PHYSICAL REVIEW B VOLUME 29, NUMBER 6 15 MARCH 1984

Universal features of the equation of state of metals

James H. Rose
Ames Laboratory—U.S. Department of Energy, Iowa State University, Ames, Iowa 50011*
and Institute for Theoretical Physics, University of California, Santa Barbara, California 93106

John R. Smith[†]
Institute for Theoretical Physics, University of California, Santa Barbara, California, 93106
and Physics Department, General Motors Research Laboratory, Warren, Michigan 48090-9055*

Francisco Guinea
Institute for Theoretical Physics, University of California, Santa Barbara, California 93106

John Ferrante
National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135

(Received 29 June 1983)

The zero-temperature equation of state of metals, in the absence of phase transitions, is shown to be accurately predicted from zero-pressure data. Upon appropriate scaling of experimental pressure-volume data a simple universal relation is found. These results provide further experimental confirmation of the recent observation that the total-binding-energy—versus—separation relations for metals obey a universal scaling relation. Important to our results is a parameter η, which is a measure of the anharmonicity of a crystal. This parameter is shown to be essential in predicting the equation of state. A simple formula is given which predicts the zero-temperature derivative of the bulk modulus with respect to pressure.

I. INTRODUCTION

Many aspects of the energetics of metals can be understood if the zero-temperature equation of state (EOS) is known. Predictions of the EOS are difficult and therefore rare. In this paper we will show that the zero-temperature EOS of metals (both alloys and elements) can rather generally be determined, in the absence of phase transitions, from a universal function. These results also allow the approximate determination of the pressure-volume relation for the experimentally inaccessible regime of negative hydrostatic pressure as well as the ultrahigh-pressure regime.

Recently, three of the authors[1–5] have examined the nature of metallic bonding. It was predicted on the basis of theoretical calculations that the binding-energy—distance relation could be *quantitatively* described in terms of a simple two-parameter scaling of a universal function and knowledge of the equilibrium specific volume per atom. The zero-temperature EOS follows directly from the universal energy relation and is specified by the zero pressure, equilibrium values of the cohesive energy ΔE, the isothermal bulk modulus B, and the specific volume per atom, which we characterize by the Wigner-Seitz equilibrium radius r_{WSE}.

The major results of this paper are as follows. Firstly, we show that in the absence of a phase transition, the EOS can be straightforwardly predicted. Secondly, we show that the experimental data can be transformed into a universal function F^* which is related to the pressure P and the volume V as $F^* \propto V^{2/3}P(V)$. The fact that a universal form emerges when $V^{2/3}P(V)$ is appropriately scaled experimentally confirms the existence of a universal binding-energy—distance relation for bulk metals under compression.

The theoretical development of the EOS from the results of Refs. 4 and 5 are carried out in Sec. II. We find a length scale l which describes the range over which strong forces act. The ratio of the size of the atomic cell to this length, $\eta \equiv r_{\mathrm{WSE}}/l$, provides a measure of the anharmonicity of a crystal. A table of this anharmonicity parameter is provided for many of the elemental metals. Other results in this section include a table characterizing the rupture pressure for a metal under negative hydrostatic pressure and a simple expression for the change in the bulk modulus with pressure.

The experimental confirmation of a universal form for the binding-energy—distance relation is given in Sec. III. First we show that given the universal energy relationship derived in Refs. 4 and 5 as well as ΔE, r_{WSE}, and the isothermal bulk modulus B, we can accurately predict the EOS for a number of elemental metals and for a representative alloy, 347 stainless steel. We collect these results and show (1) that a universal form for F^* in fact exists, and (2) that its form was predicted by theory. We conclude this section by comparing the experimental results for $(\partial B/\partial P)_T$ with the prediction of theory. Our theory predicts $(\partial B/\partial P)_T$ for the covalent semiconductors Ge and Si as well as for metals. We conclude the paper with a discussion of our results. One point of particular importance is that (to the accuracy of our results) the prediction of the EOS reduces to the prediction of the three input parameters ΔE, B, and r_{WSE}.

II. THEORY

Detailed, first-principles calculations of the cohesive energy of metals as a function of lattice parameter have appeared in recent years.[6-10] It has recently been shown[1,4,5] that the shape of these curves can be obtained from a simple two-parameter scaling of a universal function $E^*(a^*)$,

$$E(r_{\rm WS})=\Delta E\, E^*(a^*)\ . \tag{2.1}$$

Here E is the binding energy per atom, $r_{\rm WS}$ is the radius of the Wigner-Seitz sphere containing an average volume per atom, and ΔE is the equilibrium binding energy. The parameter a^* is a scaled length determined by $r_{\rm WS}$,

$$a^*=(r_{\rm WS}-r_{\rm WSE})/l\ . \tag{2.2}$$

The equilibrium radius is $r_{\rm WSE}$ and l is the length scale which we have introduced. Thus, the total energy as a function of separation relative to the equilibrium radius can be accurately represented in terms of the two parameters ΔE and l once $E^*(a^*)$ is known.

