PHYSICAL REVIEW VOLUME 144, NUMBER 2 15 APRIL 1966

Derivation of Wachtman's Equation for the Temperature Dependence of Elastic Moduli of Oxide Compounds

ORSON L. ANDERSON*
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 27 October 1965)

Recently, Wachtman and his colleagues showed that a good description of the temperature dependence of the Young's modulus of several oxides is $Y=Y_0-b_1T\exp(-T_0/T)$ where Y_0 is the modulus at absolute zero and b and T_0 are constants. Wachtman and his colleagues pointed out that they had no theoretical basis for this equation, but demonstrated that it worked very well over a large temperature range (1000°K), and they discussed the physical basis for the parameters b_1 and T_0. In this paper we show that the form of their equation for Y is equivalent to an equation for the bulk modulus derived from the Mie-Grüneisen equation of state. The Wachtman empirical equation for Young's modulus apparently is valid only when the variation of Poisson's ratio with temperature is small, for in that case $d\ln E/dT$ is equal to $d\ln B/dT$, where B is the bulk modulus.

I. INTRODUCTION

In a recent article of this journal,[1] Wachtman *et al.* suggested that an equation of the form

$$Y=Y_0-b_1T\exp(-T_0/T) \tag{1}$$

represents the variation of Young's modulus with temperature for several oxides. Here Y_0 is the modulus at absolute zero, and b_1 and T_0 are arbitrary constants, but thought to be related in some way[1] to the Grüneisen constant and the Debye temperature. This equation was later shown to hold very well for ThO_2 over a temperature range of 1300 deg.[2]

The fact that this equation is reasonable and satisfies theoretical limits was adequately pointed out by Wachtman *et al.* However, the problem remained unfinished since, as they said, ". . . No theoretical justification [of the equation] is known . . . and the physical interpretation of the parameters b and T_0 presents a challenging theoretical problem."

The purpose of this paper is to justify Wachtman's equation, and to interpret the parameters. Anticipating the later sections, it turns out that, if we consider the corresponding equation for the adiabatic bulk modulus,

$$B_s=B_{00}-bT\exp(-T_0/T), \tag{2}$$

it is shown that

$$b=3R\gamma\delta/V_0. \tag{3}$$

Here γ is the Grüneisen parameter, V_0 is the specific volume per "average" atom at absolute zero, and δ is an important physical constant (analogous to the Grüneisen constant) independent of temperature given by

$$\delta=-(1/\alpha)(\partial\ln B_s/\partial T)_p, \tag{4}$$

where α is the coefficient of volume thermal expansion, and R is the gas constant. B_{00} is the bulk modus at absolute zero and one atmosphere.

The parameter T_0 is related to a characteristic temperature Θ, and the quantity $3RT\exp(-T_0/T)$ is an empirical representation of the energy $\int C_v dT$ over the experimental range of interest.

The most important part of the derivation is the establishment of (4). This has already been done by Grüneisen[3] for the case of the Born potential (sometimes called the Mie potential):

$$\Phi=-(A/V^{m/3})+(B/V^{n/3}). \tag{5}$$

We adopt Grüneisen's result in the following sections. A derivation of the main result, (4), is given for a more general potential in the Appendix.

In deriving (4), Grüneisen used the Mie-Grüneisen equation of state relating pressure and volume:

$$PV+V(d\Phi/dV)=\gamma E, \tag{6}$$

where E is the thermal energy, and γ the Grüneisen constant.

Included in the assumptions leading to (6) are a number of important relationships. First, Φ is a function only of V as in (5), so that

$$(\partial\Phi/\partial V)=d\Phi/dV. \tag{7}$$

Second, the entropy is a function of Θ/T, where Θ is a characteristic temperature; and any function of Θ/T is independent of P if the entropy S remains constant.[3] Thus

$$\frac{\partial}{\partial P}\left\{\varphi\left(\frac{\Theta}{T}\right)\right\}_S=0. \tag{8}$$

Third, the vibrational energy is equal to the thermal energy, which has been shown[4] to result in

$$d\gamma/dT=0. \tag{9}$$

Fourth, there is only one Grüneisen parameter,

---

* Also at Lamont Geological Observatory, Columbia University, Palisades, New York.

