relatively high melting point. For elements of low melting point, such as the molecular crystals, applicability of the Murnaghan equation of state has not been verified; hence the conclusions are not necessarily valid for elements of this class, for which the Simon equation was originally devised.

The fundamental fusion criterion on this theory is Eq. (7) corresponding to the Lindemann law, from which the Simon equation follows through choice of the Murnaghan equation (or one of similar analytic form) as the equation of state of the solid. However, a treatment analogous to that given here, based on a Birch equation[19] (also derived from the theory of finite strain) or other justifiable equation of state, will not necessarily yield the analytic form of Eq. (31), but should be capable of representing the experimental facts as well, if Eq. (7) is accepted. Further, the evaluation (21) of the Simon exponent implies some dependence on the pressure range covered by the fusion curve, and the evaluation of the Simon coefficient shows a dependence on the arbitrary position of the origin of the fusion curve. These considerations suggest that the Simon equation has more the character of an interpolation formula than a basic fusion equation, at least for the elements of higher melting temperature.

The fact that the Simon equation can be derived so directly from the generalized Lindemann law of I, for low pressure, justifies to some extent the step of extrapolating the law, for high pressure, to obtain the fusion curve on the basis of the Thomas-Fermi equation of state.[20]

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Grüneisen Parameter for a Solid under Finite Strain*

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An evaluation of the Grünesisen parameter (or constant) from the equation of state of a solid has been obtained by Druyvesteyn and Meyering on the basis of the theory of finite strain. The result differs (by $-\frac{1}{3}$) from the corresponding evaluation on the Debye theory, as given by Lorentz and by Slater. The value of Druyvesteyn and Meyering is derived here without use of the formal theory of finite strain, and shown to correspond physically to a model of independent pairs of nearest neighbor atoms, rather than to the Debye model of coupled atomic vibrations. This fact resolves a paradox raised by Dugdale and MacDonald in connection with an ideal harmonic solid, and ascribed by them to neglect of finite strain. The presence of a state of finite hydrostatic pressure, upon which elastic waves or pressure changes of infinitesimal amplitude are impressed, is taken into account explicitly by means of Murnaghan's theory of finite strain, to obtain the Grüneisen parameter, as evaluated from the equation of state, on the Debye model and for a Druyvesteyn-Meyering solid. The results are identical in the two cases with the corresponding values obtained without use of the formal theory of finite strain. Hence, no basis exists for the modification at finite pressure in the Grüneisen parameter from the Debye theory, as proposed by Dugdale and MacDonald. A comparison of average values over a relatively large number of elements, of Grüneisen constants as evaluated from Grüneisen's law and from the equation of state on the Debye model, shows excellent agreement at normal and at melting temperature.

I. INTRODUCTION

FROM results of Lorentz[1] and Slater,[2,3] the Grüneisen parameter (or constant) γ_D of an isotropic solid can be evaluated from its equation of state as

$$\gamma_D = -\tfrac{2}{3} - \tfrac{1}{2}(\partial P/\partial V)^{-1}(V\partial^2 P/\partial V^2), \tag{1}$$

where P is the pressure corresponding to the volume V. As indicated by the subscript D, this result is based on the Debye theory; it presupposes that the Poisson ratio of the solid is constant. In a number of papers[4–6] concerned with the fusion curve and the behavior of solids under pressure, the author has assumed that the evaluation (1) of the Grüneisen parameter is valid at high pressure, for the Debye theory.

The question can be raised whether the theory of

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[2] J. C. Slater, Phys. Rev. **57**, 744 (1940).

[3] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 238, 394, 451.

[4] J. J. Gilvarry, this issue [Phys. Rev. **102**, 308 (1956)], referred to hereafter as I.

[5] J. J. Gilvarry, this issue [Phys. Rev. **102**, 317 (1956)], referred to hereafter as II.

