ON THE MIE–GRÜNEISEN AND HILDEBRAND APPROXIMATIONS TO THE EQUATION OF STATE OF CUBIC SOLIDS*

F. G. FUMI and M. P. TOSI

Argonne National Laboratory, Argonne, Illinois

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Abstract—An analysis is made of the conditions under which the equation of state of a cubic solid under hydrostatic pressure takes the form given by either the Mie–Grüneisen or the Hildebrand approximation. The condition of validity of the vibrational or thermal formulation of the Mie–Grüneisen approximation is reduced to the existence of a purely volume-dependent characteristic temperature for the vibrational or thermal free energy of the solid. The analysis consists then in a search for temperature ranges where these restrictions on the functional form of the free energy, and the restrictions on the form of the internal energy imposed by the Hildebrand approximation, are satisfied for a non-metal in the quasi-harmonic approximation. The main results are as follows: (1) At temperatures somewhat above the Debye characteristic temperature for the (quasi-harmonic) high-temperature heat capacity at constant volume, it is appropriate to take as equation of state the vibrational Hildebrand equation: (2) at somewhat lower temperatures, this Hildebrand equation is generally more inaccurate than the corresponding Mie–Grüneisen equation; and (3) in the low-temperature T^3 region of the heat capacity, the equation of state reduces to the thermal Mie–Grüneisen equation. The explicit forms of the vibrational and thermal Mie–Grüneisen equations of state, and of their volume derivatives at constant temperature, are reported together with the corresponding Hildebrand equations. Some corollary results are obtained, within the quasi-harmonic approximation, on the temperature variation at constant volume of the Grüneisen parameters relating the explicit volume and temperature dependence of the vibrational and thermal free energy and of the entropy of a cubic solid, and (in an Appendix) on the temperature variation of the Debye temperatures appropriate to the various thermodynamic functions of any non-metal. The available experimental and theoretical evidence on the anharmonic contributions to the thermodynamic functions of solids is briefly discussed, and points to the conclusion that their weight is quite small in the region of temperature of interest for our analysis.

1. INTRODUCTION

THE FORMULATION of the equation of a state of a cubic solid under hydrostatic pressure which is commonly adopted to determine the volume dependence of the lattice energy of the solid from empirical data is based either on the Hildebrand approximation[2] or on the Mie–Grüneisen approximation.[3] In recent years, it has been tacitly assumed that the Mie–Grüneisen equation of state, which takes approximate account of the explicit volume dependence of the (vibrational or thermal) free energy of the solid, is a better formulation to

use than the Hildebrand equation of state, which neglects the explicit volume dependence of the (vibrational or thermal) internal energy of the solid. In effect, HUANG[4] took the Mie–Grüneisen equation of state as equation of reference in analyzing the validity of the Hildebrand equation. The same attitude is implicit also in some calculations of BORN and HUANG[5], who have adopted the vibrational Mie–Grüneisen equation of state, and an approximation to its volume derivative at constant temperature, to recalculate the parameters entering the Born expression for the lattice energy of the alkali halides from empirical data at room temperature and atmospheric pressure. More recently RICE *et al.*[6] have derived the *P–V* isotherm

at 0°K for a number of metals from their shock-wave compression data by adopting the thermal Mie–Grüneisen equation of state, in an approximation proposed by DUGDALE and MACDONALD, as the equation of state appropriate above room temperature. BENEDEK[7] has used, instead, the vibrational Mie–Grüneisen equation of state, with the Grüneisen parameter γ taken as a constant, to deduce from those data the volume dependence of the lattice energy of some metals, neglecting the electronic contribution to the vibrational free energy at room temperature and zero pressure.

Here we will investigate systematically the conditions under which the equation of state of a cubic solid, subject only to hydrostatic pressure, reduces to the form given by either the Mie–Grüneisen or the Hildebrand approximation. General thermodynamic arguments, which extend previous work of BORN[8], GRÜNEISEN[3] and DAVIES[9], lead one quite easily to express the condition of validity of the vibrational or thermal formulation of the Mie–Grüneisen approximation as a restriction on the form of the vibrational or thermal free energy of the solid as a function of its volume and temperature. One can then show that the experimental observation, for a given solid, of a Grüneisen parameter γ which does not depend on temperature at constant volume in a certain range of temperature and volume does not ensure, in general, the validity in this range of either form of the Mie–Grüneisen equation of state. Thermodynamics does not allow one, instead, to establish whether the special functional form of the vibrational (or thermal) free energy, which expresses the Mie–Grüneisen approximation, is more or less restrictive than the special functional form of the vibrational (or thermal) energy, which expresses the Hildebrand approximation. Some general results on the validity of these various functional restrictions can be obtained within the quasi-harmonic approximation to the statistical mechanics of a non-metal, both at the low temperatures where only long-wave acoustic modes are thermally excited, and in the temperature range of convergence of the THIRRING–STERN[10] expansions for the thermodynamic functions, completing previous work of BORN[11] and BARRON[12, 13]. Within this approximation, the vibrational Mie–Grüneisen equation of state and the corresponding Hildebrand equation are both strictly valid only at

