

where the notation  $O[x]$  has been used for terms of order equal to or higher than that of  $x$ ; the terms indicated in this manner have already been neglected in determining the energy levels of a bond oscillator.<sup>31</sup> This potential energy contains no cubic term; that the corresponding thermal expansion vanishes follows directly from Eq. (25), within the approximation made in obtaining the energy levels. Through cubic terms, the Taylor expansion of  $u$  agrees within a proportionality factor with the potential energy  $U$  of Eq. (28) for  $m = -1$  and  $n = -2$ , if  $A$ ,  $B$ , and an added constant are selected properly. With this choice of  $m$  and  $n$ , Grüneisen's value (29) for  $\gamma_{DM}$  vanishes, as it should.

For an ideal harmonic solid of Debye type, the condition  $\gamma_D = 0$  yields

$$K = K_0(V_0/V)^{1/3}, \quad (34a)$$

$$P = 3K_0[(V_0/V)^{1/3} - 1], \quad (34b)$$

from Eq. (15), if  $K = K_0$  and  $P = 0$  at  $V = V_0$ . The equation for the bulk modulus follows directly from the condition that  $\nu_D$ , as given by Eq. (13), be constant. As one notes, the results differ from the corresponding ones of Eqs. (32) for a Druyvesteyn-Meyering solid. In contrast to the assumption of independent pairs of nearest-neighbor atoms, the Debye model postulates coupled atomic oscillations; coupling is introduced by means of the continuum approximation, by which the actual lattice vibrations are represented by elastic waves. Corresponding to these differences, the Grüneisen parameters computed on the two models do not agree exactly, and the predicted equations of state for an ideal harmonic solid differ.

The formal analog of Eq. (33) for an ideal harmonic solid of Debye type, corresponding to use of the result of  $\gamma_D = 0$  in Eq. (19), is

$$\frac{E - E_0}{3N} = -K_0 v_0^3 (r - r_0)^2 \left[ 1 + \frac{2}{3} \frac{r - r_0}{r_0} \right] + O[(r - r_0)^4], \quad (35)$$

for a simple cubic lattice. In spite of the fact that the equation contains a cubic term, one cannot use this result for  $u$  in Eq. (25) to conclude that an ideal harmonic solid of Debye type shows a nonvanishing thermal expansion, since  $(E - E_0)/3N$  cannot be interpreted as the potential energy of an independent pair of nearest neighbor atoms or of an independent atom (for one-dimensional motion) in an interatomic force field, and the validity of Eq. (25) is restricted to such a case. It goes without saying that the difference  $r - r_0$  appearing in Eq. (35) cannot be identified as the displacement which enters the expression for the potential energy of a thermal oscillator on the Debye model, since it is the normal coordinates  $q_i$  of the acoustic oscillators which enter the potential energy in the Hamiltonian  $H$  of Eq. (3). The effect of thermal expansion is to change the normal coordinates  $q_i$  to new values  $q_i'$ , where both show mean value zero, and

to change the frequencies  $\nu_i$  to new values  $\nu_i'$  given by

$$\nu_i' = \nu_i [1 - \gamma_D (V - V_0)/V_0], \quad (36)$$

which minimize the Helmholtz free energy, as Peierls<sup>33</sup> shows. Thus, Eq. (35) represents a purely formal expansion for a Debye solid.

Dugdale and MacDonald<sup>13</sup> consider a solid in which the potential energy  $\phi$  per nearest-neighbor pair of atoms is such that  $\phi \propto (R - R_0)^2$  in terms of the difference of the distance  $R$  between the pair from its normal value  $R_0$ . At zero temperature, the total internal energy in this case is proportional<sup>34</sup> to  $(V^{1/3} - V_0^{1/3})^2$ . Dugdale and MacDonald identify such a solid as an "ideal harmonic body" (this definition does not coincide with the definition of an ideal harmonic solid used in this paper). These authors note that computation of the pressure at  $T = 0$  from this total energy yields  $\gamma_D = \frac{1}{3}$  from Eq. (15) at zero pressure; since they assume that the body in question has no thermal expansion, they view this nonvanishing Grüneisen parameter as a paradox. However, even though the restoring force along a bond is strictly proportional to bond extension, resolution of the restoring forces of the bonds on the crystal axes introduces terms containing trigonometric factors in the corresponding components of the restoring force on an atom, in general, since the atoms are coupled. This effect introduces anharmonicity in the vibration of an atom in the two- or three-dimensional case, and thus a thermal expansion, as correctly predicted by the Debye theory. To suppress this behavior, one must imagine the nearest neighbor pairs of atoms as independent, in which case the body is a Druyvesteyn-Meyering solid with an internal energy proportional to  $u$  of Eq. (33), and Eq. (24) for  $\gamma_{DM}$  correctly yields  $\gamma_{DM} = 0$  at zero pressure. Note that the effect in question does not exist for the linear chain, where the restoring forces of all bonds are in the same straight line; in agreement with the discussion of Dugdale and MacDonald, one verifies independently that  $\gamma_{DM}$  and  $\gamma_D$  are identical in this case.<sup>35</sup>

It is clear, accordingly, that the paradox of Dugdale and MacDonald arises only by imputing to a Debye solid properties which belong to a Druyvesteyn-Meyering solid.

### III. CASE OF FINITE STRAIN

In the following, the presence of a state of finite hydrostatic pressure, upon which elastic waves or

<sup>33</sup> R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), p. 31.

<sup>34</sup> Strictly, the validity of this expression for the energy is incompatible with a simple cubic lattice for nearest-neighbor interactions only, since no rigidity exists in this case; in such a lattice, this expression is changed by distortion of a cubic cell into a rhomboid, but the energy is unaffected since no bonds change in length. Hence, for a cubic lattice, the result applies without qualification only in the body- or face-centered case.

<sup>35</sup> The author is indebted to Dr. W. G. McMillan in connection with the argument of this paragraph.

pressure changed, will be the formal expansion for a Debye-Meyering solid. This discussion to be lifted.

For finite pressure alone, of an ideal harmonic solid from the point  $(V_1, P_1)$  has shown<sup>17</sup> by a Taylor expansion parameter  $e$  and

$$P - P_1 = (3\lambda +$$

where  $\lambda$  and  $\mu$  are the Lamé constants at point  $(V_1, P_1)$  and  $e$  is a small parameter corresponding to the expansion connected with

which yields

$$e = -\frac{1}{3} \frac{V - V_1}{V_1}$$

by a power-series expansion. From the condition of Eq. (37) yield

where

$$(V_1, P_1)$$

One notes that the expansion of Eq. (37) for  $P - P_1$  is a power-series in  $V - V_1$  and  $P - P_1$ . The presence of the term  $P - P_1$  in the expansion corresponds to the presence of the term  $P - P_1$  in the expansion of the bulk modulus. The interpretation of the expansion must be employed in the case of  $\mu$ , and the expansion of  $P - P_1$  in terms of  $P - P_1$  and  $V - V_1$ .

By a fundamental property of an elastic body when subjected to pressure alone; the stress is superimposed on the pressure.