JOURNAL OF SOLID STATE CHEMISTRY **60**, 262–263 (1985)

On the Relationship between Coefficients of Thermal Expansion and Heat Capacities of Simple Cubic Metals

P. MOHAZZABI* AND V. G. HARRIS

School of Engineering and Architecture, Tuskegee University,
Tuskegee, Alabama 36088

Received January 8, 1985; in revised form April 29, 1985

Recently (*1*), an inverse-power-type interatomic potential energy function was employed to calculate the ratio between the thermal expansion coefficient and heat capacity of simple metals. This ratio which is known to be a constant (*2*), independent of temperature, was then compared with the experimental values for several metals. Fair to good agreement was obtained between theory and experiment. However, as different interatomic potentials usually have a varying degree of success in explaining the properties of solids (*3*), we decided to attend to the same problem by applying another widely used potential energy function, the Morse potential, and compare the results.

Let ρ be a characteristic length in the crystal lattice such as the nearest neighbor distance, the lattice parameter, etc. The total potential energy of the lattice Φ, being a function of ρ, may be expanded in a power series of $\rho - \rho_0$, where ρ_0 is the value of ρ at absolute zero temperature. Expanding Φ to the fourth power of $\rho - \rho_0$ and applying the method developed previously (*1*), we find

$$\frac{\alpha}{C_p} = -\frac{\Phi_0'''}{2(\Phi_0'')^2\rho_0} \qquad (1)$$

where Φ_0'' and Φ_0''' are the second and third derivatives of Φ, respectively, evaluated at $\rho = \rho_0$.

Under the Morse potential energy function, the total lattice energy of N atoms is given by (*3*)

$$\Phi(a) = \frac{ND}{2} e^{2\lambda r_0} \sum_j e^{-2\lambda a M_j} - NDe^{\lambda r_0} \sum_j e^{-\lambda a M_j} \qquad (2)$$

where a, being the characteristic length for our calculations, is the half-cell distance for both bcc and fcc monatomic lattices. D, λ, and r_0 are the Morse potential parameters (*3*) and M_j is defined by $M_j = r_j/a$, where r_j is the distance from the reference atom to the jth atom.

With the aid of Eqs. (1) and (2), the values of α/C_p are calculated for several metals and listed in Table I. The lattice sums needed for the calculations are evaluated by the technique described in reference (*3*). The average experimental values of α/C_p over the temperature range of 25 to 1000 K (*4*) and those obtained from the inverse-power-type potential energy function (*1*) are also listed in Table I. However, for barium and the alkali metals the experimental data are available only for limited tempera-

---

* To whom correspondence is to be addressed.

0022-4596/85 $3.00

TABLE I

VALUES OF α/C_p IN UNITS OF 10^{-6} mole/cal: (a) CALCULATED FROM INVERSE-POWER-TYPE POTENTIAL; (b) CALCULATED FROM MORSE POTENTIAL; (c) AVERAGE EXPERIMENTAL

Metal	(a)	(b)	(c)
Pb	5.29	3.80	4.43
Ag	3.35	2.69	3.25
Ni	2.42	2.12	2.02
Cu	3.06	2.59	2.89
Al	3.21	3.27	4.14
Ca	6.36	5.40	3.37
Sr	6.83	5.79	—
Mo	1.36	1.12	0.97
W	1.07	0.91	0.75
Cr	2.23	2.05	1.36
Fe	2.49	2.15	1.86
Ba	6.29	6.10	2.06
K	20.93	14.68	11.60
Na	17.38	12.48	9.50
Cs	23.74	17.62	13.18
Rb	22.55	16.79	12.41

tures, especially those for barium and cesium which may contain large errors (*4*).

The results indicate that some improvements have been achieved with the Morse potential over the inverse-power-type potential energy function. This, however, is not surprising in light of the following facts (*3*): Unlike the Morse potential, the lattice sums are independent of the homogeneous deformations of the lattice in the case of inverse-power-type potential energy function. The energy of the lattice is not, therefore, coupled with the lattice geometry in the case of the latter potential. Furthermore, some bcc lattices are unstable under the inverse-power-type potential energy function. In fact, in the case of alkali metals, this potential leads to an infinite cohesive energy.

References

1. P. MOHAZZABI AND P. C. SHARMA, *J. Solid State Chem.* **52**, 244 (1984).

2. D. MCLACHLAN AND W. R. FOSTER, *J. Solid State Chem.* **20**, 257 (1977).

3. L. A. GIRIFALCO AND V. G. WEIZER, NASA Report No. 5 (1958).

4. D. E. GRAY (Coordinating Ed.), "American Institute of Physics Handbook," 3rd ed., pp. (4)106–(4)109, Table 4e-1 and pp. (4)120–(4)134, Table 4f-1, McGraw–Hill, New York (1972).