

Stability of the Electronic Configuration and Compressibility of Electron Orbitals in Metals under Shock-Wave Compression*

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Atomic radii in metals at 0°K are calculated from shock-wave equation-of-state measurements, and are compared with the radii of various free-atom electron orbitals obtained from Hartree-Fock calculations. For metals from the long periods of the periodic table having less than half-filled conduction bands, the Z dependence of the experimental atomic radii and of the Hartree-Fock, free-atom orbital radii are found to be essentially identical at all pressures. This allows the identification of the dominant contribution to the effective interatomic interaction. In these metals it is found that the presence of a significant population in the d band appears to result in a low compressibility. An unusually high compressibility observed for the normally trivalent rare-earth metals is then taken as evidence of the promotion of a $5d$ electron to a $4f$ shell under compression. Interactions between closed electron shells in metals are estimated from the experimental equations of state of the rare gases and their isoelectronic alkali halides. In the experimental pressure range, interactions between these closed-shell cores are found to be important only for the rare-earth metals, where an observed stiffening of the Hugoniot is identified as resulting from core interactions. The limits of validity of Thomas-Fermi-like equation-of-state calculations are discussed.

1. INTRODUCTION

EQUATION-OF-STATE measurements obtained through the use of shock-wave techniques¹⁻⁷ extend to compressions of sufficient magnitude that the physical properties of metals may no longer be considered to result exclusively from interactions between the outer electrons of the constituent atoms. In this paper, such equation-of-state data are reviewed and analyzed to study the stability of the electronic configuration under compression, to estimate the contributions of electrons from different atomic orbitals to the equation of state, and to estimate the compressibility of these individual orbitals. The analysis of the equation-of-state data is made in terms of a simple theoretical framework outlined in Sec. 2. This theory is successful in accounting for several observed systematic regularities in the experimental data. The data are reviewed in Sec. 3, and the comparison of theory and experiment is carried out in some detail in Sec. 4. In Secs. 5 and 6, the results of the analysis are reviewed, and more general conclusions are drawn.

2. THEORETICAL CONSIDERATIONS

Under normal conditions of temperature and pressure, the interatomic spacings and compressibilities of

of metals are known⁸⁻¹⁰ to be governed by interactions of electrons in the conduction band,^{8,11-13} this band being made up of electrons from the incomplete outer orbitals of the atoms constituting the metal. The conduction-band electrons normally are the only electrons contributing to either the attractive or the repulsive part of the effective interatomic potential. This work is concerned almost exclusively with the repulsive part of this effective potential, which will often be termed simply the repulsive potential. The present analysis rests on the observation that the contribution of individual conduction electrons to the effective interatomic potential appears to be determined primarily by the atomic-state parentage of the electron. Since the conduction electrons are often in states hybridized from several atomic states, this assumption implies that the important characteristic of the conduction band is the degree to which the various atomic states are included in the occupied part of the conduction band.

While the electrical properties of metals depend on electrons at the Fermi surface, the equation of state or effective interatomic interaction depends, to a varying degree, on all of the conduction-band electrons. The superposition of the contributions of many electrons makes the equation of state much less sensitive to details of the band structure than are the electrical properties. Actually, one should expect the antibonding electrons at the top of a filled band and the bonding electrons at the bottom of the band to make the

* Work performed under the auspices of the U. S. Atomic Energy Commission.

¹ M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Phys.* **6**, 1 (1958).

² G. E. Duvall and G. R. Fowles, *High Pressure Chemistry and Physics*, edited by R. S. Bradley, (Academic Press Inc., London, 1963), Vol. 2, p. 209.

³ L. V. Al'tshuler, *Uspekhi Fiz. Nauk* **85**, 197 (1965) [English transl.: *Soviet Phys.—Usp.* **8**, 52 (1965)].

⁴ I. C. Skidmore, *Appl. Mater. Res.* **4**, 131 (1965).

⁵ S. D. Hamann, *Advances in High Pressure Research*, edited by R. S. Bradley, (Academic Press Inc., London, 1966), Vol. 1, p. 85.

⁶ D. G. Doran and R. K. Linde, *Solid State Phys.* **19**, 229 (1966).

⁷ B. J. Alder, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963), p. 385.

⁸ A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1954).

⁹ W. Hume-Rothery and B. R. Coles, *Advan. Phys.* **3**, 149 (1954).

¹⁰ N. F. Mott, *Advan. Phys.* **13**, 325 (1964).

¹¹ P. O. Lowdin, *Advan. Phys.* **5**, 1 (1956).

¹² J. Callaway, *Solid State Phys.* **7**, 99 (1958); *Energy Band Theory* (Academic Press Inc., New York, 1964).

¹³ S. V. Vonsovskii and Yu. A. Izyumov, *Uspekhi. Fiz. Nauk* **77**, 377 (1962); **78**, 3 (1962) [English transl.: *Soviet Phys.—Usp.* **5**, 547, (1963); **5**, 723 (1963)].

strongest contribution to the equation of state. Thus, the population of states in the middle of the band should have only a small effect on the equation of state.

