Lattice Dynamical Properties of Potassium

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The phonon dispersion, temperature dependence of the Debye temperature, Debye-Waller factor, and Grüneisen parameter of potassium are calculated using a realistic lattice dynamical model. The model considers short range pairwise forces effective upto second neighbors and an improved electron ion interaction on the lines of Bhatia. An equilibrium condition, which preserves the crystal stability, is obtained. The theoretical results are found to be in good agreement with the experimental values.

1. Introduction

Potassium is believed to represent in many respects the prototype of a free electron metal and, therefore, should confirm most closely to an idealized metallic model of free conduction electrons distributed with substantially spherical symmetry. The distance between the ion core centres compared to the actual size of the cores is large so that the contribution to the binding energy from the short range interaction is small. The Fermi surface of this monovalent metal deviates from sphericity by 0.1% in radius [1, 2] and lies entirely within the first Brillouin zone. The experimental results on elastic constants [3] and their pressure derivatives [4], specific heat [5−9], thermal expansion [10, 11], and de Haas-van Alphen measurements [12, 13] and their pressure variation [14] can be used to test the reasonableness of the interpretation in terms of the free electron model of this metal.

In the present paper, we consider a realistic lattice dynamic model, which incorporates ion-ion interaction through second neighbor pair potential [15] and the improved electron-ion interaction on the lines of Bhatia [15]. An equilibrium condition, which preserves the crystal stability, is obtained by considering the Fermi, exchange, and correlation energy of the conduction electrons. The present scheme has been utilized to compute the phonon dispersion, temperature dependence of equivalent Debye temperature, Debye-Waller factor, and Grüneisen parameter of potassium.

2. The Model

For ion-ion and electron-ion interactions, we follow our recent paper [15] and write the three equations of elastic constants and one zone boundary (ZB) frequency in [100] direction as:

$$a\,C_{11} = \tfrac{2}{3}(2A_1 + B_1) + 2B_2 + aK_e, \quad (1)$$
$$a\,C_{12} = \tfrac{2}{3}(B_1 - 4A_1 - 3A_2) + aK_e, \quad (2)$$
$$a\,C_{44} = \tfrac{2}{3}(2A_1 + B_1) + 2A_2, \quad (3)$$
$$m\,\pi^2\,\nu_T^2 = \tfrac{4}{3}(2A_1 + B_1), \quad (4)$$

where $A_j\,(=(1/r_j)\,(\mathrm{d}E^i/\mathrm{d}r_j))$ and $B_j\,(=\mathrm{d}^2E^i/\mathrm{d}r_j^2)$, with $j = 1, 2$, are respectively the tangential and radial pair potential force constants, E^i is the potential energy of the crystal corresponding to ion-ion interaction, S_i and C_i $(i = 1, 2, 3)$ are, respectively, $\mathrm{Sin}(\pi a k_i)$ and $\mathrm{Cos}(\pi a k_i)$, a is the lattice constant and K_e the bulk modulus of the electron gas. The potential energy E of the crystal is

$$E = E^i + E^e. \quad (5)$$

For lattice equilibrium the first derivative of (5) will vanish, i.e.,

$$(\mathrm{d}E^i/\mathrm{d}\Omega)_a - P^e = 0,$$
$$\text{where} \quad -P^e = \mathrm{d}E^e/\mathrm{d}\Omega, \quad (6)$$

where Ω is the crystal volume and P^e the electron pressure. Following Gellman and Brueckner [16], the Fermi, exchange and correlation parts of electron energy E^e can be written as

$$E^e = [2.21\,Z^{2/3}\,(r_0/a_0)^{-2} - 0.916\,Z^{1/3}\,(r_0/a_0)^{-1}$$
$$+ 0.622 \ln(r_0/a_0 Z^{1/3}) - 0.096]\,\mathrm{Ryd}. \quad (7)$$

The equilibrium condition (6) with the aid of (7) takes the form

$$A_1 + A_2 = \frac{27.2\,a}{\pi r_0} \tag{8}$$

$$\cdot \left[-\frac{4.41\,Z^{2/3}}{(r_0/a_0)^2} + \frac{0.916\,Z^{1/3}}{(r_0/a_0)} + 0.622\,Z^{-1/3} \right],$$

where a_0 is the Bohr radius, Z the chemical valence, and r_0 the inter electron spacing. The solution of (1−4) and (8) determines the unknown force constants in terms of the elastic constants and one ZB frequency.

