PHYSICAL REVIEW B VOLUME 14, NUMBER 8 15 OCTOBER 1976

Thermal expansion of sodium and potassium*

V. K. Jindal and K. N. Pathak

Department of Physics, Panjab University, Chandigarh-160014, India

(Received 5 May 1976)

Thermal expansion for sodium and potassium has been calculated at all temperatures using realistic potentials, obtained from one-orthogonalized-plane-wave matrix elements and screening functions of Geldart and Taylor and of Vashishta and Singwi. No significant difference between the results from these two potentials has been found. The agreement with recent experimental results of Schouten and Swenson for potassium is found to be good. In the absence of appropriate experimental data for sodium, the theoretical results have been compared with the old data on polycrystalline sodium. These are found to be in qualitative agreement.

Recently the interionic potential for sodium[1-3] and potassium[3,4] has been calculated using one-orthogonalized-plane-wave matrix elements and the dielectric function of Geldart and Taylor[5,6] and of Vashishta and Singwi.[7] These potentials have been used to discuss various lattice-dynamical properties of these metals and are believed to be reliable with either of the two screening functions.[3] In order to see how good are these potentials for the calculation of anharmonic properties, we have used them to calculate the thermal-expansion coefficient for sodium and potassium at all temperatures. Both the screening functions give thermal-expansion results sufficiently close to each other. The results have been compared with experiments. The agreement is quite good for potassium for which exhaustive experimental data on the linear-thermal-expansion coefficient have been reported very recently by Schouten and Swenson.[8] For sodium no appropriate experimental data are available to test the predictions of our theoretical results.

The thermal expansion to the lowest order can be obtained from the potential energy after expressing it as a double power series in the strain parameters and phonon coordinates. After taking the thermal average and differentiating to get the condition for equilibrium, the thermal-expansion coefficient α can be finally written[9]

$$\alpha = \frac{1}{3BV} \sum_{\vec{q}j} \gamma(\vec{q}j) C_E(\vec{q}j), \tag{1}$$

where B is the bulk modulus, V is the volume of the crystal, $C_E(\vec{q}j)$ is the Einstein specific-heat function for the mode $(\vec{q}j)$, and $\gamma(\vec{q}j)$ is the Grüneisen constant. For the case of central forces with one atom per unit cell the expression for α takes the form

$$\alpha = -\frac{\hbar^2\beta^2 k}{9MBV} \sum_{\vec{q}j} \frac{e^{\beta\hbar\omega(\vec{q}j)}}{(e^{\beta\hbar\omega(\vec{q}j)}-1)^2} \sum_{l} \left[\frac{1}{r^l}\left(\phi'''(r^l) - \frac{\phi''(r^l)}{r^l} + \frac{\phi'(r^l)}{(r^l)^2}\right) \times \sum_{yz} e_y(\vec{q}j) e_z^*(\vec{q}j) yz \sin^2\frac{\vec{q}\cdot\vec{r}^l}{2} + \left(\phi''(r^l) - \frac{\phi'(r^l)}{r^l}\right)\sin^2\frac{\vec{q}\cdot\vec{r}^l}{2} \right]. \tag{2}$$

In the above equation, ϕ', ϕ'', and ϕ''' are the first, second, and third derivatives of the potential $\phi(r)$, evaluated at $r^l = (x^2+y^2+z^2)^{1/2}$. $\vec{e}(\vec{q}j)$ are the eigenvectors, and the bulk modulus B can be obtained from the static energy. It is given by

$$B = \frac{N}{18V} \sum_{l} r_l^2 \phi''(r^l) - 2 r_l \phi'(r^l). \tag{3}$$

The interionic potential needed to calculate the thermal expansion from Eq. (2) for sodium and potassium has been obtained from first principles.[3] This is long range and oscillatory and does not contain any adjustable parameter. The calculation of thermal expansion coefficient from Eqs. (2) and (3) involves summations over the first Brillouin zone and number of neighbors. We calculated our results with a mesh size of eight and summed over the reciprocal-lattice vectors of bcc structure in the irreducible part of the Brillouin zone. The eigenvalues and polarization vectors needed were obtained after diagonalizing the dynamical matrix by Jacobi method. We recalculated our results with a mesh size of six, corresponding to 216 points in the whole zone. The difference between the two mesh size results was less than 1%. The summation of the number of neighbors posed convergence problems. The bulk modulus converges very poorly. Even up to seventh neighbor, it oscillates by as much as 10%, for obvious

