

This treatment considers only ideal perfect crystals, and ignores expansion associated with thermodynamic defects such as the Schottky or Frenkel types.¹² However, one may show that these should become important only at temperatures approaching the melting point as far as α' and $\Delta R/R_0$ are concerned. The validity of eqn. (15) is illustrated in table 2.

TABLE 2.—LINEAR EXPANSION COEFFICIENT OF METALS *

metal	T (°K)	ϕ (eV)	ϵ_0' (eV)	$2\epsilon_c$ (eV)	$\alpha' (\times 10^6)^* (\text{calc.})^\dagger$			$\alpha' (\text{obs.})$ ($\times 10^6$)
					(1)	(2)	(3)	
Cu	50	4.43	7.04	7.1	4.1	4.2		4.1
	100				10.8	11.1		10.1
	298				16.0	16.4	17.9	16.51
Ag	100	4.3	5.51	5.9	14.5	13.9		14.1
	200				17.1	16.4		18.1
	298				17.7	17.0	22.6	19.0
Au	100	5.17	5.54	7.2	14.4	12.7		11.8
	200				15.9	14.0		13.7
	298				16.3	14.4	23.4	14.2
Li	298	2.39	4.6	3.4	25.5	29.3	26	56
Na	298	2.26	3.2	2.26	37.6	42.9	45	71
K	298	2.13	2.14	1.74	48.0	49.5	71	83
Mg	298	3.48		3.12		24.7		26
Ca	298	2.74		4.18		27.1		22
Zn	298	3.74		2.34		27.2		39.7
Cd	298	3.91		2.34		26.9		29.8
Al	298	3.74		4.78		20.5		25.5
Sn	298	4.74		6.78		17.1		23
Pb	298	4.64		4.14		27.8		29.3
Fe	175	4.35		8.18		12.8		9.1
	225					14.0		10.5
	273					14.8		11.5
	298					14.9		11.7
	373					16.7		12.7
Ni	573					20.2		15.0
	298	4.78		7.40		15.3		13.3

* work potential ϕ from Michealson;¹³ ϵ_0' from Sommerfield equation: $\epsilon_0' = \frac{h^2}{2m} \left(\frac{3\rho}{8\pi} \right)^{\frac{2}{3}}$; cohesive energy ϵ_c from Mott and Jones¹⁴ and Seitz,¹⁵ observed α' data are from *Metals Handbook* (1950) and Dorsey.¹⁶

† (1) $\alpha' = C/2(\phi + 1/2\epsilon_0')$; (2) from $\alpha' = C/2(\phi + \epsilon_c)$; (3) from $\alpha' = C/\frac{h^2}{m} \left(\frac{3\rho}{8\pi} \right)^{\frac{2}{3}}$.

The same fundamental principles are applicable in describing quantitatively the compressibility $\beta = -(\partial V/\partial p)/V$. As in thermal expansion the "orbital volume" may be related reciprocally to the kinetic energy $\bar{T}$, and the compression to the change in kinetic energy in the orbital due to the applied pressure. If $\Delta\bar{T}$ is the increase in $\bar{T}$ per mole due to an applied pressure, one may write $\Delta\bar{T} = -\frac{3}{2}RFN$ where F is the total force (negative for compression) applied to an atom, in the metal along each of the three principal axes, N is Avogadro's number, and R the average diameter of the atom. The relative compression is determined by that of the valence orbital shell of the atom. Since the core or inner electron will also take up some of the force and total ΔT , one must evaluate that part F_1 and ΔT_1 of the total F and ΔT that goes only into the outermost,

or size-determining orbital. Thus, $F = \sum_{i=1}^z F_i$, where F_i is the effective force applied on each of the z electron orbitals by the total force F . Hence using ΔT_1 in place of H in

eqn. (13) one obtains for the linear compression: $\Delta R/R = -\Delta T_1/2T = 3RF_1N/4\bar{T}$ giving $\beta = -9RM^{\frac{2}{3}}N^{\frac{1}{3}}/4\rho_1^{\frac{2}{3}}\bar{T}\phi$, where M is the atomic weight, ρ_1 the density and $\phi = 1 + \sum_{i=2}^z F_i/F_1$.