temperatures where the heat capacity at constant volume has attained its classical value, but at somewhat lower temperatures the former can be expected to be less inaccurate than the latter. Furthermore, within the temperature range of convergence of the Thirring–Stern expansions, the independence of γ from temperature at constant volume does ensure the validity of the vibrational Mie–Grüneisen equation of state. The thermal Mie–Grüneisen equation, instead, is the appropriate equation of state for a non-metal in the T^3 region of the heat capacity. At moderate and high temperatures, the thermal Mie–Grüneisen and Hildebrand equations are less accurate than the correponding vibrational equations, and they become valid only if the zero-point energy of the solid becomes negligible compared to its thermal energy, so that the two formulations of each approximation coincide.

2. THERMODYNAMIC DISCUSSION OF THE MIE–GRÜNEISEN AND HILDEBRAND APPROXIMATIONS

The equation of state of a cubic solid subject only to hydrostatic pressure, $P = -(\partial F/\partial V)_T$, can be written alternatively in the so-called *vibrational* and *thermal* formulations (see, e.g., BENEDEK[7] and BARRON[12]. These correspond, respectively, to splitting the Helmholtz free energy of the solid $F(V,T)$ into the energy of the static solid of volume V in its electronic ground state [the lattice energy $W_L(V)$] plus a "vibrational" free energy $F_{vib}(V,T)$, or into the non-thermal energy [the cohesive energy $W_C(V)$ of the solid of volume V at 0°K] plus a "thermal" free energy $F_{th}(V,T)$. The free energies $F_{vib}(V,T)$, $F_{th}(V,T)$ involve, of course, the vibrational and thermal energies of the solid $W_{vib}(V,T)$ and $W_{th}(V,T)$, and the total entropy $S(V,T)$. We write the equation of state in these two completely equivalent formulations in a form which, though seemingly unduly elaborate, is particularly well suited for the subsequent thermodynamic discussion:

$$P + \frac{dW_L}{dV} = \gamma' \, \frac{W_{vib}}{V} \tag{1a}$$

$$\gamma'(V,T) = \frac{V}{T} \, \frac{[\partial(F_{vib}/T)/\partial V]_T}{[\partial(F_{vib}/T)/\partial T]_V} \tag{1b}$$

and

$$P + \frac{dW_C}{dV} = \gamma'' \frac{W_{th}}{V} \tag{2a}$$

$$\gamma''(V,T) = \frac{V}{T} \frac{[\partial(F_{th}/T)/\partial V]_T}{[\partial(F_{th}/T)/\partial T]_V}. \tag{2b}$$

The Grüneisen parameters γ' and γ'' differ, in general, from the parameter γ defined by the Grüneisen relation:

$$\gamma(V,T) = \frac{V}{T} \frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V} = \frac{V\beta}{C_V K} \tag{3}$$

where β, K and C_V are the coefficient of volume thermal expansion, the isothermal compressibility and the heat capacity at constant volume of the solid.

The vibrational formulation consists in replacing γ' in equation (1a) by γ. Similarly, the thermal formulation of the Mie–Grüneisen approximation replaces γ'' in equation (2a) of the Mie–Grüneisen approximation by γ. This is permissible in a certain range of temperature and volume when and only when γ', or γ'', does not depend explicitly on temperature in such a range, as is apparent from the equations

$$\left(\frac{\partial\gamma'}{\partial T}\right)_V = \frac{C_V}{W_{vib}}(\gamma - \gamma') \tag{4}$$

$$\left(\frac{\partial\gamma''}{\partial T}\right)_V = \frac{C_V}{W_{th}}(\gamma - \gamma'') \tag{5}$$

which re-express the temperature derivative of the equation of state at constant volume by means of the thermodynamic identity $(\partial P/\partial T)_V = \beta/\dot{K}$. This leads at once to the thermodynamic expression of the two formulations of the Mie–Grüneisen approximation, namely to the restrictions on the functional form of the thermodynamic functions of the solid which represent necessary and sufficient conditions for the validity of these formulations in a given range of temperature and volume. Indeed, the integration of equations (1b) or (2b) under the condition that γ', or γ'', be a function only of the volume of the crystal in a certain temperature range leads to the following functional form for

the vibrational free energy of the solid:

$$F_{vib}(V,T) = Tf(T/\Theta'(V)) \tag{6a}$$

or for its thermal free energy

$$F_{th}(V,T) = Tf(T/\Theta''(V)). \tag{7a}$$

Here f denotes an arbitrary function, while $\Theta'(V)$ and $\Theta''(V)$ are general characteristic temperatures, subject only to the restrictions

