

## Phonon Dispersion Relations of Body-Centered-Cubic Metals

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A model calculation for the lattice dynamics of sodium and potassium is presented. The total adiabatic potential is represented by an electrostatic interaction among the ions, and a screened electron-ion interaction. The ion-electron-ion potential is represented by a two-parameter model potential. A modified Hartree dielectric function is used to account for exchange and correlation effects. The calculated dispersion curves for sodium and potassium are compared with the experimental neutron-scattering data. The results are also discussed in the light of other theoretical models.

### INTRODUCTION

The theoretical explanation of neutron-diffraction results on phonon dispersion curves of single crystals has normally been based on several force-constant models, and also on pseudopotential formulation of electron-phonon interaction. Major work based on elastic-force models has been reported, by de Launay,<sup>1</sup> Bhatia,<sup>2</sup> and Sharma and Joshi<sup>3</sup> among others. Krebs<sup>4</sup> has calculated the dispersion curves for alkali metals based on a model which includes the central force for the nearest and next-nearest neighbors and the electron screening of the long-range Coulomb interaction between the point ions. These elastic-force models involve several arbitrary and independent parameters which, in several cases, do not necessarily bear a close relationship with the actual interactions involved in metals. Usually, the elastic constants are used to compute force constants between neighboring atoms. However, this greatly limits the usefulness of the approach because there are only a few independent elastic constants. As such, long-range interactions involving a large number of force constants can not be accounted for in this type of approach.

Toya<sup>5</sup> calculated the dispersion curves for sodium with considerable success, from first principles. This preceded the experimental measurements by a few years and proved to be in good agreement with them. In this approach, the Coulomb and Born-Mayer interactions are separated as usual.<sup>6</sup> To evaluate the contribution of the electrostatic potential to the dynamical matrix, Toya considered the change in the energy of conduction electrons in a perfect crystal in which a lattice vibration of wave vector  $\vec{q}$  is excited. This involves the matrix elements for the electron-phonon interaction. The constant energy of the phonon depends on repeated one-phonon process in which a phonon creates a electron-hole pair which recombines to emit a phonon with energy and wave vector unchanged. However, before combining, the phonon interacts

with other electrons. The matrix elements involve the Fourier transform of the gradient of the potential around the displaced ions and are evaluated on the basis of first-order perturbation theory. To account for the screening effect, the exchange interaction between conduction electrons is taken into account using Slater's approximation and introducing an exchange density which diminishes the effectiveness of the screening. The correlation effects in the motion of electrons were introduced somewhat empirically.

Several theories have been developed by Harrison<sup>7</sup> and others for the phonon spectra of simple (i. e., free-electron-like) metals using model potential and pseudopotential. For such metals it is convenient to describe the mechanical system of electrons and forces by means of pseudopotential perturbation theory. Several simple local pseudopotential models have been used to calculate the thermodynamic properties and reasonably good agreement with experiment has been obtained. For sodium and potassium, the spectra of Grüneisen parameters have been calculated by Wallace<sup>8</sup> and have been compared with experiment in the form of the thermal expansion coefficient as a function of temperature. Harrison's modified point-ion pseudopotential with two adjustable parameters was used and the Born-Mayer repulsion between ion cores was incorporated with one parameter. Using a local form of the Heine-Abarenkov model potential, the calculation of phonon frequencies of magnesium was performed by Pinder and Pynn.<sup>9</sup> The effective-mass correction suggested by Weaire<sup>10</sup> was incorporated in the model potential. It was found, however, that the calculated phonon frequencies do not agree well with those observed experimentally. Magnesium was also studied, along with sodium and potassium, by Schneider and Stoll,<sup>11</sup> who formulate the electron-phonon interaction by a pseudopotential method. Using the model pseudopotential determined from measured phonon dispersion curves, the electronic band structure, the Fermi surface, the cohesive

energy, crystal stability, the interatomic potential, and electrical conductivity have been studied in these metals.

The total crystal energy for simple metals may be divided into two parts, the electrostatic contribution of the direct Coulomb interaction of positive ions immersed in a uniform compensating background of negative charge and the other due to mutual interaction of the electrons with the screened ions. To calculate the band-structure energy for simple metals, the true ionic potentials are replaced by shallow model potential wells.<sup>12-14</sup> The energy of conduction electrons may be expanded as a perturbation series in the matrix element of model potential. We have obtained the phonon dispersion relations for body-centered-cubic lattice using a model potential to account for band-structure effects. The effects of the electron-ion interaction are taken into account in the usual way, but the effect of electron-electron interaction is accounted for by terms involving two parameters. Results are discussed for two specific cases of sodium and potassium in the light of available experimental and theoretical details.

