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Scaling relations in the equation of state, thermal expansion, and melting of metals

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A simple and yet quite accurate prediction of volume as a function of pressure for metals and alloys is presented. Thermal expansion coefficients and melting temperatures are predicted by simple, analytic expressions and results compare favorably with experiment for a broad range of metals. All of these predictions are made possible by the discovery of universality in binding energy relations for metals.

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Predictions of equations of state and thermophysical properties of solids are rare for a good reason. They depend on a knowledge of the variation of the solid's free energy with interatomic spacing—a quantity very difficult to obtain. We will show that the recently discovered universality in binding energy relations¹⁻³ allows one to obtain simple, analytic expressions for prediction of equations of state, thermal expansion coefficients, and melting temperatures. The predicted equations of state accurately agree with high pressure data. Predicted melting temperatures and thermal expansion coefficients also compare favorably with experiment.

It has been shown^{1,3} that the total internal energy of metals as a function of volume per atom exhibits universal scaling features, and can be written, to a high degree of accuracy, as

$$E(r_{ws}) = \Delta E E^*[(r_{ws} - r_{wse})/l], \quad (1)$$

where ΔE is the cohesive energy at the equilibrium lattice constant, r_{ws} and r_{wse} the Wigner Seitz radii at the given volume and at equilibrium, respectively, and l a length which describes the curvature of the function near the minimum. The quantity l can be related to the equilibrium value of the isothermal bulk modulus, B , as

$$l = (\Delta E / 12\pi r_{wse} B)^{1/2}. \quad (2)$$

The function E^* in Eq. (1) is the same for all metals.^{1,3} At zero temperature, Eq. (1) implies a universal relation

between the pressure P and the volume per atom V :

$$P = -[\Delta E / (36\pi V^2)]^{1/3} l E^{*'}(\alpha^*), \quad (3)$$

where^{4,5} $\alpha^* = (r_{ws} - r_{wse})/l$, $V = (4/3)\pi r_{ws}^3$, and the prime denotes differentiation with respect to α^* . Thus, given the zero-pressure quantities ΔE , B , and r_{wse} , which are readily available⁶ experimental numbers, one can predict the pressure as a function of volume. Evidence for Eq. (3) is found in Fig. 1, where the predicted $P(V)$ is compared to the measured values⁷⁻⁹ for Rb, Cu, Li, and stainless steel. Absolute pressures are as high as 4 Mbar, and the reductions of specific volume reach as much as $\sim 50\%$ of the equilibrium value. Note the agreement is quite good, providing a striking experimental confirmation of Eq. (3). Equations of state as well as $(\partial B / \partial P)_T$ at $P = 0$ have been predicted for a number of other metals, all exhibiting similarly accurate agreement with experiment, as will be discussed in a longer paper.

At finite temperatures, the equation of state is described by the free energy which also includes contributions from phonons and defects, the latter being only important near the melting point. For phonons in metals it is reasonable to assume that the phonon dispersion relation $\omega_s(\mathbf{k})$ depends on volume through a proportionality to $\sqrt{d^2 E(r_{ws})/dr_{ws}^2}$, where $E(r_{ws})$ is given in Eq. (1). The familiar Grüneisen¹⁰ parameter γ is then

$$\gamma = -\frac{V}{\omega_s(\mathbf{k})} \left[\frac{\partial \omega_s(\mathbf{k})}{\partial V} \right]_T = -\frac{r_{wse}}{6l} \frac{E^{*'''}(\alpha^*)}{E^{*''}(\alpha^*)}. \quad (4)$$

^{a)} Permanent addresses.

