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OF THE BULK MODULUS OF SODIUM

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ABSTRACT

Martinson's ultrasonic data of sodium is used to obtain the isothermal bulk modulus and its first and second pressure derivatives at zero pressure. The local pseudopotential method proposed by Ashcroft and Langreth is used to obtain theoretical values for these quantities. The results are compared with experimental data. The first derivative is predicted within a few percent while the theoretical and experimental values of the second derivative differ about thirty percent.

## I. INTRODUCTION

Simple local pseudopotential models have been used to calculate the binding energy and compressibility of several metals,<sup>1-3</sup> and reasonably good agreement with experiment has been obtained. In the present paper, we analyse Martinson's<sup>4</sup> ultrasonic data for sodium, and calculate the bulk modulus and its first and second pressure derivatives at zero pressure. The method proposed by Ashcroft and Langreth<sup>2</sup> has been used to derive the theoretical values of the above derivatives at absolute zero degree. The parameter  $r_c$  is obtained from the extrapolated experimental lattice constant  $a_0$  in one case and from the extrapolated experimental bulk modulus  $B_0$  in the second. The results are then compared with experimental values. In addition, results are also shown which include an ion overlap repulsion term.

## II. ANALYSIS OF DATA

We have used Martinson's notation  $\left[ \frac{\tau(0)}{\tau(p)} \right]^2 = 1 + a_1 P + a_2 P^2$

to obtain the following relations:

$$\left( \frac{\partial C^S}{\partial P} \right)_{\substack{T \\ P=0}} = C_0^S \left[ \frac{1}{3B_0^T} + a_1 \right] \quad (1)$$

$$\left( \frac{\partial^2 C^S}{\partial P^2} \right)_{\substack{T \\ P=0}} = C_0^S \left[ \frac{1 - 3B_0^{T'}}{9 B_0^{T^2}} + 2a_2 + \frac{2a_1}{3B_0^T} \right] \quad (2)$$

where  $C^S$  is the adiabatic elastic constant  $C_{11}$ ,  $C_{44}$ , or  $C'$ .  $C_O^S$ ,  $B_O^T$ ,  $B_O^{T'}$  are the adiabatic elastic constant, isothermal bulk modulus, and the first pressure derivative of isothermal bulk modulus at zero pressure, respectively. Also,  $a_1$  and  $a_2$  are the first and second order pressure coefficients listed in Table V in Martinson's paper.<sup>4</sup>

We have chosen the data at 195°K because they were taken over a wider pressure range up to 9 Kbars which would give a better estimate of the first and second pressure derivatives of the bulk modulus. The fact that Martinson assumed linearity of the pressure versus resistance change of the manganin gauge led to some minor errors in the estimation of the first and second pressure derivatives of the bulk modulus. The nonlinearity of the manganin gauge has been discussed in the literature.<sup>5</sup> We have now corrected for this effect by fitting his actual gauge with a quadratic pressure scale.

Ho and Ruoff<sup>6</sup> had also analysed Martinson's data using Cook's<sup>7</sup> analysis. In the present paper, we use Overton's<sup>8</sup> relation to calculate the first pressure derivative of isothermal bulk modulus at 195°K and zero pressure from that of the adiabatic bulk modulus. We also further generalize Overton's relation to the second pressure derivative as follows:

$$\left(\frac{\partial^2 B^T}{\partial P^2}\right)_T = \left(\frac{\partial^2 B^S}{\partial P^2}\right)_T + \Delta' \left[ 1 - \frac{2}{\beta B^T} \left(\frac{\partial B^T}{\partial T}\right)_P - 2 \left(\frac{\partial B^S}{\partial P}\right)_T \right]$$

$$+ \Delta \left[ \frac{2}{\beta^2 B^{T^3}} \left(\frac{\partial B^T}{\partial T}\right)_P^2 + \frac{2}{\beta B^{T^2}} \left(\frac{\partial B^T}{\partial P}\right)_T \left(\frac{\partial B^T}{\partial T}\right)_P - \frac{2}{\beta B^T} \frac{\partial}{\partial T} \left(\frac{\partial B^T}{\partial P}\right)_T - 2 \left(\frac{\partial^2 B^S}{\partial P^2}\right)_T \right]$$

$$+2\Delta\Delta' \left[ \left( \frac{\partial B^S}{\partial P} \right)_T - 1 - \frac{1}{\beta^2} \left( \frac{\partial \beta}{\partial T} \right)_P \right]$$

$$+\Delta^2 \left[ \left( \frac{\partial^2 B^S}{\partial P^2} \right)_T + \frac{2}{\beta^3 B T^2} \left( \frac{\partial B^T}{\partial T} \right)_P \left( \frac{\partial \beta}{\partial T} \right)_P - \frac{1}{\beta^2 B T^2} \left( \frac{\partial^2 B^T}{\partial T^2} \right)_P + \frac{2}{\beta^2 B T^3} \left( \frac{\partial B^T}{\partial T} \right)_P^2 \right]$$

