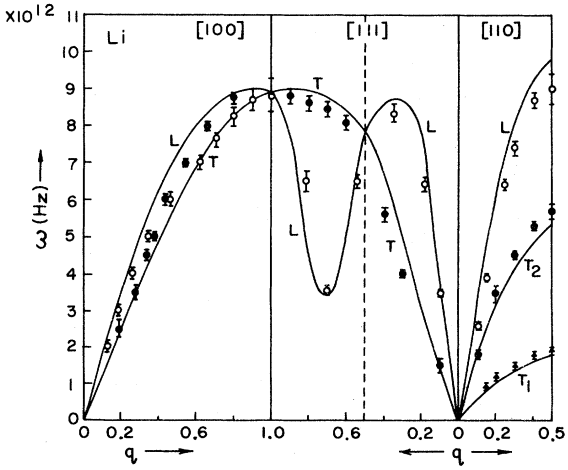

FIG. 1. Comparison of calculated and measured phonon frequencies for Li. The calculated curves are shown by solid lines, while the open and closed circles represent the data of Ref. 25.

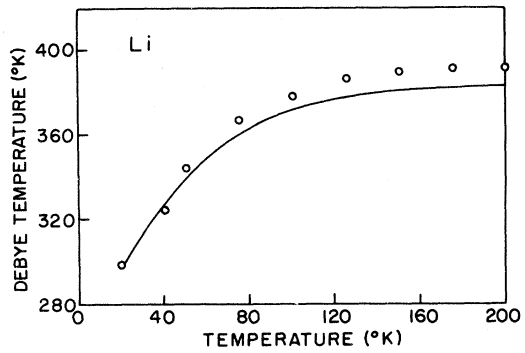

FIG. 2. Comparison of calculated and measured Debye temperature for Li. The calculated curve is shown by the solid line, while the circle represents the data of Ref. 25.

pose, the frequencies were divided into intervals of 0.5×10^{12} Hz, and the specific heats were evaluated from Einstein's function corresponding to the midpoint of each interval. These values of specific heats were converted into the corresponding Debye temperature Θ.

IV. RESULT AND DISCUSSION

The theoretical phonon dispersion curves along the three principal symmetry directions are drawn and presented in Fig. 1. It is seen that our theoretical curves are in satisfactory agreement with the neutron scattering results due to Smith *et al.*[25] In the [110] direction the longitudinal branch is nearly 8% higher than the experimental one. The experimental phonon dispersion curve of lithium, unlike that of other alkali metals, shows that the transverse branch crosses over the longitudinal branch and then becomes higher than the longitudinal branch in the [100] direction. However, we are unable to predict this peculiarity with our model potential.

The theoretical Θ-T curve for lithium is shown in Fig. 2 along with the experimental neutron data due to Smith *et al.*[25] The figure shows that our theoretical curve is in good agreement below 50 °K. In the very-low-temperature range a rigorous comparison between the experimental and theoretical Θ values is not meaningful, owing to the change in the crystal structure. This transformation causes unusual deviations in the calorimetric Debye temperature and makes a rigorous comparison based on the cubic structure rather doubtful. The sampling technique can give accurate values of C_v only when the number of frequencies falling in each frequency interval is fairly large.

V. SUMMARY AND CONCLUSIONS

The discrepancies in the theoretical and the experimental results may be attributed to the approximations adopted in the analysis.

(i) The uncertainty lies in the contribution of the exchange and correlation effects which differ in different theories.[6,21–23]

(ii) The neglect of higher-order pseudopotential terms in the dynamical matrix may affect the results significantly.[8,26]

(iii) We have assumed that the contribution due to Born-Mayer-exchange repulsion is small and negligible in this case. However, this assumption may affect the results slightly.[10,11]

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Ultrasonic Attenuation in Copper, Silver, and Gold

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Second- and third-order elastic-constant data have been used to determine the Grüneisen mode γ $\langle\gamma\rangle$, average-square Grüneisen constant $\langle\gamma^2\rangle$, and nonlinear constant D for Cu, Ag, and Au. The attenuation suffered by longitudinal ultrasonic waves propagating in the $\langle 100\rangle$ and $\langle 110\rangle$ directions and transverse waves polarized along $\langle 100\rangle$ and $\langle 1\bar{1}0\rangle$, owing to the phonon viscosity and thermoelastic phenomena, have been evaluated for the three metals at 293 °K. The phonon viscosity and dislocation drag along the $\langle 100\rangle$ and $\langle 1\bar{1}0\rangle$ directions are also discussed.

INTRODUCTION

Thermal attenuation of ultrasonic waves, particularly the part arising because of the interaction of waves with phonon gas, i.e., the phenomenon of phonon viscosity and the dislocation drag, provide a good probe[1] for the study of dislocations in solids. Ultrasonic attenuation in some dielectric and other crystals has been extensively studied in the recent past. The interaction of acoustic-wave phonons with thermal phonons accounts for a dominant portion of this attenuation. Thermal-phonon relaxation time τ_{th} decreases with an increase in temperature and generally at room temperature $\tau_{th} \ll 1/\omega$, where ω is the angular frequency of the acoustic wave.[2] Hence the interaction between various phonon modes becomes insignificant, and a statistical model of phonon gas having macroscopic parameters, which may be varied by sound energy, is described. The two well-known absorptions in this region are (i) phonon viscosity loss (Akhieser loss)[3] occurring because of the relaxational flow of thermal energy among various phonon branches at different temperatures and (ii) thermoelastic attenuation arising from the thermal conduction between the compressed and expanded parts of the acoustic waves. For shear-wave propagation, the volume remains intact and there is no heating effect. Hence the thermoelastic loss is absent in this case. The phonon viscosity in solids, which is the analog of shear viscosity in liquids, damps the motion of both the types of dislocations (screw and edge dislocations) in a crystal.[1] This damping is represented by the drag coefficient B. The acoustic attenuation, phonon viscosity, and drag coefficient are theoretically predicted for Cu, Ag, and Au at 293 °K.

THEORY

The expression for the acoustic attenuation produced because of the phonon-viscosity effect for longitudinal and shear ultrasonic waves are, respectively,

$$\alpha_l = \frac{E_0\omega^2(D_l/3)\tau_l}{2\rho V_l^3}, \tag{1}$$

$$\alpha_s = \frac{E_0\omega^2(D_s/3)\tau_s}{2\rho V_s^3}, \tag{2}$$

where the condition $\omega\tau \ll 1$ has already been assumed. Here E_0 is thermal energy density, ω is angular frequency, ρ is density, and V is the velocity of ultrasonic wave. The subscripts l and s represent longitudinal and shear. The two relaxa-

TABLE I. Primary physical constants calculated for three Debye solids.

Metal	V_l (m/sec)	V_s (m/sec)	K (cal/sec cm °K)	C_v (10^7 erg/cm^3 °K)	E_0 (10^9 erg/cm^3)	τ_{th} (10^{-10} sec)
Cu	4322	2916	1.0057	3.307	6.673	0.345
Ag	3411	2079	0.7069	2.358	5.705	1.013
Au	3161	1467	0.9177	2.401	5.742	1.354