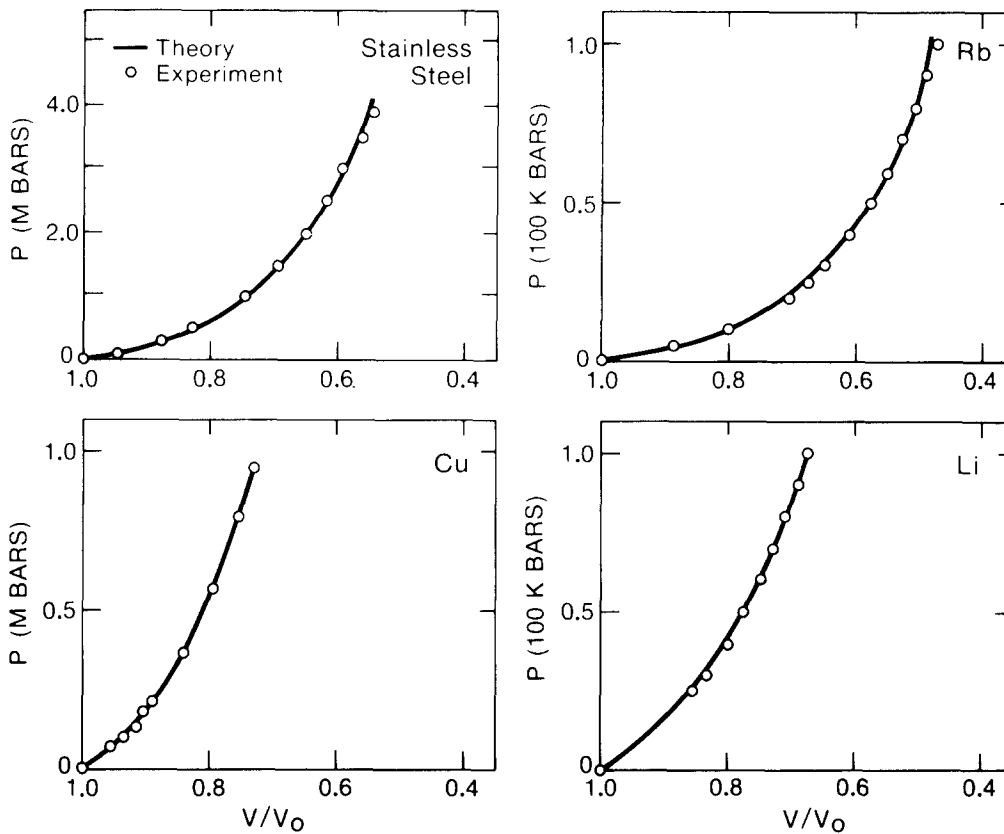


FIG. 1. Predicted (solid line) and experimental equation of state (○) is shown for four metals. Note the very different pressure scales. The Li and Rb data are due to Ref. 7, the Cu data to Ref. 8, and the stainless steel data to Ref. 9.

Substituting the derivatives of the universal binding energy relation¹⁻³ $E^*(\alpha^*)$, we have

$$\gamma = 0.38 r_{use} / l. \quad (5)$$

To assess the accuracy of this expression, one can predict the linear thermal expansion coefficient¹¹ α and compare with experiment. In particular, at temperatures of the order of the Debye temperature, it has the simple form

$$\alpha = 3.45(l / r_{us}) (k_B / \Delta E), \quad (6)$$

TABLE I. Comparison of linear thermal expansion coefficients predicted via Eq. (6) with experimental values at 293 K from Ref. 12.

Metal	$\alpha(10^{-6} \text{ K}^{-1})$	
	Theory	Experiment
W	6.0	4.5
Ir	6.7	6.5
Mo	7.7	5.0
Ta	8.0	7.3
Nb	8.4	7.1
V	11.8	7.8
Pd	12.1	11.6
Fe	12.1	11.8
Au	12.2	14.2
Ni	13.3	12.8
Cu	16.7	16.7
Ag	17.5	19.0
Al	19.6	23.0
Cu _{0.7} Zn _{0.3}	20.2	19.9
Pb	23.8	28.7
Li	60.9	46.6
Na	75.5	69.0
K	86.0	82.0
Cs	89.9	100.0

where k_B is Boltzmann's constant. Representative results are given in Table I.¹² One can see that while the experimental values vary by over an order of magnitude, the predictions agree reasonably well with experiment over the entire range. It will be shown in a subsequent publication that similar agreement can be found for a simple prediction of $(\partial B / \partial T)_P$.