$$\gamma'(V) = -\frac{d \ln \Theta'}{d \ln V} \tag{6b}$$

$$\gamma''(V) = -\frac{d \ln \Theta''}{d \ln V}. \tag{7b}$$

The conditions (6a) and (7a) are clearly less restrictive than the Debye model. It should also be stressed that the restrictions (6) and (7) are not, in general, thermodynamically equivalent, and thus the vibrational and thermal Mie–Grüneisen equations of state are not alternative formulations of the same equation, contrary to equations (1) and (2). BORN[8] had already shown, by a different procedure, that for an Einstein solid with frequency ν the validity of the vibrational Mie–Grüneisen equation of state implies that the vibrational free energy has the form $Tf[T/\nu(V)]$, while GRÜNEISEN[3] had pointed out that this equation follows from the assumption that the vibrational free energy has the form (6a).

The thermodynamic expression of the condition that γ be a purely volume-dependent function in a certain range of temperature is similarly obtained by integrating equation (3). This leads to the following functional form for the entropy of the solid:

$$S(V,T) = S(T/\Theta(V)) \tag{8a}$$

$$\gamma(V) = -\frac{d \ln \Theta}{d \ln V} \tag{8b}$$

implying that whenever γ does not depend on temperature at constant volume, it measures the logarithmic derivative of a purely volume-dependent characteristic temperature for the entropy. Condition (8a) is less restrictive than conditions (6a) and (7a), since when the vibrational or thermal free energy is of the form (6a) or (7a) in a certain

range of temperature and volume, the entropy is of the form (8a) with $\Theta(V) = \Theta'(V)$ or $\Theta(V) = \Theta''(V)$ [and the heat capacity at constant volume depends only on the ratio $T/\Theta(V)$], but the converse is not necessarily true. This implies that *the independence of γ from temperature at constant volume for a given solid in a certain range of temperature and volume, established by means of measurements of β, C_V and K, does not guarantee, in general, the validity in the same range of either formulation of the Mie–Grüneisen approximation.* However, if the entropy has the form (8a) in a temperature range from $0°K$ upwards, or if the heat capacity at constant volume has the form $C_V(V,T) = C_V(T/\Theta(V))$ in such a range and the entropy of the solid at $0°K$ is a constant, the thermal free energy has the form (7a) in the same range, with $\Theta''(V) = \Theta(V)$. DAVIES[9] had already pointed out that if the heat capacity at constant volume has a purely volume-dependent characteristic temperature in a temperature range including the absolute zero, and Nernst's theorem applies, γ and γ'' are both given by the logarithmic derivative of this characteristic temperature.

The vibrational and thermal formulations of the Hildebrand approximation are traditionally expressed through the restrictions that they impose on the functional form of the internal energy W of the solid: these read

$$W(V,T) = W_L(V) + W_{vib}(T) \qquad (9)$$

and

$$W(V,T) = W_C(V) + W_{th}(T) \qquad (10)$$

respectively. These restrictions are completely equivalent to assuming that γ' and γ'' are related to γ by the equations

$$W_{vib}\gamma'(V,T) = TC_V\gamma(V,T) \qquad (11)$$

$$W_{th}\gamma''(V,T) = TC_V\gamma(V,T) \qquad (12)$$

The vibrational and thermal Hildebrand equations of state, obtained from equations (1a) and (2a) by using equations (11) and (12), respectively, are not alternative formulations of the same equation, since the restrictions (9) and (10) are not, in general, thermodynamically equivalent.

Thermodynamically, the validity of the Hildebrand restrictions on the vibrational or thermal energy of a solid in a certain range of temperature and volume does not ensure the validity in the same range of the Mie–Grüneisen restrictions on the corresponding free energies, nor vice versa. In particular, the validity of equation (9) in a range from $T_0(V)$ to a running T implies only that $F_{vib}(V,T)/T$ is the sum of a function of the temperature and a function of the volume, while the validity of equation (6) implies only that $W_{vib}(V,T) = Tg(T/\Theta'(V))$ ith $g(x) = -x(df/dx)$. Thus, *in general, one has no thermodynamic reason o prefer either the Mie–Grüneisen or the Hildebrand approximation.* One can, on the other hand, establish thermodynamically the equivalence of the two approximations in a range of temperature and volume where the vibrational or thermal energy of the solid depends only on temperature, and in a linear way, and the vibrational or thermal free energy has the functional form $T \ln (T/\Theta(V))$, since either restriction follows from the other.