Now consider bonding in a sequence of metals adjacent to each other in the periodic table. Assume this bonding to be the result of the formation of a conduction band predominantly from the delocalization of electrons originally in a particular nl atomic orbital. Assume that it is the population of the bottom of the band that is important to the equation of state and that the changing population of the states in the middle of the band as one proceeds along the sequence has little effect on the equation of state. If none of the antibonding, upper-band states are filled, one may expect the interatomic spacings or radii of the atoms in the metal to show the same dependence on the atomic number Z as does the radius of that particular orbital in the same sequence of free, neutral atoms. The Z dependences of the individual free-atom orbital radii may be determined from published Hartree-Fock free-atom solutions.^{14,15} The analysis carried out in this work is essentially a comparison of the Z dependence of such Hartree-Fock orbital radii with the Z dependence of the experimental radii of atoms in the metal, henceforth termed the metallic radius.

The comparison of the Hartree-Fock orbital radii with the experimental metallic radii for sequences of metals is repeated at several pressures, where metallic radii are compared at constant pressure. The observation that such a comparison remains valid at different pressures gives evidence on the stability of the electronic configuration under compression, and the compressibility of the electron orbital is then taken to be the compressibility of the metals belonging to the fitted sequence. The analysis of the experimental data is devoted mainly to those metals where the Z dependence of the experimental atomic radii can be successfully fitted with a curve derived from the free-atom Hartree-Fock results. In most cases, these are metals with less than half-filled conduction bands. The compressibility of other metals is only briefly noted.

In the long periods of the periodic table, such a comparison shows that bonding in the alkali metals and alkaline-earth metals at all pressures may be associated with s electrons. Bonding in the metals of columns IIIB, IVB, VB, and VIB of the periodic table¹⁶ and in the trivalent rare-earth metals is associated with the d electrons in the s - d hybrid conduction band at zero pressure. At high pressure, this remains true of the metals of columns IIIB, IVB, VB, and VIB, but not of the rare-earth metals.

On the other hand, equations of state of materials at high compressions or high temperatures are thought to be well accounted for by a Thomas-Fermi description of the finite atom.¹⁷⁻²¹ In such a description, no electronic shell structure is included. The validity of this description is, of course, a result of the small interatomic spacings at these extreme conditions. The equation-of-state measurements made by using shock techniques extend into the beginning of the transition region between the outer-electron band description and the Thomas-Fermi description, and thus allow an estimation of the ranges of validity of these descriptions.

3. REVIEW OF THE EXPERIMENTAL EQUATION-OF-STATE DATA

Shock-wave measurements¹⁻⁷ on the equation of state of materials yield a series of (P, V, E) points related by the Rankine-Hugoniot equation for the conservation of energy,

$$\Delta E = \frac{1}{2} P (\Delta V). \quad (1)$$

The locus of such points is the Hugoniot curve or Hugoniot. Unfortunately, material at a Hugoniot point representing strong compression will be at a high temperature, primarily because of the irreversible heating associated with the shock process. In order to test the ideas outlined in the introduction, we wish to compare interatomic spacings or atomic radii derived from molar volumes at constant pressure on the 0°K isotherms of the elements, and isotherms must be calculated from the measured Hugoniot. In performing this calculation, it is usually adequate to assume a Grüneisen form for the equation of state:

$$P(V, E) = P_{0^\circ K}(V) + \gamma(V)[E - E_{0^\circ K}(V)]/V. \quad (2)$$

A further assumption about the volume dependence of γ then allows the calculation of the last term in Eq. (2), the thermal pressure on the Hugoniot, and hence a calculation of the 0°K isotherm and internal energy curve²² from Hugoniot data. As long as the thermal pressure is considerably smaller than the total pressure, the calculation of the isotherm is not particularly sensitive to the form used for $\gamma(V)$. Both the Slater and Dugdale-McDonald forms for γ have been used. At the highest pressures reached in shock experiments, thermal excitation of conduction electrons becomes important to the equation of state, and an electronic-pressure term must be added to Eq. (2).³ The coefficient of this term, the electronic γ , has been estimated³ from low-temperature specific-heat measurements. Unfortunately,

¹⁷ R. Latter, *J. Chem. Phys.* **24**, 280 (1956).

¹⁸ R. D. Cowan and J. Ashkin, *Phys. Rev.* **105**, 144 (1957).

¹⁴ R. E. Watson, Technical Report No. 12, Solid State and Molecular Theory Group, MIT, 1959 (unpublished); *Phys. Rev.* **118**, 1036 (1960); **119**, 1934 (1960); **123**, 2027 (1961).

¹⁵ F. Herman, and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

¹⁶ The designations of the columns of the periodic table are those given in *The Handbook of Chemistry and Physics* (The Chemical Rubber Publishing Company, Cleveland, Ohio, 1964).

¹⁹ N. N. Kalitkin, *Zh. Eksperim. i Teor. Fiz.* **38**, 1534 (1960) [English transl.: *Soviet Phys.—JETP* **11**, 1106 (1960)].