[1] J. B. Wachtman, Jr., W. E. Tefft, D. G. Lam, Jr., and C. S. Apstein, Phys. Rev. **122**, 1754 (1961).

[2] S. Spinner, L. Stone, and F. P. Knudsen, J. Res. Natl. Bur. Std. **67C**, 93 (1963).

[3] E. Grüneisen, Ann. Physik **39**, 257 (1912).

[4] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids **23**, 395 (1963).

defined either in terms of the frequency variation with volume,[5] or the thermal properties, by

$$\gamma = \frac{V(\partial V/\partial T)_P}{C_p(\partial V/\partial P)_S}, \tag{10}$$

or

$$\gamma = \alpha V B_S / C_p, \tag{11}$$

where α is the volume coefficient of thermal expansion, B_s is the adiabatic bulk modulus, and C_p is the specific heat.

Equations (5) through (11) are the constraints placed upon the result (4), as given by Grüneisen.

Grüneisen's approach was to take the pressure derivative of (6) at constant entropy, and redefine all the resulting differentials in terms of the one differential

$$-(\partial V/\partial P)_S = V/B_s. \tag{12}$$

To do this he invoked (7), (8), (9), and (10). The resulting expression for B_s is

$$B_s = P(1+\gamma) + (d\Phi/dV)(1+\gamma) + V(d^2\Phi/dV^2). \tag{13}$$

Equation (13) is equivalent to the expression derived for the isothermal bulk modulus given by Born and Huang.[5] Grüneisen used (5) to evaluate the last two terms of (13) as a function of volume. He then showed that the expression for B_s, (13), was equivalent to a first-order expansion in volume: However, this really involved the extra assumption that the volumes at high temperature differ little from the volume at absolute zero. The final result[3] is

$$(B_s/B_{00}) = (V_0/V)^{(m+n+2-\gamma)}, \tag{14}$$

where B_{00} is the volume at absolute zero and ambient pressure.

Equation (14) can be written in an equivalent form

$$\frac{d\ln B_s/dT}{d\ln V/dT} = -\left(\frac{m+n}{3} + 2 - \gamma\right) = -\delta, \tag{15}$$

which shows why (4) may be expected to be virtually independent of temperature.

Experimentally, the above theory can be checked by measurements of B_s and α as a function of temperature, to ascertain if γ and δ are independent of temperature as required by (9) and (15).

II. THE EXPERIMENTAL DATA FOR MgO AT HIGH TEMPERATURES

Reports in the literature on the variation of γ with temperature for MgO are conflicting. Susse[6] measured the elastic constants of MgO, and her graph of γ versus T shows that γ drops sharply with T above 500°C. White's[7] new values of α combined with Susse's values of B_s, show γ to be slowly dropping with T.[7] Other data[8] in the literature on B_s, indicate that γ rises with ascending temperature.

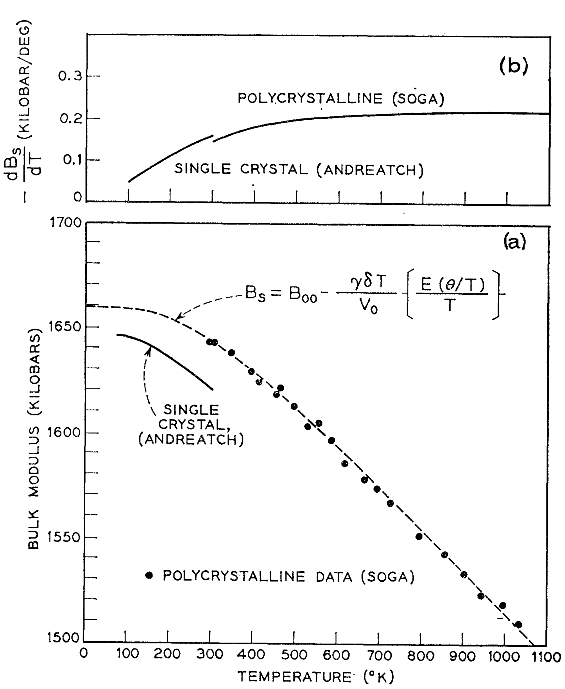

FIG. 1. (a) The variation of bulk modulus with temperature for MgO. The line indicates results for single crystals. The dots results for a polycrystal. The dashed line the theory according to (22). (b) The variation of $-dB_s/dT$ taken from (a).