3. THERMODYNAMIC FUNCTIONS AND GRÜNEISEN PARAMETERS OF A CUBIC NON-METAL IN THE QUASI-HARMONIC APPROXIMATION

To discuss the validity of the functional restrictions on the thermodynamic functions of a cubic solid under hydrostatic pressure which express the Mie–Grüneisen and Hildebrand approximations, one must resort to the statistical mechanics of the solid. We restrict ourselves to cubic non-metals, for which it is plausible to adopt the adiabatic approximation and to neglect the electronic contributions to the vibrational parts of the thermodynamic functions. In addition, we treat the lattice contributions by the quasi-harmonic approximation: namely, we assume that these contributions, taking the (constant) entropy of the solid at $0°K$ as the zero for the entropy, are given by the thermodynamic functions of an assembly of uncoupled harmonic oscillators, whose frequencies depend only on the volume of the solid. The quasi-harmonic approximation has been used quite commonly in recent years in studies of thermodynamic properties of solids (see, e.g. Refs. 12–18), and, for our purposes, it has the merit of allowing a general analysis of the functional forms of the thermodynamic functions without the adoption of particular force models.

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Admittedly, this approximation neglects specifically anharmonic contributions to the thermodynamic functions, detailed estimates of which have recently been undertaken for some simple force models,[19,20] but the available evidence, to be discussed in Section 5, suggests that these contributions are unimportant in the temperature range of utmost interest for our analysis.

A general consequence of the quasi-harmonic approximation is that, at temperatures sufficiently close to the absolute zero, the heat capacity at constant volume of a cubic non-metal is simply proportional to $[T/\Theta_D(V)]^3$, where $\Theta_D(V)$ is the elastic Debye characteristic temperature. At somewhat higher temperatures, however, the (quasi-harmonic) heat capacity contains additional terms in higher odd powers of T, originating from the dispersion of the acoustic modes and involving each the ratio between the absolute temperature and a purely volume-dependent characteristic temperature appropriate to the term and generally different from $\Theta_D(V)$.[17] This result, when combined with the thermodynamic theorem involving the heat capacity given in Section 2, allows one to state that *the T^3 region is, in general, the only low-temperature region where the thermal formulation of the Mie–Grüneisen approximation is valid, and where γ does not depend explicitly on temperature.* BORN[11] and BARRON[12, 13] had already pointed out that in the T^3 region γ and γ'' are both given by the logarithmic derivative of $\Theta_D(V)$. *The vibrational formulation of the Mie–Grüneisen approximation, instead, is not valid in the T^3 region,* contrary to what was assumed by HUANG[4], since the vibrational free energy could have the form (6a) in this region only if the zero-point energy were simply proportional to $\Theta_D(V)$; namely, if the Debye form for the vibrational spectrum were appropriate for the entire vibrational spectrum of the solid. Finally, the Hildebrand approximation for the thermal or vibrational energy is clearly not valid at low temperatures.

Another general consequence of the quasi-harmonic approximation for a cubic non-metal, pertinent to the region of moderate and high temperatures where the Thirring–Stern expansions of the thermodynamic functions converge, is easily established by inspection of these expansions, which are given in the Appendix. This is that the vibrational energy becomes explicitly independent

of volume and the vibrational free energy takes the form (6a) only at temperatures somewhat above the Debye characteristic temperature $\Theta_2(V)$ for the high temperature heat capacity at constant volume, where they approach, respectively, $3kT$ per particle and the high temperature Debye functional form $T \ln [T/\Theta_0(V)]$. On the other hand, the thermal energy per particle approaches $3kT$, and the thermal free energy approaches the high temperature Debye functional form, $T \ln [T/\Theta_0(V)]$, only at the significantly higher temperatures where the zero-point energy per particle is negligible compared to $3kT$. These results, when combined with the thermodynamic theorem given in Section 2, connecting these particular functional forms for the energies and free energies, lead one to the following conclusions: (1) *The vibrational formulation of the Mie–Grüneisen approximation becomes valid, in general, when and only when the vibrational energy per particle approaches $3kT$, namely, when and only when the Hildebrand approximation for the vibrational energy becomes valid; and* (2) *the thermal formulation of the Mie–Grüneisen approximation would generally become valid in the high-temperature region only at the very high temperatures, hardly ever attained by a solid, where the Hildebrand approximation for the thermal energy becomes valid.* BORN[11] indicated long ago that γ is a function only of the volume of the solid in the temperature range where the law of Dulong and Petit is obeyed, and BARRON[12] has pointed out that for $T \to \infty$, γ'' and γ approach a common value given by the logarithmic derivative of the Debye characteristic temperature for the entropy for $T \to \infty$. BARRON's calculations[12] of the temperature variation at constant volume of γ and γ'' for a particular quasi-harmonic model, a face-centered cubic solid with central forces between nearest neighbors, provide also an illustration of the general result, implicit in (1) and (2), that γ'' *approaches the common limit, γ_∞, of the γs at high temperatures more slowly than γ.*

