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Universal scaling relations in compressibility of solids

Brian W. Dodson
Sandia National Laboratories, Albuquerque, New Mexico 87015
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A particularly simple two-parameter scaling relation for the variation of the bulk modulus of solids with changing density has been found. The relation, although empirical, fits all metals and metal alloys tested, and also fits semiconductors, ionic crystals, and, with a lesser degree of success, organic compounds. The two parameters seem to be related to the rupture strength and the electronegativity of the solid.

I. INTRODUCTION

Attempts to form general relations for the compressive properties of metals go back to the early days of high-pressure research, when it was observed that compressibility was not constant as a sample is compressed. This lead to approximate formulas which represented little more than curve fitting to the available data.[1] The first well-founded theoretical indication that there was some degree of universality in the compressibility of metals came from the extensive density-functional calculations of the ground states of elemental solids performed by Moruzzi *et al.*[2] In the process of calculating the equilibrium lattice constant, they obtained sufficient information to numerically evaluate the bulk modulus of the elements studied at zero pressure. In addition, their muffin-tin geometry yielded an unambiguous value for the electron density in the interstitial regions. They then observed a universal relation between the bulk modulus and interstitial electron density, which appears in Fig. 1. The solid line is the compressibility of an electron gas of equal density evaluated using the Hedin-Lundqvist correlation energy.[3] Moruzzi *et al.* suggest that a reasonable physical approximation is to assume that the ionic cores are rigid and to consider the material compressibility as solely due to the interstitial electron gas. This is at least a starting point for understanding where such universal behavior can come from. Certain empirical observations of universal scaling behavior in the binding energies of metals have been reported by Rose *et al.*,[4–7] which will be discussed later. (In this paper the term empirical is used not in the rigorous sense of describing a relation derived from trends observed solely in experimental data, but also to describe trends observed in numerical data from related theoretical calculations. Thus, although the work of Rose *et al.* is based on metallic adhesive binding-energy calculations,[4] the universal scaling behavior reported by them is not the result of any underlying theory of structural energetics, and is thus empirical in nature.)

II. VARIATION OF METALLIC BULK MODULI WITH PRESSURE

The generality of the relationship of Moruzzi *et al.* can be tested by examining the variation of the bulk modulus with pressure in selected metals and seeing if the observed dependences still apply. Unless otherwise stated, all compressibilities are calculated by numerical differentiation of pressure-density curves based on zero-temperature isotherms calculated from shock-wave data.[8] Shock-wave experiments are necessary in most cases so that sufficiently large compressions can be generated. In Fig. 2, we immediately see that the simplest relation, where the interstitial electron density scales with the material density, is inadequate to explain the variation in bulk modulus. The bulk modulus of aluminum increases more slowly than that of the electron gas with increasing density under this assumption, even if one corrects for the rigidity of the ionic cores. This is true for most metals.