First-principles calculations of the cohesive energy of $\mathrm{Cu}^{(8)}$, $\mathrm{K}^{(8)}$, $\mathrm{Mo}^{(8)}$, $\mathrm{Ba}^{(7)}$, $\mathrm{Sm}^{2+(7)}$, and $\mathrm{Sm}^{3+(7)}$ have been scaled and are displayed in Fig. 1. Here ΔE and l have been chosen so that $E^*(a^*=0)=-1$, $E^{*\prime}(0)=0$, and $E^{*\prime\prime}(0)=1$, where the prime denotes differentiation with respect to a^*. As can be seen, the agreement among these different metals is good. In Refs. 4 and 5 it was further shown that the universal function $E^*(a^*)$ was not restricted to the description of the bulk binding energy of metals. Rather, as shown in Fig. 2, this same function describes *quantitatively* all first-principles calculations of bimetallic adhesion, molecular binding, cohesion, and chemisorption of gas molecules on metals. The degree to which these widely disparate phenomena can be represented by a single two-parameter function is remarkable.

The existence of such a simple form for the binding energy implies a simplification in the EOS. The pressure at $T=0$ $(P=-dE/dV)$, can be calculated using Eq. (2.1). We find

$$P(V)=-\frac{\Delta E}{4\pi r_{\rm WS}^2}\frac{1}{l}E^{*\prime}(a^*)\ . \tag{2.3}$$

Here the prime denotes the derivative with respect to a^* and $V=4\pi r_{\rm WS}^3/3$ is the volume. Note that Eq. (2.3) implies that there is no two-parameter, universal scaling relation for $P(V)$ because of the coupling between $r_{\rm WS}^2$ and a^* [Eq. (2.2)]. However, the shape of the force relation,

$$F(V)=4\pi r_{\rm WS}^2 P(V)=-\frac{\Delta E}{l}E^{*\prime}(a^*)\ , \tag{2.4}$$

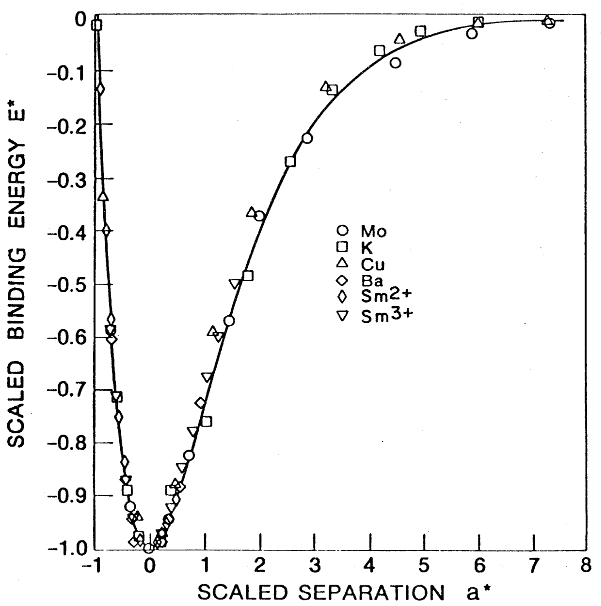

FIG. 1. Bulk energies for various metals scaled using Eqs. (2.1) and (2.2). The Mo, K, and Cu data are from Ref. 8, while the Ba, Sm^{2+}, and Sm^{3+} data are from Ref. 7.

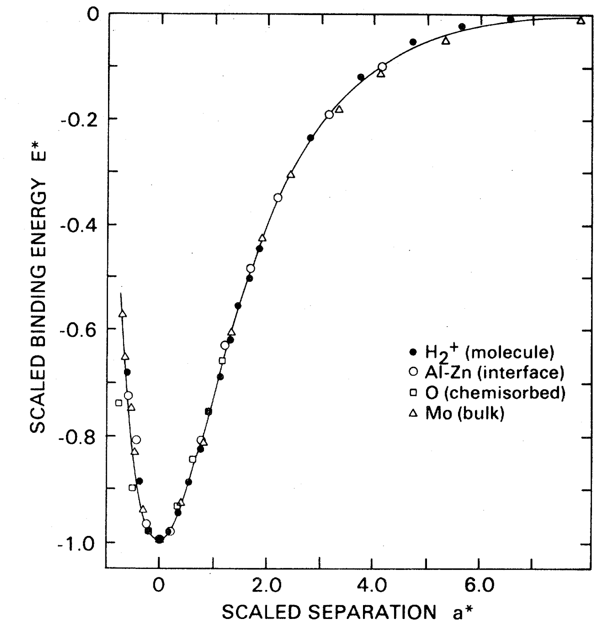

FIG. 2. Binding energy as a function of separation for four systems as noted; scaled in analogy with the bulk energy.

