

CASE FILE COPY

10-13-86

NASA Technical Memorandum 87303

Universality in the Compressive Behavior of Solids

(NASA-TM-87303) UNIVERSALITY IN THE
COMPRESSIVE BEHAVIOR OF SOLIDS (NASA) 11 p
HC A02/MF A01 CSCL 08M

N86-26775

Unclas
G3/77 43382

Pascal Vinet and John Ferrante
Lewis Research Center
Cleveland, Ohio

John R. Smith
General Motors Research Laboratories
Warren, Michigan

James H. Rose
Ames Laboratory—USDOE
Ames, Iowa

April 1986

NASA

UNIVERSALITY IN THE COMPRESSIVE BEHAVIOR OF SOLIDS

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

John R. Smith
General Motors Research Laboratories
Warren, Michigan 48090

and

James H. Rose
Ames Laboratory - USDOE
Iowa State University
Ames, Iowa 50011

SUMMARY

We have discovered that the isothermal equation of state for solids in compression is of a simple, universal form. This single form accurately describes the pressure and bulk modulus as a function of volume for ionic, metallic, covalent, and rare gas solids.

THEORETICAL ASPECTS

The various classes of solids - covalent, metallic, ionic, and rare gas - can be distinguished by their rather different types of interatomic interactions. These differences would appear to preclude a common description of the energetics of these systems.

We have found, however, that equations of state (P , V , T , relations) for these classes of solids in compression are of a universal nature. In the following we will first discuss reasons why one might expect to find a universal form for the equation of state (EOS) of solids. Next we will propose a universal expression. Finally, the considerable EOS data available will be used to test our proposed universal form.

EOS are valuable not only for prediction of thermodynamical properties but also to obtain insight into the nature of solid state and molecular theories (refs. 1 and 2). In reference 3 a general zero temperature EOS was reported which describes well the compression of metals (in the absence of phase transitions). This was derived from a cohesive energy which was found essentially to depend exponentially on the interatomic spacing. That is, it depends on the deviation of the Wigner-Seitz radius from the equilibrium value, $r_{WS} - r_{WS}^0$. (Here r_{WS} is defined in terms of the volume V per atom as $V = 4\pi r_{WS}^3/3$.)

*Visiting Scientist from Laboratoire de Technologie des Surfaces, Ecole Centrale de Lyon, B.P. 163, 69131 Ecully Cedex, France.

Wave-function-overlap interactions such as those occurring in metals are also found in varying degrees in covalent, ionic, and rare gas solids under high pressures. There are additional types of interactions important in determining the EOS of ionic and rare gas solids; however. Attractive coulombic interactions and attractive fluctuating dipole interactions are also present. In addition, if we now consider nonzero temperatures, there is a contribution to the pressure due to the variation of entropy. It is of the form $T(\partial S/\partial V)_T$ for the isothermal EOS.

The pressure contribution due to electron overlap varies essentially exponentially with $r_{WS} - r_{WSe}$. All other contributions to the pressure for solids on compression vary much less rapidly as a function of r_{WS} . For example, the entropy pressure is $T(\partial S/\partial V)_T = \alpha B T$, where α is the thermal expansion coefficient and B is the isothermal bulk modulus. The product αB is known (ref. 4) to be essentially independent of V for $T > \theta_D$, where θ_D is the Debye temperature. Thus, the entropy contribution to the pressure is expected to be nearly independent of r_{WS} , at least for $T > \theta_D$. Also the ionic or fluctuating dipole interactions depend only on powers of r_{WS} . Thus, these ionic or fluctuating dipole interactions provide a pressure component which is also relatively slowly varying with r_{WS} compared to electron overlap interactions.

Consequently, one may expect the shape of the EOS in compression to be determined essentially by the exponential wave function overlap. Note this is not true in expansion. For example, as the interatomic separation becomes significantly larger than the equilibrium separation for ionic solids, the wave-function overlap becomes small and the electrostatic interaction between the ions becomes dominant. This is quite different from metals, where it has been demonstrated (ref. 3) that the exponential interaction remains dominant well into the attractive region.

