TABLE I. Data of Brockhouse and Iyengar.[a]

	1957 Data set I	1958 Data set II
a_1	-1.091	-0.687
a_2	$+0.110$	-2.002
a_3	$+1.691$	$+4.594$
a_4	-1.283	-2.489

[a] See reference 21.

The dispersion curve in any direction is assumed to be of the same form, in reduced k, as in the [111] direction, with the initial slope determined by the sound velocity.[22] Thus

$$\frac{\omega_i}{v_i k_m}=\frac{k}{k_m}+\sum_{n=1}^{4} a_n\left(\frac{k}{k_m}\right)^{2n+1}, \qquad i=2,3. \tag{16}$$

The a_n, for the two sets of neutron spectrometry data, are given in Table I. Figures 3(a) and (b) show the data and the fitting polynomial; Fig. 3(c) shows the measured data in the [100] direction with the assumed dispersion curve. The a_n were fixed by least-squares fitting of all the data.

The longitudinal modes are approximated by the dispersion curve of the S.D.M.; a comparison with the neutron spectrometry data is shown in Figs. 3(a) and (c).

The coefficient C, fixing the limiting curvature of the reduced $\theta_D(T)$ curve [see Eq. (13)] is determined for these models by the coefficient a_1. Values for this curvature coefficient C are 98 for M.D.M. I, 62 for M.D.M. II, and 38 for S.D.M.

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Deduction of the Volume Dependence of the Cohesive Energy of Solids from Shock-Wave Compression Measurements*

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By applying the Mie-Grüneisen equation of state to measurements of the compression of solids by strong shock waves, it is possible to determine the volume dependence of the cohesive energy. The method for carrying out this deduction is presented along with a detailed exposition of the underlying assumptions. The method is applied to six metals Be, Al, Co, Ni, Cu, and Ag for which the experimental data are most extensive. The volume dependence of the cohesive energy for these six metals is presented in both analytical and graphical form.

I. INTRODUCTION

THE cohesive energy of a crystalline solid is the energy release upon assembling the constituent atoms from infinity to form the ordered array characteristic of that crystal. This energy is of fundamental significance in the theory of solids because it is a measure of the detailed nature of the spatial distribution of charge throughout the solid. The dependence of the cohesive energy Φ on the size of the atomic polyhedron is the most important factor which determines the lattice constant and the compressibility of the solid. Because of the crucial role of the cohesive energy in determining the density of the solid it is possible to deduce the volume dependence of Φ from measurements of the volume compression under pressure. The timeliness of such a deduction arises out of recent advances in the theory of cohesion,[1,2] and in the experimental methods for high-pressure compression of solids.[3,4]

The new theoretical advances[5] consist in the application of the "quantum defect" method[1] to the calculation of the volume dependence of the cohesive energy for multivalent metals with nonoverlapping cores.

The new experiments make use of strong shock waves to generate pressures which are typically in the 150 000- to 500 000-atmos region, but can be as large as 1 300 000 atmos. Under such stresses the volume compression of the solid is typically as large as 20%, but it can be as large as 40%.

The present paper applies the Mie-Grüneisen equation of state to the shock-wave data obtained by the Los Alamos group,[3] to deduce the volume dependence of Φ. A general procedure for this deduction

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† A large portion of this work was carried out while the author was a Summer Staff Member of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[1] H. Brooks and F. Ham, Phys. Rev. **112**, 344 (1958).

[2] H. Brooks, Suppl. Nuovo cimento **7**, 165 (1958).

[3] Walsh, Rice, McQueen, and Yarger, Phys. Rev. **108**, 196 (1957).

[4] Rice, McQueen, and Walsh in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6.

[5] H. Brooks (private communication).

is developed and applied to six metals: Be, Co, Ni, Cu, and Ag, and 24*ST* aluminum[6] for which the shock compression measurements are most extensive.

II. THE MIE-GRÜNEISEN EQUATION OF STATE[7]

The Mie-Grüneisen equation of state relates implicitly the strain of a solid to the applied stress and the temperature. This equation of state owes its simplicity to two assumptions. The first is that the applied stress is limited to hydrostatic pressure. The second is that under this stress the unit cell can always be described by means of a single parameter which is usually taken to be its volume. The latter assumption is satisfied by those solids possessing cubic symmetry, and is approximately true for solids with hexagonal symmetry providing that the c/a ratio remains close to the ideal value of 1.633.

If the solid is envisioned as a lattice whose periodicity is disturbed only by the lattice vibrations, it is possible to write its Helmholtz free energy as a sum of two terms. The first is the free energy Φ required to assemble the atoms from infinity to form the rigid lattice. This term is the cohesive energy. To this must be added the Helmholtz free energy of the lattice vibrations. Since the Helmholtz free energy F_μ of a normal mode of lattice vibration, whose frequency is ν_μ, is given by $F_\mu = kT\ln[2\sinh(h\nu_\mu/2kT)]$, it follows that the total Helmholtz free energy of the solid can be written as

$$F=\Phi(v)+kT\sum_{\mu=1}^{3N}\ln\left[2\sinh\left(\frac{h\nu_\mu(v)}{2kT}\right)\right]. \tag{1}$$

In the interest of normalization the free energy F, the cohesive energy Φ, the number of atoms N, and the volume v are all taken to be per unit mass. In Eq. (1) we note that Φ and ν_μ are implicit functions of the volume only. In the case of a metal it is possible to add a term which represents the temperature dependence of the free energy of the conduction electrons.[8] This term is much smaller than those already included and hence will be neglected.