[6] J. J. Gilvarry, preceding paper [Phys. Rev. **102**, 325 (1956)], referred to hereafter as III.

finite strain may not modify Eq. (1) at high pressure. On the basis of Duhem's formulation[7] of the theory of finite strain, Druyvesteyn and Meyering[8] have obtained a value γ_{DM} for the Grüneisen parameter of a solid as evaluated from the equation of state, which can be expressed as

$$\gamma_{DM}=\gamma_D-\tfrac{1}{3}, \tag{2}$$

in terms of γ_D of Eq. (1). The presumption in their work is that the conflict of Eq. (2) with Eq. (1) arises from consideration of finite strain. Further, Druyvesteyn[9] has used Murhaghan's theory[10,11] of finite strain, with some drastic assumptions, to evaluate the Grüneisen parameter of a solid in terms of its Poisson ratio alone. In later work,[12] however, he pointed out that values of the Grüneisen constant obtained from Grüneisen's law show only poorly the predicted correlation with Poisson ratio; hence, this result of Druyvesteyn will not be considered further in what follows.

Of late, this question of the possible effect of finite strain has been reopened by Dugdale and MacDonald.[13] These authors point out that Eq. (1) yields a value $\gamma_D=\frac{1}{3}$ when applied to the equation of state of a solid which they believe should show no thermal expansion; since γ_D does not vanish, Grüneisen's law implies a thermal expansion. Dugdale and MacDonald ascribe the paradox to neglect of finite strain in the derivation of Eq. (1). They attempt to resolve the paradox by postulating (apparently without formal derivation from the theory of finite strain) an expression for the Grüneisen parameter as evaluated from the equation of state, which coincides with Eq. (2) of Druyvesteyn and Meyering at zero pressure, and thus yields a vanishing Grüneisen parameter for the case in question.

The infinitesimal theory of elasticity describes an isotropic solid by means of two elastic parameters, which can be taken as the two Lamé constants or as the bulk modulus and the Poisson ratio. These coefficients yield directly the values of such derivatives as $\partial P/\partial V$ or $\partial^2E/\partial V^2$, where E is the total energy. To evaluate the corresponding higher derivatives, the formal theory of finite strain introduces three additional coefficients for an isotropic solid, which can be taken as the three Brillouin[14,15] or the three Murnaghan[10,11] parameters. These parameters yield directly the values of such derivatives as $\partial^2P/\partial V^2$ or $\partial^3E/\partial V^3$. Since Eq. (1) contains $\partial^2P/\partial V^2$, though not expressed in terms of Brillouin or Murnaghan parameters, it involves consideration of finite strain. Hence, Eq. (1) for the Grüneisen parameter on the Debye model should contain no restriction to infinitesimal strain (a point which has also been made by Slater[16]).

In this paper, Eq. (2) for γ_{DM} will be derived without recourse to the formal mechanics of the theory of finite strain. The derivation brings out clearly the area of physical validity of the result; it applies to a model of independent pairs of nearest neighbor atoms. Druyvesteyn and Meyering obtained the expression by virtue only of tacit limitation to such a solid. Hence, the difference between Eqs. (1) and (2) lies in the model employed. The former equation corresponds to a Debye solid, in which coupling of the vibrations of the individual atoms is taken into account. These considerations yield an immediate resolution of the paradox of Dugdale and MacDonald.

Murnaghan has reduced the theory of finite strain to a form very tractable for physical applications.[17] The consistency of his results with the very extensive earlier work has been shown by Truesdell.[18] The formalism of the Murnaghan theory will be used in this paper to derive the value of the Grüneisen parameter under finite strain, as evaluated from the equation of state for a Debye solid, on the basis of an assumption corresponding to that of constant Poisson ratio. The result is identical with that of Eq. (1), as one should expect on the usual assumption that the presence of a uniform finite pressure affects the velocities of elastic waves of infinitesimal amplitude only through its effect upon the density and the elastic parameters. In point of fact, this assumption has been justified by Biot[19] on his formulation of the theory of finite strain, by a general argument. The value of Eq. (2) is found for the Grüneisen parameter of a Druyvesteyn-Meyering solid under finite strain.