3. Numerical Computation

Experimental values of the elastic constants and other parameters at 4.2 K used in the calculations are $C_{11} = 0.416$, $C_{12} = 0.341$, $C_{44} = 0.286$ (all in units of 10^{11} dyn cm^{-2} [3]), $a = 5.226$ Å, density $= 0.903$ g cm^{-3}, $\nu_T(100) = 2.21$ THz [17], and $(m^*/m) = 0.99$ [18]. The calculated values of the force constants are

$$A_1 = 11.0130, \quad B_1 = -19.6787,$$
$$A_2 = -0.0351, \quad B_2 = -21.7949,$$

and $aK_e = 44.1990$ (all in units of 10^3 dyn cm^{-1}).

These force constants are used to calculate frequency vs. wave vector dispersion relations along the principal symmetry directions. The lattice specific heat at constant volume and Debye-Waller (DW) factor are calculated as described earlier [15].

To calculate the Grüneisen parameter, we follow our earlier paper [19]. In the present scheme, the four force constants are related to three elastic constants and one ZB frequency. Hence to evaluate the microscopic Grüneisen parameter $\nu_{q,j}$ one must know the pressure derivative of both elastic constants and ZB frequency. As the pressure derivative of ZB frequency is not known, the four parameters (A_1, A_2, B_1, B_2) have been reduced to three (A_1, B_1, B_2) by taking a suitable ratio of A_1/A_2 which gives a better fit of our phonon dispersion curves with experiment. In the present calculations, both elastic constants and the lattice parameter were used at the respective temperature for which the computation is made. The temperature dependent values of the elastic constants and the lattice parameter habe been borrowed from Marquardt and Trivisonno [3] and Pearson [20] respectively. The pressure derivatives of the elastic constants dC_{ij}/dP at room temperature are taken from Smith and Smith [4], Suzuki et al. [21], Lincoln et al. [22] and Mathur and Sharma [23]. We have been compelled to use the room temperature values of dC_{ij}/dP, as the temperature variation of the dC_{ij}/dP values is not available.

4. Results and Discussion

We display our theoretical results for phonon dispersion along with the experimental measurements [17] in Figure 1. The agreement between theory and experiment is very good.

The lattice specific heat extracted from experiments [5−9] and our theoretical results are converted into equivalent Debye temperatures Θ. These
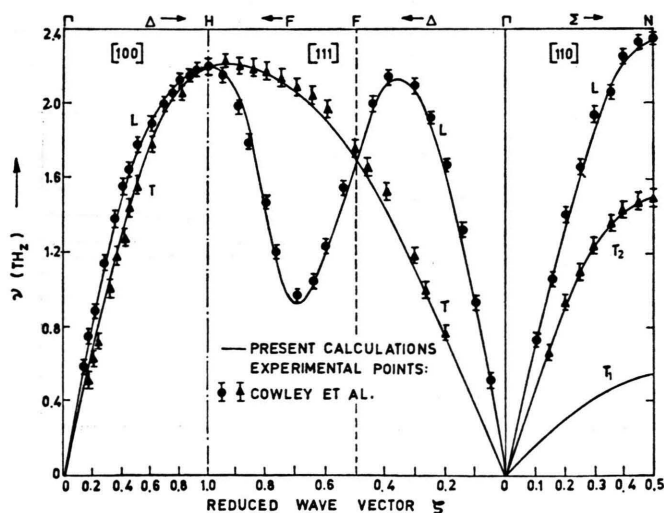

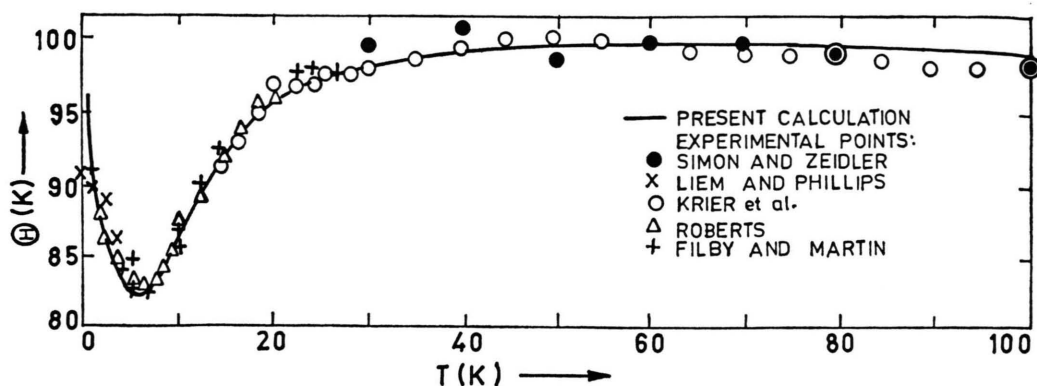Fig. 1. Phonon dispersion curves of potassium along symmetry directions.

