relatively accurate values are available in few cases. Grüneisen[24] and Birch[8] provide tables of η for elements and some compounds.

As noted, the parameter ξ of the multiplicative correction (5) to the Birch equation as expressed in the form (4), has a value quite close to zero for very many (if not most) elements and compounds. When ξ does not vanish but is independent of temperature, it is clear from the derivation that the generalized relation (15) is valid within the approximations made, when multiplied by the correction factor (5). However, the experimental results of Swenson[9] for the alkali metals at low temperature show that ξ depends on temperature when it does not vanish for these elements. But whether ξ depends on temperature or not, one notes that the generalized relation (15), when multiplied by the correction factor (5), reduces at any fixed temperature precisely to the general form of the isothermal Birch equation, because of the physical significance of the parameters $\mathcal{V}$ and $\mathcal{K}$. Thus, no reason seems to exist why the generalized Birch equation should not be reliable for arbitrary temperature when the factor (5) is included and ξ depends on temperature. This statement should be true within the approximations entailed in Birch's derivation of the isothermal form, and implies that the difficulty raised by Eq. (31) in representing correctly the temperature dependence of K is a shortcoming of Birch's equation in the form (4), and not of the analysis employed here.

IV. THERMAL PROPERTIES OF THE SOLID

In this section, the salient thermal properties of the solid will be examined, as implied by the generalized equation of state. Inasmuch as $\xi=0$ for the majority of solids, the discussion will be restricted to this case for simplicity.

In the Mie-Grüneisen theory of the thermal pressure of a lattice, the total pressure P is expressed in terms of a volume-dependent pressure p and a thermal component P_T of pressure, by[15,16]

$$P=p+P_T. \qquad (41)$$

If the volume variation of all lattice frequencies ν_i is the same, so that the Grüneisen parameter γ can be defined by

$$\gamma=-(\partial \ln\nu_i/\partial \ln V)_T, \qquad (42)$$

the basic result of the theory is

$$P_T=\gamma E_T/V, \qquad (43)$$

where E_T is the thermal energy of the lattice.[15,16] One obtains

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P_T}{\partial T}\right)_V = \gamma\frac{C_V}{V}+\left(\frac{\partial \gamma}{\partial T}\right)_V \frac{E_T}{V} \qquad (44)$$

directly, where C_V is the heat capacity of the solid at constant volume. The generalization (15) has been

required to meet Eq. (17) through terms of first order in P/K. To this order, therefore, for a solid to which the Mie-Grüneisen theory is applicable, the generalized equation of state satisfies

$$K\alpha=\gamma C_V/V+(\partial\gamma/\partial T)_V E_T/V, \qquad (45)$$

which represents Grüneisen's law.

The usual statement of Grüneisen's law differs from Eq. (45) by omission of the term involving $(\partial\gamma/\partial T)_V$, in conformity with Grüneisen's postulate that the lattice frequencies are a function only of the volume.[15,24] When this hypothesis is not satisfied, the general form (45) follows from the fundamental result (43). By use of the Lorentz-Slater formula (12), one obtains

$$\gamma=\frac{1}{2}\frac{n^2(\mathcal{V}/V)^n-m^2(\mathcal{V}/V)^m}{n(\mathcal{V}/V)^n-m(\mathcal{V}/V)^m}-\frac{1}{6} \qquad (46)$$

as the Grüneisen parameter corresponding to the generalization (15) of the isothermal equation of state. In general, this expression for γ depends on the temperature through the parameter $\mathcal{V}$ (although it does not involve $\mathcal{K}$). However, it has been noted that $V=\mathcal{V}$ for zero pressure. Hence, Eq. (46) yields the result that γ at any temperature has the strictly constant value given by Eq. (14), if the pressure is zero. In this case, the last term in the form (45) of Gruneisen's law vanishes. Therefore, Grüneisen's postulate is satisfied for zero pressure.

To discuss the temperature dependence of γ for nonvanishing pressure, it is convenient to make use of the volume v possessed by the solid at zero temperature, rather than the actual volume V. These two quantities are related to each other at the same pressure by

$$V=v \exp\int_0^T \alpha dT. \qquad (47)$$

The bulk modulus K will be written in a form corresponding to Eq. (41), as

$$K=k+K_T, \qquad (48)$$

where k (like p in this case) depends only on v, and K_T (like P_T) is a temperature-dependent component. If the exponentials in Eqs. (27) and (32) are expanded to first order, and Birch's approximation (25) is used, γ of Eq. (46) can be written to first order as

$$\gamma=\gamma_0-\left[\frac{d\gamma_0}{d \ln v}\int_0^T \eta_0\alpha_0 dT\right]\frac{p}{k}, \qquad (49)$$

where

$$\gamma_0=\frac{1}{2}\frac{n^2(v_0/v)^n-m^2(v_0/v)^m}{n(v_0/v)^n-m(v_0/v)^m}-\frac{1}{6} \qquad (50)$$

and

$$\frac{d\gamma_0}{d \ln v}=\frac{1}{2}\frac{nm(n-m)^2(v_0/v)^{n+m}}{[n(v_0/v)^n-m(v_0/v)^m]^2} \qquad (51)$$