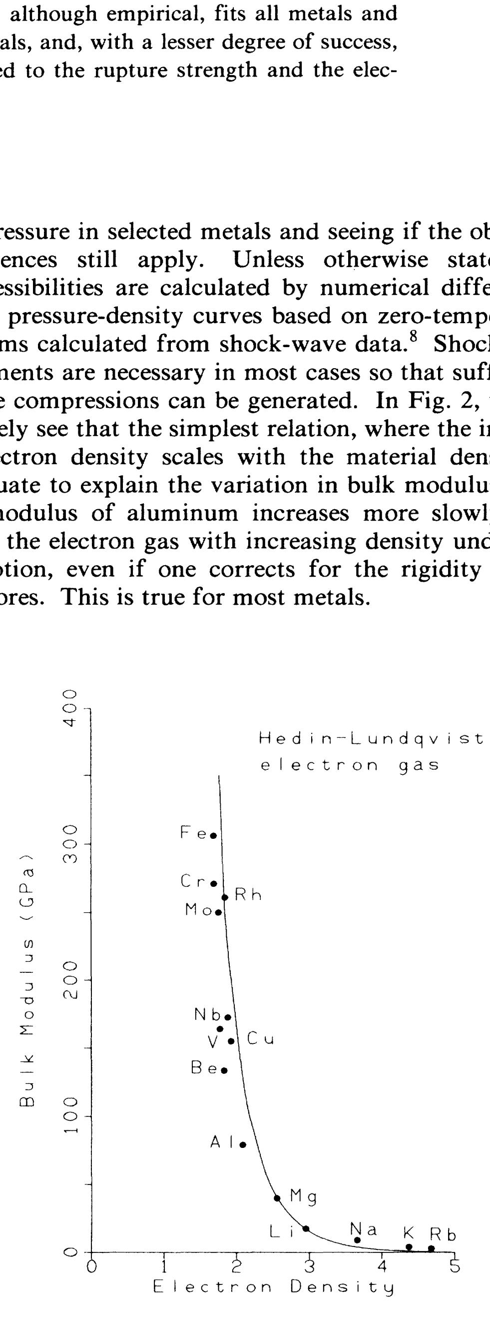

FIG. 1. Bulk modulus versus interstitial electron density expressed in terms of r_s ($4\pi r_s^3 = \rho_e$). The data points result from the density-functional calculations of Moruzzi *et al.* in Ref. 2, and the solid line is the bulk modulus of a homogeneous electron gas. The figure is reproduced from Ref. 2.

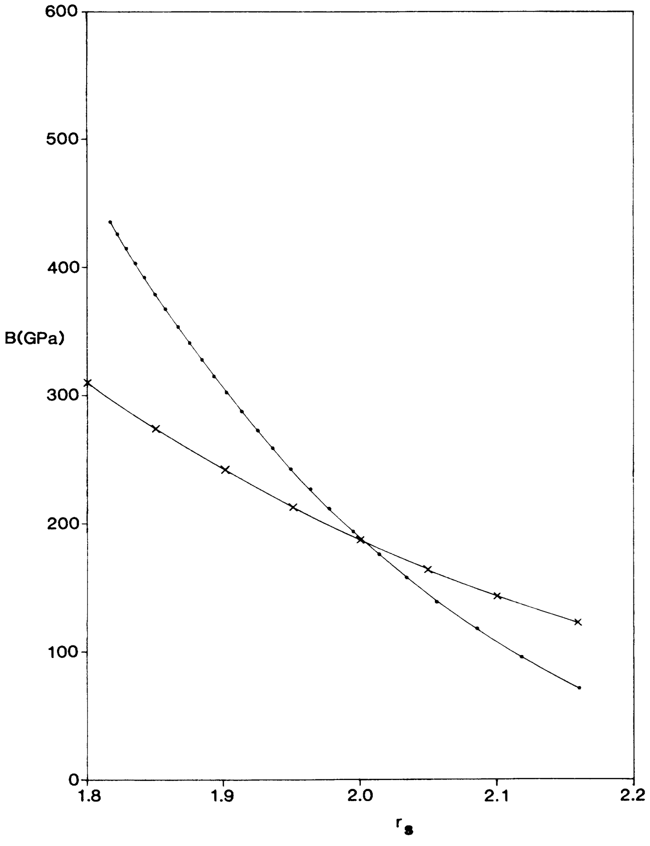

FIG. 2. Bulk modulus versus electron density for aluminum (×) and a homogeneous electron gas (●). The assumption of rigid Al ionic cores is made, and thus r_s^{-1} for the experimental Al moduli varies as the cube root of the material density. The resulting curves do not agree.

Recalling that the Moruzzi *et al.* relationship is based on results from a muffin-tin calculation, however, allows for a simple generalization of this viewpoint. In such a calculation, the number of interstitial electrons per atom is a variable, depending on the crystal structure and density. It is therefore possible to conjecture that the number of interstitial electrons per atom in the calculation changes with density, and thus that the interstitial electron density rises slower than does the material density. We have found that the simple relation

$$e^{-}/\text{atom}=\eta(\rho_0/\rho)+\lambda \tag{1}$$

for the number of interstitial electrons per atom, where ρ_0 is the zero-pressure material density, ρ is the material density, and η and λ are material-dependent parameters, gives quite a good fit to the observed variation of bulk modulus with material density.

The above treatment of the experimental compressibility data works reasonably well, but the procedure has no physical significance as the rough model of Moruzzi *et al.* for electron density versus bulk compressibility has been used far outside its regime of applicability. However, the success of Eq. (1) in fitting the experimental data offers promise for finding a simple universal variation of metallic bulk modulus, and thus of compressibility and the equation of state, with density. We have indeed found a simple two-parameter scaling relation for the bulk modulus as a function of material density:

$$B(\rho)=\alpha(\nu-\beta)^2\ , \tag{2}$$

where $\nu=(\rho/\rho_0)^{1/3}$ (the inverse of a normalized interatomic spacing), and α and β are material-dependent parameters, α having units of GPa. In Fig. 3 are displayed fits to Eq. (2) for compressibility data for a large number of metals and alloys. (The parameter values used appear in Table I.) The fits are at least as good as the data, with correlation coefficients[9] in excess of 0.9999 being common in the pressure range 0—100 GPa, which for these metals corresponds to maximum densities of roughly $1.25\rho_0-1.6\rho_0$.