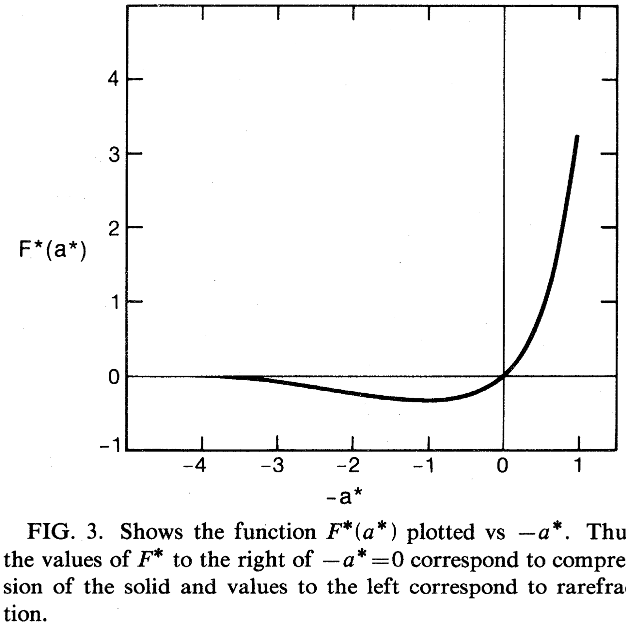

FIG. 3. Shows the function $F^*(a^*)$ plotted vs $-a^*$. Thus, the values of F^* to the right of $-a^*=0$ correspond to compression of the solid and values to the left correspond to rarefraction.

can be scaled into a universal form under a two-parameter transformation. We write

$$F(V)=\Delta F\, F^*(a^*)\ , \tag{2.5}$$

where $\Delta F=\Delta E/l$ and $F^*(a^*)=-E^{*\prime}(a^*)$. Figure 3 shows the universal function $F^*(a^*)$. Note that F^* has a minimum at $a^*\approx 1$.

A second universal function, $G^*(a^*)$, which may have use in experimental data analysis, can be derived from Eq. (2.5). We note that the force depends linearly on a^* near equilibrium. Thus, we can rewrite $F^*=a^*G^*$. Explicitly, G^* is given by

$$G^*(a^*)=\frac{4\pi r_{\mathrm{WS}}^2 l^2}{\Delta E\,(r_{\mathrm{WS}}-r_{\mathrm{WSE}})}P(V)\ . \tag{2.6}$$

If zero-pressure data are available for a given phase then ΔE and r_{WSE} can be determined directly from the equilibrium specific volume and cohesive energy. The length scale l can then be fixed in terms of ΔE and the isothermal bulk modulus B by requiring that $E^{*\prime\prime}(0)=1$. We find, after taking two derivatives of Eq. (2.1),

$$l=\left[\frac{\Delta E}{12\pi B r_{\mathrm{WSE}}}\right]^{1/2}\ . \tag{2.7}$$

The length scale l describes the width of a binding-energy curve. Consequently, it describes the distance over which strong forces act when the crystal is uniformly dilated. In confirmation of this point of view, it has been shown in Ref. 1 that l is given to fair accuracy by an appropriate screening length of the metal. Since l sets the range over which strong forces act, it also sets the range of the Hooke's-law region. A crystal will be said to be strongly anharmonic if it exceeds the Hooke's-law regime for a relatively small change of its initial volume. On the other hand, in a more harmonic crystal, the Hooke's-law region is not exceeded until a relatively larger change in the initial volume is reached. We can consequently measure the anharmonicity of a crystal in terms of the ratio $\eta=r_{\mathrm{WSE}}/l$. If l, and consequently the Hooke's-law region, are small compared to the size of the crystal cell, η is large and the crystal is more anharmonic. Small values of η correspond to more harmonic crystals. In Table I, l, r_{WSE}, and η are listed for many of the elemental metals. The three input parameters for evaluation of the EOS of many of the elemental metals are given in Tables I and II. Values of ΔE and r_{WSE} (deduced from the specific volume) were taken from Kittel's book.[11] The values of B were taken from the lowest-temperature result in the tables of Simmons and Wang[12] with the exception of the values in parentheses which were taken from Kittel.[11]

The anharmonicity parameter η can be written simply in terms of the three input parameters as

$$\eta=\left[\frac{12\pi B r_{\mathrm{WSE}}^3}{\Delta E}\right]^{1/2}\ . \tag{2.8}$$

This relation can be used to explain the trends exhibited by η across the Periodic Table which are considerable, as η varies by a factor ~ 2.6. First, η tends to increase along the alkali-metal column. The large increase in r_{WSE}^3 down the column is compensated by a similarly large decrease in

TABLE I. Scaling length l [Eq. (2.7)], equilibrium Wigner-Seitz radius (Ref. 11), and dimensionless parameter, $\eta=r_{\mathrm{WSE}}/l$, which describes the anharmonicity are given. For each element, first line gives value of l (in Å), second line gives value of r_{WSE} (in Å), and third line gives value of η.