II. HARMONIC SOLIDS

A harmonic solid is one in which the thermal behavior can be represented by a set of lattice oscillators whose Hamiltonian H is

$$H=\tfrac{1}{2}\textstyle\sum_i(p_i^2+4\pi^2\nu_i^2q_i^2), \tag{3}$$

where the range of i corresponds to all normal modes of oscillation, p_i is the generalized momentum corresponding to the oscillator coordinate q_i, and ν_i is an oscillator frequency. The Grüneisen parameter γ of the solid is defined by

$$\gamma=-\partial\ln\nu_i/\partial\ln V, \tag{4}$$

on the Grüneisen postulate that all lattice frequencies

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[8] M. J. Druyvesteyn and J. L. Meyering, Physica 8, 851 (1941).

[9] M. J. Druyvesteyn, Physica 8, 862 (1941).

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[16] J. C. Slater (private communication).

[17] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley and Sons, Inc., New York, 1951), Chap. 4.

[18] C. Truesdell, J. Rational Mech. and Anal. 1, 173 (1952).

[19] M. A. Biot, J. Appl. Phys. 11, 522 (1940).

ν_i vary with volume in the same manner.[20] The thermal pressure P_l of the lattice is given by

$$P_l=\gamma E_l/V, \tag{5}$$

where the thermal energy E_l of the lattice is defined by

$$E_l=\langle\textstyle\sum_i\frac{1}{2}p_i^2\rangle_{\mathrm{Av}}+\langle\sum_i 2\pi^2\nu_i^2q_i^2\rangle_{\mathrm{Av}}, \tag{6}$$

in which the averages of the kinetic and potential energies which appear must be computed from quantum statistical mechanics. The volumetric coefficient α of thermal expansion for a harmonic solid can be found from Grüneisen's law

$$K\alpha=\gamma C_V/V, \tag{7}$$

in which K is the bulk modulus (inverse compressibility) and C_V is the heat capacity at constant volume. This result follows directly from Eq. (5), on the Grüneisen assumption that γ is a function only of volume.

The thermal oscillators, whose coordinates appear in Eq. (3) for H, may be the virtual oscillators of the acoustic field as in a Debye solid (which shows a spectrum of frequencies), or they may be material oscillators, as in the Druyvesteyn-Meyering solid (where only one frequency appears) discussed below. Such harmonic solids stand in contrast to the anharmonic solids treated by Born and Brody,[21] or by Hooton.[22]

A. Debye Solid

For purposes of later reference, a prefatory discussion of a Debye solid will be given.

The Debye frequency ν_D of an isotropic monatomic solid is defined by

$$3N=(4/3)\pi V(c_l^{-3}+2c_t^{-3})\nu_D^3, \tag{8}$$

where N is Avogadro's number, V is the atomic volume, and c_l and c_t are the velocities of longitudinal and transverse elastic waves, respectively; this definition corresponds to the Debye assumption of an average wave velocity for the two types of waves. The wave velocities are given for an isotropic solid by

$$c_l^2=(\lambda+2\mu)/\rho,\quad c_t^2=\mu/\rho, \tag{9}$$

if ρ is the density and λ and μ are the Lamé parameters. The definition of the bulk modulus by

$$K=-V\partial P/\partial V \tag{10}$$

yields the result

$$K=\lambda+\tfrac{2}{3}\mu \tag{11}$$

on the infinitesimal theory of elasticity. Use of this relation and the definition,

$$\sigma=\tfrac{1}{2}\lambda/(\lambda+\mu), \tag{12}$$

of Poisson's ratio σ permits one to write Eq. (8), in the form of I and II, as

$$\nu_D=s_DN^{1/3}M^{-1/2}K^{1/2}V^{1/6}, \tag{13}$$

where M is the atomic weight and $s_D(\sigma)$ is defined by

$$s_D=\left[\frac{3}{2(1+\sigma)}\right]^{\frac{1}{2}}\left[\frac{9/4\pi}{[2(1-\sigma)]^{-\frac{3}{2}}+2[1-2\sigma]^{-\frac{3}{2}}}\right]^{\frac{1}{3}}. \tag{14}$$

Thermodynamic functions on the Debye model, such as the thermal energy E_l of Eq. (6), are given directly by standard results[23] in terms of $h\nu_D/kT$, where h and k are the Planck and Boltzmann constants respectively, and T is the absolute temperature.