The parameters α and β can be derived from zero-pressure compressibility data. By differentiating Eq. (2) with respect to ν and manipulating, we obtain an expression for β:

$$\beta=1-\tfrac{2}{3}[\partial B(P)/\partial P]^{-1}\ ,\quad \nu=1\ (\text{or } P=0)\ , \tag{3}$$

where P is the pressure. One then immediately obtains

$$\alpha=B(\nu)(1-\beta)^{-2}\ ,\quad \nu=1\ , \tag{4}$$

where $\nu=1$ represents zero-pressure conditions. The parameters needed to predict the high-pressure bulk modulus of metals are thus the zero-pressure density, bulk modulus, and $(\partial B/\partial P)_{\rho_0}$.

The bulk sound speed as a function of density can also be evaluated using Eq. (2). The bulk sound speed is expressed as

$$c^2=B/\rho\ , \tag{5}$$

where c is the bulk sound speed and ρ is the material density. By substituting Eq. (2) for B and observing that $\rho=\rho_0\nu^3$, we obtain

$$c^2=(\alpha/\rho_0)(\nu-\beta)^2\nu^{-3}\ . \tag{6}$$

Equation (6) is quite successful at predicting the sound speeds along the zero-temperature isotherms obtained from Ref. 8. This correspondence is shown in Fig. 4.

The bulk modulus, expressed by Eq. (2), can be integrated to give pressure and specific energy as functions of ν, while still retaining only the two material-dependent parameters. The pressure is given by

$$\begin{aligned}P(\nu)&=\int(3/\nu)B(\nu)d\nu\\&=(3\alpha/2)(\nu^2-4\beta\nu+2\beta^2\ln\nu+4\beta-1)\end{aligned} \tag{7}$$

and the specific energy by

$$\begin{aligned}E(\nu)&=3\int\nu^{-4}P(\nu)d\nu\\&=\alpha\{3(1-\beta)+\beta^2-(9/2\nu)+(9\beta/\nu^2)\\&\qquad-[3(4\beta-1)/(2\nu^3)]-\beta^2[(3\ln\nu+1)/\nu^3]\}\ .\end{aligned} \tag{8}$$