#### THEORETICAL MODEL

The total potential of the lattice is separated into three components, viz., the electrostatic energy  $E_s$ , the ion core exchange energy  $E_e$ , and the band-structure energy  $E_{bs}$  which represents the screened electron-ion potential. The long-range nature of the Coulomb potential gives rise to the convergence problem in the dynamical matrix for  $E_s$ . Kellerman,<sup>15</sup> following Ewald<sup>16</sup> gave a method to evaluate the electrostatic part of the dynamical matrix for body-centered-cubic and face-centered-cubic lattices. The core exchange term, which is taken to be of the Born-Mayer type, is much smaller for metals owing to different core configurations<sup>17</sup> and is neglected here. Phillips and Kleinman<sup>18</sup> treated the effective electron-ion interaction using a pseudopotential which is small within the core and is treated by the perturbation method.

We evaluate the band-structure energy using a two-parameter model potential. The total ion potential can be separated into individual overlapping ion potentials centered upon individual ions at position  $\vec{r}_i$ ,

$$W(\vec{r}) = \sum_i w(|\vec{r} - \vec{r}_i|). \quad (1)$$

This when Fourier transformed gives

$$W_q = \frac{1}{\Omega} \sum_i e^{-i\vec{q} \cdot \vec{r}_i} \int e^{-i(\vec{k} + \vec{q}) \cdot \vec{r}} w(r) e^{+i\vec{k} \cdot \vec{r}} d^3r. \quad (2)$$

The structure factor  $S(\vec{q})$  is defined as

$$S(\vec{q}) = \frac{1}{N} \sum_i e^{-i\vec{q} \cdot \vec{r}_i} \quad (3)$$

and the form factor  $w_q$  as

$$w_q = \frac{1}{\Omega_0} \int e^{-i(\vec{k} + \vec{q}) \cdot \vec{r}} w(\vec{r}) e^{+i\vec{k} \cdot \vec{r}} d^3r. \quad (4)$$

$\Omega_0$  and  $\Omega$  are the atomic and crystal volumes, respectively. The electron-phonon matrix element is written as

$$W_q = \langle \vec{K} + \vec{q} | w(\vec{r}) | \vec{K} \rangle = S(\vec{q}) w_q. \quad (5)$$

For  $w(\vec{r})$  we adopt the model potential of the form

$$w(\vec{r}) = -\frac{Ze^2}{r} + \left( \frac{Ze^2}{r} + \beta \right) e^{-\alpha r}. \quad (6)$$

$\alpha, \beta$  are two parameters. The Fourier transform of the above potential gives

$$w_q = -\frac{1}{\Omega_0} \frac{4\pi Ze^2}{q^2 + \alpha^2} \left( -\frac{\alpha^2}{q^2} + \frac{\alpha\beta}{q^2 + \alpha^2} \right). \quad (7)$$

The effect of screening on band-structure energy was first discussed by Bardeen<sup>19</sup> who assumed that each ion potential is screened independently. Taking this into consideration, the first-order matrix element of the screening potential comes out as

$$W_q \left( \frac{1}{\epsilon(q)} - 1 \right),$$

where  $\epsilon(q)$  is the Hartree dielectric function for the noninteracting electron gas and is given by

$$\epsilon(q) = 1 + S_0(q)/q^2, \quad (8)$$

where

$$S_0(q) = \frac{2mZe^2k_F}{\pi\hbar^2} \left[ 1 + \left( \frac{4k_F^2 - q^2}{4k_F q} \right) \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right], \quad (9)$$

$k_F$  is the Fermi wave vector.

However, in order to introduce the exchange and correlation effects in the electron-electron interaction, Hubbard,<sup>20</sup> Sham,<sup>21</sup> and Geldart and Vosko<sup>22</sup> suggested various modifications to the Hartree dielectric function. In the scheme of Geldart and Vosko one writes

$$\epsilon(q) = 1 + S_V/q^2, \quad (10)$$

where

$$S_V = S_0(q)/[1 - f(q)S_0(q)]. \quad (11)$$

The function  $f(q)$  is defined by

$$f(q) = 1/2(q^2 + \xi k_F^2) \quad (12)$$

and  $\xi$  is a function of electron density only.