²⁰ V. P. Kopyshchev, *Dokl. Akad. Nauk SSSR, Ser. Mat. Fiz.* **161**, 1067 (1965) [English transl.: *Soviet Phys.—Doklady* **10**, 338 (1965)].

²¹ H. M. Schey and J. L. Schwartz, *Phys. Rev.* **137**, A709 (1965).

²² G. B. Benedek, *Phys. Rev.* **114**, 467 (1959).

there is considerable question as to the applicability of the value of the electronic γ so obtained because of probable changes in the density of states at the Fermi surface under compression. At these highest pressures, the thermal pressure of the lattice may contribute one-half or more of the total pressure on the Hugoniot, and the uncertainty in the calculation of the last term in Eq. (2) further increases the uncertainty in the calculation of the isotherm.

In many cases, 0°K isotherms have been published with the Hugoniot data and may be obtained directly from the literature. In cases where this was not true, the 0°K isotherms were calculated from the Hugoniots with the use of the Grüneisen equation and with the assumption of the Dugdale-McDonald form for γ .²³ Electronic effects were ignored. The results are tabulated in the Appendix, together with references to the original work.

The repulsive interaction between the inner-electron closed-shell cores of metal atoms should be the same as that between atoms of the preceding rare gas. Hugoniot equation-of-state measurements have been reported on liquid argon and liquid xenon, and from these measurements an effective interatomic potential was derived.^{24,25} This potential is in agreement with theoretical calculations^{26,27} and with other experimental work.²⁶ The potential was then used to calculate 0°K isotherms for fcc solid argon and xenon. In this calculation, only nearest-neighbor interactions were included, pairwise additivity was assumed, and the resulting total energy was differentiated with respect to volume to obtain the pressure. The 0°K isotherms for solid argon and xenon so calculated are essentially identical at high pressures to the isotherms for the isoelectronic alkali halides KCl and CsI as calculated from Hugoniot data, and this agreement lends credence to the isotherms. No data are available for neon or krypton; the isotherms for isoelectronic NaF and RbBr are used to estimate core effects.

There is some uncertainty in the calculated isotherms for the alkali metals. The large shock compressions observed for these materials result in high temperatures on the Hugoniot even at 0.25 Mbar,²⁸ and the calculation of the isotherm, therefore, involves the calculation of a large and somewhat uncertain thermal-pressure term. For lithium, sodium, and potassium, isotherms have been calculated both with and without electronic contributions, and the two results differ significantly. Probably electronic effects are also im-

portant for rubidium and cesium though they have not been calculated. The isotherm for cesium was only crudely estimated. Furthermore, there appear to be small differences in the Hugoniots for lithium, sodium, and potassium as measured in two different laboratories. The alkaline earths, calcium, strontium, and barium are also very compressible, and calculations of the isotherms involve the same problems as the calculations for the alkali metals. The problem is not as severe, however.

Further uncertainties in the calculation of the isotherms of calcium, strontium, barium, iron, germanium, antimony, and bismuth arise from kinks in the experimental Hugoniots, associated with polymorphic phase transitions at pressures of the order 0.1 to 0.2 Mbar.²⁹ The phase transitions have not been properly accounted for in the calculation of the isotherms. Because of this, the molar volumes at 0.25 Mbar on the calculated isotherms are somewhat uncertain for these elements, though the volumes at higher pressures should be less uncertain because of the steepening of the repulsive part of the effective interatomic potential.

At 1 Mbar, data are available only for the less compressible materials. For these materials, the isotherms and Hugoniots are not far apart, reflecting a small thermal-pressure contribution, and volumes on the calculated isotherms should be reasonably accurate. The calculated isotherms at 4 Mbar are uncertain because of high thermal-pressure contributions and high electronic-pressure contributions, both associated with the high temperatures reached on the Hugoniot.

4. ANALYSIS OF THE DATA

The analysis of the experimental data is best done with the aid of Figs. 1–4, where the metallic radius is shown versus atomic number at several pressures. The metallic radius, or radius of an atom in the metal, is taken as the Wigner-Seitz radius, defined in terms of the experimental molar volume by the relation

$$(\text{molar volume}) = A/\rho = N_0(4\pi/3)(R_m)^3. \quad (3)$$

Note that the radius so defined is independent of the crystal structure. Since crystal structures at high pressures are usually not known, such a radius seems most appropriate for comparisons of the interatomic spacings of different elements. The figures show the atomic radii to become more nearly alike for the various elements at high pressures, as has been noted from similar plots of atomic volume versus atomic number.³

The lines drawn in Figs. 1–4 show the Z dependence of the radii of particular nl Hartree-Fock electron shells as normalized to the experimental metallic radii. The normalization is carried out by taking the Z dependence of these electron-shell radii in the form $B_{nl}(P)R_{nl}(Z)$. The function $R_{nl}(Z)$ is determined from the Hartree-Fock free-atom solutions,^{14,15} where the radius of an

²³ The code for this calculation was written by V. Davis, and is based on earlier work of R. Grover. See Physics Department Progress Report No., UCRL-14360, Lawrence Radiation Laboratory, University of California 1965, p. 62 (unpublished).