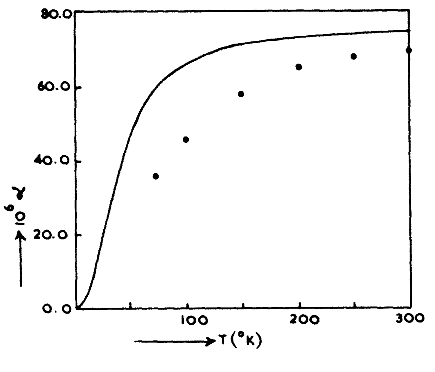

FIG. 1. Linear-thermal-expansion coefficient of sodium up to 300 °K. Experimental points for polycrystalline sodium are from Ref. 1.

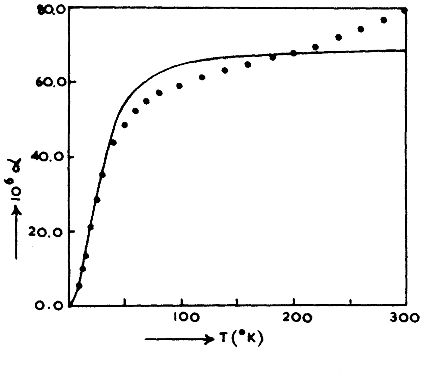

FIG. 2. Linear-thermal-expansion coefficient of potassium up to 300 °K. Experimental points are from Ref. 8.

reasons. As with the addition of every neighbor, the computer time increases sufficiently, we have not gone beyond seventh. If we give allowance for the poor convergence of bulk modulus by the amount they differ from experimental values, our results should be decreased by about 10% for sodium and about 3% for potassium. The results for the linear expansion coefficients at all temperatures up to 300 °K have been plotted in Figs. 1 and 2 for sodium and potassium using the potentials obtained from the one-orthogonalized-plane-wave matrix elements and the dielectric function of Vashishta and Singwi. The results obtained from Geldart and Taylor screening function do not differ more than 2%. In absence of the results of linear-thermal-expansion coefficient for single-crystal sodium, experimental results for polycrystalline sodium[10] have been used for comparison. Experimental points have been shown as filled circles. There are about 12% deviations in results for potassium over a small region around 100 and 300 °K. For higher temperatures, the expansion coefficient rises with temperature, indicating the necessity of taking into account higher-order anharmonic contributions to the thermal expansion. For sodium, there is a maximum deviation of 40% a major part of which is believed to be due to nonavailability of appropriate experimental data.

In this note, we have reported the results for the thermal-expansion coefficient for sodium and potassium using first-principle potentials. The results for potassium are more than satisfactory and a maximum deviation of 12% can be attributed partially to poor convergence of the lattice sums. In the high-temperature region, clearly, higher-order anharmonic effects can only take care of the rising portion of the curve. For sodium, deviations as large as 40% are noted. Although the reasons for the deviation in the results in case of potassium are also valid here, we however feel that the experimental numbers which are for polycrystalline sodium, may be quite off from those of single-crystal sodium.

---

[*] Work supported in part by NSF under Grant No. GF-36470.

[1] D. J. W. Geldart, R. Taylor, and Y. P. Varshni, Can. J. Phys. 48, 183 (1970).

[2] Z. S. Basinski, M. S. Duesbery, A. P. Pogany, R. Taylor, and Y. P. Varshni, Can. J. Phys. 48, 1480 (1970).

[3] V. K. Jindal, Can. J. Phys. 53, 1507 (1975).

[4] M. S. Duesbery and R. Taylor, Phys. Rev. B 8, 1372 (1973).

[5] D. J. W. Geldart and R. Taylor, Can. J. Phys. 48, 155 (1970).

[6] D. J. W. Geldart and R. Taylor, Can. J. Phys. 48, 167 (1970).

[7] P. Vashishta and K. S. Singwi, Phys. Rev. B 6, 875 (1972).

[8] D. R. Schouten and C. A. Swenson, Phys. Rev. B 10, 2175 (1974).

[9] R. A. Cowley, Rep. Prog. Phys. 31, 123 (1968).

[10] *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963), pp. 4–66.