Li .553 1.719 3.10	Be .312 1.25 4.01											B	C	N	O	F	Ne
Na .562 2.080 3.70	Mg .316 1.77 5.60											Al .336 1.58 4.71	Si 0.344 1.68 4.88	P	S	Cl	Ar
K .651 2.573 3.94	Ca .483 2.18 4.52	Sc --	Ti .340 1.62 4.76	V .310 1.49 4.81	Cr .254 1.42 5.59	Mn --	Fe .274 1.41 5.16	Co .262 1.39 5.31	Ni .270 1.38 5.11	Cu .272 1.41 5.20	Zn .215 1.54 7.16	Ga --	Ge 0.348 1.76 5.05	As	Se	Br	Kr
Rb .658 2.750 4.18	Sr --	Y .47 1.99 4.23	Zr .395 1.77 4.48	Nb .336 1.63 4.84	Mo .265 1.55 5.85	Tc --	Ru .245 1.48 6.04	Rh --	Pd .237 1.52 6.41	Ag .269 1.60 5.94	Cd .214 1.73 8.08	In .360 1.84 5.11	Sn	Sb	Te	I	Xe
Cs .714 2.977 4.17	Ba .558 2.46 4.41	La --	Hf .373 1.74 4.66	Ta .330 1.62 4.92	W .274 1.56 5.69	Re .247 1.52 6.15	Os --	Ir .230 1.50 6.52	Pt .237 1.53 6.47	Au .236 1.59 6.75	Hg --	Tl .331 1.90 5.74	Pb .303 1.93 6.37	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce .648 2.02 3.11	Pr	Nd	Pm	Sm	Eu .478 2.27 4.75	Gd .467 1.99 4.27	Tb	Dy .404 1.96 4.85	Ho	Er .393 1.94 4.94	Tm	Yb .506 1.99 3.94	Lu
Th .483 1.99 4.12	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

TABLE II. Cohesive energy and the bulk modulus are tabulated for many metals (Refs. 11 and 12). In addition, the theoretical limit for the characteristic negative hydrostatic pressure, P_R/B, at which a metal ruptures, is tabulated. For each element, first line gives value of ΔE (eV), second line gives value of B (10^{12} dyn/cm^2), and third line gives value of $-P_R/B$.

Li 1.65 .133 .21	Be 3.33 1.144 .17											B	C	N	O	F	Ne
Na 1.13 .0729 .19	Mg 1.53 .369 .14											Al 3.34 .794 .15	Si 4.64 0.99	P	S	Cl	Ar
K .941 .0366 .18	Ca 1.825 (.152) .16	Sc --	Ti 4.86 1.097 .15	V 5.30 1.570 .15	Cr 4.10 1.901 .14	Mn --	Fe 4.29 1.724 .14	Co 4.39 1.948 .14	Ni 4.435 1.876 .15	Cu 3.50 1.420 .14	Zn 1.35 .804 .11	Ga --	Ge 3.87 0.77	As	Se	Br	Kr
Rb .858 .0306 .17	Sr --	Y 4.39 .423 .17	Zr 6.32 .973 .15	Nb 7.47 1.730 .15	Mo 6.810 2.653 .13	Tc --	Ru 6.62 3.152 .13	Rh --	Pd 3.936 1.955 .12	Ag 2.96 1.087 .13	Cd 1.16 .621 .10	In 2.6 .464 .14	Sn	Sb	Te	I	Xe
Cs .827 .0231 .17	Ba 1.86 (.103) .16	La --	Hf 6.35 1.106 .16	Ta 8.089 1.942 .15	W 8.66 3.142 .13	Re 8.10 3.715 .13	Os --	Ir 6.93 3.704 .12	Pt 5.852 2.884 .12	Au 3.78 1.803 .12	Hg --	Tl 1.87 .382 .13	Pb 2.04 .488 .12	Bi	Po	At	Rn
Fr --	Ra --	Ac --															

Ce 4.77 (.239) .21	Pr	Nd	Pm	Sm	Eu 1.80 (.147) .15	Gd 4.14 .405 .17	Tb	Dy 3.1 .411 .15	Ho	Er 3.3 .468 .15	Tm	Yb 1.6 (.133) .17	Lu
Th 5.926 (.543) .17	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

B. The decrease in ΔE leads to the increase in η. Note that η peaks roughly in the middle of each $3d$, $4d$, or $5d$ transition-metal row and generally increases in going down the columns of transition metals. This is in spite of the similar variation of ΔE, given that the cohesive energy ΔE and η are inversely related. It is consistent with the variation of the bulk modulus B, however. The large values for Zn, Cd, Mg, and Ca relative to their neighbors is due to smaller cohesive energies and larger r_{WSE}, and occur despite their small bulk moduli.

An accurate, analytic representation of $E^*(a^*)$ is needed to practically evaluate the pressure. The most rapid variation in the binding energy as a function of separation is assumed to be exponential. Hence, we propose to approximate $E^*(a^*)$ using the function

$$E^*(a^*)\approx f^*(a^*)e^{-a^*}\;, \tag{2.9}$$

where f^* is assumed to be slowly varying. Consequently, f^* can be represented by a low-order polynomial (if $a^*<1$). We assume that

$$f^*(a^*)\approx f_0^*+f_1^*a^*+f_2^*a^{*2}+f_3^*a^{*3}\;. \tag{2.10}$$

The constraints introduced by $E^*(0)=-1$, $E^{*\prime}(0)=0$, and $E^{*\prime\prime}(0)=1$ require that $f_0^*=-1$, $f_1^*=-1$, and $f_2^*=0$. We fix f_3^* from the thermal expansion of Cu (Ref. 13) to be $f_3^*=-0.05$. Higher-order terms in the polynomial are expected to be small and are neglected here.