Thus, again within the regime of applicability of Eq. (2),

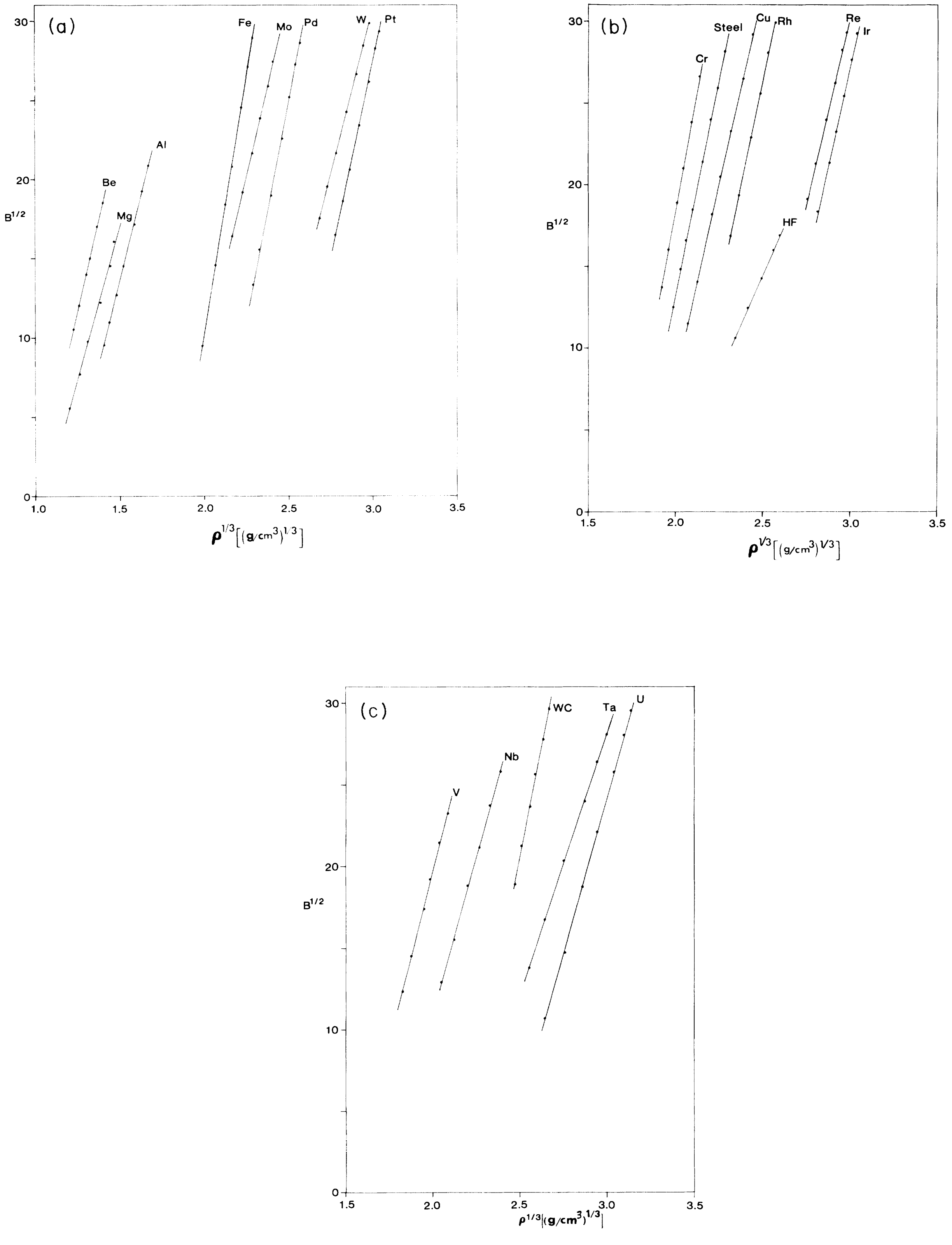

FIG. 3. Fits of experimental bulk moduli of various elemental metals and alloys to Eq. (2). The axes are $B^{1/2}$ and $\rho^{1/3}$ so that the theoretical relation gives a straight line. The figure is separated into three separate graphs for clarity: (a) Al, Be, Fe, Mg, Mo, Pd, Pt, and W; (b) Cr, Cu, Hf, Ir, Re, Rh, and 304 stainless steel; (c) Nb, Ta, U, V, and WC.

TABLE I. Universal compressibility parameters for metals.

Metal	α (GPa)	β	$-P_r$ (GPa)
Be	3300	0.817	22.5
Mg	2210	0.885	3.46
Al	4290	0.870	9.75
V	5860	0.838	26.0
Cr	13 100	0.880	23.3
Fe	16 400	0.926	6.8
Cu	9940	0.885	15.6
Nb	6020	0.833	29.3
Mo	9830	0.835	46.1
Rh	14 100	0.858	41.9
Pd	15 300	0.892	19.8
Hf	3280	0.815	21.8
Ta	6690	0.831	33.8
W	12 000	0.840	51.2
Re	16 420	0.851	56.5
Ir	20 590	0.872	44.6
Pt	18 850	0.880	33.6
U	9980	0.893	12.6
Steel	11 100	0.881	19.3
WC	17 140	0.855	54.3

