

Pseudopotential Calculation of Phonon Frequencies and Grüneisen Parameters for Lithium*

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Phonon frequencies and Grüneisen parameters are calculated from a local pseudopotential model for bcc lithium. Two pseudopotential parameters and a Born-Mayer repulsive potential parameter were adjusted to fit the measured crystal binding energy, lattice spacing, and compressibility; in this fitting procedure the Born-Mayer repulsive energy turned out to be essentially zero. The phonon frequencies are in good qualitative agreement with experiment, except that the crossing of longitudinal and transverse branches along the [001] direction is not reproduced by the theory. The Kohn anomalies are too small to be seen in the calculated phonon frequency curves, but are apparent in the Grüneisen-parameter curves.

I. INTRODUCTION

WE have recently used a local pseudopotential model to calculate lattice dynamical properties of sodium and potassium.¹ The same model is used here to calculate phonon frequencies and Grüneisen parameters for body-centered cubic (bcc) lithium. The calculations are described in Sec. II, and the results are presented and discussed in Sec. III.

II. DESCRIPTION OF CALCULATIONS

We follow exactly the theory described in Ref. 1. The total adiabatic potential is the sum of electrostatic interactions among the ions and conduction electrons, Born-Mayer repulsion between the ions, a local pseudopotential interaction between ion cores and conduction electrons, and conduction electron kinetic, exchange, and correlation energies. The Born-Mayer repulsion is represented by a potential $\varphi(r)$ between two ions separated by a distance r , where

$$\varphi(r) = \alpha e^{-\gamma r}, \quad (1)$$

and with α and γ adjustable positive parameters. The bare pseudopotential form factor w_{Bq} is represented by Harrison's² modified point-ion model, which contains two parameters β and ρ :

$$w_{Bq} = \frac{1}{\Omega_a} \left[-\frac{4\pi Z e^2}{q^2} + \frac{\beta}{(1+q^2\rho^2)^2} \right], \quad (2)$$

where Ω_a = volume per atom and Z = number of conduction electrons per ion.

The Born-Mayer repulsive potential parameters and the pseudopotential parameters were determined by fitting the theory to experimental values of the crystal binding energy, lattice spacing, and compressibility for bcc lithium at 100°K. This procedure is approximate in that we are using a zero-temperature theory and

neglecting the small vibrational energy at 100°K. The fitting calculations required α to be quite small, so we set $\alpha=0$. The resulting values of the parameters are

$$\begin{aligned} \alpha &= 0, \\ \beta &= 23 \text{ Ry } a_0^3, \\ \rho &= 0.33 a_0, \end{aligned} \quad (3)$$

where a_0 is the Bohr radius.

With the parameters so determined, we calculated the dynamical matrices $\mathbf{a}_{\mathbf{k}}$ for \mathbf{k} vectors along symmetry directions in the Brillouin zone. The eigenvalues of $\mathbf{a}_{\mathbf{k}}$ are $M\omega_{\mathbf{k}s}^2$, $s=1, 2, \text{ and } 3$, where M = mass of the ions, and $\omega_{\mathbf{k}s}$ = phonon circular frequencies. We also calculated the matrices which are volume derivatives of the $\mathbf{a}_{\mathbf{k}}$, and then obtained the phonon Grüneisen parameters $\gamma_{\mathbf{k}s}$ with the aid of the Hellmann-Feynman theorem.¹ The $\gamma_{\mathbf{k}s}$ are defined by

$$\gamma_{\mathbf{k}s} = -(d \ln \omega_{\mathbf{k}s} / d \ln \Omega_a). \quad (4)$$

The i, i' element of the matrix $\mathbf{a}_{\mathbf{k}}$, where $i, i' = x, y, \text{ and } z$, contains a contribution of the form¹

$$2\Sigma_Q F_{Q+k}(\mathbf{Q}+\mathbf{k})_i(\mathbf{Q}+\mathbf{k})_{i'}, \quad (5)$$

where Q are reciprocal lattice vectors and F_Q is the energy-wave-number characteristic. F_Q contains the Hartree dielectric function, which has weakly singular behavior at $Q=2k_F$, where k_F = Fermi wave-vector magnitude. This singular behavior gives rise to Kohn anomalies,³ which are wiggles in the curves of $\omega_{\mathbf{k}s}$ versus \mathbf{k} at points, where $|\mathbf{Q}+\mathbf{k}|=2k_F$ for some reciprocal lattice vector \mathbf{Q} . The Kohn anomalies are expected to be quite small in the alkali metals, since the band-structure contribution given by (5) is only a small part of the total dynamical matrix. However, the volume derivative of $\mathbf{a}_{\mathbf{k}}$ contains a contribution which is the volume derivative of (5). The singular behavior of the dielectric function is magnified in the volume derivative of F_Q , and hence the Kohn anomalies should be magnified in the curves of $\gamma_{\mathbf{k}s}$ versus \mathbf{k} .