Since

$$F = \phi F_1 = p/n_0^{\frac{2}{3}} = p(M/N\rho_1)^{\frac{2}{3}},$$

one therefore obtains

$$\beta = 2 \times 10^{-6} RM^{\frac{2}{3}}/\bar{T}\phi\rho_1^{\frac{2}{3}}. \quad (16)$$

for R in Å, T in eV and ρ_1 in g cm⁻³.

To estimate ϕ it is here assumed that $F_i \propto \bar{r}_i^2$, where $\bar{r}_i$ is the effective average orbital radius of the i th electron. Then from the Fermi-Thomas model one obtains $F_i/F_k = E_k/E_i$,

and $\phi = 1 + \sum_{i=2}^z E_1/E_i$, where E_i is the electronic energy level of the i th electron. Since

each orbital in a closed shell contains two electrons of opposite spin one may evaluate E_1/E_i with sufficient accuracy by building up the core in pairs assuming perfect screening by inner filled orbitals. The only difficulty comes in knowing E_i for $i < \text{about } 6$. Fortunately one may frequently determine these from measured ionization potentials taking into account the valence structure of the atom. It is, of course, important to know whether valence electrons are coupled as in helium (two electron bonds) or are uncoupled in effectively single electron bonds as in metals. The ϕ s are sufficiently sensitive to the type of coupling that one should have little difficulty in deciding the valence structure from the observed β_0 (the low pressure value of β). This is justified from the excellent agreement in cases where there is no uncertainty in this factor, e.g., lithium and sodium. One finds, for example, that the outer three electrons of aluminium should be treated as a one-electron bond with two underlying coupled electrons, rather than to assume that all three valence electrons have equal energy.

Our interest here concerns β at very large pressures. This may be obtained from the value at atmospheric pressure β_0 and the variations of R , $\bar{T}$ and ϕ with pressure by the application of eqn. (16). If one assumes that only E_1 is influenced significantly when pressure is applied, one finds that

$$\begin{aligned} \beta &= \beta_0 + \int_0^p \frac{\partial \beta}{\partial p} dp = \beta_0 + \int_0^p \beta \left\{ \frac{1}{V} \frac{\partial V}{\partial p} - \frac{1}{\bar{T}} \frac{\partial \bar{T}}{\partial p} - \frac{1}{\phi} \frac{\partial \phi}{\partial p} \right\} dp \\ &= \beta_0 + \int_0^p \beta \left\{ \frac{1}{V} \frac{\partial V}{\partial p} + \frac{2}{3V} \frac{\partial V}{\partial p} + \frac{2}{3V} \frac{\partial V}{\partial p} \left(1 - \frac{1}{\phi_0} \right) \right\} dp = \beta_0 - \int_0^p a\beta^2 dp. \end{aligned}$$

Hence, taking $a = 2.33 - 0.67\phi_0^{-1}$, one obtains

$$\beta = \beta_0 \sum_{i=0}^{\infty} (-a\beta_0 p)^i. \quad (17)$$

Mott and Jones showed that the $\beta(T)$ relation is $\frac{1}{\beta} \frac{\partial \beta}{\partial T} = \frac{\alpha}{\gamma} V^2 \frac{d^2 \ln \nu}{dV^2}$, where α is the volume expansion coefficient, and $\gamma = \alpha V_0 \beta_0^{-1} C^{-1} = -d \ln \nu / d \ln V$, ν being the characteristic frequency and C the heat capacity. Hence, applying the above theory one obtains the very simple relation

$$d \ln \beta / dT = a\alpha = 3a\alpha'. \quad (18)$$

Bridgman's results are expressed by the equation $\beta = a' \times 10^{-7} - 2b \times 10^{-12}p$ and apply up to about 50 to 100 kilobars. Hence one expects to find $\beta_0 = a' \times 10^{-7}$ and $a\beta_0^2 = ab \times 10^{-12}$. Table 3A evaluates this comparison and shows that the theoretical values of β_0 are in remarkable agreement but that the ratio $2b \times 10^{-12}/a\beta_0^2$ (theoretically unity) ranged from 1.0 for strontium to 12.6 for platinum. This indicates that the semi-empirical method used here for handling the pressure coefficient of β while not exact is correct as to order of magnitude. Table 3B compares results of V/V_0 (total compression) at 200-400 kilobars measured by Walsh and Christian¹⁸ with results computed from the equation

$$V/V_0 = \exp \left[+ \sum_{i=1}^{\infty} (-a\beta_0 p)^i / a_i \right]. \quad (19)$$