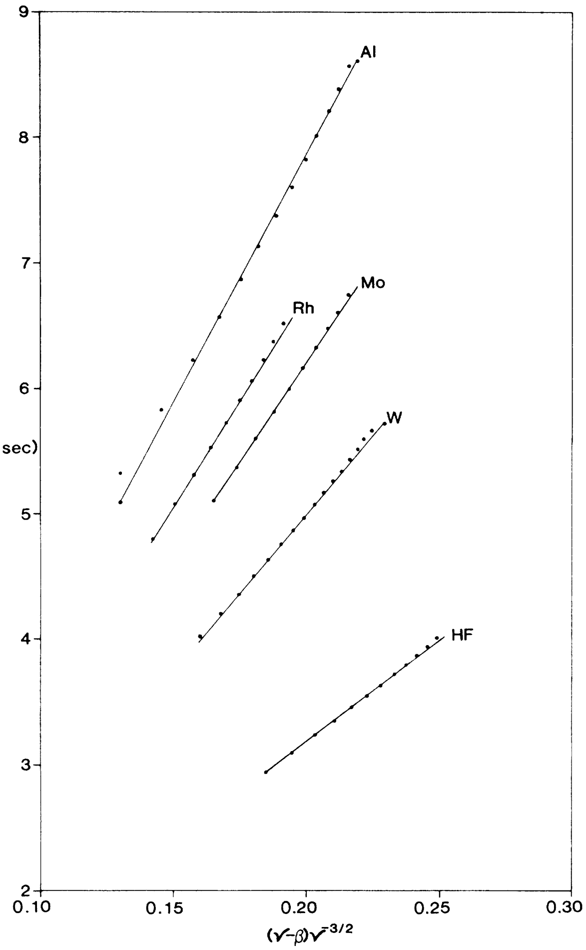

FIG. 4. Bulk sound speed calculated using Eq. (6) versus $(\nu-\beta)\nu^{-3/2}$ (ν is the inverse of a normalized interatomic spacing and β is one of the material-dependent parameters describing the universal compressive behavior. The x-axis function is chosen so that the theoretical sound-speed dependence will be a straight line.) The metals displayed are Al, Hf, Mo, Rh, and W.

the pressure and compressive energy take on the form of simple analytic universal functions having two material-dependent parameters. In Fig. 5 is shown experimental pressure-density data on 19 metals and alloys compared to the universal relation of Eq. (7).

One is tempted to extend the relations given above into the dilatational regime in order to extract some information concerning materials in tension. It is clear that the form of Eq. (2) limits the extent to which this can be accomplished, since it defines a positive-definite bulk modulus, which does not allow for rupture of materials, and is thus unphysical in this regime. However, it does seem reasonable to suggest that rupture would occur, in a perfect crystal, near where the bulk modulus goes to zero in the current model. This occurs when $\nu=\beta$, which varies between 0.90 and 0.81 for most of the metals studied here. These values are typical of ultimate crystalline strength calculations.[10] If one then evaluates the pressure at this value of ν, a (negative) rupture pressure P_r is obtained, which is listed in Table I. The value of this rupture pressure is between 10% and 20% of the zero-pressure bulk modulus. Similar calculations have been performed by Rose *et al.*[7] Their values for P_r agree with ours within about 15%.

III. UNIVERSAL COMPRESSIVE BEHAVIOR OF NONMETALS

In the preceding section we established that the two-parameter universal scaling relationship for compressive properties established by Eq. (2) accurately predicts the behavior of metals and alloys. In this section we investigate the extent to which this relationship will predict the compressive behavior of various classes of nonmetals. There are essentially three classes of nonmetals which will be considered: covalently bound crystals, ionic crystals, and van der Waals systems, such as organic materials. In Fig. 6 we display fits based on Eq. (2) for selected members of these classes, for which we have $T=0$ isotherms based on shock-wave data.[8] (The fit parameters appear in Table II.) We observe that the fits of covalently bound crystals, represented by SiC and Al_2O_3, ionic crystals, represented by NaCl and LiF, and organic solids, represented by paraffin (a mixture of medium-length hydrocarbon chains) and by polymethylmethacrylate (PMMA), a structural polymer, all work very well over a range of pressure corresponding to maximum compressions to $1.6\rho_0$–$1.7\rho_0$. Beyond these compressions in the ionic crystals and organics, the calculation of the isotherms is somewhat questionable because of the extremely high temperatures attained in the shock-wave experi-