The EOS is determined from Eqs. (2.3) and (2.10),

$$\frac{P(V)}{B}=\frac{3[(V/V_0)^{1/3}-1]}{(V/V_0)^{2/3}}e^{-a^*}(1-0.15a^*+0.05a^{*2})\;. \tag{2.11}$$

Here $V_0=4\pi r_{\text{WSE}}^3/3$. Two quantities which are characteristic of the pressure can be extracted from this equation. The bulk modulus is characteristic of the behavior near the minimum. The second characteristic pressure corresponds to a theoretical limit on the *negative* hydrostatic pressure at which a solid ruptures. This pressure, P_R, corresponds to the minimum in Eq. (2.11). Typically, P_R is 10–20 % of the bulk modulus. As a fraction of the bulk modulus, P_R is largest for the more harmonic solids (η small) and smallest for the anharmonic solids. Values of P_R for many elemental metals are included in Table II.

The description given above allows the derivative of the bulk modulus with pressure to be determined, starting from the definition

$$B=-V\left[\frac{\partial P}{\partial V}\right]_T\;. \tag{2.12}$$

After taking the derivative of this equation with respect to pressure and using Eq. (2.7) we find at $T=0$ K,

$$\left[\frac{\partial B}{\partial P}\right]_T=1-\frac{r_{\text{WSE}}}{3l}\frac{E^{*\prime\prime\prime}(0)}{E^{*\prime\prime}(0)}\;. \tag{2.13}$$

$E^{*\prime\prime}(0)$ and $E^{*\prime\prime\prime}(0)$ can be evaluated from the information given above and are 1 and -2.3 explicitly. Consequently,

$$\left[\frac{\partial B}{\partial P}\right]_T=1+\frac{2.3}{3}\frac{r_{\text{WSE}}}{l}\;. \tag{2.14}$$

A similar although more tedious derivation can straightforwardly be carried through for $(\partial^2B/\partial P^2)_T$ and higher-order derivatives.

III. EXPERIMENTAL VERIFICATION OF THE UNIVERSAL BONDING RELATION

In this section we collect experiments on the compression of metals with pressure $[V(P)]$ and use them to test our hypothesis of a universal form for $E^*(a^*)$ and $F^*(a^*)$. Two types of experiment were considered. First, there are static press measurements which were made by Bridgman up to 100 kbar.[14] The second class of experiments involve shock-wave experiments[15] in which metals are collided at high velocities. Very large compressions $(V/V_0 \sim \frac{1}{2})$ and pressures (up to 10 Mbar) have been achieved by this technique. Unfortunately, the determination of both the pressure and volume are indirect. For example, in a shock-wave experiment on Pd, the internal temperature is as high as 7000 K.[15] From a model of the shock-wave experiment, the experimentalist predicts a zero-temperature isotherm. Clearly, some room for systematic error lies here. Mao *et al.*[16] have used shock-wave data[17] for four elements (Pd, Ag, Cu, and Mo) to establish a high-pressure scale based on a ruby crystal fluorescence line. Given the importance of this scale, we have included these four elements in our studies. Agreement between theory and experiment not only tests the hypothesis, but also tests the accuracy of the shock-wave data and analysis.

In Fig. 4 we show the experimental EOS's for four metals and compare them with the theory. Similarly, Fig. 5 shows the same comparison for four other metals. Note particularly that an alloy [stainless steel 347 (Ref. 18), taken as 70% Fe, 19% Cr, and 11% Ni for our calculations] has been included. The data for Li and Rb come from Bridgman's work[14] and thus are independent of the shocked-wave analysis. The theory curves use Eq. (2.11) and the zero-pressure data in Tables I and II. The elemental input data have been taken from handbook values extrapolated to zero temperature and have not been adjusted to improve agreement. In the case of stainless steel the bulk modulus was determined from the experimental data and l was found by an average over the concentration for the constituent elements. As can be seen, the overall agreement for the eight metals plotted is good. For five of the cases (Li, Rb, Ag, Cu, and stainless steel) the agreement is essentially exact. For Pd, Mo, and Pt the small discrepancy is unexplained. Its origin may lie either in a small correction to our hypothesis or more probably in the analysis of the shock-wave data. Overall the agreement between theory and experiment is satisfactory.

