

energy u of the oscillator becomes

$$u = \pi^2 m \nu_{DM}^2 (r - r_1)^2 [1 - 2\gamma_{DM}(r - r_1)/r_1], \quad (55)$$

analogous to Eq. (18). By means of Eqs. (52) and (53), an alternative expansion of u in powers of $r - r_1$ can be obtained. Comparison of the result with u as defined by Eq. (55) yields

$$\nu_{DM} = s_{DM} N^{1/3} M^{-1/2} K_1^{1/2} V_1^{1/6} \quad (56)$$

as the characteristic frequency, if note is taken of Eq. (41a), and yields

$$\gamma_{DM} = -\frac{1}{2} - \frac{1}{6}(18l + 2n - P_1)/(3\lambda + 2\mu + P_1) \quad (57)$$

directly as the corresponding Grüneisen parameter in terms of Lamé and Murnaghan parameters. One obtains

$$\gamma_{DM} = -\frac{1}{2} [1 + (\partial \ln K / \partial \ln V)_1] \quad (58)$$

from Eqs. (41); this result corresponds exactly with Eq. (24) obtained for zero pressure. By direct use of Eq. (25) to calculate $\langle r - r_1 \rangle_{Av}$, one can verify Grüneisen's law under finite strain. The analog of Eq. (27) becomes

$$(\partial^3 u / \partial r^3)_1 = -54\gamma_{DM} K_1, \quad (59)$$

which, with reference to Eq. (57), brings out a point emphasized by Druyvesteyn and Meyering, that the anharmonic term in the potential energy of an atom in the interatomic force field is a function of the second-order elastic coefficients.

For an ideal harmonic solid of Druyvesteyn-Meyering type, integration of the relation $\gamma_{DM} = 0$ for an arbitrary point and evaluation of the constant of integration at the point (V_1, P_1) yields

$$P = P_1 + K_1 [(V_1/V) - 1], \quad (60)$$

as the equation of state. This expression reduces to Eq. (32b) by use of Eqs. (32) to evaluate K_1 and P_1 ; thus the equation of state shows a transitivity property (as noted for the corresponding Debye solid). Note that $\lambda + (2/3)\mu$ must be such a function of pressure that Eqs. (32a) and (41a) are satisfied simultaneously. For u in the case of this ideal solid, one obtains an expression corresponding exactly to Eq. (33), from which direct use of Eq. (25) to compute $\langle r - r_1 \rangle_{Av}$ yields a vanishing thermal expansion.

IV. COMPARISON WITH EXPERIMENTAL DATA

It is clear from the foregoing that the two evaluations, γ_D and γ_{DM} , for the Grüneisen parameter as evaluated from the equation of state, correspond to two different models. That both models represent approximations follows from the more refined analysis of Barron,³⁷ and from considerations noted by Slater³ and Zener³⁸ in connection with the Debye model. However, from

³⁷ T. H. K. Barron, *Phil Mag.* 46, 720 (1955).

³⁸ C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), p. 30.

TABLE I. Comparison of average Grüneisen constants from equation of state and from Grüneisen's law.

	γ_D	γ_{DM}	$\gamma_{m,D}$	$\gamma_{m,DM}$	γ (Grüneisen law)
Average of 19 elements	1.92 ^a	1.59 ^a			1.96 ^b
Average of 14 elements			1.8 ^c	1.5 ^c	1.8 ^c

^a Values for 10 elements (Mn, Fe, Co, Ni, Cu, Pd, Ag, W, Pt, and Pb) from Slater (reference 3); values for 9 elements (Li, Na, K, Rb, Cs, Al, Au, Mo, and Ta) from Gilvarry (reference 39).

^b Values from Grüneisen (reference 20), revised in the cases of the alkali metals and of Al, Au, Mo, and Ta to correspond to incompressibilities given by Gilvarry (reference 39).

^c From Table V of I (values for Ga, Bi, and Sb excluded).

the artificial nature of the Druyvesteyn-Meyering solid as compared to the Debye model, one expects γ_D to represent a better approximation than γ_{DM} . Dugdale and MacDonald state that use of γ_{DM} , as against γ_D , improves slightly the over-all agreement of values of the Grüneisen constant from the equation of state and from Grüneisen's law, for the elements in Slater's tabulation.³ However, this tabulation shows large deviations in the two evaluations of the constant for the three alkali metals included and for some relatively incompressible metals (Au, Mo, and Ta). A redetermination by the author³⁹ of compressibility parameters for these elements (with inclusion of Rb and Cs) from more recent experimental data of Bridgman reduced the discrepancies in these cases, so that the contention of Dugdale and MacDonald could not be maintained.

One should expect the inevitable experimental inaccuracies to cancel to a significant extent in a comparison of the averages for a reasonably large number of elements, of evaluations of the Grüneisen constant on particular models. In Table I, average values for 19 elements of γ_D and γ_{DM} , as obtained from the equation of state for zero pressure, are compared with the corresponding average obtained with use of thermal parameters from Grüneisen's law (7); one notes that agreement of γ_D with the value from Grüneisen's law, shown in the last column, is excellent. An average value for 14 elements is shown likewise for the Grüneisen constant $\gamma_{m,D}$ of the solid at fusion, given in I as

$$\gamma_{m,D} = \frac{1}{3} + \frac{1}{2} q K_m \Delta V / L, \quad (61)$$

where K_m is the bulk modulus of the solid at melting, ΔV and L are the volume change and latent heat of fusion, respectively, and q is a parameter of the order of unity. This equation has been derived in I on the basis of Eq. (15) for the Grüneisen parameter, and thus is valid on the Debye theory; the corresponding value $\gamma_{m,DM}$ for a Druyvesteyn-Meyering solid is $\gamma_{m,D} - \frac{1}{3}$. The agreement shown by the table is exact, within the accuracy of the data, between $\gamma_{m,D}$ and the corresponding value derived from application of Grüneisen's

³⁹ J. J. Gilvarry, *J. Chem. Phys.* 23, 1925 (1955).