The expression for  $E_{bs}$  may be written as<sup>7</sup>

$$E_{bs} = \sum_q' S^*(q) S(q) F(q), \quad (13)$$

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

$$F(q) = -\frac{\Omega_0 q^2}{8\pi Z e^2} \left| w_q \right|^2 \left( \frac{\epsilon(q) - 1}{\epsilon(q)} \right). \quad (14)$$

When exchange and correlation effects, as mentioned

earlier, are introduced, then

$$\frac{\epsilon(q) - 1}{\epsilon(q)} = \frac{S_0(q) |q^2}{1 + S_0(q)(1 - \xi q^2) |q^2} \quad (15)$$

Electron interaction, however, makes  $E_{\text{bs}}$  slightly more negative. The parameter  $\xi$  in some recent calculations<sup>22</sup> is computed from the compressibility of an electron gas. This leads to

$$\xi = 2/[1 + 0.153(\pi a_0 k_F)^{-1}], \quad (16)$$

$a_0$  being the Bohr radius.

The secular determinant for calculating phonon frequencies is obtained in the usual way,

$$|D_{\alpha\beta}(q) - \omega^2 m I| = 0, \quad (17)$$

where  $m$  is the mass of the atom,  $I$  is the unitary matrix, and  $\omega$  is the circular frequency. In this approach the dynamical matrix consists of two major contributions, viz.,  $D_{\alpha\beta}^C(q)$  due to electrostatic energy between the ions, and  $D_{\alpha\beta}^E(q)$  due to band-structure energy. Thus

$$D_{\alpha\beta}(q) = D_{\alpha\beta}^C(q) + D_{\alpha\beta}^E(q). \quad (18)$$

Expressions for  $D_{\alpha\beta}^C(q)$  in the case of a body-centered-cubic lattice are taken from Kellerman's work:

$$D_{\alpha\beta}^C(q) = Ne^2 \left( \frac{4\pi}{3} \delta_{\alpha\beta} + G_{\alpha\beta}(q) - H_{\alpha\beta}(q) - \frac{16}{3\sqrt{\pi}} \eta^3 \delta_{\alpha\beta} \right), \quad (19)$$

where

$$G_{\alpha\beta}(q) = 4\pi \sum_H \left[ \frac{(\vec{q} + \vec{H})_\alpha (\vec{q} + \vec{H})_\beta}{|\vec{q} + \vec{H}|^2} \right] e^{-|\vec{q} + \vec{H}|^2 / 4\eta^2}$$

and

$$H_{\alpha\beta}(q) = 4 \sum_{l \neq 0} \left[ -f(l) \delta_{\alpha\beta} + g(l) \frac{l_\alpha l_\beta}{l^3} \right] \cos(\vec{q} \cdot \vec{l}),$$

with

$$f(l) = \frac{2}{\sqrt{\pi}} \frac{\eta}{l^3} e^{-\eta^2 l^2} + \frac{\text{erfc}(\eta l)}{l^3},$$

$$g(l) = \frac{4}{\sqrt{\pi}} \eta^2 e^{-\eta^2 l^2} + 3f(l),$$

and

$$\text{erfc}(Z) = \frac{2}{\sqrt{\pi}} \int_Z^\infty e^{-t^2} dt.$$

$\eta$  is a parameter chosen to make both the series  $\sum_H$  and  $\sum_{l \neq 0}$  rapidly convergent,

$$H = |\vec{H}| = (H_x^2 + H_y^2 + H_z^2)^{1/2}$$

and

$$l = |\vec{l}| = (l_x^2 + l_y^2 + l_z^2)^{1/2}, \quad |\vec{q}| = a/\lambda = a|\vec{k}|,$$

and is the lattice constant of the direct cell ( $H_x, H_y, H_z$ ), and  $(l_x, l_y, l_z)$  cover all sets of integers so that for a body-centered lattice  $(l_x, l_y, l_z)$  are either all odd or all even and  $\sum_x H_x$  is even.