Since the hydrostatic pressure (P) on the solid is related to the volume dependence of the free energy by the thermodynamic relation

$$P=-(\partial F/\partial v)_T, \tag{2}$$

the desired implicit relation between P, v, and T is obtained by differentiating (1). This yields the Mie-Grüneisen equation of state:

$$P=-\frac{\partial\Phi(v)}{\partial v}+\frac{\gamma(v,T)U_{\text{vib}}(v,T)}{v}, \tag{3}$$

where

$$\gamma=\sum_{\mu=1}^{3N}\left(-\frac{\partial\ln\nu_\mu}{\partial\ln v}U_\mu\right)\Big/\sum_{\mu=1}^{3N}U_\mu, \tag{4}$$

$$U_\mu=h\nu_\mu\left(\frac{1}{2}+\frac{1}{e^{h\nu_\mu/kT}-1}\right), \tag{5}$$

$$U_{\text{vib}}=\sum_{\mu=1}^{3N}U_\mu. \tag{6}$$

The quantity γ is the average of the logarithmic volume derivative of ν_μ weighted over the energies U_μ of each mode of lattice vibration. This quantity will be referred to as Grüneisen's parameter. This parameter should be distinguished from the γ' in Grüneisen's relation

$$\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P=\gamma'\frac{C_v}{v}\left[\frac{-1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]. \tag{7}$$

In this relation γ' is given by

$$\gamma'=\sum_\mu\left(-\frac{\partial\ln\nu_\mu}{\partial\ln v}\frac{\partial U_\mu}{\partial T}\right)\Big/\sum_\mu\frac{\partial U_\mu}{\partial T}, \tag{8}$$

as may be seen[9] by differentiating Eq. (3) relative to the temperature to give Eq. (7). In the high-temperature region, $\gamma'=\gamma$; but at low temperatures the weighting factors in the two averages can lead to a difference between γ and γ'.

U_μ is the energy of the μth mode of lattice vibration, and U_{vib} is the total vibrational energy of the solid.

III. THE SHOCK-WAVE HUGONIOTS

The shock-wave compression experiments subject the back surface of a sample pellet to an explosively established high pressure. As a result a shock wave passes into the pellet. The shock wave is characterized by a shock front which moves through the sample with velocity $U_s(t)$. Behind the shock front the material in the pellet moves with a velocity U_p which is in general a function of time and position behind the shock front. Henceforth, we shall denote as $U_p(t)$ the particle velocity of the material directly behind the shock front.

It can be shown with great generality[10] that if the shock front is thin, that the density ρ', pressure P', and internal energy/unit mass E' directly behind the shock front can be related to the density ρ_0, the pressure P_0, and the internal energy per unit mass E_0 before the shock front by means of the velocities U_s and U_p. In particular, the application of the conservation of mass, Newton's second law, and the conservation of energy across the shock front yields the following relations of

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[6] 24*ST* aluminum is an alloy of aluminum consisting of 4.5% Cu, 0.6% Mn, and 1.5% Mg.

[7] E. Grüneisen, *Handbuch der Physik* (Springer-Verlag, Berlin, 1926), Vol. 10, p. 1.

[8] S. Visvanathan, Phys. Rev. **81**, 626 (1951).

[9] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

[10] R. Courant and K. Friedrichs, *Supersonic Flow and Shock-waves* (Interscience Publishers, Inc., New York, 1948).

Rankine and Hugoniot:

$$\begin{aligned}&(1)\ \rho'(U_s-U_p)=\rho_0U_s; \quad \text{conservation of mass}\\&(2)\ U_p\rho_0U_s=P'-P_0; \quad \text{Newton's second law}\\&(3)\ P'U_p=\tfrac{1}{2}U_s\rho_0U_p^2+U_s\rho_0(E'-E_0); \quad \text{conservation of energy.}\end{aligned}\tag{9}$$

The quantities U_s and U_p can be accurately determined experimentally.[3,4] Thus ρ', P', and E' directly behind the shock front can be determined immediately from the three Rankine-Hugoniot relations above. If a sequence of U_s, U_p pairs is measured by generating shocks of different strength, one can make plots of P' and E' *vs* ρ'. Each such curve is called a Hugoniot.

Because of the novelty of these shock-wave compression studies, it seems appropriate to dwell briefly on the assumptions underlying the determination of the shock-front and shock-particle velocities and the Rankine-Hugoniot relations.

1. The Condition of Constant Velocity

The shock-front velocity U_s and shock-particle velocity U_p are determined by time-of-flight measurements over measured distances. The measured velocities U_s and U_p are therefore averages over the length of the traversal distances. The Rankine-Hugoniot relations require that U_s and U_p correspond to the same instant of time. If U_s and U_p are constants, the measured velocities would be identical with the required instantaneous ones. In order that the shock velocities be constant it would be necessary that the explosive be a semi-infinite block. In practise of course this is not the case and the velocities do change somewhat over the traverse lengths. The Los Alamos group has made measurements[11] of this effect and estimate that U_s typically decreases by 0.75% and U_p by 1.75% for a $\frac{1}{4}$-in. traverse distance. Thus the departure of U_s and U_p from constancy over the measured path is not large. To improve the situation further, the measurements of U_s and U_p *vs* distance are used[11] to correct the time-of-flight measurements so that the values of U_s and U_p correspond to the same time. As a result of these corrections, it is felt[11] that any systematic error produced by the nonsimultaneity of U_s and U_p is less than the experimental accuracy with which U_s and U_p are measured.

2. The Condition of Thermal Equilibrium

In its passage from the unshocked to the shocked condition, each point in the solid is successively subjected to a sudden change in temperature and pressure. The question arises as to how far between the leading edge of the shock front one must go in order to find the lattice in a state of thermal equilibrium. If Δl is the distance required to reach thermal equilibrium and τ ($\sim10^{-11}-10^{-13}$ sec) is the mean time between phonon collisions, it is reasonable to expect $\Delta l\sim\tau U_s$, where U_s is the shock-front velocity. On the other hand, the width of the shock front ($\Delta l'$) can be expected to be of the order of the phonon mean free path, i.e., $\Delta l'\sim\tau v$ where v is the mean phonon velocity. Since $U_s\simeq v\simeq5\times10^5$ cm/sec, it follows at once that one can expect $\Delta l\simeq\Delta l'$. Thus under normal conditions it is reasonable to assume that the material directly behind the shock front is in a state of thermal equilibrium. However, in the case of shocks which generate phase transitions[12,13] such as melting or slow recrystallization, the time required for the establishment of the new phase may be many orders of magnitude larger than the phonon collision time. Under these conditions the material directly behind the shock front may not have time to make the transition, and as a result may not be in a state of equilibrium.