In the region of intermediate temperatures, where the Thirring–Stern expansions converge but the vibrational energy per particle has not yet attained the value $3kT$, the validity of the Hildebrand approximation for the vibrational energy requires that the pertinent even moments μ_{2n} of the frequency distribution of the normal modes of the solid be independent of the volume of the solid. On

the other hand, the validity of the Mie–Grüneisen approximation for the vibrational free energy, as well as the condition that γ be a purely volume-dependent function, require only that the volume dependence of the roots $(\mu_{2n})^{1/2n}$ of the pertinent even moments of the vibrational spectrum be the same as that of the geometric means of the normal-mode frequencies, a less restrictive condition than the validity of the Debye functional form for the vibrational free energy (see Appendix). The corresponding conditions for the validity of the thermal formulations involve also the moment μ_1. Clearly, one cannot make any general statement on the actual validity of either formulation of the Mie–Grüneisen or Hildebrand approximation, but *one has some reason to expect either formulation of the Mie–Grüneisen approximation to be less inaccurate than the corresponding formulation of the Hildebrand approximation in the region of moderate temperatures*. One can also state that *within the region of convergence of the Thirring–Stern expansions, the temperature ranges in which γ and γ' do not depend on temperature at constant volume coincide*. Thus the calculations of the temperature variation at constant volume of the parameter γ for simple quasi-harmonic models of rare-gas solids, performed by BARRON[12] and by HORTON and LEECH[18], which show that in these cases γ remains practically constant down to temperatures of the order of one third of the Debye characteristic temperature, do confirm that in these cases the vibrational Mie–Grüneisen approximation is in fact less inaccurate than the vibrational Hildebrand approximation at these temperatures.

The Thirring–Stern expansions for the entropy and the vibrational free energy allow one also to show that *the rates of approach of γ and γ' to γ_∞ are equal in absolute value but opposite in sign*. This result, together with equation (4), allows one to predict that for any model for which γ increases monotonically with temperature from $0°K$ upwards (and in which one neglects the effect of thermal expansion on the vibrational frequencies), as is the case, for example, for most of the quasi-harmonic models of rare-gas solids treated by BARRON[12] and by HORTON and LEECH[18], γ' will be larger than γ_∞ and will increase steadily with decreasing temperature down to $0°K$, where $(\partial\gamma'/\partial T)_V$ must vanish. One can envisage this result as a particularly dramatic illustration of the general

result that γ' differs from γ at very low temperatures.

A condition for the validity, within the quasi-harmonic approximation, of *both* formulations of the Mie–Grüneisen approximation over the *entire* range of temperatures has recently been given by BLACKMAN[14]. If one rewrites the quasi-harmonic expressions

$$\gamma' = -\sum_j \frac{d\ln\nu_j}{d\ln V}\, W_{\text{vib}}^{(j)}/W_{\text{vib}}$$

and

$$\gamma'' = -\sum_j \frac{d\ln\nu_j}{d\ln V}\, W_{\text{th}}^{(j)}/W_{\text{th}}$$

in integral form, it is in effect apparent that the condition in question is that the arithmetic average of $d\ln\nu/d\ln V$ for all vibrations lying between ν and $\nu+\Delta\nu$ be a constant, independent of the frequency. This is clearly more restrictive than the conditions for the validity of either formulation of this approximation at intermediate temperatures, that we have given above.

4. THE MIE-GRÜNEISEN AND HILDEBRAND EQUATIONS OF STATE

The formulations (1) and (2) of the equation of state of a cubic solid under hydrostatic pressure, and their first volume derivatives at constant temperature:

$$-\frac{1}{K} + V\frac{d^2 W_L}{dV^2} = \frac{\gamma'^2}{V}(TC_V - W_{\text{vib}})$$

$$+ \gamma'\frac{W_{\text{vib}}}{V}\left[\frac{V}{\gamma'}\left(\frac{\partial\gamma'}{\partial V}\right)_T + T\left(\frac{\partial\gamma'}{\partial T}\right)_V - 1\right] \quad (13)$$

$$-\frac{1}{K} + V\frac{d^2 W_C}{dV^2} = \frac{\gamma''^2}{V}(TC_V - W_{\text{th}})$$

$$+ \gamma''\frac{W_{\text{th}}}{V}\left[\frac{V}{\gamma''}\left(\frac{\partial\gamma''}{\partial V}\right)_T + T\left(\frac{\partial\gamma''}{\partial T}\right)_V - 1\right] \quad (14)$$

can be easily reduced to the special forms appropriate in the Mie–Grüneisen and Hildebrand approximations. One uses the Mie–Grüneisen and Hildebrand approximations to $\gamma'(V,T)$ and $\gamma''(V,T)$, together with the thermodynamic

expressions of $(\partial\gamma/\partial V)_T$ and $(\partial\gamma/\partial T)_V$,