To satisfy Grüneisen's postulate,[20] that all the frequencies vary with volume in the same manner, it is essential that the Poisson ratio σ be constant; otherwise the frequencies of the longitudinal and transverse waves show different variations.[3] With this assumption, use of Eq. (13) in Eq. (4) yields

$$\gamma_D=-\tfrac{1}{6}-\tfrac{1}{2}\partial\ln K/\partial\ln V \tag{15}$$

for the Grüneisen parameter γ_D on the Debye model. This form for γ_D is essentially that of Lorentz; by Eq. (10), it is equivalent to Eq. (1) of Slater, which, one notes, does not contain explicitly the Lamé parameters λ and μ characteristic of the infinitesimal theory of elasticity.

It is common in the theory of elasticity of solids to consider only adiabatic and isothermal processes, in which cases a strain-energy function can be defined[24]; thus, the distinction between the energy and the Helmholtz free energy will be ignored, in general. It is known that the bulk modulus for a solid can be taken indifferently as adiabatic or isothermal at low pressure,[25] and the result for a solid at high pressure follows from the Thomas-Fermi atomic model, for temperatures low in the sense of the model.[26] Hence, qualification of a partial derivative with respect to volume as adiabatic or isothermal will be omitted, on the basis above, and on the basis of Grüneisen's assumption that the characteristic frequency is a function only of volume.

B. Druyvesteyn-Meyering Solid

In this section, the Grüneisen parameter given by Druyvesteyn and Meyering will be obtained from an atomistic model. Consider a monatomic solid with a simple cubic lattice. Assume that each atom shares a bond with each of its six nearest neighbors, and with no neighbors more remote. Let each bond be represented

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[24] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), fourth edition, pp. 94, 99, 104.

[25] H. Jeffreys, Proc. Cambridge Phil. Soc. **26**, 101 (1930).

[26] J. J. Gilvarry, Phys. Rev. **96**, 934 (1954).

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 ν 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 γ_{DM} is the corresponding Grüneisen parameter, ν_{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

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

for the Grüneisen parameter of a solid of independent pairs of nearest-neighbor atoms. This expression differs from γ_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

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

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 nonvanishing 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-

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[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].

pression

$$(\partial^3 u/\partial r^3)_0 = -54\gamma_{DM} K_0, \tag{27}$$

obtained by Druyvesteyn and Meyering from prior work of Ornstein and Zernike.[30]

For a solid with a simple cubic lattice, in which the potential energy U of an atom in the interatomic force field is given, in terms of the interatomic distance r, by

$$U = -A/r^m + B/r^n, \tag{28}$$

where m and n are constants, and A and B are lattice sums which are computed for pairwise interaction of the atom with all others (considered fixed), and which are constant for deformation without distortion, Grüneisen[20] determined the characteristic frequency directly to obtain the expression

$$(m+n+3)/6 = \gamma_{DM} \tag{29}$$

for the Grüneisen constant at normal volume. The equation of state corresponding to the potential energy (28) can be evaluated as

$$P = 3K_0(n-m)^{-1}[(V_0/V)^{n/3+1} - (V_0/V)^{m/3+1}], \tag{30}$$

where K_0 is the bulk modulus corresponding to the normal volume V_0. If the bulk modulus K is determined from this equation, one verifies that Eq. (24) for γ_{DM} reproduces correctly Grüneisen's value of Eq. (29) for the parameter at normal volume. Slater[3] has given the value $(n+6)/6$ for the Grüneisen constant at normal volume of a solid for which $m=1$ in Eq. (28); the difference from the value $(n+4)/6$ corresponding to Eq. (29) of Grüneisen is due to the fact that Slater based his result on Eq. (15) for the Debye model.