New data on the elastic constants of MgO have been obtained by the writer and his colleagues. The variation of B_s with T between 78 and 300°K on single-crystal MgO by Anderson and Andreatch,[9] and the variation of B_s with T between 295 and 1050°K on polycrystalline MgO by Soga and Anderson[10] are given in Fig. 1. These data used in (11) along with the value of α obtained by White,[7] show that γ is independent of temperature, and that δ is virtually independent of temperature, as shown in Fig. 2.

On the basis of these measurements on MgO, and also the results of Al_2O_3 reported elsewhere,[10] the theory of Grüneisen described in the previous section would appear to be applicable to oxide solids.

III. THE BULK-MODULUS TEMPERATURE EQUATION

Substituting (11) in (15), we have

$$dB_s/dT = -(\delta\gamma)(C_p/V). \tag{16}$$

---

[5] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956).

[6] C. Susse, J. Rech. Centre Nat. Rech. Sci. Lab. Bellevue (Paris) **54**, 23 (1961).

[7] G. White and O. L. Anderson, J. Appl. Phys. **37**, 430 (1966).

[8] D. H. Chung and W. G. Laurence, J. Am. Ceram. Soc. **42**, 254 (1959).

[9] O. L. Anderson and P. Andreatch, J. Am. Ceram. Soc. (to be published).

[10] N. Soga and O. L. Anderson, J. Am. Ceram. Soc. (to be published).

In the previous section, we presented the evidence that δ and γ are independent of temperature for MgO. Assuming this as a general condition,

$$\int dB_s=-\delta\gamma\int\left(\frac{C_p}{V}\right)dT. \tag{17}$$

We now derive the constant b in Wachtman's empirical equation. We need the following approximation:

$$\int_0^T \frac{C_p}{V}dT\cong\frac{1}{V_0}\int_0^T C_v dT. \tag{18}$$

The approximation inherent in (18) can be checked experimentally by observing whether the measured value of $-dB_s/dT$ has the features of a C_v curve; i.e., a check for flatness at high temperature in the plot $-dB_s/dT$ versus T. This is demonstrated for MgO in the top of Fig. 1. To obtain some idea of the error made in (18) we replace C_p and V by expressions in α and T. Thus, taking

$$C_p\cong C_V(1+T\alpha\gamma), \tag{19}$$

$$V\cong V_0(1+\alpha T), \tag{20}$$

we have

$$\int_0^T \frac{C_p}{V}dT=\frac{1}{V_0}\int_0^T\left(\frac{1+T\alpha\gamma}{1+\alpha T}\right)C_v\,dT. \tag{21}$$

For a rigorous solution, (21) is integrated by parts taking into account the temperature variation of α. We merely note that for MgO, $1+\alpha T$ changes by about 3% in 1000°, with the result that the coefficient of C_v in (21) changes by 2%. The approximation inherent in (18) is the same as replacing the quantity in parentheses in (21) by unity.

We recall that $\int C_v dT$ is the thermal energy E in (6), so that the solution for B_s as a function of T is

$$B_s=B_{00}-(\gamma\delta/V_0)E. \tag{22}$$

Using the Debye approximation for E, the thermal energy for a gram atom of a monatomic isotropic substance is

$$E=3RTH\left(\frac{\Theta}{T}\right); \tag{23}$$

$$H(x)=\frac{3}{x^3}\int_0^x\frac{\xi^3}{e^{\xi}-1}d\xi, \tag{24}$$

where Θ is the Debye temperature. Thus,

$$B_s=B_{00}-\frac{3R\gamma\delta}{V_0}TH\left(\frac{\Theta}{T}\right), \tag{25}$$

where V_0 is the volume of the "average" gram atom, defined by the ratio of "mean" atomic weight to density.