²⁴ M. van Thiel and B. J. Alder, *J. Chem. Phys.* **44**, 1056 (1966); R. N. Keeler, M. van Thiel, and B. J. Alder, *Physica* **31**, 1437 (1965).

²⁵ M. Ross and B. J. Alder, *J. Chem. Phys.* **46**, 4203 (1967).

²⁶ A. A. Abrahamson, *Phys. Rev.* **130**, 693 (1963).

²⁷ G. M. Gandel'man, *Zh. Eksperim. i Teor. Phys.* **48**, 578 (1965) [English transl.: *Soviet Phys.—JETP* **21**, 501 (1965)].

²⁸ 1 bar = 10^6 dyn/cm² = 1 atm. 1 Mbar = 10^8 kbar = 10^6 bar.

²⁹ V. V. Evdokimova, *Uspekhi. Fiz. Nauk* **88**, 93 (1966) [English transl.: *Soviet Phys.—Usp.* **9**, 54 (1966)].

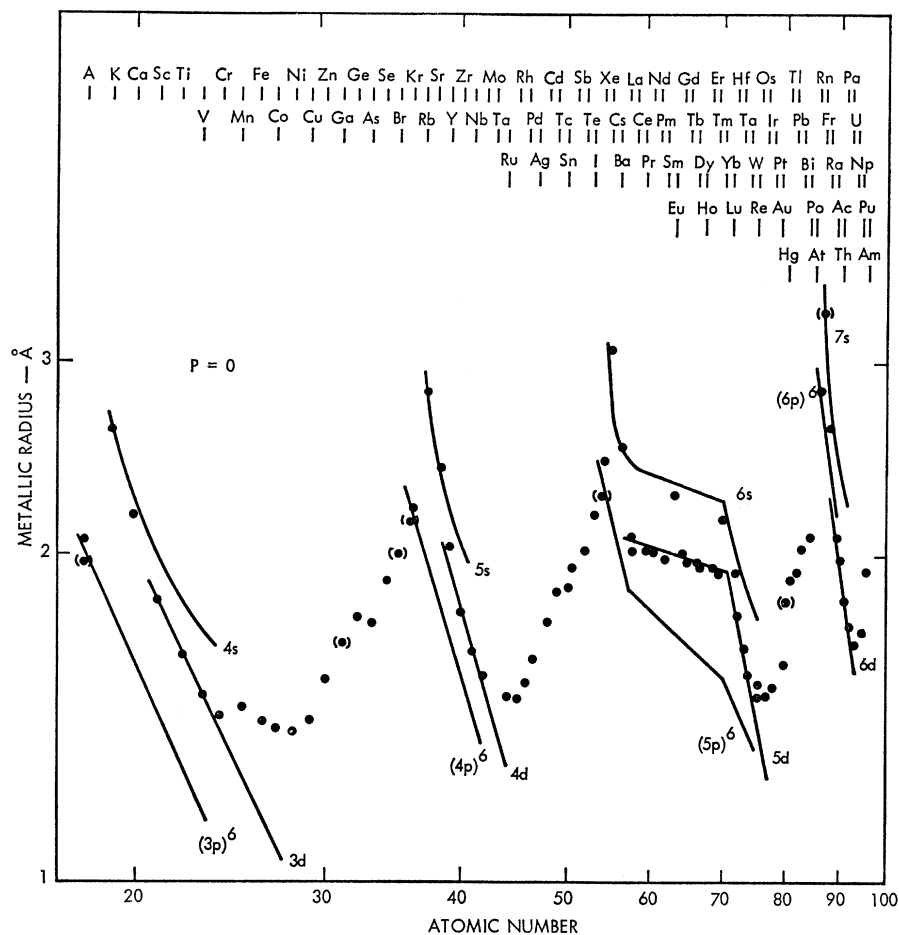


FIG. 1. Atomic radius versus atomic number at zero pressure. The dots are experimental data, and the lines show the Z dependences obtained from the Hartree-Fock free-atom solutions as normalized to the experimental data. Parentheses indicate questionable experimental points.

orbital is taken as the outermost radius at which the wave function attains half of its value at the outermost extremum. Except for s -electron orbitals $R_{nl}(Z)$ may be approximated by Z^{-m} over a limited range of Z , though the actual $R_{nl}(Z)$ functions in graphical form were used in this work. The function $B_{nl}(P)$ depends on the details of the bonding states formed and the exact definition of the radius of the free-atom orbital. It is assumed to be independent of Z and is used as an adjustable parameter for each particular pressure and particular orbital. This allows the curve for the Z dependence of the Hartree-Fock free-atom orbital radius to be normalized to the experimental metallic radius of *one* element. In fact, several elements will usually fall on the same line, confirming the assumed

TABLE I. Values of the scaling factor $B_{nl}(P=0) = R_m(P=0)/R_{nl}$, where R_m is the experimental metallic radius and R_{nl} the Hartree-Fock free-atom orbital radius.