$$\left(\frac{\partial\gamma}{\partial V}\right)_T = \frac{\gamma}{V} - \frac{\gamma}{C_V}\left(\frac{\partial C_V}{\partial V}\right)_T$$
$$+ \frac{1}{C_V K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right] \qquad (15)$$

$$\left(\frac{\partial\gamma}{\partial T}\right)_V = \frac{V}{TC_V}\left(\frac{\partial C_V}{\partial V}\right)_T - \frac{\gamma}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V \qquad (16)$$

which follow from equation (3), the first one by transforming $[\partial(\beta/K)/\partial V]_T$ into pressure derivatives at constant temperature, noting then that $(\partial\beta/\partial P)_T = -(\partial K/\partial T)_P$. In the vibrational formulation of the Mie–Grüneisen approximation, the resulting equations have the form

$$P + \frac{dW_L}{dV} = \frac{T\beta}{K}\frac{W_{\text{vib}}}{TC_V} \qquad (17)$$

$$-\frac{1}{K} + V\frac{d^2W_L}{dV^2}$$
$$= \frac{V\beta^2}{C_V^2 K^2}W_{\text{vib}}\left[\frac{TC_V}{W_{\text{vib}}} - 1 - \frac{T}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V\right]$$
$$+ \frac{W_{\text{vib}}}{TC_V}\frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]; \qquad (18)$$

while in the thermal formulation they read

$$P + \frac{dW_C}{dV} = \frac{T\beta}{K}\frac{W_{\text{th}}}{TC_V} \qquad (19)$$

$$-\frac{1}{K} + V\frac{d^2W_C}{dV^2}$$
$$= \frac{V\beta^2}{C_V^2 K^2}W_{\text{th}}\left[\frac{TC_V}{W_{\text{th}}} - 1 - \frac{T}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V\right]$$
$$+ \frac{W_{\text{th}}}{TC_V}\frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]. \qquad (20)$$

In the corresponding formulations of the Hildebrand approximation, they are instead:

$$P + \frac{dW_L}{dV} = \frac{T\beta}{K} \qquad (21)$$

$$-\frac{1}{K} + V\frac{d^2W_L}{dV^2} = \frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right] \qquad (22)$$

and

$$P + \frac{dW_C}{dV} = \frac{T\beta}{K} \qquad (23)$$

$$-\frac{1}{K} + V\frac{d^2W_C}{dV^2} = \frac{T}{K^2}\left[\left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]. \qquad (24)$$

HUANG[4] assumed equations (17) and (19) as valid at all temperatures and attempted to investigate the validity of the Hildebrand approximation for a non-metal by searching for temperature ranges where equations (21) and (23) coincide with equations (17) and (19), respectively, computing the ratios W_{vib}/TC_V and W_{th}/TC_V by means of the Debye model. Clearly this procedure does not establish the relative merits of the Hildebrand and Mie–Grüneisen approximations. Thus HUANG's result that the ratio W_{vib}/TC_V approaches unity at temperatures somewhat above the Debye characteristic temperature, while the ratio W_{th}/TC_V approaches unity only at much higher temperatures, represents only a numerical verification for the Debye model of the general result to this effect which is apparent from the Thirring expansions for the vibrational and thermal energies. BORN and HUANG[5], on the other hand, have used equation (17) for the alkali halides at room temperature, adopting, however, an approximate expression for its volume derivative at constant temperature derived by neglecting the volume dependence of γ.

5. DISCUSSION OF THE RESULTS

A few definite statements on the validity of the Mie–Grüneisen and Hildebrand approximations to the equation of state of cubic solids under hydrostatic pressure are possible within the quasi-harmonic approximation. The thermal Mie–Grüneisen equation of state is correct for a non-metal in the T^3 region of the heat capacity, and the validity of the Debye model for the thermal thermodynamic functions in this region, which

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implies that

$$\frac{TC_V}{W_{th}} = 1 + \frac{T}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V = 4,$$

ensures a welcome simplification of the form of this equation, and of its volume derivative at constant temperature. At temperatures somewhat above the Debye characteristic temperature $\Theta_2(V)$ for the (quasi-harmonic) heat capacity at high temperature, the appropriate equation of state is the vibrational Hildebrand equation, which has of course the advantage that its use, and that of its volume derivative, does not require the knowledge of the vibrational energy of the solid as a function of temperature and volume. At somewhat lower temperatures, the vibrational Mie–Grüneisen equation is the appropriate equation of state for solids in which γ is essentially a purely volume-dependent function at these temperatures; however, the use of this equation, and of its volume derivative, does require the knowledge of the vibrational energy of the solid $W_{vib}(V,T)$, and this has the Debye functional form with $\Theta_2(V)$ as the Debye characteristic temperature in the temperature region where its Thirring expansion can be truncated after the T^{-2} term (see Appendix). One may also add that the thermal Mie–Grüneisen and Hildebrand equations involve generally greater errors than the corresponding vibrational equations when used at the same temperature in the region of moderate temperatures. The various statements pertaining to moderately high temperatures can be assumed to apply to metals, as well as non-metals, since at these temperatures the electronic terms in the vibrational thermodynamic functions of the solid are generally small compared to the lattice terms.