A NEW EQUATION OF STATE FOR SOLIDS

From the foregoing discussion, we propose that an exponential expression similar to that found (ref. 3) for metals applies to all classes of solids in compression over a range of temperatures excluding phase transitions. This expression has the form

$$P(X, T) = 3B_T [(1 - X)/X^2] \exp[\eta_T(1 - X)] \quad (1)$$

where B_T is the isothermal bulk modulus at zero pressure, $X = (V/V_0)^{1/3}$ ($V_0 = 4\pi r_{WSe}^3/3$ is the equilibrium atomic volume), and

$$\eta_T = 3[(\partial B/\partial P)_T - 1]/2 \quad (2)$$

Equation (2) follows from equation (1), where $(\partial B/\partial P)_T$ is evaluated at zero pressure. To test this, we first rearrange terms:

$$H(X, T) \equiv \ln[PX^2/3(1 - X)] = \ln B_T + \eta_T(1 - X) \quad (3)$$

If our expression were universal, then one would expect isothermal plots of experimental $H(X, T)$ to be linear in $1 - X$, with intercept and slope yielding

B_T and $(\partial B/\partial P)_T$, respectively. The effects of entropy and forces other than those due to wave-function overlap enter only through these two parameters and V_0 .

We have tested equation (3) against high pressure data from all classes of solids, excluding materials which have phase transitions within the experimental pressure range. We found it to be remarkably successful. In figure 1 we have examples from each class of solid at a variety of temperatures: solid hydrogen (4.2 K data, ref. 5), solid xenon (150 K, ref. 6), cesium (295 K, ref. 7), molybdenum (293 K, ref. 8), sodium chloride (298 K, ref. 9, see also ref. 10), and magnesium oxide (293 K, ref. 8).

Despite the fact that all classes of solids are represented from a variety of experimental methods, the data are linear in $(1 - X)$ as predicted by equation (3). This graphically illustrates that EOS are, in fact, universal in form, our primary result.

One may also find this way of plotting the data convenient for analyzing it. The values of B_T and $(\partial B/\partial P)_T$ obtained from intercept and slope of these plots as listed in the caption of figure 1 are in very good agreement with experimental values available in the literature (see, e.g., refs. 1, 5, and 11).

One need only know two zero pressure equilibrium numbers, B_T and $(\partial B/\partial P)_T$, at each temperature to obtain the pressure-volume curve through equation (3). Many of these equilibrium values are available in the literature. For example, one can use ultrasonic values of B_T and $(\partial B/\partial P)_T$ to predict $P(V)$ through equation (1) and compare it with independent high pressure experimental results. This is shown in figure 2 for NaCl. NaCl was chosen because of the large amount of experimental data available which allows it to be used as a high pressure reference scale (refs. 1 and 10). Values of $B_T = 2.34 \times 10^{10}$ Pa and $(\partial B/\partial P)_T = 5.35$ were taken from ultrasonic experiments (ref. 1). The agreement between the predicted pressures (eq. (1), solid curve), and the experimental data is very good over a broad range of V/V_0 .

Another gauge of the accuracy of equation (1) is found from a comparison with the Murnaghan EOS:

$$P(X, T) = [B_T / (\partial B / \partial P)_T] \left[X^{-3(\partial B / \partial P)_T} - 1 \right] \quad (4)$$

Equation (4) is obtained by integrating the linear approximation

$$B(P, T) = B_T + (\partial B / \partial P)_T P \quad (5)$$

so that equation (4) has increasing accuracy as $P \rightarrow 0$. The Murnaghan EOS is perhaps the most extensively used EOS for solids and has been argued (refs. 1 and 2) to be one of the "best" two-parameter EOS available. The dashed curve in figure 2 is a plot of the Murnaghan EOS (eq. (4)). While good agreement with the data and equation (1) is obtained at low pressures, the Murnaghan expression deviates from both at larger pressures. This is a critical test of the universal expression equation (1), because it shows that the exponential form correctly describes the nonlinear pressure contributions which are not included in equation (5).

A more severe test of nonlinear pressure effects is shown in figure 3, where hydrogen data is plotted for relative compressions of over 50 percent in volume. The data are due to Anderson and Swenson (ref. 5). The predicted pressures from the universal expression, (eq. (1)), are shown in figure 3(a) as the solid curve while the Murnaghan prediction, (eq. (4)), is the dashed curve. The input values used in both predictions are $B_T = 1.7 \times 10^8$ Pa and $(\partial B / \partial P)_T = 7.0$, as listed in reference 5. Note these input values are quite close to those obtained from the intercept and slope, respectively, in figure 1. Again, the agreement between equation (1) and experiment is good, while at the higher pressures the Murnaghan prediction deviates significantly. Bulk modulus data are also given in reference 5, which provides another test. From equation (1) we have

$$B(X,T) = (B_T/X^2)[2 + (\eta_T - 1)X - \eta_T X^2] \exp[\eta_T(1 - X)] \quad (6)$$

Figure 3(b) compares the experimental data (circles) with the predictions of equation (6) (solid curve) and of Murnaghan (eq. (5), dashed curve). Again, the prediction from the universal expression, (eq. (6)), agrees well with the data, while the linear (Murnaghan) prediction deviates at high pressures.