A solid of the type of Druyvesteyn and Meyering shows thermal vibrations corresponding to the single frequency given by Eq. (17). Hence, thermodynamic functions, such as the thermal energy E_l of Eq. (6), can be expressed in terms of $h\nu_{DM}/kT$ by making use of results from Einstein's theory[23] of the heat capacity of solids. The properties discussed above, depending on the cubic term in the interatomic potential energy, are consistent with the usual thermodynamic functions derived directly from the partition function $Q = \sum_n \times \exp[-(n+\frac{1}{2})h\nu_{DM}/kT]$, since the energy levels of an anharmonic oscillator are independent of the cubic term within first-order perturbation theory.[31]

Lattices more general than the simple cubic can be treated by following Slater's procedure,[3] used in his heuristic representation of the metallic bond by a diatomic molecule, of writing the volume per atom as cr^3 in terms of the interatomic distance r of nearest-neighbor atoms, where the constant c is characteristic of the lattice type. In such a case, Eq. (20) remains valid, since each oscillator introduces a generalized coordinate $q_i = r - r_0$ to describe the solid, which has $3N$ degrees of freedom. Taylor expansion of $V = Ncr^3$ changes the constant factor in Eq. (21) for u, however. For the more general lattices in question, therefore, the value of s_{DM} in Eq. (23) for ν_{DM} becomes $3^{1/2}c^{1/3}/2^{1/2}\pi$, but Eq. (24) for γ_{DM} remains unchanged. For such lattices, Grüneisen's law in the form (26) can be verified by means of Eq. (25).

The preceding results can be generalized directly to the case of a simple cubic lattice where the mass of an atom differs from the common mass of its six nearest neighbors, as in the structure of the alkali halides. If the mass ratio is significantly different from unity, the value of s_{DM} approaches $\sqrt{3}/2\pi$. This value is quite close to the corresponding coefficient, as noted above, obtained by Einstein; in point of fact, both Madelung and Einstein had ionic crystals of the type of the alkali halides in mind in their treatments. For the degenerate case of mass ratio very different from unity, the Druyvesteyn-Meyering solid can be viewed as a solid of independent (light) atoms, where the coupling to the heavy atoms serves the function of providing an interatomic force field for the light atoms. The Grüneisen parameter γ_{DM} is independent of the mass ratio.

C. Ideal Harmonic Solid

An ideal harmonic solid will be defined as one in which the oscillator frequencies ν_i are strict constants. The constancy of the frequencies demands that the Grüneisen parameter vanish, from Eq. (4). It follows from Grüneisen's law (7) that the coefficient of thermal expansion vanishes, and, from Eq. (5), that the thermal pressure P_l vanishes. The latter conclusion is in agreement with the virial theorem, which one derives as[32]

$$\langle \sum_i \tfrac{1}{2} p_i^2 \rangle_{\mathrm{Av}} - \langle \sum_i 2\pi^2 \nu_i^2 q_i^2 \rangle_{\mathrm{Av}} = \tfrac{3}{2} P_l V, \tag{31}$$

for an ensemble of purely harmonic oscillators; since the average kinetic and average potential energies which enter are equal, one has $P_l = 0$. As will appear, the Debye and the Druyvesteyn-Meyering models make different predictions on the equation of state of an ideal harmonic solid.

From Eq. (24) for the Grüneisen parameter of a Druyvesteyn-Meyering solid, the condition $\gamma_{DM} = 0$ yields

$$K = K_0(V_0/V), \tag{32a}$$

$$P = K_0[(V_0/V) - 1], \tag{32b}$$

for the bulk modulus and equation of state (corresponding to $P=0$ for $V=V_0$) of an ideal harmonic solid on this model. In this case, Eq. (18) or Eq. (21) yields the potential energy u of a bond oscillator as

$$u = (3/2)K_0 v_0^{1/3}(r-r_0)^2 + O[(r-r_0)^4], \tag{33}$$

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[30] L. S. Ornstein and F. Zernike, Proc. Roy. Acad. Amsterdam **19**, 1289, 1304 (1916).

[31] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 160.

[32] H. C. Corben and P. M. Stehle, *Classical Mechanics* (John Wiley and Sons, Inc., New York, 1950), p. 202.

