by an oscillator consisting of the two atoms connected by a nonlinear spring along their join, and assume that each such oscillator is independent. The Grüneisen parameter for such a solid of independent pairs of nearest-neighbor atoms will be obtained by extension of a method given by Madelung[27] and Einstein[28] to evaluate the characteristic frequency of a solid in terms of its elastic parameters. The model in question is equivalent to one in which each bond is replaced by a diatomic molecule. It is clearly artificial, but not entirely so; Slater[3] has pointed out the similarity between the metallic bond and the homopolar bond, and has used the Morse potential for the interatomic potential in a metal to obtain values of the Grüneisen constant showing reasonable agreement with values from Grüneisen's law.

The volume variation of the frequency $\nu$ of a single bond oscillator is given to first order, from Eq. (4), by

$$\nu = \nu_{DM}[1 - \gamma_{DM}(V - V_0)/V_0], \tag{16}$$

where $\gamma_{DM}$ is the corresponding Grüneisen parameter, $\nu_{DM}$ is a constant frequency, and $V_0$ is the normal value of the volume $V$. Since the volume per atom for a simple cubic lattice is $r^3$ in terms of the interatomic distance $r$, one obtains

$$\nu = \nu_{DM}[1 - 3\gamma_{DM}(r - r_0)/r_0], \tag{17}$$

if $r_0$ is the normal value of $r$; note that the nonlinear spring forming a bond is such that increase of its length $r$ lowers its force constant. The independent oscillation corresponding to a bond takes place with the center of mass of the two atoms fixed. Using reduced coordinates, one can express the total potential energy $u$ of this oscillator of variable frequency (and force constant) as

$$u = \pi^2 m \nu_{DM}^2 (r - r_0)^2 [1 - 2\gamma_{DM}(r - r_0)/r_0], \tag{18}$$

if $m$ is the mass of an atom.

The change $E - E_0$ in the total energy of a solid on compression can be expressed as a Taylor series through third-order terms in the volume change as

$$E - E_0 = \frac{1}{2} \frac{K_0}{V_0}(V - V_0)^2$$
$$\times \left\{ 1 + \frac{1}{3}\left[\left(\frac{\partial \ln K}{\partial \ln V}\right)_0 - 1\right]\frac{V - V_0}{V_0}\right\}, \tag{19}$$

by means of Eq. (10), if $E_0$, $K_0$, and the partial derivative represent values corresponding to the normal volume $V_0$. For the model of a solid in question, the work of compression can be viewed as expended against the potential energy of the independent bond oscillators. For $N$ atoms in volume $V$, one obtains

$$E - E_0 = 3Nu, \tag{20}$$

if $u$ is the energy of a single oscillator (since a unit cell of a simple cubic lattice corresponds to one atom and has twelve edges, each of which is common to four unit cells). Taylor expansion of $V = Nr^3$ yields

$$u = \frac{3}{2}K_0 v_0^{\frac{1}{3}}(r - r_0)^2 \left\{ 1 + \left[1 + \left(\frac{\partial \ln K}{\partial \ln V}\right)_0\right]\frac{r - r_0}{r_0}\right\} \tag{21}$$

from Eqs. (19) and (20), if $v_0$ is the normal volume per atom corresponding to the normal value $r_0$ of $r$.

Comparison of the leading terms of Eqs. (18) and (21) for $u$ yields the form

$$\nu_{DM} = s_{DM}m^{-1/2}K_0^{1/2}v_0^{1/6}, \tag{22}$$

with $s_{DM} = 3^{1/2}/2^{1/2}\pi$, for the characteristic frequency of a solid of independent pairs of nearest neighbor atoms. In his evaluation of the characteristic frequency of a solid from elastic parameters, Einstein obtained the somewhat different value $(\pi/6)^{1/3}(3^{1/2}/2^{1/2}\pi)$ for the coefficient corresponding to $s_{DM}$, by taking into account the presence of 26 neighbors of each atom in a simple cubic lattice. If $N$ is Avogadro's number and $V_0$ the normal atomic volume, Eq. (22) yields

$$\nu_{DM} = s_{DM}N^{1/3}M^{-1/2}K_0^{1/2}V_0^{1/6}, \tag{23}$$

which corresponds to Eq. (13) for the Debye frequency.[29]

A corresponding comparison of the second terms of Eqs. (18) and (21) for $u$ yields

$$\gamma_{DM} = -\frac{1}{2}[1 + (\partial \ln K/\partial \ln V)_0] \tag{24}$$

for the Grüneisen parameter of a solid of independent pairs of nearest-neighbor atoms. This expression differs from $\gamma_D$ of Eq. (15) by $-\frac{1}{3}$; it is identical with the result of Druyvesteyn and Meyering, and agrees with the result of Dugdale and MacDonald for zero pressure. Note that no use of the formal theory of finite strain has been made in the derivation.

On the assumption of independent bond oscillations, the thermal expansion of the lattice can be determined directly in the classical limit by means of the expression

$$\langle r - r_0 \rangle_{Av} = \left[\int_{-\infty}^{\infty} e^{-u/kT}dx\right]^{-1}\int_{-\infty}^{\infty} xe^{-u/kT}dx, \tag{25}$$

where $x = r - r_0$. From Eq. (18) or Eq. (21), one obtains Grüneisen's law in the form

$$K_0\alpha = \gamma_{DM}(3k)/v_0, \tag{26}$$

as a check on the results. Equation (25) yields a non-vanishing thermal expansion from $u$ of Eq. (18) or Eq. (21) only because of existence of the anharmonic terms, corresponding to which one obtains the ex-

[27] E. Madelung, Physik. Z. 11, 898 (1910).
[28] A. Einstein, Ann. Physik 34, 170, 590 (1911).

[29] If the value of $s_{DM}$ noted above is equated to $s_D$ of Eq. (14), one obtains $\sigma = 0.36$ as the equivalent Poisson ratio, which may be compared with the average value $\frac{1}{3}$ over the metals [C. Zwikker, *Physical Properties of Solid Materials* (Interscience Publishers, Inc., New York, 1954), p. 90].