3. The Condition of No Radiation or Conduction Loss

The derivation of the third Rankine-Hugoniot relation involves the assumption that the work put into the solid by the explosion goes entirely into an increase in kinetic energy and an increase in internal energy. Since the shocked material heats up ~ to 500°C for ~500 000 atmos, energy can be lost due to radiation or conduction. Owing to the high conductivity of the metal pellets, there is no loss of energy due to radiation from the internal volume of the pellet. In view of the short times available for radiation and conduction from the surface, the assumption of no radiation or conduction loss is probably quite well satisfied.

4. The Assumption of Equivalence

The assumption of equivalence states that a solid which is subject to an external *hydrostatic* pressure (P), and which has an internal energy/unit mass (E), has the same density (ρ) as does the shocked solid which is characterized by the pressure P' and energy E', provided that $P=P'$ and $E=E'$. In other terms, it is assumed that the material behind the shock front at pressure P' and temperature T has the same density as that solid would have if subjected to a hydrostatic pressure P' and temperature T. With this assumption, the shock compression measurements of P', v', E' points are equivalent to hydrostatic pressure measurements. In view of the one-dimensional nature of the shock wave, there is no clear *a priori* evidence to support this assumption. However, it can, in principle, be checked by direct experimental comparisons of the volume compression under shock and hydrostatic conditions at the same temperature. The difficulty in

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[11] J. M. Walsh (private communication).

[12] R. H. Christian and B. J. Alder, Bull. Am. Phys. Soc. Ser. II, **3**, 290 (1958).

[13] R. E. Duff and F. S. Minshall, Bull. Am. Phys. Soc. Ser. II, **3**, 291 (1958).

carrying out this procedure in detail lies in the fact that the shock-wave measurements begin at about 150 000 atmos and Bridgman's measurements end at around 100 000 atmos. Furthermore, the Hugoniots are not isotherms. Extensive graphical comparisons[3] of the hydrostatic pressure isotherms and shock-wave Hugoniots indicate a fairly close joining of the two in the region around 150 000 atmos. A more sensitive test is the extrapolation of the compressibility data into the shock-wave region. Such a comparison has been made by Borelius[14] for Cu and Al. A satisfactory junction of the two results is indicated.[14a] Thus, *a posteriori* experimental evidence, at least in the 150–200 thousand atmos range, indicates the validity of the equivalence assumption. As a result, the primes will be dropped from $\rho'=1/v'$, P', and E' in the Rankine-Hugoniot relation so as to make these symbols identical with those appearing in the hydrostatic Mie-Grüneisen equation of state.

The Rankine-Hugoniot relations formally represent a system of three equations in the five variable U_s, U_p, ρ, P, E. The specification of any two of these variables fixes the value of the remaining three. It has been found[4] that within the limits of experimental error the relation between U_s and U_p is linear. Thus, for each metal there exists a relation

$$U_s=c+sU_p, \tag{10}$$

where s and c are determined experimentally. Equation (10) added to (9) enables the specification of any four of the variables in terms of the remaining one. It is useful to choose as the independent variable the volume v, or more conveniently the volume decrement x:

$$x=(v_0-v)/v_0=(1-\rho_0/\rho). \tag{11}$$

By using Eqs. (10) and (11) in Eq. (9) we can eliminate U_s and U_p to obtain P and $E-E_0$ as functions of x, *viz*:

$$P=c^2x/[v_0(1-sx)^2], \tag{12}$$

$$E-E_0=\tfrac{1}{2}c^2x^2/(1-sx)^2. \tag{13}$$

Equations (12) and (13) show explicitly the form of the Hugoniot in a form which is particularly useful for the extrapolation of the shock-wave data beyond or below the experimentally attainable region. This extrapolation is valid insofar as the relation between U_s and U_p remains linear. Data on 24*ST* aluminum up to pressures as high as 1.3 million atmospheres indicates that over this range the linear relation between U_s and U_p is maintained.

IV. DEDUCTION OF THE VOLUME DEPENDENCE OF THE COHESIVE ENERGY FROM THE SHOCK-WAVE HUGONIOTS

The equation of state [Eq. (3)] may be regarded as a differential equation for $\Phi(v)$, which can be integrated if P, γ, and U_{vib} are known as functions of the volume for corresponding temperatures. We may write Eq. (3) as

$$\frac{d\Phi}{dv}=-P+\frac{\gamma U_{\text{vib}}(v_0,T_0)}{v}+\frac{\gamma}{v}[U_{\text{vib}}(v,T)-U_{\text{vib}}(v_0,T_0)]. \tag{14}$$

In this equation the vibrational energy has been split into two terms. The first is the vibrational energy at some initial volume and temperature v_0 and T_0. The second is the change in U_{vib} as the state is changed from the initial state v_0, T_0 to some final state v, T. v_0 and T_0 will be taken as the state at the foot of the Hugoniot, i.e., at $P=1$ atmos and $T=20°\text{C}$. Along the Hugoniot P is known as a function of volume as is shown by Eq. (12). Also, $E(v,T)-E(v_0,T_0)$, the change in the total internal energy/unit mass, is known as a function of volume from Eq. (13), for each point on the Hugoniot. In our simple model of the solid, the total internal energy is the sum of the cohesive energy Φ and the vibrational energy U_{vib}. Therefore, we have

$$E(v,T)-E(v_0,T_0)=[\Phi(v)-\Phi(v_0)]+[U_{\text{vib}}(v,T)-U_{\text{vib}}(v_0,T_0)]. \tag{15}$$

The solid is presumed perfectly periodic except for the lattice vibrations. In order to include lattice imperfections, it would be necessary to reformulate the equation of state by including the free energy of the imperfections. It would also be necessary to modify (15) to include the change in energy of the lattice imperfections. In writing Eq. (15) in the form given above, we are explicitly assuming that a negligible amount of the shock-wave energy goes into the production of imperfections in the lattice. Substituting Eq. (15) into Eq. (14), we find

$$\frac{d}{dv}[\Phi(v)-\Phi(v_0)]=-P+\frac{\gamma U(v_0,T_0)}{v}+\frac{\gamma}{v}[(E-E_0)-(\Phi-\Phi_0)]. \tag{16}$$

This is a differential equation for $[\Phi(v)-\Phi(v_0)]$ in which all the entering quantities except γ are known as functions of the volume along the Hugoniot.