n	$(np)^6$ closed shell	$(n+1)s$	nd
3	1.52	0.65	1.35
4	1.48	0.69	1.05
5	1.33	0.67	1.03
6	1.41	0.65	0.92

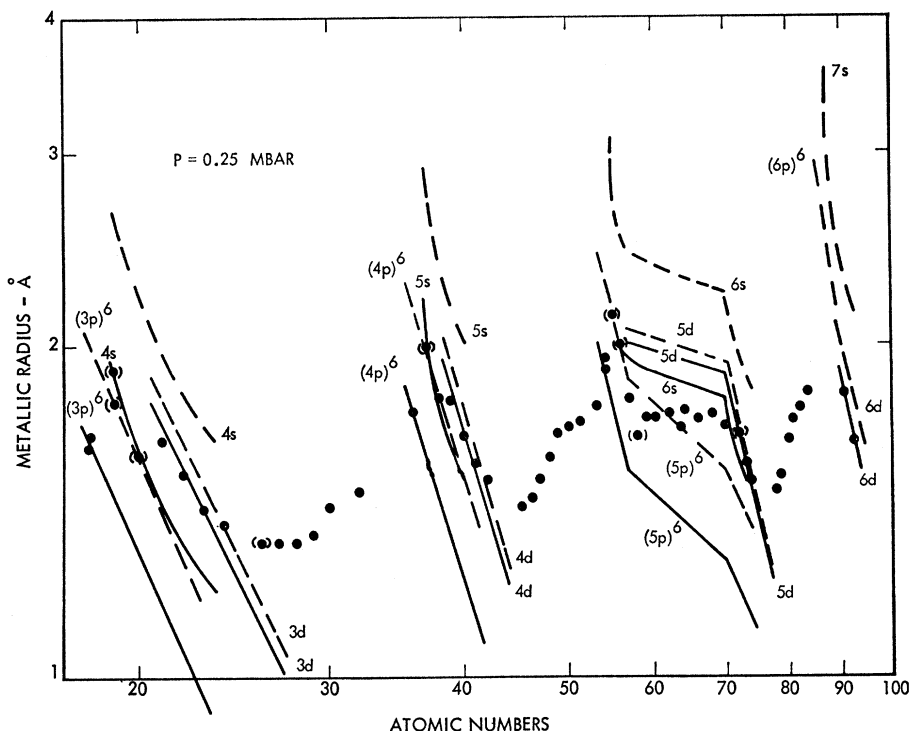
existence of similar bonding in the sequence of metals, and lending credence to the simple theory outlined previously. Note that the use of a log-log plot of atomic radius versus Z makes this curve fitting particularly simple. The predetermined function $R_{nl}(Z)$ fixes the shape of the curves; the only adjustment allowed is a vertical translation.

This procedure is repeated at several pressures, in order to examine the stability of the electronic configuration and the electron-shell compressibility at high pressure. The success of the fitting procedure indicates that there are approximate universal compression curves for groups of metals whose bonding is governed by the same electron orbitals, provided the metallic radii are appropriately scaled with Z . The steepness of the effective repulsive potential eliminates the necessity of scaling the pressure with Z as well.

TABLE II. Values of the scaling factor $B_{nl}(P=0.25 \text{ Mbar})$.

n	$(np)^6$ closed shell	$(n+1)s$	nd
3	1.23	0.47	1.27
4	1.17	0.51	0.98
5	1.08	0.53	0.99
6	0.84

FIG. 2. Atomic radius versus atomic number at a pressure of 0.25 Mbar. The dots are experimental radii on the 0°K isotherms as calculated from Hugoniot data. The solid lines show the Z dependences obtained from the Hartree-Fock free-atom solutions as normalized to the experimental data at this pressure. The broken lines are the Hartree-Fock Z -dependences at zero pressure, taken from Fig. 1. Parentheses indicate questionable experimental points.



Tables I-IV give the values of $B_{nl}(P)$ resulting from the fitting procedure.

A. The (3d, 4s, 4p) Period

Now consider the (3d, 4s, 4p) period at zero pressure. Potassium and calcium fall on a curve representing 4s bonding, the dependence of the atomic radii on Z being that of the 4s orbital in the free atoms. Scandium, titanium, vanadium, and chromium all fall on the line whose slope is determined by the 3d orbital in the free atom. Thus, although the conduction band in these metals is a 3d4s hybrid, the 3d component apparently dominates in determining the interatomic spacing.

Turning to the high-pressure data, one finds that potassium and calcium still fall on a 4s curve, though the atoms are quite appreciably compressed. Scandium, titanium, vanadium, and chromium continue to fall on a 3d curve, and are only slightly compressed. This difference in compressibility between the 4s shell and 3d shell is so marked that the radius of the 4s shell falls inside the radius of the 3d shell under compression, though it falls outside the 3d shell at zero pressure, if one makes the comparison at the same value of Z .