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.[31] 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 γ_{DM} vanishes, as it should.

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

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

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

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 ν_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

$$\frac{E-E_0}{3N}=\frac{3}{2}K_0v_0^{\frac{1}{3}}(r-r_0)^2\left[1+\frac{2}{3}\frac{r-r_0}{r_0}\right]+O[(r-r_0)^4], \tag{35}$$

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 Debey 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 ν_i to new values ν_i' given by

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

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

Dugdale and MacDonald[13] consider a solid in which the potential energy ϕ 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[34] 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 γ_{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 γ_{DM} and γ_D are identical in this case.[35]

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

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[33] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), p. 31.

[34] 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.

[35] The author is indebted to Dr. W. G. McMillan in connection with the argument of this paragraph.

pressure changes of infinitesimal amplitude are impressed, will be taken into account explicitly by means of the formal theory of finite strain, to justify Eq. (1) for a Debye solid and Eq. (2) for a Druyvesteyn-Meyering solid. Thus, any restriction in the preceding discussion to the case of infinitesimal strain will be lifted.

A. Debye Solid

For finite deformation, under hydrostatic pressure alone, of an isotropic elastic solid about the arbitrary point (V_1,P_1) on its pressure-volume curve, Murnaghan has shown[17] that the change $P-P_1$ in pressure of the silid from the point (V_1,P_1) to the point (V,P) is given by a Taylor series through second-order terms in a parameter e as

$$P-P_1=(3\lambda+2\mu+P_1)e-\tfrac{1}{2}(18l+2n-6\lambda-4\mu-3P_1)e^2, \quad (37)$$

where λ and μ are Lamé parameters evaluated at the point (V_1,P_1), and l and n are Murnaghan parameters corresponding to the same point. The variable e is connected with the volumes by the exact relation

$$1-2e=(V/V_1)^{2/3}, \quad (38)$$

which yields

$$e=-\frac{1}{3}\frac{V-V_1}{V_1}+\frac{1}{18}\left(\frac{V-V_1}{V_1}\right)^2-\frac{2}{81}\left(\frac{V-V_1}{V_1}\right)^3 \quad (39)$$

by a power-series expansion.

From the definition (10) of the bulk modulus K, Eq. (37) yields

$$K=K_1-3(V\partial K/\partial V)_1 e, \quad (40)$$

where

$$K_1=\lambda+\tfrac{2}{3}\mu+\tfrac{1}{3}P_1, \quad (41a)$$

$$(V\partial K/\partial V)_1=2l+(2/9)n-(1/9)P_1. \quad (41b)$$

One notes that inclusion of the second-order term in Eq. (37) for P makes the graph of $P-P_1$ against the dilatation $(V-V_1)/V_1$ a parabola, instead of the straight line corresponding to the first-order term in e. The presence of the finite pressure introduces the correction term P_1 to $3\lambda+2\mu$ in the first term of Eq. (37) for $P-P_1$, which, by Eq. (41a), changes the physical interpretation of the Lamé parameters in terms of the bulk modulus at finite pressure, as compared to the interpretation of Eq. (11) for infinitesimal pressure. It must be emphasized that the Lamé parameters λ and μ, and the Murnaghan parameters l and n, are functions of P_1, in general.

By a fundamental theorem of Murnaghan,[17] an elastic body which is initially isotropic remains so when subjected to a finite strain due to hydrostatic pressure alone; the initial state (V_1,P_1) above must be produced in this manner. If a general infinitesimal stress is superposed in this situation, the body remains approximately isotropic. Hughes and Kelly[36] have extended a prior result of Murnaghan[17] to show that the response of the solid to the superposed infinitesimal stress in this case is completely specified by two generalized Lamé parameters L and M, in a manner entirely analogous to the specification by λ and μ in the infinitesimal case. The values of L and M are given by

$$L=\lambda+P_1-(6l-2m+n-2\lambda-2\mu-P_1)e, \quad (42a)$$

$$M=\mu-P_1-(3m-\tfrac{1}{2}n+3\lambda+3\mu+P_1)e, \quad (42b)$$

in which m, like l and n, is a Murnaghan parameter evaluated at (V_1,P_1).