There is now available no direct experimental evidence which will determine $\gamma(v,T)$ along the Hugoniot. It is, however, possible to make use of a theory due to Slater[15] to estimate the volume

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[14] G. Borelius, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6.

[14a] Recent measurements by Doran, Fowles, and Peterson [Phys. Rev. Letters 1, 402 (1958)] are also in support of the assumption of equivalence.

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

dependence of γ. Slater has shown that γ can be related to the curvature of the P-v isotherms as follows:

$$\gamma(v)=-\tfrac{2}{3}+\tfrac{1}{2}\left[\frac{vd^2v/dP^2}{(dv/dP)^2}\right]_v. \tag{17}$$

In spite of the crudeness of the assumptions on which this relation is based, values of γ obtained from it, using Bridgman's P-v data, are in good agreement[15,16] with γ' as determined from the Grüneisen relation [Eq. (7)]. The volume range available using Bridgman's data was so limited that (d^2v/dP^2) could be evaluated only very near v_0. The availability of the shock-wave data over a much wider volume range has enabled the Los Alamos group to determine γ as a function of volume using isotherms deduced from the Hugoniots.[3] To be sure, they used the Dugdale-MacDonald relation.[17] However, the resulting volume dependence of γ is nearly the same as that given by the Slater relation. We have presented Slater's equation because the theoretical basis of the Dugdale-MacDonald relation has been called into serious question.[18] The Los Alamos results indicate that the percentage change of γ upon changing the volume is about the same as the percentage volume change itself: i.e., $(1/\gamma)[\partial\gamma/(\partial v/v_0)]$ $\sim$1-2. Since γ is independent of the temperature at constant volume for temperatures above the Debye temperature,[9] the percentage change in γ along a Hugoniot is of the same size as the percentage change in volume. In view of the weakness of the volume dependence of γ in comparison with the volume dependence of P, it is possible, in the first approximation, to regard γ as a constant independent of the volume along the Hugoniot insofar as the calculation of Φ is concerned. This approximation can be justified as follows. $[\Phi(v)-\Phi(v_0)]$ is determined by the volume dependence of the right-hand side of Eq. (14). The first of these terms, P, starts from 1 atmos and rises to $\sim$500 000 atmos for $x=(v_0-v)/v_0\sim0.25$. The second term is the so-called internal pressure set up by the lattice vibrations. Its magnitude is $\sim$25 000 atmos. Thus, in the low-pressure range below about 70 000 atmos, this term is very important in determining Φ. However, in this region the volume has not changed much and γ changes by less than $\sim$10%. In the high-pressure region where γ has changed the most, the internal pressure is relatively small compared to the P term, and the neglect of the volume dependence of γ is suppressed. The last term in Eq. (14), which represents the change in the vibrational energy along the Hugoniot, can be estimated from calculations[3] of the temperature along the Hugoniots. For pressures of 500 000 atmos, the change in temperature of the shocked material is about 400°K[4] for metals such as those dealt with here. The order of magnitude of the last term is $\sim(\gamma/v)(3Nk\Delta T)\sim30\,000$ atmos for $\Delta T=400°$K. Thus, at 500 000 atmos the last term is less than 10% of the P term. For larger pressures this term is larger, and at lower pressures it is relatively smaller. Thus again we see that the effect of any change in γ along the Hugoniot is suppressed insofar as the determination of $[\Phi-\Phi(v_0)]$ is concerned. We shall therefore neglect the volume dependence of γ in the integration of Eq. (16). For those applications for which more accurate results are required, the volume dependence of γ as determined by the Los Alamos group can be used. We shall, *a posteriori*, roughly estimate the effect of γ on $\Phi-\Phi(v_0)$ by plotting $\Phi(v)-\Phi(v_0)$ as determined from Eq. (16) for various values of γ.

Under the assumption that γ is a constant, Eq. (16) for Φ can be written as

$$\frac{d}{dx}[\Phi(x)-\Phi(0)]-\frac{\gamma}{(1-x)}[\Phi(x)-\Phi(0)]=+\frac{c^2x}{(1-sx)^2}-\frac{\gamma c^2x^2}{2(1-x)(1-sx)^2}-\frac{\gamma U_{\text{vib}}(v_0,T_0)}{(1-x)}. \tag{18}$$

Since this is an ordinary first order differential equation, the solution can be presented formally. This solution is

$$\Phi(x)-\Phi(0)=(1-x)^{-\gamma}\int_0^x\frac{c^2\zeta(1-\zeta)^\gamma}{(1-s\zeta)^2}\left(1-\frac{\gamma}{2}\frac{\zeta}{(1-\zeta)}\right)d\zeta-U_{\text{vib}}(v_0,T_0)\left(\frac{1}{(1-x)^\gamma}-1\right). \tag{19}$$

The integral in Eq. (19) cannot be evaluated in terms of elementary functions because of the appearance of the irrational function $(1-\zeta)^\gamma$ in the integrand. If an exact solution of (18) is required, the solution (19) can be computed numerically by machine. Instead of employing the machine calculation of (19), it is possible to determine $\Phi(x)-\Phi(0)$ approximately by solving Eq. (16), using a method of successive approximation. This approach is based on the smallness of the last term in Eq. (16). In the zeroth approximation we may neglect the changes in vibrational energy entirely and write Eq. (16) as

$$\left(\frac{\partial\Phi}{\partial v}\right)^{(0)}=-P+\frac{\gamma U(v_0,T_0)}{v}. \tag{20}$$

In the first approximation we substitute $\Phi^{(0)}$ for Φ in the last term of Eq. (16), giving

$$\left(\frac{\partial\Phi}{\partial v}\right)^{(1)}=\left(\frac{\partial\Phi}{\partial v}\right)^{(0)}+\frac{\gamma}{v}[(E-E_0)-(\Phi-\Phi_0)^{(0)}]. \tag{21}$$

If this procedure is carried out successively, we find in

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

[17] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **89**, 832 (1953).

