Temperature Effects on the E.O.S. of Solids from Thermal Pressure Considerations: a Thermodynamic Discussion

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The equation of state (E.O.S.) of solids at high temperatures is frequently formulated by distinguishing two contributions to the equilibrium pressure at T, V, *viz.*,

$$P(T,V)= P(0,V) + P_{th}(T,V)$$

where P(0,V) is the equilibrium pressure at zero kelvin, and P_{th}, which is usually called the thermal pressure, is the increase in P associated to the change in temperature from T=0 to the actual T, while the volume is kept constant. In connection with the description of the thermal effects on the P *vs.* V relation, two generalizations about P_{th} have often been applied, which may be traced back to early work by Hildebrand [1], *viz.*: (i) it is assumed that P_{th} is independent of volume at high T and, (ii) P_{th} is treated as a linear function of T. If (i) holds, then $\partial P/\partial T|_V$ and the isothermal bulk modulus (B) are independent of V. Moreover, if (ii) also holds, $\partial P/\partial T|_V$ is independent of T, as well. Hence, the simultaneous application of (i) and (ii) at high temperatures implies that the quantity $\partial P/\partial T|_V$ is treated as a constant, an approximation discussed by Swenson [2] decades ago. More recently, the interest in the combination of (i) and (ii) has been renewed since Vinet, Smith, Ferrante and Rose (VSFR) [3] proposed it as a way of introducing temperature effects in a general, so-called "universal" form of the E.O.S. of solids. In the present paper a critical analysis is presented of the use of such a combination for predicting the temperature dependence of B' ($= \partial B/\partial P|_T$). This quantity plays a key role in the Murnaghan model, and other forms of the EOS of solids, but its variation with T [4] is poorly known from experiments. Our approach is as follows. By combining the approximation $\partial P/\partial T|_V$ = constant with general thermodynamic relations we derive two relations between B' and the temperature derivatives of two measurable parameters of the solid, *viz.*, the thermal expansion coefficient (α) and the bulk modulus B, respectively. By integrating these relations, new expressions are obtained, which allow the mean value of B' in a given temperature range to be calculated from directly measured quantifies. Next, these relations are applied to experimental data on three solids with different bonding types for which experimental data are available, *viz.*, Au, Xe and NaCl. Detailed comparisons between predictions and experiments are presented, and various observed trends are considered. Finally, the approach of Vinet *et al*. [4] to incorporating temperature effects in the E.O.S. of solids is discussed in light of the present findings.

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[2] C.A. Swenson, *J. Phys. Chem. Solids* **29**, 1337 (1968).
[3] P. Vinet, J.R. Smith, J .Ferrante, and J.H. Rose, *Phys. Rev***. B35**, 1945 (1987).
[4] A.F. Guillermet, *Int. J. Thermophysics* **16,** 1009 (1995).