The speeds C_l and C_t of longitudinal and transverse waves, respectively, of infinitesimal amplitude superposed on a state of finite strain due to hydrostatic pressure, are given by equations analogous to Eqs. (9) in the infinitesimal case, as

$$C_l^2=(L+2M)/\rho, \quad C_t^2=M/\rho, \quad (43)$$

where ρ is the density corresponding to the volume V. Hughes and Kelly give expressions for L and M which omit terms in P_1, since these authors referred the body to an initial state of zero pressure, for experimental purposes. If use is made of the relation $\rho=\rho_0(1+3e)$ obtained from Eq. (39), for ρ in terms of an initial density ρ_0, Eqs. (43) reduce to the corresponding expressions of Hughes and Kelly for $P_1=0$, and agree with the corresponding relations of Brillouin.

With K given by Eq. (40), the values of L and M satisfy the relation

$$K=L+\tfrac{2}{3}M, \quad (44)$$

analogous to Eq. (11) in the infinitesimal case. The expression (12) for the Poisson ratio in the infinitesimal case must be replaced for finite strain by a generalized Poisson ratio Σ defined by

$$\Sigma=\tfrac{1}{2}L/(L+M). \quad (45)$$

The stability conditions[24] K, $M\geq 0$ require that $\Sigma\leq\frac{1}{2}$, and one obtains $\Sigma\rightarrow\sigma$ in the limit P_1, $P\rightarrow 0$. With introduction of Σ, the response of the solid under finite strain to a superposed infinitesimal stress of general type can be described completely by the two parameters K and Σ, instead of L and M.

Use of Eqs. (44) and (45) in the analog of Eq. (8) obtained by replacing c_l and c_t by C_l and C_t, respectively, yields

$$\nu_D=SN^{1/3}M^{-1/2}K^{1/2}V^{1/6} \quad (46)$$

for the Debye frequency ν_D, where $S=s_D(\Sigma)$ in terms of s_D of Eq. (14). Corresponding to the case of Sec. IIA, it is necessary that Σ be constant to satisfy the Grüneisen postulate that the frequencies of the longitudinal and transverse waves show the same volume variation. Under this assumption, the definition (4)

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[36] D. S. Hughes and J. L. Kelly, Phys. Rev. **92**, 1145 (1953).

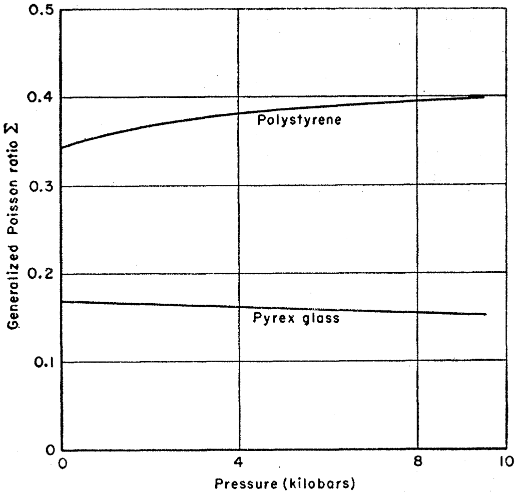

FIG. 1. The generalized Poisson ratio Σ as a function of pressure for polystyrene and for Pyrex glass, from data of Hughes and Kelly.

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

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

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

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

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

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

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

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

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 Murnaghan[17] 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 expression[17]

$$E-E_1 = V_1[3P_1e + (3/2)(3\lambda+2\mu)e^2 - (9l+n)e^3], \quad (51)$$

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

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

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

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

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 energy u of the oscillator becomes

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

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

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

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

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

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

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

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

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

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

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

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 $\langle r-r_1\rangle_{\mathrm{Av}}$ yields a vanishing thermal expansion.

IV. COMPARISON WITH EXPERIMENTAL DATA

It is clear from the foregoing that the two evaluations, γ_D and γ_{MD}, 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 Slater[3] and Zener[38] in connection with the Debye model. However, from 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 author[39] 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.