TABLE III. Values of the scaling factor $B_{nl}(P=1.0 \text{ Mbar})$.

n	$(np)^6$ closed shell	$(n+1)s$	nd
3	1.08	...	1.16
4	0.90
5	0.95	...	0.96
6	0.75

The curve for the Z dependence of the radius of the argon $(3p)^6$ core is determined from Hartree-Fock solutions in the same way as the curves for the open shells. It is fitted to the experimental radius either for argon or KCl. In this way, the cores are found to be quite compressible; in fact, almost as compressible as the open 4s shell. It should be noted, however, that since the attractive potential in the solid rare gases and alkali halides is weaker than in many metals, this apparent large core compressibility is due, in part, to the large interatomic spacing. At small interatomic spacings, the core repulsion is probably large, and the core should be expected to be relatively incompressible. Because of the high core compressibility at the atomic spacings of interest here, none of the elements is compressed to the point where core interactions dominate in determining the interatomic spacing. However, experimental compressions are clearly adequate to cause some hybridization of core and outer electron states to be expected at the highest pressures, and this effect probably should not be ignored in detailed calculations of the electronic structure under pressure. At compressions beyond the present experimental limits, a more complete hybridization of core and outer electron

TABLE IV. Values of the scaling factor $B_{nl}(P=4.0 \text{ Mbar})$.

n	$(np)^6$ closed shell	$(n+1)s$	nd
3	0.97
4	0.82
5	0.88
6

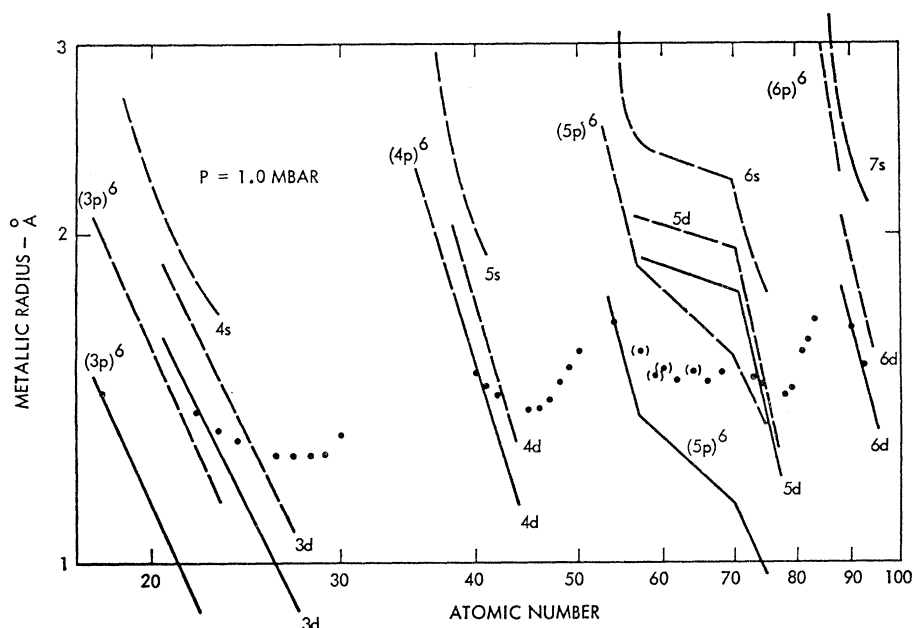


FIG. 3. Atomic radius versus atomic number at 1.0 Mbar, as in Fig. 2.

states will, of course, bring many electrons into play in determining the interatomic potential; shell structure will become less important; and the Thomas-Fermi statistical model will become more applicable.

At 1 Mbar, the sequence of elements titanium, vanadium, and chromium does not follow the $3d$ curve as well as at 0.25 Mbar or at zero pressure. Vanadium and chromium are not as compressible as they would be expected to be. Probably this is a result of the presence of more than one $3d$ electron for these elements.

Interatomic spacings for manganese and the succeeding elements at all pressures are greater than would be predicted by simple ideas presented here, although compressibilities are comparable to the early elements of the $3d$ period. This behavior is easily accounted for when it is realized that the sd hybrid conduction bands in which the outer electrons find themselves are more than half full for these elements. The occupation of the more antibonding states near the top of the band³⁰ presumably gives rise to a sufficiently strong repulsive potential to move the minimum in the interaction energy curve to a greater interatomic spacing. The simple arguments used in this analysis are no longer directly applicable. In terms of the previously defined functions, for these materials $B_{ni}(P)$ continues to show the same dependence on P but is no longer independent of Z .

Band calculations³¹⁻³³ and cohesive energy calculations³⁴⁻³⁶ confirm the s character of bonding in potas-

sium and support the identification of the compressibility of potassium with the compressibility of the $4s$ shell. Experimentally, there is no evidence of the existence of any pressure-induced phase transition from the normal bcc structure, though melting should be expected at a fairly small Hugoniot pressure for all the alkali metals.^{37,38} The measured Hugoniot is smooth at all pressures above 45 kbar, so the latent heat and volume change on melting are probably small. Static high-pressure measurements³⁹ show no discontinuities in the volume under isothermal compression. The discontinuities in resistance at 280 and 360 kbar are observed⁴⁰ only at low temperature and are apparently not reflected in the equation of state. These experimental results support the assumption that the $4s$ configuration is stable at all pressures reached.