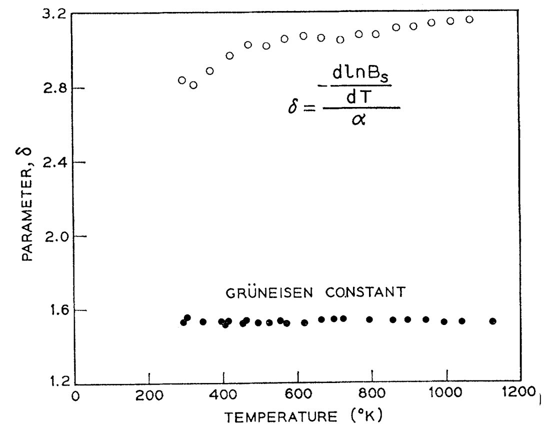

FIG. 2. The variation of the Grüneisen constant γ with temperature for MgO. The variation of the parameter $-(d\ln B_s/dT)/\alpha$ with temperature for MgO.

Comparing (25) with (2) it is apparent that the empirical constant b of Wachtman's equation is given by

$$b=3R\gamma\delta/V_0. \tag{26}$$

Equation (26) should hold irrespective of the special relationship chosen between E and T, of which (23) is one example. It is apparent that the term $\exp(-T_0/T)$ of Wachtman's equation is empirically related to E in much the same way that (24) is related to E.

We now show how the magnitude of Wachtman's parameter T_0 is related to Θ. At high temperatures the limits of integration in (24) are close, so that to a good degree of approximation

$$H(x)\cong\frac{x}{e^x-1}$$

$$\cong\left[1+\left(\frac{\Theta/2}{T}\right)+\frac{2}{3}\left(\frac{\Theta/2}{T}\right)^2+\cdots\right]^{-1}.$$

Expanding Wachtman's factor at high T,

$$e^{-T_0/T}=[1+(T_0/T)+\tfrac{1}{2}(T_0/T)^2+\cdots]^{-1}.$$

At high temperatures the two expansions yield the same numerical result if T_0 is close to the value $\Theta/2$. This accounts for the fact that the empirical values of T_0 quoted by Wachtman *et al.*[1] are close to one-half the value of the corresponding Debye temperatures.

Since E/T according to (24) is tabled[11] for a given Θ/T, a convenient form of (24) is

$$B_s=B_{00}-\frac{\gamma\delta}{V_0}T\frac{E(\Theta/T)}{T}. \tag{27}$$

Equation (25) is the important result of this paper. By using it, the bulk modulus can be estimated at high

---

[11] See *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), Chap. 7, Table IV.

temperature from measurements of elastic constants taken over a limited temperature range, providing data on α exist at all temperatures considered.

At low temperatures, the thermal energy varies as T^4, so that for $\Theta/T\gg 1$,

$$B_{00}-B_s\sim T^4. \tag{28}$$

The difference between the temperature variation of T^4 and $\exp(-T_0/T)$ is of no practical significance.

The variation of B_s with T for MgO according to (27) is shown as the dotted line in Fig. 1. The parameters used are $\gamma=1.53$, $\delta=3.1$, $V_0=5.56$, and $\Theta=930°$. These parameters were determined near room temperature. The one arbitrary parameter is $B_{00}=1660$ kbars.

IV. THE YOUNG MODULUS AND THE SHEAR-MODULUS EQUATION

We relate Y to B and σ, the Poisson ratio, by

$$Y=3(1-2\sigma)B, \tag{29}$$

and

$$\frac{d\ln Y}{dT}=\frac{d\ln B}{dT}-\frac{2}{(1-2\sigma)}\frac{d\sigma}{dT}.$$

Hence,

$$\frac{dY}{dT}=3(1-2\sigma)\frac{dB}{dT}-6B\frac{d\sigma}{dT}. \tag{30}$$

Taking $d\sigma/dT$ as constant

$$Y-Y_{00}\approx 3(1-2\sigma)\int\left(\frac{dB}{dT}\right)dT-6B\left(\frac{d\sigma}{dT}\right)T. \tag{31}$$

A similar relationship holds for the shear modulus G.

Consequently (31) reduces to (1) only if $d\sigma/dT$ is sufficiently small and a constant. For thoria and Al_2O_3, $d\sigma/dT$ is sufficiently small.[2] For MgO, however, there is some doubt that $d\sigma/dT$ is small enough. A plot of $d\sigma/dT$ for MgO and ThO_2 is given in Fig. 3. The application of (1) to some compounds may be questionable. Forcing Y and G to fit (1) may result in distortions in the computed value of B_s versus T.