[18] J. J. Gilvarry, Phys. Rev. **102**, 331 (1956).

the nth order approximation that

$$\left(\frac{\partial\Phi}{\partial v}\right)^{(n)}=\left(\frac{\partial\Phi}{\partial v}\right)^{(0)}+\frac{\gamma}{v}[(E-E_0)-(\Phi-\Phi_0)^{(n-1)}]. \tag{22}$$

It is consistent with the approximation of neglecting the volume dependence of γ to stop after the first approximation. The range of x for which this first approximation is accurate will be shown later to be quite wide. If Eqs. (12) and (13) are substituted into Eq. (20), we find that in terms of the volume decrement $x=(v_0-v)/v_0$ the expression for $(\partial\Phi/\partial v)^{(0)}$ becomes

$$\frac{\partial\Phi^{(0)}}{\partial x}=\frac{c^2x}{(1-sx)^2}-\frac{\gamma U_{\text{vib}}(v_0,T_0)}{(1-x)}. \tag{23}$$

Integrating to find Φ in the zeroth order gives

$$[\Phi(x)-\Phi(0)]^{(0)}=\frac{c^2}{s^2}\left[\frac{sx}{(1-sx)}-\ln\left(\frac{1}{1-sx}\right)\right]$$
$$-\gamma U_{\text{vib}}(v_0,T_0)\ln\left(\frac{1}{1-x}\right). \tag{24}$$

The differential equation for Φ in the first order therefore becomes

$$\left(\frac{d\Phi}{dx}\right)^{(1)}=\left(\frac{d\Phi}{dx}\right)^{(0)}-\frac{\gamma}{1-x}$$
$$\times\left\{\frac{1}{2}\frac{c^2x^2}{(1-sx)^2}-\frac{c^2}{s^2}\left[\frac{sx}{1-sx}-\ln\left(\frac{1}{1-sx}\right)\right]\right.$$
$$\left.+\gamma U_{\text{vib}}\ln\left(\frac{1}{1-x}\right)\right\}. \tag{25}$$

The result of integrating (25) is

$$[\Phi(x)-\Phi(0)]^{(1)}$$
$$=\frac{c^2}{s^2}\left[\frac{sx}{(1-sx)}-\ln\left(\frac{1}{1-sx}\right)\right]-\gamma U_{\text{vib}}\ln\left(\frac{1}{1-x}\right)$$
$$-\frac{\gamma c^2}{s^3}(sx)^4G(s,x)-\frac{\gamma^2}{2}U_{\text{vib}}[\ln(1-x)]^2, \tag{26}$$

where

$$\begin{aligned}
&\text{(a)}\quad G(s,x)=\sum_{n=0}^{\infty}b_n(s)(sx)^n,\\
&\text{(b)}\quad b_n(s)=a_n(s)/(n+4),\\
&\text{(c)}\quad a_n(s)=\frac{a_{n-1}}{s}+\left(\frac{n}{2}+\frac{1}{n+3}\right),\\
&\text{(d)}\quad a_0=\tfrac{1}{3},\quad a_1=\frac{1}{3s}+(\tfrac{1}{2}+\tfrac{1}{4}).
\end{aligned} \tag{27}$$

It is possible to interpret physically the meaning of the zeroth and first approximations for $\Phi(v)$ [Eqs. (24) and (26)] within the framework of the assumption that γ is independent of v. If P could be measured as a function of v along a curve for which the vibrational energy is a constant, then $d\Phi/dx$ would be given exactly by Eq. 23. Thus, the zeroth approximation for Φ regards the Hugoniot as identical with the path of constant vibrational energy. However, the Hugoniot rises more rapidly than an isotherm.[3] Thus the first order expression for Φ includes, as the last two terms, the reduction which must be made to account for the fact that the Hugoniot rises more steeply than the curve of constant vibrational energy.

Using Eq. (26), we may examine how closely the first order approximation approaches the exact value for $\Phi(v)-\Phi(v_0)$ represented in Eq. (19). The first order corrections are most important at large x. In this region, the dominant zeroth order and first order correction terms are

$$(c^2/s^2)\{[sx/(1-sx)]+\ln(1-sx)\}$$

and

$$(\gamma c^2/s^3)(sx)^4G(s,x),$$

respectively. The ratio of the latter to the former term is $\sim x^2$, as may be seen from a power series expansion of each term. Thus for the maximum comparison attained in 24*ST* aluminum for a pressure of 1 megabar, namely $x=0.40$, the dominant first order correction term is about 16% of the dominant zeroth order term. It is to be expected that the second order corrections will in their turn be x^2 as big as the first order corrections. Hence again, for the largest available compression, $x=0.40$, the second order correction can be expected to contribute only about 2.5% of the zeroth order terms even in the most unfavorable case. Therefore, the error produced by stopping after the first approximation is small, certainly much smaller than the errors introduced by neglecting the volume dependence of γ.

TABLE I. Values of parameters required for the determination of $\Phi(v)-\Phi(v_0)$.

Metal	c (km/sec)	s	γ	Θ_0 (°K)	Θ (°K)
Be	8.15±0.1	1.01±0.05	1.17[a]	1160[d]	1000[d]
Al	5.35	1.34	2.37[b]	419[e]	394[h]
Co	4.73±0.03	1.39±0.05	1.87[c]	443[f]	375[i]
Ni	4.77±0.03	1.27±0.02	1.88[c]	413[g]	390[i]
Cu	3.9 ±0.1	1.60±0.1	1.96[c]	345[h]	315[e]
Ag	3.25±0.02	1.58±0.03	2.43[b]	225[d]	215[e]

[a] Rice, McQueen, and Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 61.