In calcium bonding cannot be purely s like, since the material would then have to be an insulator, and a small overlap between s and d bands has been calculated.^{41,42} The present analysis of the compression of calcium under high pressure, however, would indicate that there is only a small d component to the bonding, since the compression of calcium follows that of potassium quite closely. A break in the Hugoniot in the vicinity of 180 kbar and a discontinuity in the statically measured P - V curve³⁹ at 63 kbar indicate phase transitions, the lower of which may be a phase transition from fcc to

³⁷ G. C. Kennedy, A. Jayaraman, and R. C. Newton, *J. Geophys. Res.* **67**, 2559 (1962).

³⁸ G. C. Kennedy, A. Jayaraman, and R. C. Newton, *Phys. Rev.* **126**, 1363 (1962).

³⁹ Work of P. W. Bridgman; see F. P. Bundy and H. M. Strong, *Solid State Phys.* **13**, 81 (1962).

⁴⁰ R. A. Stager and H. G. Drickamer, *Phys. Rev.* **132**, 124 (1963).

⁴¹ M. F. Manning and H. Krutter, *Phys. Rev.* **51**, 761 (1937).

⁴² B. Vasvari, A. O. E. Animalu, and V. Heine, *Phys. Rev.* **154**, 535 (1967).

³⁰ L. F. Mattheiss, *Phys. Rev.* **134**, A970 (1964).

³¹ F. S. Ham, *Phys. Rev.* **128**, 82 (1962); **128**, 2524 (1962).

³² J. Callaway, *Phys. Rev.* **103**, 1219 (1956).

³³ L. C. Allen, Quarterly Progress Report, Solid State and Molecular Theory Group, MIT, 1958, p. 45 (unpublished) (Quoted by Ham, Ref. 28).

³⁴ J. Callaway, *Phys. Rev.* **119**, 1012 (1960).

³⁵ H. Brooks, *Nuovo Cimento Suppl.* **7**, 165 (1958).

³⁶ H. Brooks, *Trans. AIME* **227**, 546 (1963).

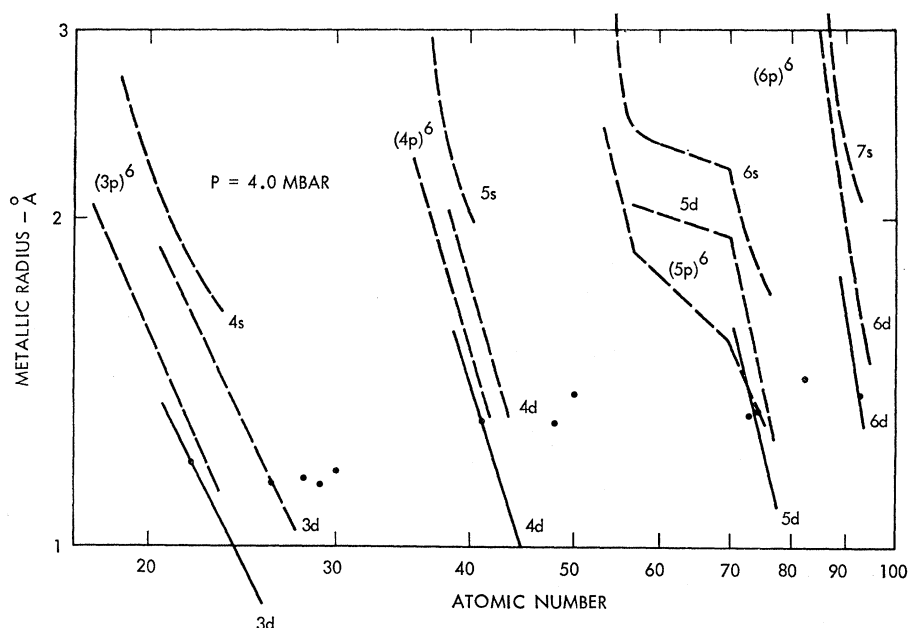


FIG. 4. Atomic radius versus atomic number at 4.0 Mbar, as in Fig. 2.

bcc, as has been observed⁴³ for strontium at 35 kbar. However, other evidence⁴⁴ indicates that this lower transition is probably spurious. Probably the large compressibility observed may be taken as evidence that neither of these transitions is accompanied by a large electronic transition to d bonding.

Band calculations⁵⁰ on the $3d$ metals from titanium through zinc indicate that there should be significant s - d hybridization and broadening of the d band, and hence, that the d electrons probably play a significant role in bonding. For iron further band calculations^{50,45,46} and calculations of the cohesive energy,⁴⁷ based on band calculations, all confirm overlap of the s and d bands and significant d -electron participation in bonding, as do calculations for chromium,^{48,49} vanadium,⁴⁹ and titanium.^{50,51} Even for copper, where the $3d$ bands are presumably filled, the calculations^{50,52,53} indicate a strong s - d interaction, and broadening of the d band, which should be accompanied by an effect of the d electrons on binding. The presence of d -electron bonding and the apparent qualitative difference between d - and s -electron bonding noted in this work may account for the poor success of the application of the quantum-defect method to the calculation of the cohesive energy

⁴³ D. B. McWhan and A. Jayaraman, *Appl. Phys. Letters* **3**, 129 (1963).

