



FIG. 1. The generalized Poisson ratio Σ as a function of pressure for polystyrene and for Pyrex glass, from data of Hughes and Kelly.

yields Eq. (15) for the Grüneisen parameter on the Debye theory, which is the result obtained without use of the formal theory of finite strain. By application of Eq. (15) at the point (V_1, P_1) , with use of Eqs. (41), the expression for γ_D becomes

$$\gamma_D = -\frac{1}{6} \left[1 + (18l + 2n - P_1) / (3\lambda + 2\mu + P_1) \right], \quad (47)$$

in terms of Lamé and Murnaghan parameters.

For an ideal harmonic solid of Debye type, the requirement that γ_D of Eq. (15) vanish yields

$$P = P_1 + 3K_1 \left[(V_1/V)^{1/3} - 1 \right] \quad (48)$$

as the corresponding equation of state, if the constant of integration is evaluated at the point (V_1, P_1) . One recovers Eq. (34b) if use is made of Eqs. (34) to relate K_1 and P_1 to the bulk modulus K_0 at the normal volume V_0 ; thus the equation of state shows a transitivity property. Use of the same relations for K_1 and P_1 in Eq. (41a) yields

$$\lambda + \frac{2}{3}\mu = K_0, \quad (49)$$

so that the combination of Lamé parameters on the left is a constant. From Eq. (41b), one obtains

$$6l + \frac{2}{3}n = -K_0, \quad (50)$$

in which the combination of Murnaghan parameters is constant. The last equation imposes no restriction on the second-order coefficient m ; this parameter must be chosen as a function of volume so that Σ of Eq. (45) has the value σ , which must be taken as a constant, so that the Grüneisen postulate is satisfied for the frequencies. Accordingly, the Lamé parameters λ and μ have constant values separately for an ideal harmonic solid of Debye type.

The fact that the Lamé parameters are constant for an ideal Debye solid means that the equation of state is identical with that obtained by Murnaghan¹⁷ on

the linear theory of finite strain. The equation of state given by Murnaghan, corresponding to the "integrated linear theory of finite strain," which was used in III to derive the Simon equation for the fusion curve, reduces to Eq. (34b) if the Grüneisen parameter of the solid on the fusion curve vanishes. One notes that the sign of the combination of Murnaghan parameters in Eq. (50) is negative, which is agreement with the general results of measurements of these parameters made by Hughes and Kelly on various solids. The signs of the second-order coefficients were predicted by Brillouin to be negative in general, as is necessary if the wave velocities increase with pressure.

As a check on the assumption of constant Σ , values of this parameter from experimental results of Hughes and Kelly for polystyrene and for Pyrex glass are shown in Fig. 1, as a function of pressure. Comparison of Fig. 1 with Fig. 1 of I and Fig. 1 of II shows that the assumption is fulfilled reasonably as compared to the corresponding assumption on σ .

B. Druyvesteyn-Meyering Solid

For the change $E - E_1$ in total energy of a solid from the point (V_1, P_1) to the point (V, P) under a change in hydrostatic pressure, Murnaghan has given the expression¹⁷

$$E - E_1 = V_1 \left[3P_1 e + (3/2)(3\lambda + 2\mu)e^2 - (9l + n)e^3 \right], \quad (51)$$

which, as one verifies, yields Eq. (37) for $P - P_1$, with use of Eq. (38). By means of the expansion (39), one obtains

$$E - E_1 = -P_1(V - V_1) + \frac{1}{6}(3\lambda + 2\mu + P_1) \times (V - V_1)^2 / V_1 + (1/54)(18l + 2\mu - 9\lambda - 6\mu - 4P_1)(V - V_1)^3 / V_1^2. \quad (52)$$

The first term in this expression is an energy of compression whose presence ensures that $-(\partial E / \partial V)_1 = P_1$, corresponding to the fact that the total energy of the solid cannot possess a minimum at (V_1, P_1) unless $P_1 = 0$. For a Druyvesteyn-Meyering solid of N atoms in volume V , the remaining energy of compression can be represented as the potential energy of $3N$ independent bond oscillators of potential energy u by

$$E - E_1 + P_1(V - V_1) = 3Nu, \quad (53)$$

which replaces Eq. (20) in the infinitesimal case. In contrast to E , u is such that $(\partial u / \partial V)_1 = 0$, corresponding to the fact that the potential energy of an oscillator must possess a minimum at (V_1, P_1) .

The definition (4) of the Grüneisen parameter yields

$$\nu = \nu_{DM} \left[1 - 3\gamma_{DM}(r - r_1) / r_1 \right] \quad (54)$$

for the frequency ν of a bond oscillator, if r_1 is the value of the interatomic distance r corresponding to the point (V_1, P_1) ; this expression replaces Eq. (17) in the infinitesimal case. The corresponding potential

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³⁸ C. Zener, *E* Chicago Press, C