

modulus by the relationship,

$$B_S = B_T(1 + (TV\beta^2/k_T C_V)) = B_T(1 + \beta\Gamma T), \quad (24)$$

where Γ is defined by the right-hand-side of equation (19b). The pressure derivative of B_S is given by,

$$\begin{aligned} (\partial B_S / \partial P)_T &= (\partial B_T / \partial P)_T(1 + \beta\Gamma T) + B_T(\partial_\beta \Gamma T / \partial P)_T \\ &= (\partial B_T / \partial P)_T(1 + \beta\Gamma T) - \\ &\quad VT(\partial\beta\Gamma / \partial V)_T. \end{aligned} \quad (25)$$

The variation of $\beta\Gamma$ with volume can be estimated from Fig. 5, equation (5) and the relationship that β/k_T is constant for a given temperature. Since both β and Γ decrease with decreasing volume, the effect of this second term is such as to decrease the difference between the pressure derivatives of the isothermal and adiabatic bulk moduli. In particular, at room temperature, B_S and B_T differ by about seven per cent, but the effect of the second term in equation (25) is to reduce the difference between their pressure derivatives to four per cent.

The data shown in Fig. 5 can be combined with zero pressure values of the entropy and equation (13) to ascertain qualitatively the validity of the Debye model as it applies to sodium. First, tables of the Debye functions⁽²⁶⁾ can be used to calculate the Debye θ at zero pressure by determining the values of θ/T to which the experimentally determined entropies correspond. The entropy at 20,000 atm can be calculated from equation (13), and a value for θ at 20,000 atm can be found similarly. Finally, the ratio $(\theta_{20,000}/\theta_0)$ can be obtained by integration of the left-hand-side of equation (19b) and from equation (21). The results of these calculations are given in Table 4 for

Table 4. Comparison of the change in characteristic temperature in 20,000 atm as given by the Debye model expression for the entropy and the Mie-Grueneisen equation of state

T °K	θ_0 °K	$(\theta_{20,000}/\theta_0)_{\text{Debye}}$	$(\theta_{20,000}/\theta_0)_{\text{MG}}$
100	157	1.20	1.16
200	152	1.28	1.23
300	146	1.27	1.27

100°K, 200°K and 300°K. It again is not surprising that the results are in best agreement at room temperature where the small temperature dependence of Γ implies that a model containing a characteristic temperature is most likely to be correct.

The failure of our simple assumption that the volume dependence of the thermodynamic functions depends only on a characteristic temperature is not surprising. This postulate requires that the lattice frequency distribution function first be independent of the temperature at constant volume, and, second, be unchanged in shape (although the magnitudes may be a function of volume) upon change in volume. Practically, this means that Poisson's ratio must not be a function of pressure or volume.⁽⁶⁾ Recent ultrasonic measurements on the variation of single crystal elastic constants with pressure have furnished data which allow a direct test of this assumption.^(13,27-30)

Two different Poisson's ratios can be defined for a cubic crystal,

$$\begin{aligned} \sigma_{100} &= (3B_S - 2C')/(6B_S + 2C') \\ \sigma_{111} &= (3B_S - 2C_{44})/(6B_S + 2C_{44}), \end{aligned} \quad (26)$$

where $C' = (C_{11} - C_{12})/2$ and $B_S = (C_{11} + 2C_{12})/3$.⁽³¹⁾ It can be seen by inspection that the logarithmic pressure derivatives of the elastic constants $[(\partial \ln B_S / \partial P)_T, (\partial \ln C_{44} / \partial P)_T, (\partial \ln C' / \partial P)_T]$ must be identical if the Γ 's are to be unchanged by pressure. DANIELS' data give (in units of 10^{-11} (dyne⁻¹ cm⁻²)), $(\partial \ln B_S / \partial P)_T = 5.45$, $(\partial \ln C_{44} / \partial P)_T = 3.89$, and $(\partial \ln C' / \partial P)_T = 3.86$. Obviously, the condition that the Poisson's ratios are unchanged by pressure is not satisfied.

The variation of these ratios with volume can be calculated to give,

$$\begin{aligned} (\partial \ln \sigma_{100} / \partial \ln V)_T &= -0.10, \\ (\partial \ln \sigma_{111} / \partial \ln V)_T &= -0.94. \end{aligned}$$

SLATER draws an analogy between the effects of temperature and pressure on volume, and predicts that these derivatives should be positive.⁽⁶⁾ His discussion does not take into account the fact that σ can have an explicit temperature dependence at constant volume which can be different from the above in sign. The necessary data are not available for sodium, but calculations which can be made from more complete data for Cu, Ag, Au⁽²⁹⁾ and