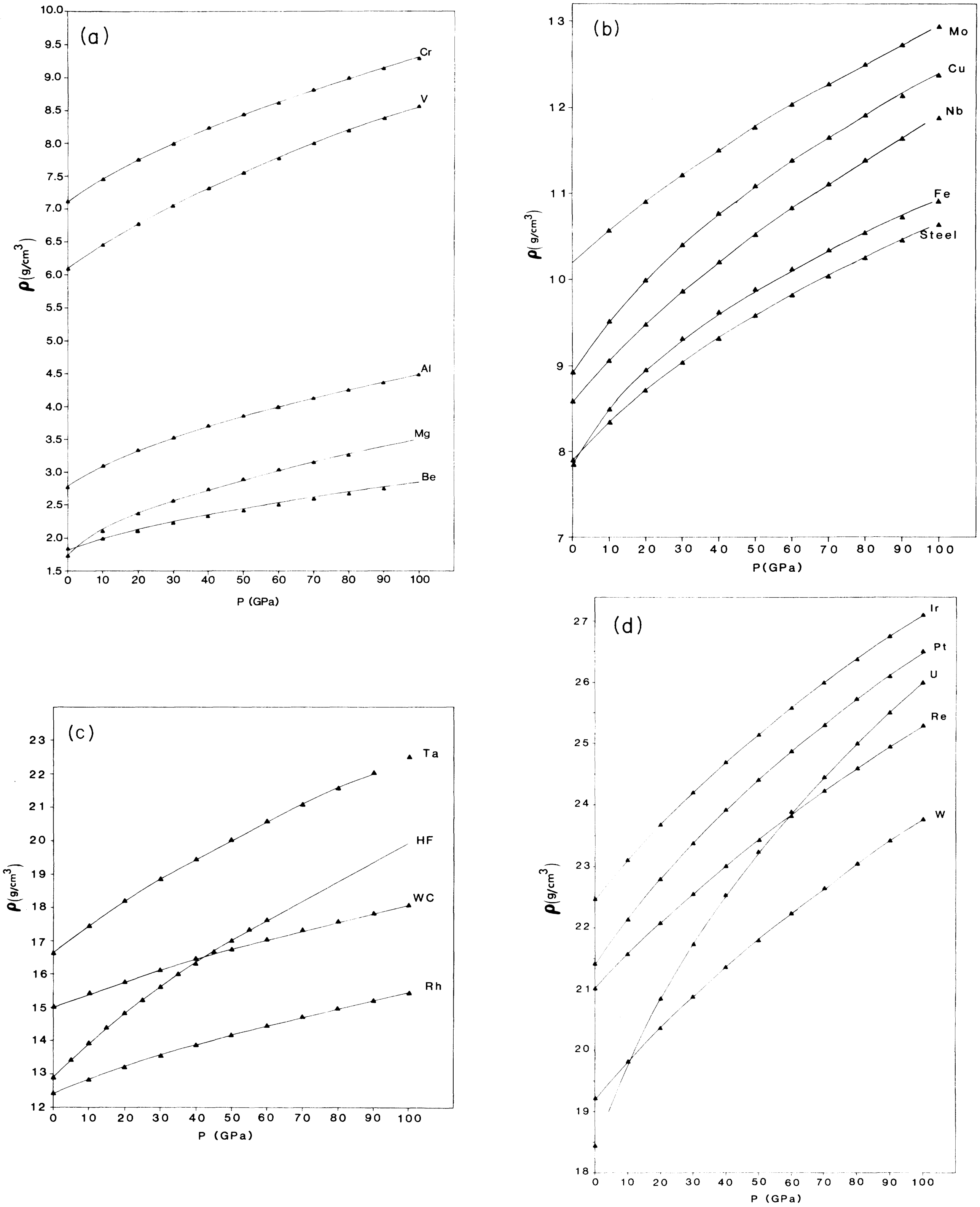

FIG. 5. Material density versus pressure for various metals and alloys. The pressure range is 0 to 100 GPa. The solid lines are the theoretical fits resulting from Eq. (7). .The isolated points are data resulting from experimental zero-temperature isotherms derived from shock-wave data (see Ref. 8). Again, for clarity the figure is separated into four simpler graphs. (a) Al, Be, Cr, Mg, and V; (b) Cu, Fe, Mo, Nb, and 304 stainless steel; (c) Hf, Rh, Ta, and WC; (d) Ir, Pt, Re, U, and W. In all cases the fits are as good as the experimental data.