[b] C. S. Smith (private communication).

[c] J. C. Slater, Phys. Rev. **57**, 744 1940.

[d] M. Blackman, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7, Part I (see p. 368 for Θ_0 for Ag).

[e] J. A. Kok and W. H. Keesom, Physica **3**, 1035 (1936).

[f] G. Duykaerts, Physica **6**, 817 (1939).

[g] W. H. Keesom and C. W. Clark, Physica **2**, 513 (1935).

[h] J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 2.

[i] K. Clusius and L. Schachinger, Z. Naturforsch. **7A**, 185 (1952).

V. NUMERICAL RESULTS

In order to establish Φ as a function of x, using Eq. (26), c, s, γ and $U_{\text{vib}}(v_0,T_0)$ must be determined, for each metal. In columns 1 and 2 of Table I are listed the values of c and s determined directly from the intercept and slope of a line drawn through the experimental values[3] of U_s *vs* U_p. The metals chosen, Be, 24*ST* Al, Co. Ni, Cu, and Ag, are those for which the experimental measurements are most extensive. The values of c and s listed here are slightly different from those listed in Table X, reference 4. In column 3, Table I are listed values of γ determined by using Grüneisen's relation [Eq. (7)], along with literature references.

The vibrational energy at 20°C and 1 atmosphere, $U_{\text{vib}}(v_0,T_0)$, consists of the zero-point vibrational energy of the normal modes at $T=0°\text{K}$ plus the energy required to heat the lattice at the constant volume v_0 from 0°K to 293°K. Thus we can write

$$U_{\text{vib}}(v_0,T_0)=U_{\text{vib}}(v_0,0)+\int_0^{T_0} C_{v_0}dT. \tag{28}$$

The zero-point energy is given by

$$U_{\text{vib}}(v_0,0)=\int_0^{\nu_m} \tfrac{1}{2}h\nu g(\nu)d\nu, \tag{29}$$

where $g(\nu)$ is the density of normal modes at frequency ν, and ν_m is the maximum vibration frequency. Since there are $3N$ modes of vibration of a lattice with N atoms, there is a normalization condition on $g(\nu)$, *viz.*:

$$\int_0^{\nu_m} g(\nu)d\nu=3N. \tag{30}$$

From Eqs. (29) and (30) it follows that the vibrational energy at 0°K is $3Nh\langle\nu\rangle/2$, where $\langle\nu\rangle$ is the average vibration frequency weighted over the density of modes. In order to determine $\langle\nu\rangle$ accurately, the detailed form of the density of modes is needed. Since there is no direct experimental information on the detailed form on the density of modes, we shall use the Debye approximation, i.e., that

$$g(\nu)=3N(3\nu^2/\nu_m{}^3). \tag{31}$$

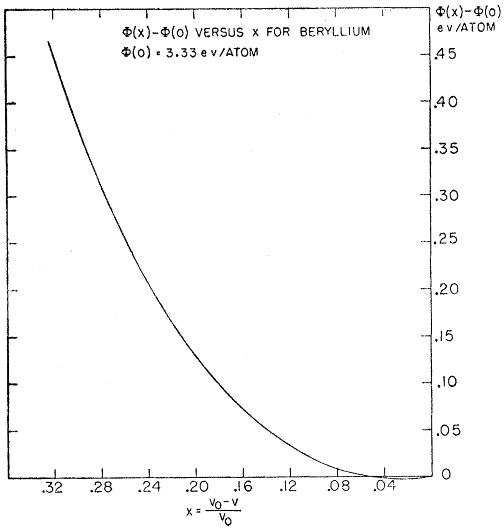

FIG. 1. The change in the cohesive energy $[\Phi(x)-\Phi(0)]$ of beryllium as a function of the volume decrement $x=(v_0-v)/v_0$. v_0 is the volume/unit mass at 20°C and $P=1$ atmos. $\Phi(0)$ is the cohesive energy at $v=v_0$.

TABLE II. Values of C^2, $U_{\text{vib}}(v_0,T_0)$ and $\Phi(v_0)$ used in the determination of $\Phi(v)$.

Metal	c^2 (ev/atom)	$U_{\text{vib}}(v_0,T_0)$ (ev/atom)	$\Phi(v_0)$ (ev/atom)
Be	6.20±2.4%	0.1303	3.33
Al	8.00[a]	0.0849	3.23
Co	13.7 ±1.2%	0.0883	4.56
Ni	13.8 ±1.2%	0.0846	4.40
Cu	10.0 ±5%	0.0829	3.52
Ag	11.8 ±2%	0.0787	3.00

[a] No error is listed for the 24*ST* Al data because the published results represent smoothed values of U_s and U_p obtained from a very large number of measurements.

The average frequency for this distribution is $\frac{3}{4}\nu_m$. Thus the zero point energy can be written as

$$U_{\text{vib}}(v_0,0)=(9/8)Nh\nu_m=(9/8)Nk\Theta_0; \tag{32}$$

where Θ_0 is defined by $k\Theta_0=h\nu_m$. The value of Θ_0 used in calculating $U_{\text{vib}}(v,0)$ from Eq. (32) will be obtained from measurements of the specific heat at low temperature. With this choice of Θ_0 the density of modes $g(\nu)$ will have the same curvature in the low-frequency region as the actual density of modes in the solid. If the Debye model is also used to estimate the integral of the specific heat from 0°K to 293°K, then Eq. (28) can be written as

$$U_{\text{vib}}(v_0,T_0)=3NkT\left[\frac{3}{8}\frac{\Theta_0}{T}+B(y_m)\right], \tag{33}$$

where

$$B(y_m)=3\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta/T}\frac{z^3dz}{(e^z-1)}, \tag{a}$$

$$y_m=\Theta/T. \tag{b}$$

The function $B(y_m)$ has been calculated by Beattie.[19] The value of Θ used in calculating U_{vib} from Eq. (33) is the value appropriate to the high-temperature region $T\sim\Theta$. In this way we get the best fit of the Debye function to the specific heat data in the region of temperature which makes the largest contribution to U_{vib}. The values of Θ_0 and Θ required for the determination of $U_{\text{vib}}(v_0,T_0)$ are listed in columns 5 and 6 of Table I, along with literature references. It should be

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[19] J. A. Beattie, J. Math and Phys. 6, 1 (1926).