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¹ D. C. Wallace, Phys. Rev. **176**, 832 (1968).

² W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

³ W. Kohn, Phys. Rev. Letters **2**, 393 (1959).

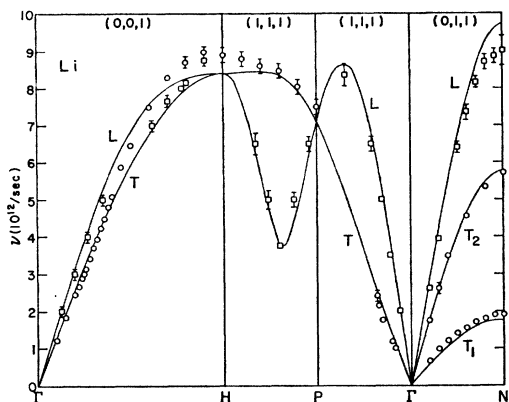


FIG. 1. Calculated phonon frequencies (solid lines) compared with the 98°K measurements of Smith *et al.* (Ref. 4) for lithium.

III. RESULTS AND DISCUSSION

Figure 1 compares the calculated phonon frequencies $\nu_{\mathbf{k}s} = (\omega_{\mathbf{k}s}/2\pi)$ for bcc lithium with the 98°K measurements of Smith *et al.*,⁴ at Oak Ridge. The agreement between theory and experiment is qualitatively good. However, the theory does not reproduce the crossing of longitudinal and transverse branches for \mathbf{k} along $[00\zeta]$. Furthermore, we have been unable to cause these branches to cross by varying the parameters of the theory. A similar result is found in our calculations for sodium and potassium.¹ The measured longitudinal-phonon-frequency curve along $[00\zeta]$ shows a dip in sodium and potassium at $\zeta \approx 0.7$; the calculations, on the other hand, showed no dips. Thus, the physical property which causes this behavior for the alkali metals is not contained in our simple model.

In this connection we have studied the convergence of lattice sums and reciprocal lattice sums which appear in the dynamical matrices.¹ The frequencies shown in Fig. 1 were calculated to an accuracy of 0.2%. We have found, however, that if inverse lattice sums such as given by (5) are not carried to good convergence, the longitudinal branch along $[00\zeta]$ will cross the transverse branch at $\zeta \approx 0.7$; the poor convergence is then apparent by a discrepancy between the two branches at $\zeta = 1$.

⁴ H. G. Smith, G. Dolling, R. M. Nicklow, P. R. Vijayaraghavan, and M. K. Wilkinson, *Colloque Ampère* (to be published). More extensive and much more refined data, shown in Fig. 1, are from H. G. Smith (private communication).

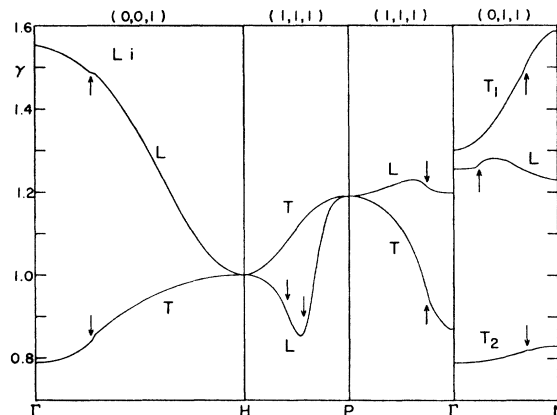


FIG. 2. Calculated Grüneisen parameters for lithium. Arrows show the places where Kohn anomalies should be observable.

The phonon frequencies have previously been calculated for lithium by Animalu *et al.*⁵ Although for this calculation the longitudinal mode falls below the transverse mode for \mathbf{k} along $[00\zeta]$, the frequencies are uniformly 50% higher than the measured values of Ref. 4.

The Grüneisen parameters calculated for bcc lithium are shown in Fig. 2. We note these curves show large variations over the zone, the $\gamma_{\mathbf{k}s}$ varying from ~ 0.8 to ~ 1.6 . We also find, as expected from the comments in Sec. II, that while the Kohn anomalies are not discernible on our phonon-frequency curves, they do show up on the Grüneisen-parameter curves. The nine places where Kohn anomalies should appear in the $\gamma_{\mathbf{k}s}$ curves are shown in Fig. 2; the anomalies may be seen in all cases except on the longitudinal branch along $[\zeta\zeta\zeta]$ at $\zeta = 0.716$ and at $\zeta = 0.794$. There are seven more places in Fig. 2 where anomalies might occur, but the magnitudes are either zero or extremely small for the $\gamma_{\mathbf{k}s}$ curves.

ACKNOWLEDGMENT

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⁵ A. O. E. Animalu, F. Bonsignori, and V. Bortolani, *Nuovo Cimento* **44**, 159 (1966).