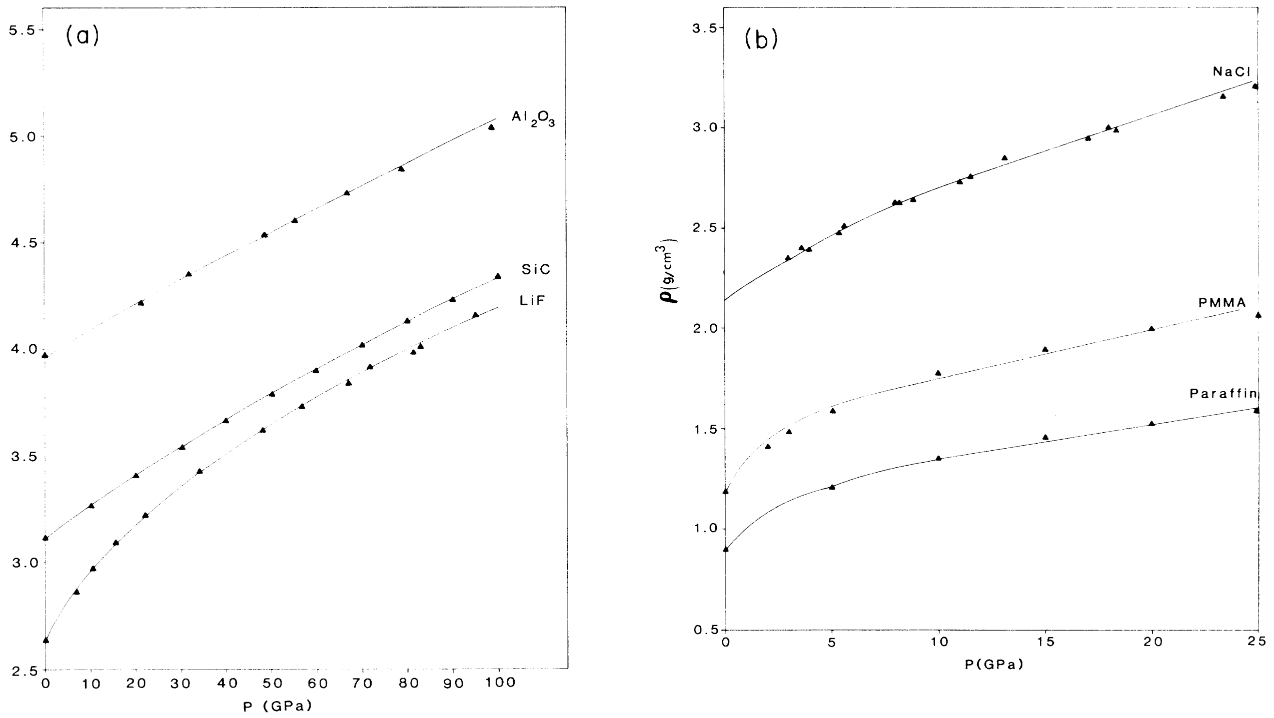

FIG. 6. Material density versus pressure for select nonmetallic solids. The solid lines are theoretical fits based on Eq. (7). The isolated points are data from zero-temperature isotherms from Ref. 8 for SiC, PMMA (Plexiglass), and paraffin, and from shock-wave hugoniots from Ref. 13 for Al_2O_3, LiF, and NaCl. (a) shows data for Al_2O_3, SiC, and LiF up to 100 GPa, and (b) shows data for NaCl, PMMA, and paraffin to 25 GPa. In both figures the maximum degree of compression is similar, since those materials in (b) are much more compressible than those in (a). Again, the fit is as good as the data, indicating that the universal relation expressed by Eq. (2) also applies to certain classes of nonmetallic solids.

ments. We are thus faced with the surprising result that all classes of materials, from metals to van der Waals solids, obey Eq. (2) closely over a large range of compression.

IV. DISCUSSION

These results have the same flavor as the observation by Rose *et al.* of universal scaling in the binding energy curves of metallic systems.[4–7] They observed that the binding energy of metals can be expressed in terms of a two-parameter scaling of an empirical universal binding-energy function.[4] They have established that this function and the scaling relationships quantitatively describe bimetallic adhesion, molecular binding, cohesion, and chemisorption on metals.[6] An expression for the mechanical response of metals based on this universal binding-energy function has been developed,[7] but is said to apply only to metals (and Si and Ge). Other materials, because of differing electronic overlap interactions, are believed to require a different description. By contrast, through the present study we have been able to establish that not only does the mechanical response of metals depend solely on two parameters, but that one can express, at least in the compressive regime, the mechanical response of (apparently) all materials in terms of a simple two-parameter scaling relation.

TABLE II. Universal compressibility parameters for nonmetals.