where  $\Delta = \frac{TV\beta^2 B^T}{C_P}$

$$\Delta' = \frac{\partial \Delta}{\partial P} = \Delta \left[ \frac{1}{B^T} \left( \frac{\partial B^T}{\partial P} \right)_T - \frac{1}{B^T} + \frac{2}{\beta B T^2} \left( \frac{\partial B^T}{\partial T} \right)_P \right]$$

$$+\Delta^2 \left[ \frac{1}{B^T} + \frac{1}{B^T \beta^2} \left( \frac{\partial \beta}{\partial T} \right)_P \right]$$

The second pressure derivative of the isothermal bulk modulus is then calculated. Since we calculate these derivatives at zero pressure, the knowledge of the pressure dependence of the thermal properties is not necessary. We have used the data of Siegel and Quimby<sup>9</sup> to calculate the volumetric thermal expansion coefficient  $\beta$  and its temperature derivative  $\frac{\partial \beta}{\partial T}$ , and correct the temperature variation of density. The value of specific heat  $C_p$  is from Martin's<sup>10</sup> work. We also neglect the small contributions from  $\frac{\partial}{\partial T} \left( \frac{\partial B^T}{\partial P} \right)$  and  $\left( \frac{\partial^2 B^T}{\partial^2 T} \right)_P$  at 195°K and zero pressure. The results are listed in Table I, where we extrapolate the value of  $B_0$  to 0°K using Martinson's data.<sup>11</sup>

Table I

Parameter	195°K	0°K
$B_O^T$	69.26 kb	77 kb
$B_O^{T'}$	3.904	3.904*
$B_O^{T''}$	-0.0696 kb <sup>-1</sup>	-0.0696 kb <sup>-1</sup> *

\*We assume that the isothermal pressure derivatives do not vary with temperature. This is discussed by Swenson<sup>12</sup> for  $B_O^{T'}$ .

### III THEORETICAL CALCULATION

In order to calculate the values of the bulk modulus and its pressure derivatives at zero pressure, we have to know the total energy of the solid as a function of volume analytically. The method proposed by Ashcroft and Langreth<sup>2</sup> is used in the present calculation. The total energy of the solid per electron (assuming a static lattice) at 0°K is expressed as:

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

where  $\frac{4}{3} \pi r_s^3 = v = \frac{1}{n}$  is the average volume per electron,  $Z$  is the number of free electrons per ion,  $\alpha = 4\pi r_c^2$  is the parameter to be determined by the zero pressure condition  $\frac{dE}{dr_s} = 0$ ,  $E_B$  is the contribution due to band structure effects.

Barrett<sup>13</sup> first reported a partial phase transformation of sodium from bcc to hcp near 35°K. Microscopic experiments have shown such a transformation is of the martensitic type. In the present calculation, we have assumed that sodium is in the bcc

phase all the way down to 0°K. Also, the value of  $B_0^T$  extrapolated to 0°K at zero pressure is based on the data obtained for the bcc phase.

From thermodynamic definitions, we have at the absolute zero of temperature:

$$P = - \frac{dE}{dV} \quad (5)$$

$$B_0 = \lim_{\substack{P \rightarrow 0 \\ V \rightarrow V_0}} \left( V \frac{d^2 E}{dV^2} \right)$$

$$B_0' = \lim_{\substack{P \rightarrow 0 \\ V \rightarrow V_0}} \left[ - \left( \frac{V}{B} \frac{d^2 E}{dV^2} + \frac{V^2}{B} \frac{d^3 E}{dV^3} \right) \right]$$

$$B_0'' = \lim_{\substack{P \rightarrow 0 \\ V \rightarrow V_0}} \left[ (1+B') \frac{V}{B^2} \frac{d^2 E}{dV^2} + (3+B') \frac{V^2}{B^2} \frac{d^3 E}{dV^3} + \frac{V^3}{B^2} \frac{d^4 E}{dV^4} \right]$$

For the bcc phase, the relation between the lattice constant  $a$  and the parameter  $r_s$  is

$$a = \left( \frac{8\pi}{3} \right)^{1/3} r_s.$$

Using Siegel and Quimby's<sup>9</sup> thermal expansion data, again assuming no phase change, we estimate the value of  $r_s$  at 0°K and zero pressure as 3.936 in Bohr units. From this value, we evaluate