The clearest demonstration of a universal relation results from scaling the experimental data using the zero-pressure data r_{WSE}, ΔE, and B. As discussed in Sec. II the function $F^*(a^*)$ is expected to have a universal form. F^* can be related to experimental results via Eqs. (2.4) and (2.5), which yield

$$F^*(a^*)=\frac{1}{3}\frac{r_{\mathrm{WSE}}}{l}\left[\frac{V}{V_0}\right]^{2/3}\frac{P(V)}{B} . \tag{3.1}$$

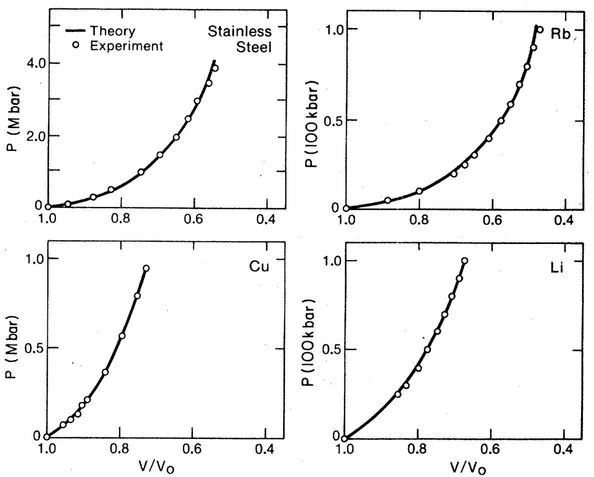

FIG. 4. Predicted (solid line) and experimental EOS (○'s) is shown for four metals. Note the very different pressure scales. Rb and Li are from Ref. 14, stainless steel from Ref 18, and Cu from Refs. 16 and 17.

Figure 6 shows the results of transforming the data for the eight metals previously cited. As can be seen, a single functional relation clearly emerges. We note that a^* is defined by Eq. (2.2). Thus, only ΔE, B, and r_{WSE} enter in the determination of Eq. (3.1). A theoretical estimate for $E^*(a^*)$ is given by Eqs. (2.2) and (2.10), which allows us to approximately predict F^* as

$$F^*(a^*)=a^*e^{-a^*}[1-0.15a^*+0.05a^{*2}] . \tag{3.2}$$

The theoretical estimate is in complete agreement with the function determined by scaling the experimental data. The range of data used in deriving F^* is quite wide. The Rb data were taken below 100 kbar while the stainless steel represents pressures up to 4 Mbar. Thus, a factor of 50 exists in the measured pressure for comparable points on the curves. It is not possible for us to decide if the small deviations from the predicted curves represent small errors in our hypothesis or if they result from the experimental method and analysis.

Finally, some experimental data exists for the derivative of the bulk modulus with pressure, $\partial B/\partial P$. The last systematic compilation (of which we are aware) for this

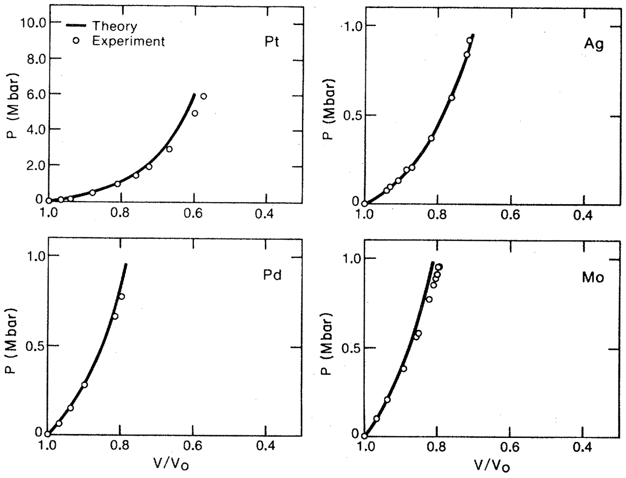

FIG. 5. Predicted (solid line) and experimental EOS (○'s) is shown for four metals. Note the very different pressure scales. Ag, Pd, and Mo data are from Refs. 16 and 17. Pt data are from Ref. 15.

quantity is that of Swenson[19] in 1968, who reports results at room temperature for 10 metallic elements. Recently, Anderson and Swenson have obtained accurate results for Na, K, and Rb and a new value for Cs.[20] A value for Li was given recently.[21] Also, a careful study (small quoted error bars) has been made of Au, Ag,and Cu (Refs. 22 and 23) as a function of temperature down to 77 K. Results for the covalent semiconductors Ge and Si are also available.[9] The theoretically predicted value is in good agreement with those metals for which we have found accurate experimental values which can be extrapolated to zero temperature (i.e., Au, Ag, Cu, Na, K, and Rb) as shown in Table III. The other experimental results, primarily measured at room temperature, are in fairly good agreement across the Periodic Table including Si and Ge. Discrepancies occur for the bcc transition elements.[19,24] These discrepancies are not currently explained. It should be remarked that the experimental values are difficult to measure and somewhat uncertain.