We conclude that the EOS of all classes of solids in compression is, to a good approximation, a universal function. It can be represented by a simple exponential form which yields at each temperature accurate predictions of pressure and bulk modulus versus volume.

ACKNOWLEDGMENT

One of us (P.V.) would like to thank the French "Ministère des relations extérieures" for providing him a grant. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract number W-7405-ENG-82 and this work was supported by the Director of Energy Research, U.S. Office of Basic Energy Sciences. We would also like to thank Professor C.S. Smith for helpful discussions.

REFERENCES

1. A.L. Ruoff and L.C. Chhabildas, in High Pressure Science and Technology, Sixth AIRAPT Conference, Vol. 1, edited by K.D. Timmerhaus and M.S. Barber (Plenum Press, New York, 1978), pp. 19-32.
2. J. Ross Macdonald, Rev. Mod. Phys. 41, 316 (1969).
3. J.H. Rose, J.R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B 29, 2963 (1984).
4. C.A. Swenson, J. Phys. Chem. Solids 29, 1337 (1968).
5. M.S. Anderson and C.A. Swenson, Phys. Rev. B 10, 5184 (1984).
6. J.R. Packard and C.A. Swenson, J. Phys. Chem. Solids 24, 1405 (1963).
7. M.S. Anderson and C.A. Swenson, Phys. Rev. B 31, 668 (1985).

8. W.J. Carter, S.P. Marsh, J.N. Fritz, and R.G. McQueen, in Accurate Characterization of the High Pressure Environment, Natl. Bur. Std. (U.S.) Special Publication No. 326, edited by E.C. Lloyd (Natl. Bur. Std., Washington, D.C., 1971), p. 147.
9. D.L. Decker, J. Appl. Phys. 42, 3239 (1971).
10. S.D. Wood and V.E. Bean, High Temp.-High Pressures 15, 715 (1983).
11. Z.P. Chang and G.R. Barsch, J. Geophys. Res. 74, 3291 (1969).
12. E.A. Perez-Albuerne and H.G. Drickamer, J. Chem. Phys. 43, 1381 (1965).
13. S.N. Vaidya and G.C. Kennedy, J. Phys. Chem. Solids 32, 951 (1971).
14. J.S. Weaver, T. Takahashi, W.A. Basset, in Accurate Characterization of the High Pressure Environment, Natl. Bur. Std. (U.S.) Special Publication No. 326, edited by E.C. Lloyd (Natl. Bur. Std., Washington, D.C., 1971), p. 189.
15. J.N. Fritz, S.P. Marsh, W.J. Carter, and R.G. McQueen, in Accurate Characterization of the High Pressure Environment, Natl. Bur. Std. (U.S.) Special Pub. No. 326, edited by E.C. Lloyd (Natl. Bur. Std., Washington, D.C., (1971), p. 201.
16. L. Thomsen, J. Phys. Chem. Solids 31, 2003 (1970).
17. P.W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 1 (1945).