$r_c$  from the zero pressure equilibrium condition  $\frac{dE}{dr_s} = 0$  as follows:

$$\frac{dE}{dr_s} = 0 = -\frac{4.42}{r_s^3} - \frac{9r_c^2}{r_s^4} + \frac{2.708}{r_s^2} + \frac{0.031}{r_s} + \frac{dE_B}{dr_s} \quad (6)$$

$$\text{and } \frac{dE_B}{dr_s} = 0.2036 \Sigma \frac{1}{x^4} \frac{0.166 F_L(x)}{r_s + 0.166 \frac{r_s^2 F_L(x)}{x^2}} \left[ \cos^2 y - y \sin 2y - \frac{\cos^2 y}{(1 + \frac{0.166 r_s F_L(x)}{x^2})} \right]$$

where  $x$  is a reciprocal lattice vector measured in units of twice the Fermi wave vector, and

$$y = 3.84 x r_c / r_s, \text{ and}$$

$$F_L(x) = \frac{1}{2} + \frac{1}{4x}(1-x^2) \ln \left| \frac{x+1}{x-1} \right|$$

The value of  $r_c$  is evaluated as 1.970. We then use eq. (4) and (5) to calculate  $B_0$ ,  $B_0'$  and  $B_0''$ . The results are listed in the second column of Table II.

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Table II

	Expt'l	Theory (based on experimental $a_0$ )	Theory (Born Repulsive term included)
$B_0^T$	77 kb*	82.36 kb	87.06 kb
$B_0^{T'}$	3.904**	3.926	4.096
$B_0^{T''}$	$-0.0696\text{kb}^{-1}$ **	$-0.0461\text{kb}^{-1}$	$-0.0441\text{kb}^{-1}$

\* extrapolated 0°K value

\*\* 195°K value

If, instead, we use the following two conditions

$$P=0 = - \frac{1}{4\pi r_s^2} \frac{dE}{dr_s}$$

$$B_0 = \frac{1}{12\pi r_s} \frac{d^2E}{dr_s^2}$$

and the extrapolated 0°K value of  $B_0$  to determine the value of  $r_c$  and the equilibrium value of  $r_s$ , we obtain  $r_s=4.038$ ,  $r_c=2.047$ . Again using eq. (4) and (5) to calculate  $B_0$ ,  $B_0'$  and  $B_0''$ , we obtain the results shown in Table III.

In the previous calculation the Born repulsive energy due to ion-ion overlap was not considered. It would be interesting to see the effect of adding this term to the total energy. A Huggins-Mayer type expression for the Born repulsive energy

is used:

$$E_{\text{rep}} = \frac{1}{2} M \beta_{++} b_+^2 \exp\left(-\frac{A r_s}{\rho}\right)$$

where  $M$  is the number of nearest neighbors, and the parameters  $b_+$  and  $\rho$  are from Fumi and Tosi's<sup>14</sup> calculation. Although the value of  $E_{\text{rep}}$  is nearly negligible compared to the rest of the terms in the expression for the total energy, it becomes increasingly important after repeated differentiations with respect to  $r_s$ . Similar calculations of  $B_0$ ,  $B_0'$  and  $B_0''$  with this repulsive term included have been carried out, and the results are listed in the third column of Tables II and III. However, the results are of questionable validity, because as remarked by Tosi<sup>15</sup>, there are uncertainties in these parameters  $b_+$  and  $\rho$  arising from the uncertainties in the experimental values used in their determination.

Table III

	Expt'l	Theory (based on experimental $B_0$ )	Theory (Born repulsive term included)
$B_0^T$	77 kb <sup>*</sup>	77 kb	77 kb
$B_0^{T'}$	3.904 <sup>**</sup>	3.945	4.092
$B_0^{T''}$	-0.0696 kb <sup>-1**</sup>	-0.0508 kb <sup>-1</sup>	-0.0519 kb <sup>-1</sup>

\* extrapolated 0°K value

\*\* 195°K value

#### IV CONCLUSION

Previously, Simon<sup>16</sup>, Saxena<sup>17</sup> et al. and Brown<sup>18</sup> have calculated certain elastic properties of sodium. Saxena<sup>17</sup> et al. calculated the binding energy and compressibility both for bcc and hcp phases; however, the Born repulsive term was not included. Simon<sup>16</sup> has done similar calculations on the elastic modulus and its first pressure derivative using an improved theory of Gombas.<sup>19</sup> The theoretical results were compared with experimental values obtained by Diederichs and Trivisonno<sup>20</sup> and Daniels<sup>21</sup>. Quite a discrepancy was found for the bulk modulus and its pressure derivative. The present calculation shows much better agreement between the theoretical values and experimental values for the isothermal bulk modulus and its first pressure derivative. There is a slight discrepancy in the second pressure derivative. However, if we consider the simplicity of the theory and the fact that there is an estimated 10% standard error in the experimental value for the second derivative the result is actually fairly good.

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The values of  $b^+$  and  $\rho$  are taken from 1st set of data in Table 2.
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