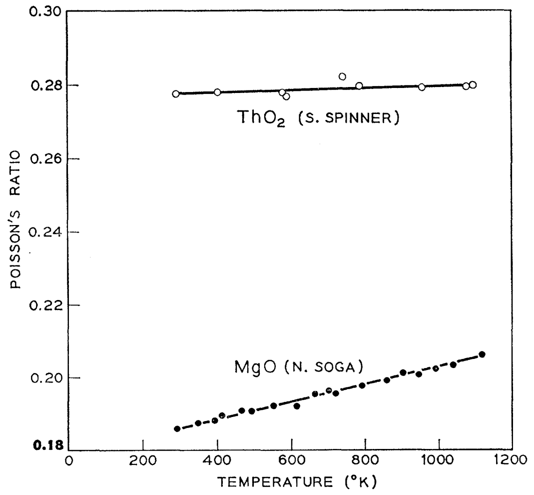

FIG. 3. The variation of $d\sigma/dT$ with temperature for MgO and for ThO_2.

V. DISCUSSION

Wachtman's equation has been derived from the Mie-Grüneisen equation of state, except that his Young modulus is replaced by bulk modulus.

There are several incidental results of importance to experimenters. It should turn out that $-dB_s/dT$ is proportional to C_v which serves as a good cross check on the measured results of the elastic constants versus T. Thus, at temperatures above Θ, dB_s/dT should be independent of T, and at temperatures around $\Theta/2$, $-dB_s/dT$ should rise with T. Equation (16) can be used to estimate $-dB_s/dT$ from C_p, provided there is information of δ and γ. The variation of $d\ln B_s/dT$ can be estimated from α using (15) if δ can be estimated.

Equation (22) is the basis for extrapolation into high temperatures. Since, for example, (22) adequately represents the data for MgO from liquid-nitrogen temperature to 1200°C, it should also hold up to close to the melting temperature.

ACKNOWLEDGMENT

The writer is especially indebted to N. Soga, who performed the experiments shown in Figs. 1–3.

APPENDIX

We determine the conditions for deriving the result

$$\frac{d\ln B_s/dT}{d\ln V/dT}=\text{const} \tag{A1}$$

from a more general potential than given by (5), and assuming the Mie-Grüneisen equation of state.

We consider the cohesive potential

$$\Phi=-(a/r^m)+f(r), \tag{A2}$$

instead of (5), where r is a representative interatomic distance. The value of m can be, for example, 1 for the Coulomb potential or 6 for the Leonard-Jones potential. The repulsion potential $f(r)$ can be, for example, the Born repulsion of (5), or a Morse potential, or a sum of terms including various interactions such as the van der Waals interaction.

For convenience, (A2) is redefined in terms of the volume V

$$\Phi=-(A/V^{m/3})+f(V). \tag{A3}$$

We need the derivatives of Φ as given in (13). The first derivative of (A3) is

$$\frac{d\Phi}{dV}=\frac{m}{3}\frac{A}{V^{m/3+1}}+f'(v). \tag{A4}$$

From equilibrium conditions, we have

$$\left(\frac{d\Phi}{dV}\right)_{P=0,T=0}=0. \qquad \text{(A5)}$$

The second derivative of (A3) gives

$$V\frac{d^2\Phi}{dV^2}=-\frac{m}{3}\left(\frac{m}{3}+1\right)\frac{A}{V^{m/3+1}}+Vf''(V). \qquad \text{(A6)}$$

(A4) and (A6) are now substituted in (13). The problem is to express the quantity $B_s-P(1+\gamma)$ in terms of the volume ratio V/V_0 and presumably other constants which vary quite slowly with volume. To do this we use (A4) and (A5). Thus, (A6) becomes by using (A4):

$$V\frac{d^2\Phi}{dV^2}=\left(\frac{m}{3}+1\right)[f'(V)-d\Phi/dV]\times\left\{1+\frac{Vf''(V)}{(m/3+1)[f'(V)-d\Phi/dV]}\right\}. \qquad \text{(A7)}$$

The quantity in braces is important in subsequent expressions:

$$K=1+\frac{Vf''(V)}{(m/3+1)[f'(V)-d\Phi/dV]}. \qquad \text{(A8)}$$

For most standard potentials, $d\Phi/dV$ is small compared to $f'(V)$. We now assume that the repulsion potential is such that $d\Phi/dV$ is small compared to $f'(V)$ at all temperatures we consider, and that K is slowly varying with V, or constant with V, as V increases with T.