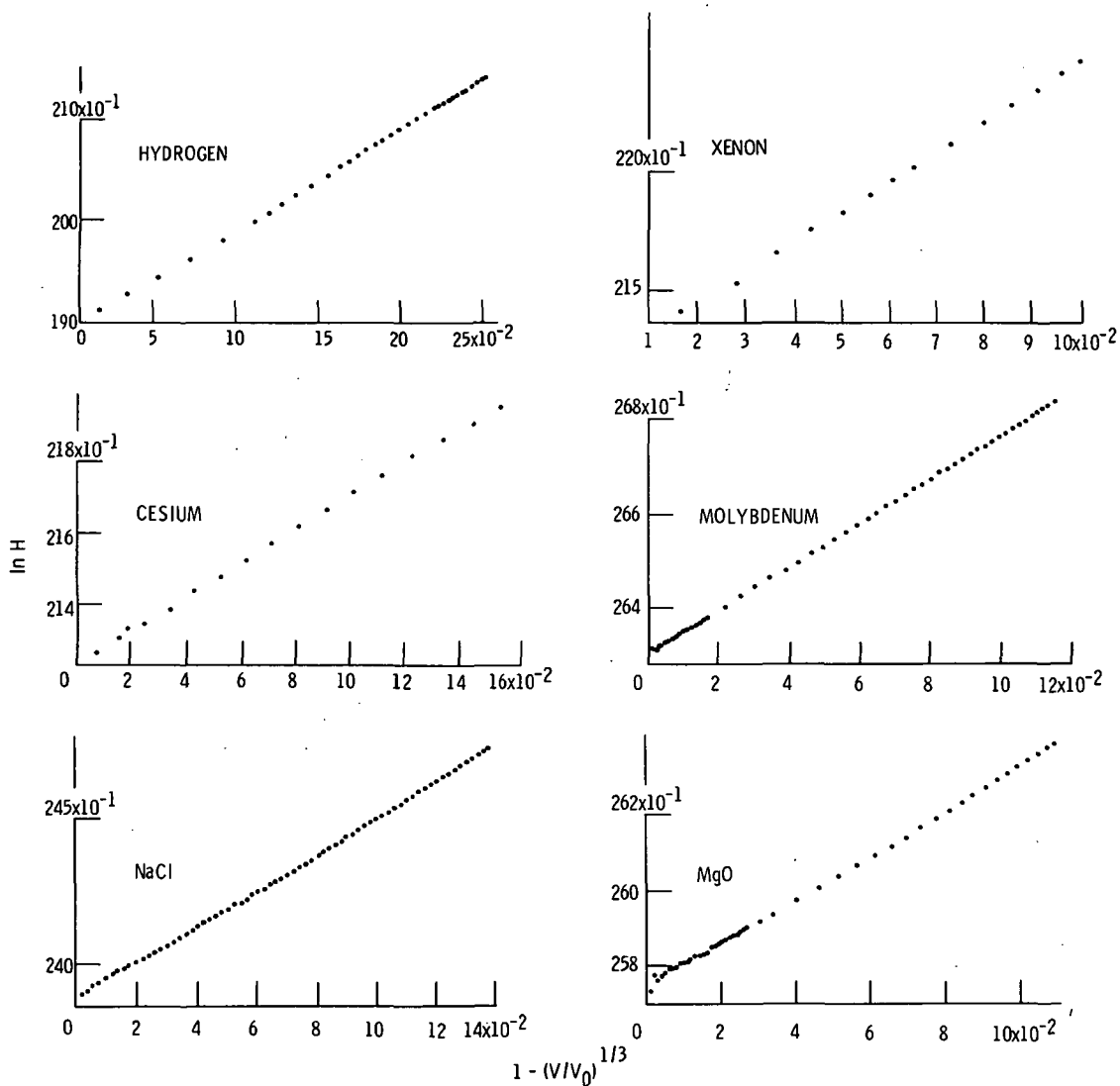


Figure 1. - Experimental values of $H(X,T) \equiv \ln [PX^2/3(1-X)]$ versus $1-X$, where $x \equiv (v/v_0)^{1/3}$ and v_0 is the equilibrium volume per atom. The source of the data and values of B_T and $(\partial B/\partial P)_T$ as obtained from the intercept and slope of the plots of figure 1 are respectively: hydrogen, ref. 5, 1.66×10^8 Pa, 7.33; xenon, ref. 6, 1.63×10^9 Pa, 8.87; cesium, ref. 7, 1.68×10^9 Pa, 4.07; molybdenum, ref. 8, 2.66×10^{11} Pa, 3.99; sodium chloride, ref. 9, 2.35×10^{10} Pa, 5.15; and magnesium oxide, ref. 8, 1.52×10^{11} Pa, 4.81.

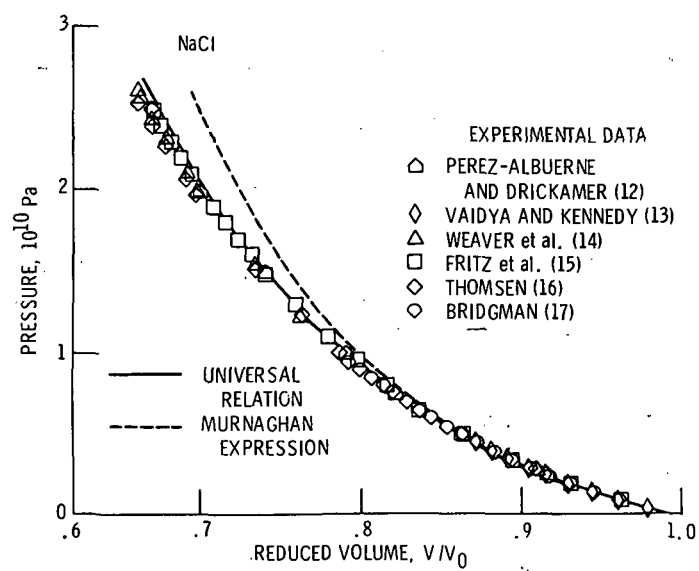


Figure 2. - Pressure versus reduced volume for NaCl. Solid curve, Eq. (1). Dashed curve, Murnaghan expression, Eq. (4).