The applicability of these quasi-harmonic results to a particular solid depends naturally on the weight of the anharmonic contributions to its thermodynamic functions in the various ranges of temperature and volume. The available experimental evidence indicates that in the region of temperature around and below Θ_2 the anharmonic contributions to the thermal thermodynamic functions are quite small in a number of solids. Quite accurate evidence to this effect has been provided by BARRON et al.[21], who have shown

that the weight of the anharmonic contributions to the heat capacity at constant volume of various alkali halides at atmospheric pressure is still less than 1 per cent at temperatures around Θ_2. SALTER[16] has also pointed out that the entropy of copper and aluminum at atmospheric pressure remains apparently quasi-harmonic at least up to 300°K, since it has essentially the functional form $\ln(T/\Theta)$ in the temperature range from about 200°K to at least 300°K. An analogous test for sodium, using the data reported by MARTIN[22], reveals that the logarithmic functional form for the entropy at atmospheric pressure applies in the range extending roughly from 100°K to 200°K. On the other hand, an analysis of the available calculations of the anharmonic contributions to the vibrational thermodynamic functions, which concern simple force models of a linear chain of a face-centered cubic solid,[19] shows that the contributions to the vibrational free energy at temperatures around and somewhat below the appropriate Θs are at most comparable to the contributions to TC_V. Under these conditions, the characteristic temperature for the logarithmic term of the vibrational free energy is affected by the anharmonic terms only by a percentage comparable to their fractional weight in the heat capacity.

In the temperature range where the entropy of a solid has the functional form $\ln[T/\Theta(V)]$, γ must of course be a purely volume-dependent function, and one would actually expect γ not to vary significantly with temperature also at somewhat lower temperatures, where the following terms of the Stern expansion of the entropy are still small and a different volume dependence of the characteristic temperatures appropriate to the various terms of the expansion (see Appendix) is hardly detectable. These expectations are confirmed by the measurements of BIJL and PULLAN[23] which show that in copper and aluminum γ at atmospheric pressure does not vary with temperature in the range from 273°K to below 150°K. For sodium, one anticipates that γ at atmospheric pressure should not vary with temperature in the range extending roughly from 200°K to 100°K. An experimental verification of this prediction, when compared with the observation[24] that γ'' for sodium depends explicitly on temperature in this range, would provide also a verification of the quasi-harmonic theorem that γ'' approaches the

limiting high temperature value of the γs more slowly than γ. Of course this theorem leads one further to anticipate that γ'' for copper and aluminum should not be independent of temperature in the entire range in which this holds for γ. For the alkali halides for which BARRON *et al.*[21] have proved the accuracy of the quasi-harmonic approximation to the thermal thermodynamic functions at moderate temperatures, one would again expect that γ at atmospheric pressure should not vary significantly with temperature in a region around and below the pertinent Θ_2. The measurements of RUBIN *et al.*[25] prove that this is true for sodium chloride.

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APPENDIX

The Quasi-Harmonic Approximation at Moderate Temperatures and the Debye Model

At temperatures above $h\nu_m/2\pi k$, where ν_m is the highest vibrational frequency of the solid, the thermodynamic functions of a quasi-harmonic non-metal are represented by their Thirring–Stern expansions[10] in inverse powers of the absolute temperature:

$$\frac{F_{\text{vib}}}{3NkT} = \frac{F_{\text{th}}}{3NkT} + \frac{1}{2}\frac{h}{kT}\mu_1$$

$$= \ln\left[\frac{h}{kT}(\textstyle\prod_j \nu_j)^{1/3N}\right] \tag{A.1}$$

$$- \sum_{n=1}^{\infty}(-1)^n\frac{B_{2n}}{2n(2n)!}\left(\frac{h}{kT}\right)^{2n}\mu_{2n}$$

$$\frac{S}{3Nk} = -\ln\left[\frac{h}{kT}(\textstyle\prod_j \nu_j)^{1/3N}\right]$$

$$+1-\sum_{n=1}^{\infty}(-1)^n\frac{B_{2n}}{(2n)!}\frac{2n-1}{2n}\left(\frac{h}{kT}\right)^{2n}\mu_{2n} \tag{A.2}$$

$$\frac{W_{\text{vib.}}}{3NkT} = \frac{W_{\text{th.}}}{3NkT} + \frac{1}{2}\frac{h}{kT}\mu_1 = 1$$

$$- \sum_{n=1}^{\infty}(-1)^n\frac{B_{2n}}{(2n)!}\left(\frac{h}{kT}\right)^{2n}\mu_{2n} \tag{A.3}$$