The change in the band-structure energy caused by a periodic disturbance  $q$  is calculated by expanding the structure factor and retaining terms only up to the second order in the amplitudes of normal coordinates. The resulting elements of the dynamical matrix are

$$D_{\alpha\beta}^E(q) = \frac{1}{\Omega_0} \left( \sum_H (\vec{q} + \vec{H})_\alpha (\vec{q} + \vec{H})_\beta F(\vec{q} + \vec{H}) \right)$$

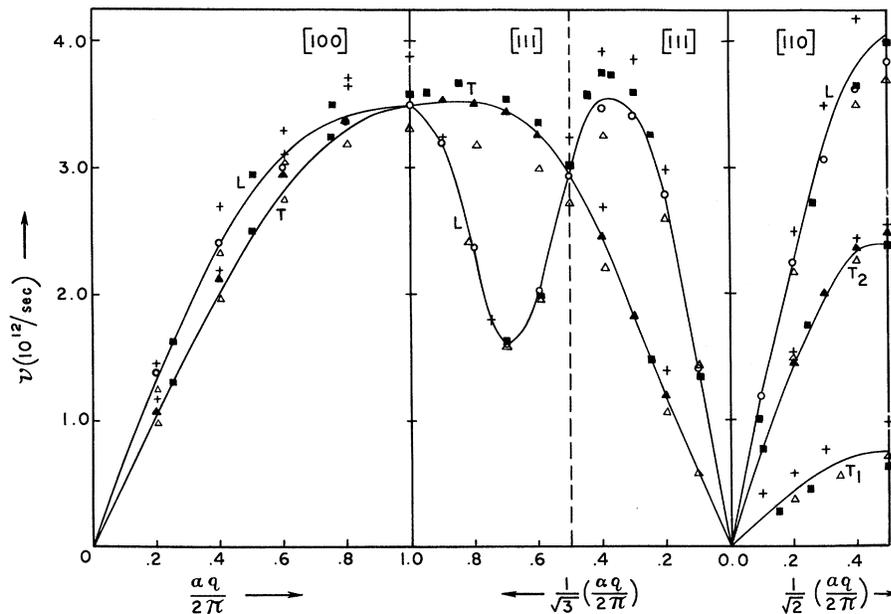


FIG. 1. Phonon dispersion curve for sodium. Experimental points for longitudinal branches (open circle) and transverse branches (solid triangle) along (100), (111), and (110) are also shown, along with the results of Sham (open triangle), Ho (solid square), and Vosko (plus).

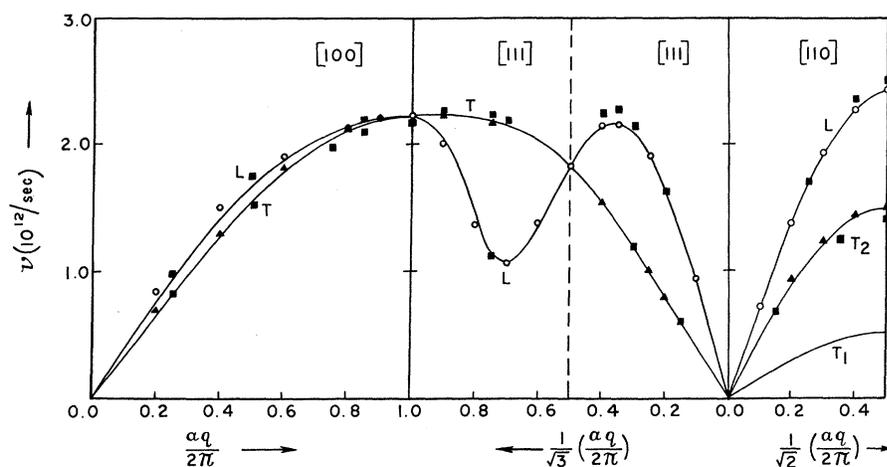


FIG. 2. Phonon dispersion curves for potassium. Experimental points for longitudinal branches (open circle) and transverse branches (solid triangle) along (100), (111), and (110) symmetry directions are also shown for comparison along with the results obtained by Ho (solid square).

$$-\sum_{H \neq 0} \vec{H}_\alpha \vec{H}_\beta F(\vec{H}) \quad (20)$$

### RESULTS

The potential of the electron due to the presence of the other electrons has been taken as

$$Ze^2/r + \beta,$$

which, of course, gives a constant value of the potential for large values of  $r$ . The convergence problem in the calculation of matrix element  $D_{\alpha\beta}^E(q)$  due to oscillations of Fourier transform of the actual potential  $w(\vec{r})$  at large  $k$  values has been eliminated by the multiplication of a factor  $e^{-\alpha r}$ . However, to ensure proper convergence for lattice sums, we have included 683 reciprocal-lattice vectors. The parameters  $\alpha$  and  $\beta$  have been determined by fitting the experimental quantities on the right-hand side of the following equations:

$$U/N = -U_b - U_i, \quad (21)$$

$$\Omega_0 \left( \frac{d(U/N)}{d\Omega_0} \right) = -\Omega_0 P = 0. \quad (22)$$