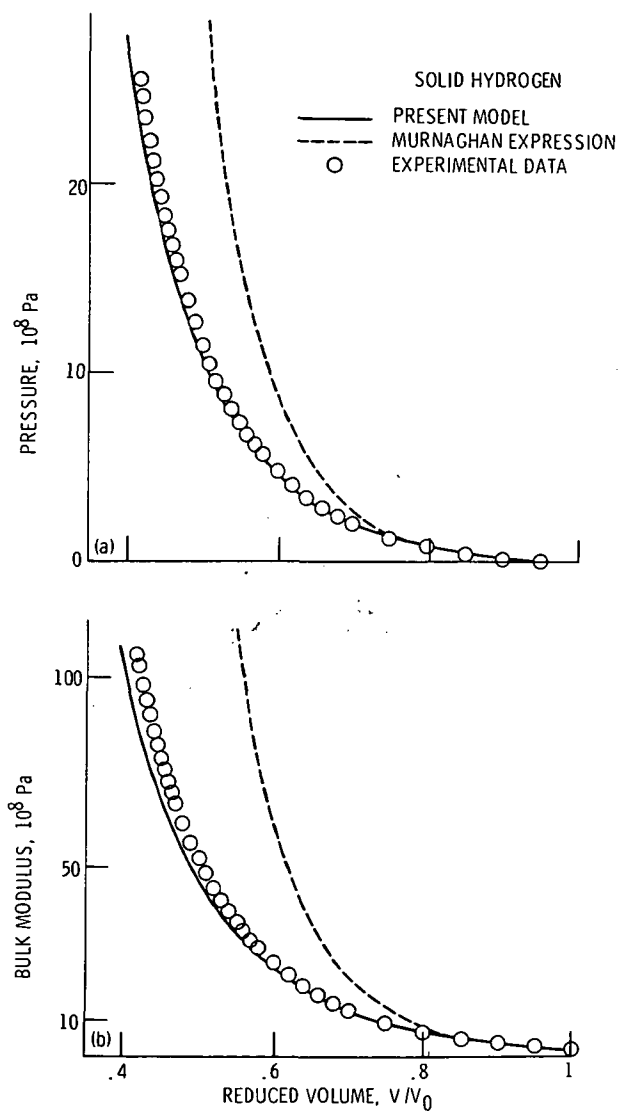


Figure 3. - Pressure (3a) and isothermal bulk modulus (3b) versus reduced volume for solid hydrogen. Experimental data is from ref. 5. Present model is Eqs. (1) and (6). Murnaghan expressions are Eqs. (4) and (5).

1. Report No. NASA TM- 87303		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Universality in the Compressive Behavior of Solids				5. Report Date April 1986	
				6. Performing Organization Code 506-53-12	
7. Author(s) Pascal Vinet, John Ferrante, John R. Smith, and James H. Rose				8. Performing Organization Report No. E-2702-1	
				10. Work Unit No.	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Pascal Vinet, Visiting scientist from Laboratoire de Technologie des Surfaces, Ecole Centrale de Lyon, B.P. 163, 69131 Ecully Cedex, France; John Ferrante, NASA Lewis Research Center; John R. Smith, General Motors Research Laboratories, Warren, Michigan 48090; James H. Rose, Ames Laboratory - USDOE, Iowa State University, Ames, Iowa 50011.					
16. Abstract We have discovered that the isothermal equation of state for solids in compression is of a simple, universal form. This single form accurately describes the pressure and bulk modulus as a function of volume for ionic, metallic, covalent, and rare gas solids.					
17. Key Words (Suggested by Author(s)) Equation of state Bulk modulus Compressibility				18. Distribution Statement Unclassified - unlimited STAR Category 77	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages	
				22. Price*	

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio 44135

Official Business
Penalty for Private Use \$300

SECOND CLASS MAIL

ADDRESS CORRECTION REQUESTED



Postage and Fees Paid
National Aeronautics and
Space Administration
NASA-451

NASA
