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Pressure derivatives of the isothermal bulk moduli of alkali metals

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The local-pseudopotential method proposed by Ashcroft and Langreth is used to calculate the isothermal bulk moduli and their first and second pressure derivatives for alkali metals. The results are compared with various experimental works. It suggests that the Grover-Getting-Kennedy representation might be the best model to be used in *P*-*V* data analysis.

I. INTRODUCTION

Recently, Grover, Getting, and Kennedy[1] (GGK) proposed a two-parameter equation of state of the form $\ln B = \ln B_0 + B_0'(\Delta V/V)$ for a large number of solids. Barsch and Chang[2] measured the pressure derivatives of the bulk moduli of cesium halides and discussed various models of empirical equations of state. Dunn and Ruoff[3] also studied the theoretical and some empirical equations of state. Among all these empirical representations of equations for solids, the isothermal bulk modulus and its pressure derivatives at zero pressure are often used as parameters which are determined from experiments. In the present paper, we have calculated the isothermal bulk moduli and their first and second pressure derivatives at zero pressure of lithium, sodium, potassium, and rubidium using the pseudopotential theory proposed by Ashcroft and Langreth.[4] The theoretical results are compared with the experimental measurements. A discussion is presented in Sec. III.

II. THEORETICAL CALCULATION

The pseudopotential used here is a Ashcroft empty-core type. The core radius r_c is determined by the zero-pressure condition using the extrapolated experimental lattice constant. The second pressure derivative of the bulk modulus involves the fourth derivative of the total energy with respect to the volume. Thus it is a severe test to the theory.

Following Ashcroft and Langreth,[4] the total energy of the static lattice per atom can be written (in a.u.)

$$E = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - (0.115 - 0.031 \ln r_s) - \frac{1.792 Z^{2/3}}{r_s} + \frac{3\alpha}{4\pi r_s^3} + E_B \,. \tag{1}$$

We will not repeat the detailed steps in calculating the bulk modulus and its pressure derivatives since they have been given elsewhere.[5] In the present calculation, we did not neglect the contributions arising from differentiating the denominator of $(\epsilon - 1)/\epsilon$ as Ashcroft and Langreth[4] did in their calculation.

Although it has been reported that there are phase transformations for some of the alkali metals at low temperatures, it is assumed here that all of them are in bcc phase at 0 °K. The theoretical results are compared with experimental results obtained for the bcc phase. The linear extrapolation of the lattice constant is based on Barrett's[6] x-ray data. The parameters used in and the results of the present calculation, and also the results of various experimental works are shown in Table I.

III. DISCUSSION

Although experimentally the isothermal bulk moduli of alkali metals at zero pressure show some temperature dependence, their first pressure derivatives vary slightly with temperature as Martinson[7] has shown for sodium. As shown in Table I, the present calculation at 0 °K is compared with the room-temperature results of static measurements by Vaidya *et al.*,[8] with results derived from the GGK representation, with those deduced from shock-wave experiments using the Dugdale-MacDonald equation of state by Keeler,[9] and those obtained from ultrasonic work by Dunn and Ruoff,[5] Smith and Smith,[10] and Pauer.[11] Here, the first- and second-order Murnaghan equations used in data analysis are abbreviated as ME_1 and ME_2, respectively. We see that for the isothermal bulk modulus at zero pressure, the theory predicts the right order of magnitude. For the first pressure derivative at zero pressure, the theoretical result and the experimental results are reasonably close. However, for the second pressure derivative at zero pressure, quite a discrepancy is observed. There is also large disagreement between various experimental measurements concerning the latter quantity. As Dunn[12] has shown, the widely used quadratic-fit model in ultrasonic data analysis is not adequate for a maximum pressure of 10 kbar. The contributions from the third-order term $\frac{1}{6}B_0''P^3$ and perhaps some other higher-order terms are not negligible. The same argument can be applied to the state of the second-order Murnaghan equa-

TABLE I. Isothermal bulk moduli and their pressure derivatives of alkali metals.

Element	r_c	r_s	T (°K)	B_0^T (kbar)	$B_0^{T\prime}$	$B_0^{T\prime\prime}$ (kbar^{-1})	Ref.
Li	3.246	1.416	0	137.70	3.537	−0.0202	Present calculation
			0	137.70	3.537	−0.0257	GGK[a]
			RT	117.4	3.62	−0.0308	GGK[b]
				(±0.9)	(±0.02)		
			RT	118.0	3.33		Vaidya *et al.* (Ref. 8) (ME_1)
				(±0.2)	(±0.09)		
			RT	109.1	3.06		Keeler (Ref. 9) (ME_1)
Na	3.936	1.940	0	79.17	3.766	−0.0417	Present calculation[c]
			0	79.17	3.766	−0.0476	GGK[a]
			RT	59.9	4.06	−0.0678	GGK[b]
				(±0.5)	(±0.07)		
			RT	61.31	3.69	−0.019	Vaidya *et al.* (Ref. 8) (ME_2)
				(±0.05)	(±0.04)	(±0.006)	
			RT	60.6	3.62	−0.017	Keeler (Ref. 9) (ME_2)
			195	69.26	3.904	−0.0696	Dunn and Ruoff (Ref. 5) (ME_2)
K	4.875	2.634	0	43.9	3.925	−0.0889	Present calculation
			0	43.9	3.925	−0.0911	GGK[a]
			RT	31.0	3.93	−0.1268	GGK[b]
				(±0.2)	(±0.02)		
			RT	31.2	3.65	−0.039	Vaidya *et al.* (Ref. 8) (ME_2)
				(±0.2)	(±0.09)	(±0.006)	
			RT	29.70	3.68	−0.052	Keeler (Ref. 9) (ME_2)
			295	30.87	3.98		Smith and Smith (Ref. 10)
Rb	5.200	2.872	0	35.75	3.957	−0.1110	Present calculation
			0	35.75	3.957	−0.1107	GGK[a]
			RT	24.9	4.12	−0.1655	GGK[b]
				(±0.3)	(±0.04)		
			RT	26.0	3.37	−0.009	Vaidya *et al.* (Ref. 8) (ME_2)
				(±0.1)	(±0.06)	(±0.005)	
			RT	21.0	3.34	−0.026	Keeler (Ref. 9) (ME_2)
			195	26.3	3.79		Pauer (Ref. 11)

[a] B_0^T and $B_0^{T\prime}$ are theoretical values.

[b] The values of B_0^T and $B_0^{T\prime}$ are obtained from Ref. 1.

[c] The present calculation is slightly different from that of Ref. 5. Some modification in the reciprocal-lattice summation of E_B has been made.

tion of state used in the P-V data analysis by Vaidya *et al.*[8] and Keeler.[9] This systematic error in data analysis would yield a less negative value for the second pressure derivative. And this is just the general case, as shown in Table I, when one compares the experiments with the theory. The second pressure derivative of the bulk modulus at zero pressure for the two-parameter (B_0 and B_0') GGK representation can be obtained through direct differentiation

$$B_0'' = -B_0'/B_0 . \qquad (2)$$

Using the values of B_0 and B_0' determined by Grover *et al.*[1] at room temperature and also those determined by theory at 0°K, the B_0'''s are calculated and listed in Table I. The results of the GGK representation, while comparing with other results derived from different empirical models, are most close to the theory. Assuming the theory is correct, the GGK model might be the best one to be used in data analysis.

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