Ordinarily, K is a negative number larger than unity. This results from the fact that the repulsion curve is steeper than the attraction curve. For example, for the Born repulsion as given by (5), $K=(n+m)/(m+3)$ when $d\Phi/dV=0$.

Replacing (A4) and (A7) in (13), we have

$$B_s-P(1+\gamma)=(1+\gamma)\frac{m}{3}\frac{A}{V^{m/3+1}}+(1+\gamma)f'(V)-K\frac{m}{3}\left(\frac{m}{3}+1\right)\frac{A}{V^{m/3+1}}.$$

Factoring out the far term on the right,

$$B_s-P(1+\gamma)=-K\frac{m}{3}\left(\frac{m}{3}+1\right)\frac{A}{V^{m/3+1}}\times\left\{1-\frac{(1+\gamma)f'(v)}{K(m/3)(m/3+1)V^{m/3+1}}-\frac{(1+\gamma)}{K(m/3+1)}\right\}. \qquad \text{(A9)}$$

Using (A4)

$$B_s-P(1+\gamma)=-K\frac{m}{3}\left(\frac{m}{3}+1\right)\frac{A}{V^{m/3+1}}\times\left\{1+\frac{(1+\gamma)}{K(m/3+1)}\left[\frac{f'(V)}{f'(V)-d\Phi/dV}-1\right]\right\}. \qquad \text{(A10)}$$

The terms within the brackets cancel at absolute zero where $d\Phi/dV$ is small compared with $f'(V)$. At absolute zero and $P=0$, we have from (A10),

$$-B_{00}=-K_0\left(\frac{m}{3}\right)\left(\frac{m}{3}+1\right)\frac{A}{V_0^{m/3+1}}. \qquad \text{(A11)}$$

Thus,

$$-K\left(\frac{m}{3}\right)\left(\frac{m}{3}+1\right)\frac{A}{V^{m/3+1}}=\left(\frac{K_0}{K}\right)B_{00}\left(\frac{V_0}{V}\right)^{m/3+1}. \qquad \text{(A12)}$$

We factor out (A12) from (A10) and obtain

$$\frac{B_s-P(1+\gamma)}{B_{00}}=\left(\frac{V_0}{V}\right)^{m/3+1}\frac{K_0}{K}\times\left\{1+\frac{(1+\gamma)d\Phi/dV}{K(m/3+1)[f'(V)-d\Phi/dV]}\right\}. \qquad \text{(A13)}$$

We now obtain the desired result from (A13) provided the quantity in braces is a slowly varying function of volume. It is not readily obvious that this will be so for most potentials at all temperatures. However, we may constrain the potential to produce the desired result. Consequently, we replace the coefficient of $(V_0/V)^{m/3+1}$ in (A13) by an expansion in V_0/V, e.g.,

$$\frac{K_0}{K}\left\{\quad\right\}\cong1-\omega\left(\frac{V-V_0}{V}\right)=\left(\frac{V_0}{V}\right)^{\omega}, \qquad \text{(A14)}$$

where ω is a function of γ and K. In order to justify (A14) the potential must be such that (1) $d\Phi/dV$ is small compared to $f'(V)$ at all temperatures considered, and (2) $Vf''(V)/[f'(V)-d\Phi/dV]$ must be a slowly varying function of volume, or independent of volume, at all temperatures considered. Placing (A14) in (A13), we have

$$B_s/B_{00}=(V_0/V)^{m/3+1+\omega}. \qquad \text{(A15)}$$

Taking the derivative of (A15) with respect to T at constant P we have

$$\frac{d\ln B_s/dT}{d\ln V/dT}=-\left(\frac{m}{3}+1+\omega\right)=\text{const.}$$