Here  $U_b$  is the binding energy per atom of the metal and the ionization energy of each ion is  $U_i$ . The zero-point vibrational energy has been neglected, since this is about 0.001 Ry for Na and K. The experimental values of the binding energy for Na and K are 0.08 and 0.07 Ry, respectively, while the ionization energies are 0.38 and 0.32 Ry, respectively. By slight adjustment of these parameters we can bring the calculated curves with the measurements within experimental errors. The values of  $\alpha$  and  $\beta$  obtained in the present work are

2 and 10, respectively, for sodium and 2 and 18 for potassium.

The parameter  $\xi$  as calculated using Eq. (16) comes out to be 1.86 for sodium and 1.82 for potassium. Ho<sup>23</sup> has taken  $\xi$  as an adjustable parameter and his values are 1.78 for sodium and 1.87 for potassium.

In Figs. 1 and 2 we have plotted the dispersion curves along the symmetry direction [100], [111], and [110] for sodium and potassium. We have compared our results with those of Ho, who has formed the screened potential by linearly screening a Heine-Abarenkov-type<sup>12</sup> ion potential. To include approximately the exchange and correlation effects, a modified Hartree dielectric function was used and the model parameters were determined using experimental elastic constants. In case of sodium, we have also plotted the results obtained by Vosko and Sham. In sodium, along the [111] symmetry direction the agreement with experimental results in our case is distinctly better. Along the other two symmetry directions, the degree of agreement is the same. In potassium, better agreement has been obtained along the [110] direction.

Investigations are in progress for determining other related properties of these and certain other metals and will be reported in due course.

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## Effect of the Dielectric Function on the Phonon Spectrum of Magnesium<sup>†</sup>

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In this paper we demonstrate that an excellent fit to the phonon spectrum of a simple metal, magnesium, may be obtained with a local pseudopotential containing only two adjustable parameters. We compare the spectrum obtained with a fixed pseudopotential using different dielectric response functions. The Hubbard dielectric function yields phonon frequencies 30% greater than the Kleinman-Langreth one, with the random-phase approximation yielding intermediate frequencies.

### I. INTRODUCTION

There have recently appeared a plethora of calculations of the phonon spectrum of magnesium. The first to appear, that of Roy and Venkataraman,<sup>1</sup> unfortunately contained errors in the secular determinant. Schneider and Stoll<sup>2</sup> obtained a nearly perfect fit to the experimental curves in the [0001] and [01 $\bar{1}$ 0] wave-vector directions using a pseudopotential containing four adjustable parameters, whereas Brovman, Kagan, and Holas<sup>3</sup> needed to introduce, in addition to the pseudopotential, four short-range force constant parameters to obtain a good fit. Pindor and Pynn<sup>4</sup> used the optimized model potential (whose parameters are obtained by fitting the atomic spectra and not adjusted to fit the phonon spectrum) to obtain a poor fit to the phonon spectrum. Gilat, Rizzi, and Cubiotti<sup>5</sup> obtained a nearly perfect fit using the same method by arbitrarily replacing the electron mass with an effective mass  $m^* = 1.60m$ .

Shaw and Pynn,<sup>6</sup> taking exchange and correlation into account, effected a large improvement on the results of Pindor and Pynn<sup>4</sup> but still did not achieve a perfect fit to the experimental spectrum. Most recently, Prakash and Joski,<sup>7</sup> using a "first-principles" potential containing a Kohn-Sham<sup>8</sup> exchange potential screened by a procedure<sup>9</sup> we believe to be incorrect,<sup>10</sup> obtained a poor fit to the experimental phonon spectrum.

A secondary purpose of this paper is to demonstrate that a very good fit of phonon spectrum of magnesium can be obtained using a local pseudopotential containing only two adjustable parameters. When such a local pseudopotential is used, all exchange and correlation interactions between conduction electrons enter the calculation through the dielectric response function. It is the primary purpose of this paper to study the effect of various dielectric functions on the phonon dispersion curves. Because there is no way of knowing the "correct"