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	1.9_2[a]	1.5_9[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).

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 everage value for 14 elements is shown likewise for the Grüneisen constant $\gamma_{m,D}$ of the solid at fusion, given in I as

$$\gamma_{m,D}=\tfrac{1}{3}+\tfrac{1}{2}qK_m\Delta V/L, \tag{61}$$

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

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[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.

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

law to the solid at the melting point. These data suggest that the assumptions underlying the evaluation of the Grüneisen parameter from the equation of state on the Debye model are met reasonably well by elementary solids, on the average.

V. CONCLUSION

The results obtained show that formal consideration of finite strain leaves the evaluation of the Grüneisen parameter from the equation of state unaltered, for either a Debye solid or a Druyvesteyn-Meyering solid. Hence, no reason exists on the basis of the theory of finite strain for the arbitrary modification in the evaluation of the parameter for a Debye solid, as proposed by Dugdale and MacDonald. This statement presupposes that the wave amplitudes of the lattice vibrations are infinitesimal. It is not denied that an intrinsically anharmonic theory, such as that of Born and Brody[21] or of Hooton,[22] may demand revision of the value of the Grüneisen parameter as determined from the equation of state, but such a model likewise requires revision of the value of the characteristic frequency, as fixed by Eq. (8) on the Debye theory. Underlying the definition of the Grüneisen parameter is the postulate that all lattice frequencies vary with volume in the same manner; it is not obvious, *a priori*, that this requirement can be met within the framework of an essentially anharmonic theory.

The development of I, II, and III is based on the Debye-Waller theory derived from the Debye model, in contrast to the original Lindemann theory based on an Einstein model. Since the form of Grüneisen parameter taken in the papers in question corresponds to the Debye theory, it is felt that in this respect the results have been justified fully.

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Auger Electron Emission in the Energy Spectra of Secondary Electrons from Mo and W

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With the aim of determining to what extent the energy distribution of secondary electrons from targets of Mo and W may contain fine structure, measurements have been made using primary energies from 100 to 2000 electron volts. An electrostatic analyzer of the 127-degree type having an experimentally determined resolution of one percent was used. Observations of the pressure in the vacuum system, after heating the target above 2000°K and cooling to room temperature, showed that an energy spectrum could be recorded before formation of the first monolayer of contamination on the target surface.

Energy distribution measurements revealed: (1) Several subsidiary maxima at fixed differences in energy from the primary energy, these differences being characteristic of the target material and independent of the primary energy itself. (2) Several subsidiary maxima in the energy distribution at fixed positions along the energy scale lying between 10 and 500 electron volts, characteristic of the target material, and independent of the primary voltage. The maxima described in (1) are considered to be primary electrons reflected after suffering discrete losses of energy to the target. These discrete losses are believed to indicate the positions of the higher energy levels of the target material. The maxima described in (2) are interpreted as Auger electrons. Combining the energy level values determined from the discrete loss measurements with energy values for the deeper lying levels available from x-ray studies, it is possible to predict the energies with which Auger electrons might be expected to be emitted. Some of the predicted energies for Auger electrons agree reasonably well with with the energies observed experimentally both for Mo and for W.

I. INTRODUCTION

THE general shape of the energy distribution of secondary electrons from a metal target is that of a smooth curve whose two principal features are a large maximum of slow secondaries occurring near two or three volts and a sharper, usually smaller maximum, caused by elastically reflected primaries. Furthermore, several workers have observed some fine structure in the energy spectrum of secondaries from a number of different metals. Rudberg,[1] studying Cu, Ag, and Au, reported inelastic reflection of primary electrons that had suffered discrete losses of energy, these losses being independent of the primary energy and characteristic of the target material. Haworth[2,3] made similar observations for targets of Mo and Cb but observed further that

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[1] E. Rudberg, Phys. Rev. 50, 138 (1936).

[2] L. J. Haworth, Phys. Rev. 48, 88 (1935).

[3] L. J. Haworth, Phys. Rev. 50, 216 (1936).