$$\frac{C_V}{3Nk} = 1 + \sum_{n=1}^{\infty} (-1)^n \, B_{2n} \frac{2n-1}{(2n)!} \left(\frac{h}{kT}\right)^{2n} \mu_{2n}$$

$$(A.4)$$

Here the Bs are the Bernoulli numbers[26] and $\mu_n = \sum_j v_j^n/3N$ is the nth moment of the frequency distribution of the $3N$ normal modes of the solid and depends only on its (homogeneous) strain state. The expansion of the thermal free energy, whence the other expansions follow straightforwardly, is obtained quite easily by integration of the Taylor expansion of the function $d/dx\{\ln[(1-e^{-x})/x]\}$, and this involves the Bernoulli expansion[26] of the function $x/(1-e^{-x})$, which converges for $|x| < 2\pi$. The region of convergence of the Thirring–Stern expansions extends to below 80°K even for a value of v_m equal to $10^{13}\,\text{sec}^{-1}$.

Each term of the Thirring–Stern expansions is a function of the ratio between the absolute temperature and an appropriate (purely strain-dependent) characteristic temperature. We define the characteristic temperature appropriate to the logarithmic term of the entropy, Θ_0, and the characteristic temperature for the term of the expansions containing the nth moment of the frequency distribution, Θ_n, as follows:

$$\Theta_0 = \exp\left(\frac{1}{3}\right) \frac{h}{k} (\textstyle\prod_j v_j)^{1/3N} \qquad (A.5)$$

$$\Theta_n = \left(\frac{n+3}{3}\right)^{1/n} \frac{h}{k} \mu_n^{1/n} / (n = 1, 2, 4, 6, \ldots) \qquad (A.6)$$

This choice of the numerical factors, which are *a priori* arbitrary, ensures that when all these characteristic temperatures are taken as equal the expansions (A.1) to (A.4) reduce to the well-known Debye expansions.

For each thermodynamic function there is clearly a high-temperature region, generally of different width for different functions, where only the leading strain-dependent term of its Thirring–Stern expansion is relevant. Thus the correct quasi-harmonic expression coincides with the Debye expression at these classical or nearly classical temperatures. However, the appropriate Debye characteristic temperatures for the entropy and for the heat capacity are different (see, for example, Ref. 12) and differ also from the one appropriate for the thermal energy, being given by Θ_0, Θ_2 and Θ_1 respectively;

on the other hand, the appropriate Debye characteristic temperatures for the (vibrational and thermal) free energies and for the vibrational energy coincide, respectively, with those for the entropy and for the heat capacity. Numerical values of these Θs for some alkali halides, referred to the volume at 0°K and atmospheric pressure, are given in the paper by BARRON *et al.*[21]; e.g. for potassium iodide one has $\Theta_0 = 142{\cdot}8°\text{K}$, $\Theta_1 = 152{\cdot}9°\text{K}$ and $\Theta_2 = 162{\cdot}5°\text{K}$. The experimental Debye temperatures, obtained by fitting the appropriate Debye formulae to the measured values of the entropy, thermal energy and heat capacity of a non-metal, will not actually tend to Θ_0, Θ_1 and Θ_2 at high temperatures, owing to the presence of anharmonic contributions. However, while these affect the experimental Debye temperature for the heat capacity by a percentage much larger than their fractional weight in the heat capacity, as BARRON *et al.*[21] have dramatically illustrated for some alkali halides, they affect the experimental Debye temperature for the entropy only by a percentage comparable to that fractional weight.

At lower temperatures, where several strain-dependent terms of the Thirring–Stern expansion of a given thermodynamic function are relevant, the Debye temperature appropriate to this function, determined by fitting the truncated Debye expansion to the truncated Thirring–Stern expansion, will depend explicitly on temperature whenever the values of the characteristic temperatures pertinent to the relevant terms of the Thirring–Stern expansion are numerically different, because the relative weights of these terms change with temperature. DOMB and SALTER[15] have expressed this temperature dependence for the Debye temperature for the heat capacity analytically, as an expansion in inverse powers of the absolute temperature, and analogous expansions can be easily obtained for the Debye temperatures pertinent to the other thermodynamic functions. These expansions are of course different for different thermodynamic functions, and should represent rather accurately the temperature dependence of the experimental Debye temperatures for the various functions in the region of relatively low temperatures. As yet, this has been shown to be the case only for the DOMB and SALTER expansion.[21] A final remark, of some interest, is that even if the numerical values of the characteristic temperatures (A.5) and (A.6) pertinent to the relevant terms of the Thirring–Stern expansion of a given thermodynamic function are different, so long as their strain dependence is the same, the function depends only on the ratio between the absolute temperature and a unique (purely strain-dependent) characteristic temperature, but the dependence on this variable is not of the Debye form.