Material	α (GPa)	β
	Covalently bound	
Al_2O_3	1675	0.550
SiC	3090	0.745
	Ionic crystals	
NaCl	1040	0.830
LiF	6440	0.905
	Organic compounds	
Plexiglass	2060	0.965
Paraffin	1800	0.960

It is of interest to investigate the degree to which Eq. (2) will describe the behavior of a simple analytical model. Consider the example of a perfectly harmonic solid, i.e., one in which the interatomic interaction is described by

$$\Phi(l)=K(l-l_0)^2/l_0^2\ , \qquad (9)$$

where l is the interatomic spacing and l_0 is the zero-pressure equilibrium spacing. Differentiation of Eq. (9) twice gives an analytical expression for the bulk modulus, which can then be fit to Eq. (2). When this is done for ν

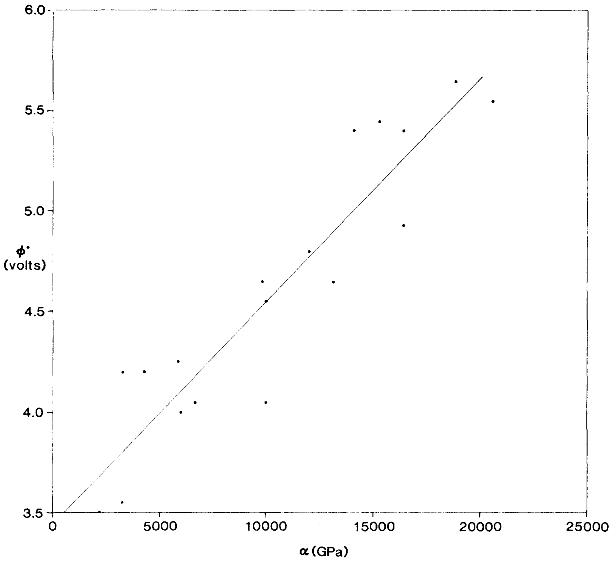

FIG. 7. ELectronegativity ϕ^* versus the material-dependent parameter α. The electronegativity scale chosen is due to Miedema (Ref. 11). There appears to be a reasonably strong linear correlation between ϕ^* and α, with a least-squares fit giving $\phi^* = 1.1\times10^{-4}\alpha+3.44$. Since electronegativity and electron density are closely related, it appears that our α is also related to electron density.

values from 1 to 1.2 (representing compression to $1.73\rho_0$), the bulk modulus is described by $\beta=0.3245$ with a correlation coefficient in excess of 0.99999 [α is arbitrary in this example because K in Eq. (9) is unknown]. This is an extremely good fit, even though the functional form of $B(v)$ resulting from Eq. (9) is slightly different than that of Eq. (2). The extraordinarily small value of β is an artifact resulting from the fact that a harmonic solid cannot rupture.

We also find a significant correlation between the values of the parameter α in Eq. (2) and the electronegativities of the corresponding metals. In Fig. 7 is plotted the electronegativity versus α for the metallic elements studied in this paper. (The electronegativity scale is that of Miedema and de Chatel.[11]) The electronegativity appears to depend linearly on α within the considerable uncertainties in both the values for α and the electronegativity. Specifically, a least-squares fit yields

$$\phi^* = 1.11\times10^{-4}\alpha+3.44 \qquad (10)$$

with a correlation of 0.925. This provides an interesting connection back to the picture proposed by Moruzzi *et al.*,[2] since the electronegativity and the interstitial electron density are closely related, as is also the chemical potential in the density-functional approach to many-body solid-state theory.[12] Thus Eq. (2) may appear more similar to Eq. (1), the compression-dependent interstitial electron population, than seemed true at first.

In this paper we have demonstrated that the compressive properties of most solids (not simply metals and possibly some covalent semiconductors, as in Ref. 7) display universal behavior which is accurately described over a large range of densities by the two-parameter universal scaling function appearing in Eq. (2). The parameter α has a linear correlation with elemental electronegativity in the metals, and the parameter β is tentatively identified with the rupture strength of an ideal crystal. Although identification of the material-dependent parameters with real and appropriate physical constants in this manner strongly suggests that there is some first-principles basis for Eq. (2), a fundamental derivation is currently unknown.

Note added. After submitting this paper, we received a copy of work by Vinet, Ferrante, Smith, and Rose[14] describing an empirical relation based on their previous work on metals[4–7] but requiring additional assumptions, which models the compressive P-V relations of all classes of materials. Although our explicit formulas differ, both relations depend on the same input data [ρ_0, $B(\rho_0)$, and $(\partial B/\partial P)_{\rho_0}$], and the accuracy of description seems to be similar. A fundamental derivation of the universal scaling behavior is still lacking.

ACKNOWLEDGEMENT

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