Now let us go higher in temperature, near the melting point. Melting has been predicted to occur through the proliferation of dislocations and other defects,¹³ as it has been shown to happen in simpler 2D systems and spin models.¹⁴ Despite the importance of and interest in melting, this first-order phase transition is still not completely described. One reason for this is our inability until now to determine quantitatively the anharmonicity that could lead to lattice instability. Equation (1) predicts strong anharmonic forces when the atoms deviate from their equilibrium positions by a distance of order l . In particular, the inflection point in the universal binding energy curve is at $r_{us} - r_{use} \cong l$; this implies that beyond this distance restoring forces decrease with increasing deviations from equilibrium. It can be shown¹⁵ for simple models that fluctuations beyond the inflection point lead to the formation and growth of defects.

We can now compute for each metal the temperature at which the root-mean-square displacement of each atom from its equilibrium position is equal to the distance to the corresponding inflection point. From a Debye model at high temperatures¹⁶ the root-mean-square amplitude of vibration of each atom about its lattice site is

$$\langle u^2 \rangle^{1/2} = (9\hbar T / M k_B \Theta_D^2)^{1/2}, \quad (7)$$

where M is the atomic mass. For metals the Debye tempera-

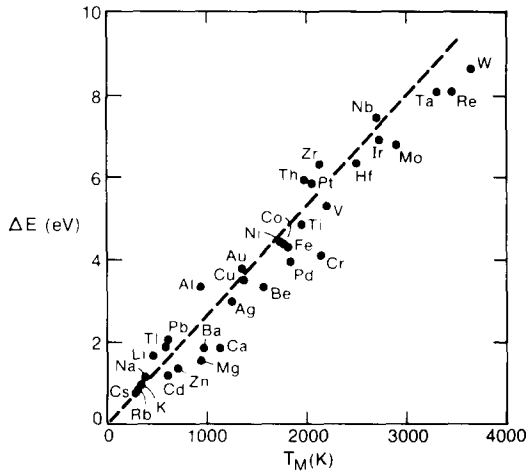


FIG. 2. Predicted [dashed line-Eq. (9)] and experimental (dots) melting temperatures T_M as a function of the cohesive energies ΔE .

ture Θ_D can be accurately computed by assuming that the longitudinal speed of sound is given by $\sqrt{B/\rho}$, where ρ is the mass density of the solid. Then

$$\langle u^2 \rangle^{1/2} = (0.827 k_B T / r_{wse} B)^{1/2}. \quad (8)$$

From Eqs. (8) and (2) with $\langle u^2 \rangle^{1/2} = l$, we have

$$T_M = 0.032 \Delta E / k_B, \quad (9)$$

where T_M is the melting temperature. An empirical correlation between cohesive energies and melting points has long been known and now we see that it can be derived. Equation (9) is the dashed line drawn in Fig. 2. The prediction agrees rather well with experiment.

Lindemann¹⁷ long ago proposed a relation between thermal fluctuations and T_M , but his criterion was based on the fluctuations exceeding a fixed fraction of r_{wse} rather than the inflection point l . As T_M depends on the square of this distance [see Eq. (8)], the ratio of our estimates of T_M to Lindemann's is $(l/r_{wse})^2$. This ratio is a measure of the anharmonicity of the lattice and varies by a factor of ~ 7 for the metals in Fig. 2. It is clear then that a knowledge of anharmonicity—not possible at the time of Lindemann's prediction—is an essential ingredient to the theory.

In summary, we have seen how a knowledge of universality in total energy relations can lead to simple, accurate

predictions of the equations of state for metals and alloys. Thermophysical properties such as thermal expansion and melting also can be simply treated, given the universal binding energy relation. We have seen that both the melting temperature and thermal expansion coefficient are simply related to lattice anharmonicity, and predicted values agree well with experiment for a broad range of metals.

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