Fig. 2. Equivalent Debye temperature of Potassium as a function of temperature.

are plotted in Figure 2. The theory exhibits good agreement with the experiments. In Fig. 3, the calculated DW factors as a function of temperature
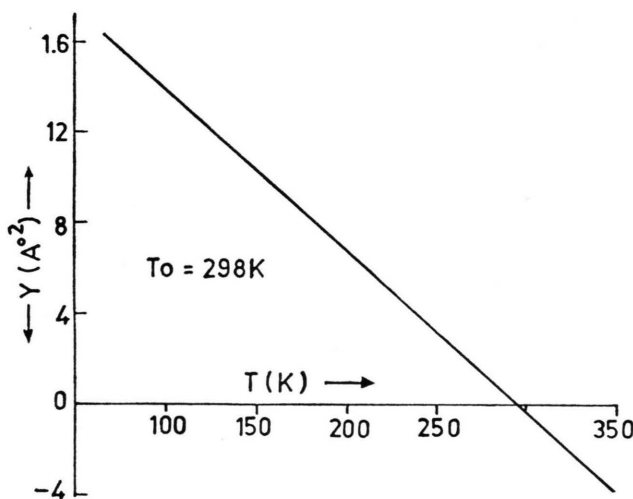

Fig. 3. Debye-Waller factor of potassium as a function of temperature.

are shown. Since no experimental or theoretical results are available, a comparative study was not possible. These results will act, however, as an information for experimental and theoretical workers and we feel that the present investigation will accelerate the future developments in this direction.

Figure 4 exhibits the calculated values of the Grüneisen parameter as a function of temperature. For comparison, we have also shown the values reported [24], and derived from experimental thermal expansion [10, 11] and specific heat [5, 8] data. It is shown from Fig. 4 that the general shape of the theoretical and experimental $\mathscr{V} - T/\Theta$ curves is similar in spite of the fact that the observed values of Monfort and Swenson [11], and Martin [24] show large scatter at certain points. The experiment of Schouten and Swenson [10] represents detailed and improved measurements. The theoretical results using Smith and Smith [4] $\mathrm{d}C_{ij}/\mathrm{d}P$ values show very good agreement with the measurements of Schouten and Swenson [10]. The theoret-
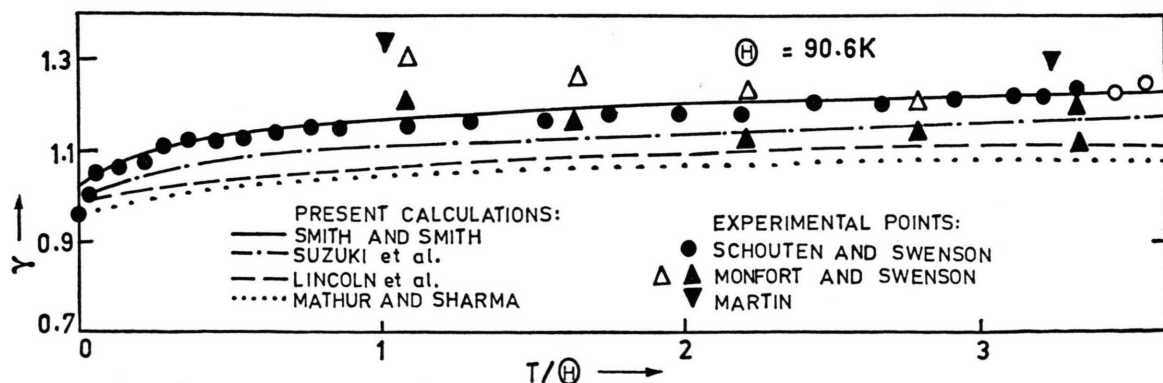

Fig. 4. Temperature variation of the Grüneisen parameter of potassium.

ical $\mathscr{V} - T/\Theta$ curves using dC_{ij}/dP values of Suzuki et al. [21], Lincoln et al. [22], and Mathur and Gupta [23] are slightly lower than the measurements of Schouten and Swenson. The present results are in better agreement than those reported earlier [19]. Our results corroborate Barron's [25] prediction that $\mathscr{V}$ remains constant to a few percent down to about $\Theta/3$, and below this temperature the uncertainty is relatively large; however $\mathscr{V}$ does decrease with falling temperature below about $\Theta/5$.

Barron [25] predicted for a cubic lattice a value of 0.3 for the difference between the high and low temperature limits for nearest neighbor central interaction and a decrease of this value when higher neighbors also interact. The present study lends support to this statement.

The present study demonstrates that the simple model provides a good overall understanding of the phonon spectrum and thermophysical properties of potassium.

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