IV. DISCUSSION

The compilation of many first-principles calculations has recently been used to show that the metallic binding-energy—distance relation exhibits an unexpected simplicity. In particular in the region of strong bonding it is adequate to assume there is a single length scale l which describes the range over which strong forces act. For this region the entire bonding curve was described by the universal function $E^*(a^*)$ and two parameters l and ΔE. In this paper we have shown that the EOS can be determined from these two parameters, r_{WSE} and the derivative

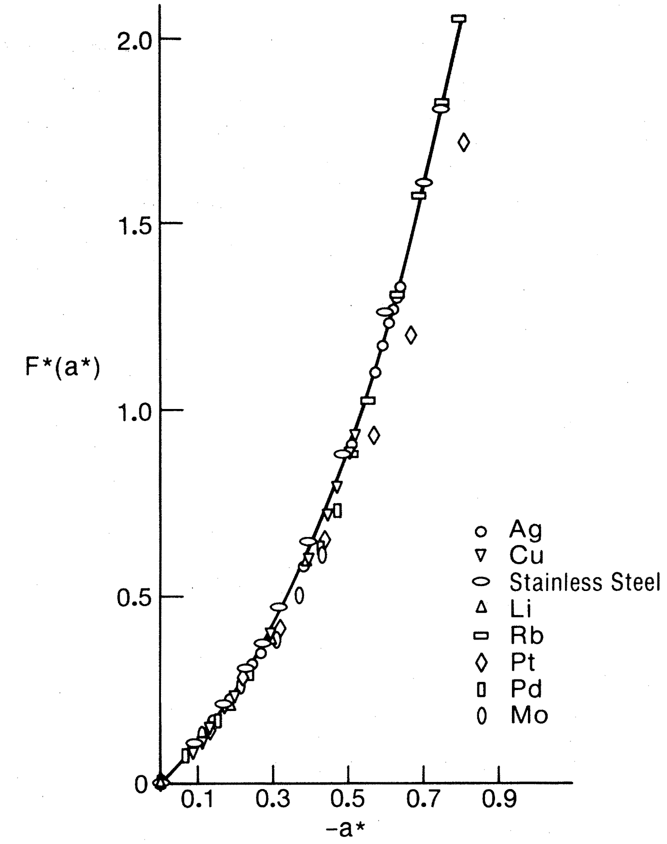

FIG. 6. Result of scaling the experimental pressure-volume data as in Eq. (3.1). The solid line is the result of the theoretical estimate given by Eq. (3.2).

TABLE III. $(\partial B/\partial P)_{T=0}$ is predicted for many of the elemental metals and compared with experiment when it is available. Experimental results for Na, K, Rb, and Cs are from Ref. 20; Li from Ref. 21; Al from Ref. 19; Cu, Ag, and Au from Refs. 22 and 23; Si and Ge from Ref 9; Nb, Mo, Ta, and W from Ref. 24; Pb from Ref. 25; and Fe from Ref. 26. For each element, the first line gives the value of $\partial B/\partial T \mid_{T=0}$ from theory, and the second line gives the value from experiment.

Li 3.38 3.5	Be 4.07											B	C	N	O	F	Ne
Na 3.84 3.90	Mg 5.29											Al 4.61 4.72	Si 4.74 4.2	P	S	Cl	Ar
K 4.02 4.07	Ca 6.28	Sc	Ti 4.65	V 4.69	Cr 5.29	Mn	Fe 4.96 5.29	Co 5.07	Ni 4.92	Cu 4.99 5.25	Zn 6.49	Ga	Ge 4.84 4.6	As	Se	Br	Kr
Rb 4.20 4.07	Sr	Y	Zr 4.43	Nb 4.72 4.1	Mo 5.49 4.7	Tc	Ru 5.63	Rh	Pd 5.91	Ag 5.55 5.87	Cd 7.19	In 4.92	Sn	Sb	Te	I	Xe
Cs 4.20 3.98	Ba 4.38	La	Hf 4.57	Ta 4.77 3.8	W 5.36 4.5	Re 5.72	Os	Ir 6.00	Pt 5.96	Au 6.18 5.90	Hg	Tl 5.40	Pb 5.88 5.45	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce 3.39	Pr	Nd	Pm	Sm	Eu 4.64	Gd 4.27	Tb	Dy 4.72	Ho	Er 4.79	Tm	Yb 4.02	Lu
Th 4.16	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

of E^*, i.e., $F^*(a^*) = -E^{*\prime}(a^*)$. Good agreement was obtained with experimentally measured values of EOS's. We then inverted the procedure and scaled the experimental data to obtain an experimental estimate for $F^*(a^*)$. This curve was in good agreement with the predicted $F^*(a^*)$. Thus we have experimentally verified the universal scaling relations (in the region of compressive loading of bulk metals) proposed earlier.[1-5]

The fact that the scaling results exist focuses attention on ΔE, B, and r_{WSE} as crucial variables in the theory of the EOS. If these quantities could be predicted we would have a complete theory of the zero-temperature EOS in the absence of phase transitions. It is thus of some interest to see if these quantities can be predicted empirically, using the quantum-defect method as discussed by Bloch and collaborators,[27] or the approach of Miedema.[28]

Other equations[29] (e.g., that of Murnaghan[30]) have been used to represent the high-pressure EOS of metals. These equations have the common feature that they represent a fit to the high-pressure data. For example, $\partial B/\partial P$ is required as an input. Such equations are unlike the present results since our work predicts the pressure and $\partial B/\partial P$ from zero-pressure measurements.