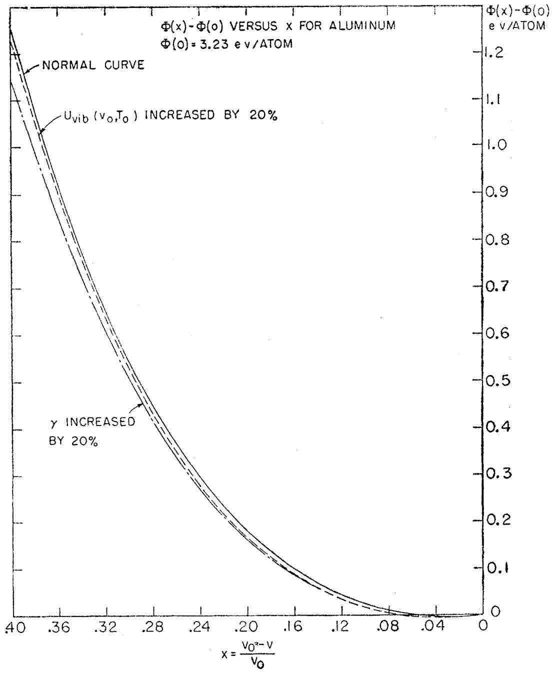

FIG. 2. The change in the cohesive energy $[\Phi(x)-\Phi(0)]$ of 24*ST* aluminum as a function of the volume decrement $x=(v_0-v)/v_0$. The normal curve uses the parameters listed in Tables I and II. The comparison curves show the effect of increasing the vibrational energy $U_{\text{vib}}(v_0,T_0)$ or Grüneisen parameter γ by 20%.

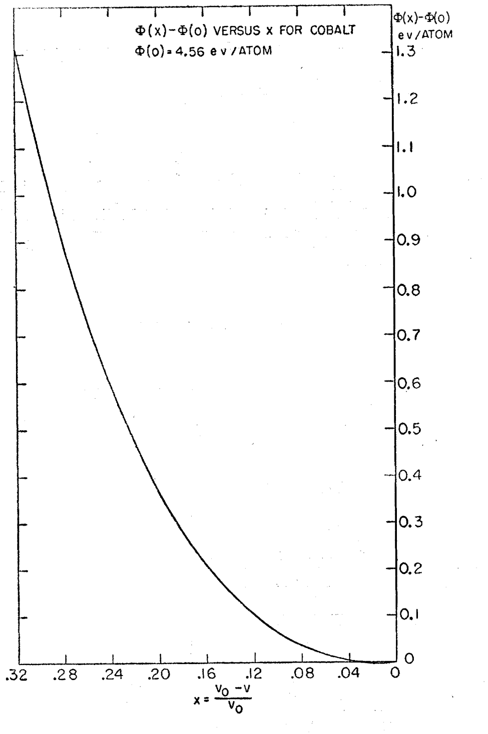

FIG. 3. The change in the cohesive energy $[\Phi(x)-\Phi(0)]$ of cobalt as a function of the volume decrement $x=(v_0-v)/v_0$. v_0 is the volume/unit mass at 20°C and $P=1$ atmos. $\Phi(0)$ is the cohesive energy at $v=v_0$.

noted that these values of Θ are appropriate if the density of the solid is the same as at absolute zero. Actually we should use the values of Θ which correspond to the density at 293°K. Since $\partial \ln\Theta/\partial \ln v \simeq -\gamma$, the change in Θ due to the volume expansion from 0°K to 293°K is a few percent. In view of the approximate nature of the method for estimating U_{vib}, and the uncertainty in the experimental values of Θ, due to the temperature dependence of Θ, no correction was made to account for this small volume dependence.

It is difficult to estimate the error introduced by using the Debye approximation in place of the actual distribution of modes in the evaluation of the two contributions to $U_{\text{vib}}(v_0,T_0)$. It is expected though that the estimated values of U_{vib} are probably correct to within $\sim 25\%$. The U_{vib} term is important in determining $\Phi(v)-\Phi(v_0)$ only in the region of small x where $\Phi(v)-\Phi(v_0)$ is small anyhow. Thus errors in the estimation of U_{vib} are suppressed in the calculation of $\Phi(v)$ as may be seen in Fig. 2.

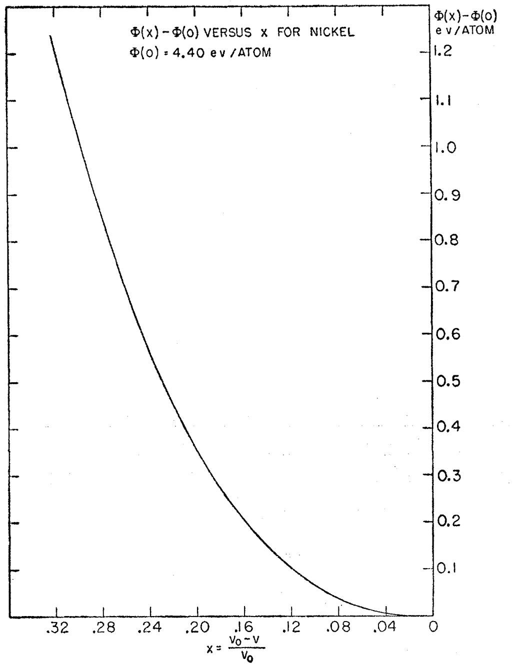

FIG. 4. The change in the cohesive energy $[\Phi(x)-\Phi(0)]$ of nickel as a function of the volume decrement $x=(v_0-v)/v_0$. v_0 is the volume/unit mass at 20°C and $P=1$ atmos. $\Phi(0)$ is the cohesive energy at $v=v_0$.