The accuracy of our predictions for $P(V)$ must be determined by comparison with experiment. This comparison is quite good, as shown in the preceding section. We cannot determine from the current data whether apparent discrepancies between the experiment and theory are due to inaccuracies of the model or systematic errors in the experimental data. We note that the overall good agreement between theory and experiment lends support to the current pressure scale which was deduced from shock-wave experiments.

In conclusion, the EOS for metals at zero temperature in the absence of a phase transition has been determined from the universal form for the total-energy—distance relation proposed earlier.[1-5] A universal form, $F^* \propto V^{2/3}P(V)$, was predicted. These predictions were compared with experiment and found to be in good agreement with the data. This work thus serves as a direct verification of the universal binding-energy relation in the compressive region.

ACKNOWLEDGMENTS

Two of us (J.H.R.) and (J.R.S.) would like to thank the Institute for Theoretical Physics, Santa Barbara, for its very kind hospitality. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. 2-7405-ENG-82. This work was supported by the Director of Energy Research, U.S. Office of Basic Energy Sciences, and by the National Science Foundation under Grant No. PHY-77-27084.

---

[*] Permanent address.

[†] Also at Physics Department, University of Michigan, Ann Arbor, MI 48109.

[1] J. H. Rose, J. Ferrante, and J. R. Smith, Phys. Rev. Lett. 47, 675 (1981).

[2] J. R. Smith, J. Ferrante, and J. H. Rose, Phys. Rev. B 25, 1419 (1982).

[3] J. Ferrante, J. R. Smith, and J. H. Rose, in *Microscopic Aspects of Adhesion and Lubrication,* Proceedings of the French Society of Chemical Physics Conference, edited by J. M. Georges (Elsevier, Amsterdam, 1982).

[4] J. H. Rose, J. Ferrante, and J. R. Smith, Phys. Rev. B 28, 1835 (1983).

[5] J. Ferrante, J. R. Smith, and J. H. Rose, Phys. Rev. Lett. 50, 1385 (1983).

[6] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[7] J. F. Herbst, Phys. Rev. B 24, 608 (1981); J. F. Herbst and J. W. Wilkins, *ibid.* 24, 1679 (1981).

[8] A. E. Carlsson, C. D. Gelatt, and H. Ehrenreich, Philos. Mag. A 41, 241 (1980).

[9] M. T. Yin and M. L. Cohen, Phys. Rev. B 26, 5668 (1982).

[10] B. Delley, D. E. Ellis, A. J. Freeman, E. J. Baerend, and D. Post, Phys. Rev. B 27, 2132 (1983).

[11] C. Kittel, *Introduction to Solid State Physics,* 4th ed. (Wiley, New York, 1971).

[12] G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook,* 2nd ed. (MIT Press, Cambridge, Mass., 1971).

[13] F. Guinea, J. R. Smith, J. H. Rose, and J. Ferrante, Appl. Phys. Lett. 44, 53 (1984).

[14] P. W. Bridgman, *Collected Experimental Papers* (Harvard University Press, Cambridge, Mass., 1964), Vol. 6, pp. 3819 and 3835.

[15] J. A. Morgan, High Temp. High Pressures 6, 195 (1974), and references therein.

[16] H. K. Mao, P. M. Bell, J. W. Shaver, and D. J. Steinberg, J. Appl. Phys. 49, 3276 (1978).

[17] W. J. Carter, S. P. Marsh, J. N. Fritz, and R. G. McQueen, Nat. Bur. Stand. (U.S.) Spec. Publ. 326, 147 (1971).

[18] J. A. Morgan, High Temp. High Pressures 7, 65 (1975).

[19] C. A. Swenson, J. Phys. Chem. Solids 29, 1337 (1968).

[20] M. S. Anderson and C. A. Swenson, Phys. Rev. B 28, 5393 (1983); the tentative value for Cs is due to M. S. Anderson and C. A. Swenson (unpublished).

[21] R. A. Felice, J. Trivisonno, and D. E. Scheule, Phys. Rev. B 16, 5173 (1977).

[22] P. Van't Klooster, N. J. Trappeniers, and S. N. Biswas, Physica (Utrecht) 97B, 65 (1979).

[23] S. N. Biswas, P. Van't Klooster, and N. J. Trappeniers, Physica (Utrecht) 103B, 235 (1981).

[24] K. W. Katahara, M. H. Manghnani, L. C. Ming, and E. S. Fisher, in *High Pressure Research Applications in Geophysics,* edited by M. H. Manghnani and Syun-iti Akimoto (Academic, New York, 1977), p. 351.

[25] R. A. Miller and D. E. Schuele, J. Phys. Chem. Solids 30, 589 (1969).

[26] M. W. Guinan and D. N. Beshers, J. Phys. Chem. Solids 29, 541 (1968).

[27] For example, G. Schattner, and A. Bloch, in *Structure and Bonding in Crystals,* edited by M. O'Keefe and A. Navrotsky (Academic, New York, 1981), Vol. 1, p. 49.

[28] A. R. Miedema, Philips Tech. Rev. 36, 217 (1975).

[29] J. R. MacDonald and D. R. Powell, J. Res. of the Nat. Bur. Stand. Sect. A 75, 441 (1971).

[30] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA 30, 244 (1944).