In Table II we list the values of $U_{\text{vib}}(v_0,T_0)$ which are calculated from Eq. (33) using the values of Θ_0 and Θ listed in Table I. $U_{\text{vib}}(v_0,T_0)$ is given in units of ev/atom, as is c^2 which is also included in Table II. In column 4 are given values of the cohesive energy $\Phi(v_0)$ obtained from sublimation measurements.[20]

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[20] F. D. Rossini *et al.*, *Selected Values of Chemical Thermodynamic Properties* (U. S. Government Printing Office, Washington, D. C., 1952).

The results of calculating $\Phi(x)-\Phi(0)$ from Eq. (26) using the values of c, s, γ, and U_{vib} listed in Tables I and II are shown in Figs. 1–6. In the case of Be, Co, Ni, Cu, and Ag the experiments achieved a volume decrement between 20% and 25%. Figures 1, 3, 4, 5, and 6 present $\Phi(x)$ as large as 32%. The values of Φ beyond the experimental range represent extrapolation of the linear U_s, U_p relation into the region $0.20 \leq x \leq 0.32$. In the case of 24*ST* aluminum the shock compression measurements extend to $x=0.40$ and U_s is observed to be a linear function of U_p throughout this range.

Because of the smallness of the scale, it is difficult to see graphically that the minimum of $\Phi(x)$ is somewhat to the left of $x=0$. At $x=0$ the volume of the solid is that corresponding to $P=1$ atmos and $T=20°\mathrm{C}$. For $P\sim 0$ the equation of state requires that $\partial\Phi/\partial v = +\gamma U_{\mathrm{vib}}(v_0,T_0)/v_0$, i.e., $\partial\Phi/\partial v$ is positive at $v=v_0$.

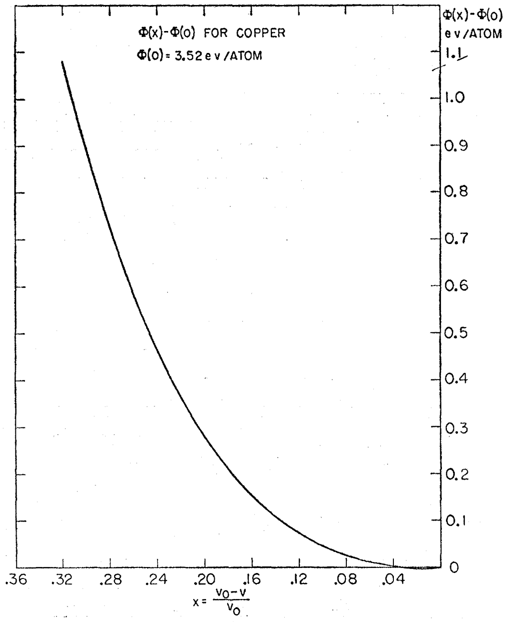

FIG. 5. The change in the cohesive energy $[\Phi(x)-\Phi(0)]$ of copper as a function of the volume decrement $x=(v_0-v)/v_0$. v_0 is the volume/unit mass at 20°C and $P=1$ atmos. $\Phi(0)$ is the cohesive energy at $v=v_0$.

In Fig. 2, which gives $\Phi(x)$ for aluminum, the curve marked "normal" uses the data in Tables I and II. The two comparison curves show the effect of increasing the vibrational energy $U_{\mathrm{vib}}(v_0,T_0)$ or the Grüneisen parameter γ by 20%. It is clear that a 20% change in U_{vib} does not affect $\Phi(x)$ much. The effect of changing γ is somewhat greater and becomes more important as x is increased.

VI. CONCLUSIONS

It has been shown that within the framework of certain assumptions, the most important of which is the assumption of the equivalence of the shock and hydrostatic compression, it is possible to deduce the volume dependence of the cohesive energy Φ directly from measurements of the relation between the shock-front and shock-particle velocities. Although the shock compressions are limited generally to $\Delta v/v\sim 25\%$, the present method is well suited for extrapolation beyond the experimental region.

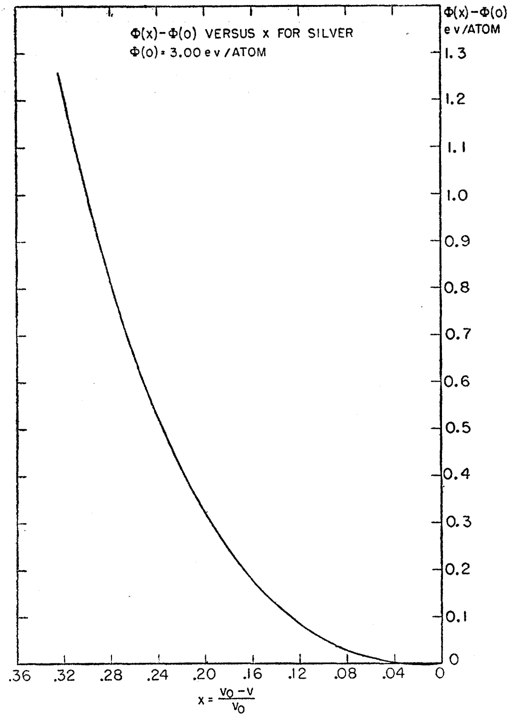

FIG. 6. The change in the cohesive energy $[\Phi(x)-\Phi(0)]$ of silver as a function of the volume decrement $x=(v_0-v)/v_0$. v_0 is the volume/unit mass at 20°C and $P=1$ atmos. $\Phi(0)$ is the cohesive energy at $v=v_0$.

The accuracy of the deduction of $\Phi(v)$ is limited by the simplifying assumption that γ is independent of volume. Because of the weakness of the volume dependence of γ this assumption introduces little error in the deduction of $\Phi(v)$ except in the case of very large compressions, $\Delta v/v \gtrsim 40\%$. In this volume range, or if a more accurate calculation of $\Phi(v)$ is required in the region $\Delta v/v \gtrsim 30\%$, the volume dependence of γ can be taken into account by making use of Slater's[15] relation for γ in conjunction with the isotherms deduced from the Hugoniots.[4]

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