⁴⁴ A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **132**, 1620 (1963).

⁴⁵ J. Callaway, *Phys. Rev.* **99**, 500 (1955).

⁴⁶ J. H. Wood, *Phys. Rev.* **117**, 714 (1960); **126**, 517 (1962).

⁴⁷ F. Stern, *Phys. Rev.* **116**, 1399 (1959).

⁴⁸ M. Asdente and J. Friedel, *Phys. Rev.* **124**, 384 (1961); **127**, 1949 (1962).

⁴⁹ W. M. Lomer, *Proc. Phys. Soc. (London)* **80**, 489 (1962).

⁵⁰ B. Schiff, *Proc. Phys. Soc. (London)* **A68**, 686 (1955).

⁵¹ S. L. Altmann and N. V. Cohen, *Proc. Phys. Soc. (London)* **71**, 383 (1958); *Proc. Roy. Soc. (London)* **A244**, 141 (1958).

⁵² B. Segall, *Phys. Rev.* **125**, 109 (1962).

⁵³ G. A. Burdick, *Phys. Rev.* **129**, 138 (1963).

and compressibility of $3d$ metals at low pressure.⁵⁶ Under high compressions, relatively simple calculations⁵⁴ using a Thomas-Fermi potential have been fairly successful in reproducing the equation of state of iron. These calculations confirm the importance of the d electrons in determining the equation of state. They also indicate that the $(3p)^6$ argon cores will not be important at less than 6-fold compression, in agreement with the general conclusions reached here. The phase transition in iron at 130 kbar from bcc to hcp^{55,56} may be associated with the increased d character in the bonding predicted at high pressure; the calculations do not indicate any p character in this pressure range.

B. The $(4d, 5s, 5p)$ Period

The $(4d, 5s, 5p)$ period shows essentially the same behavior as the $(3d, 4s, 4p)$ period. Rubidium and strontium are characterized by $5s$ bonding and are quite compressible. Yttrium, zirconium, niobium, and molybdenum are much less compressible and are characterized by $4d$ bonding. Again, under compression the s shell moves inside the d shell, though it normally lies outside the d shell. The compressibility of the krypton $(4p)^6$ core was determined from RbBr data and indicates that the core repulsion will not dominate the equation of state until pressures well above the present upper limit are attained. Some hybridization with outer electron bands may be expected in the experimental range, however.

⁵⁴ G. M. Gandelman, *Zh. Exptim. i Teor. Fiz.* **43**, 131 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 94 (1963)].

⁵⁵ D. Bancroft, E. L. Peterson and F. S. Minshall, *J. Appl. Phys.* **27**, 557 (1956).

⁵⁶ J. C. Jamieson and A. W. Lawson, *J. Appl. Phys.* **33**, 776 (1962); T. Takahashi and W. A. Bassett, *Science* **145**, 483 (1964); R. L. Clendennen and H. G. Drickamer, *J. Phys. Chem. Solids* **25**, 865 (1964).

For rubidium and cesium under compression, there is the possibility of an electronic phase transition,^{57,58} in which the bottom of the d band drops below the Fermi level. This should give rise to some d character in the normally s -like bonding indicated by band calculations³¹ and cohesive-energy calculations.^{35,36,59} Quasiclassical calculations⁵⁸ of the wave functions in a Thomas-Fermi potential indicate that this transition in rubidium should take place at a pressure of the order of 200 kbar. Discontinuities in the resistance of rubidium are seen at 75 and 190 kbar in static high-pressure experiments,^{60,40} though no volume discontinuities are seen below 100 kbar.³⁹ The lower transition may be a phase transition from bcc to fcc with only a very small volume change. The Hugoniot is smooth from 55 to over 400 kbar. However, there appears to be a slight stiffening of the Hugoniot in the vicinity of 300 kbar, which may be associated with the 190-kbar resistance discontinuity observed statically or with a broad resistance maximum in the vicinity of 400 kbar.⁴⁰ It seems possible that this stiffening of the Hugoniot is associated with the electronic transition to partial d bonding; such a conclusion is consistent with the present work.

The 35-kbar transition in strontium from fcc to bcc has already been mentioned.⁴³ A further reported transition at 65 kbar³⁹ was apparently spurious. A break is seen on the Hugoniot near 60 kbar and may result from the fcc \rightarrow bcc transition. As in the case of calcium, the present arguments indicate that there is not a large d contribution to the binding in strontium, though there is presumably some small overlap between the s and d bands.

As in the previous period, band calculations are consistent with the idea that the d electrons play a significant role in bonding for zirconium⁶¹ and molybdenum.⁴⁹

C. The ($4f$, $5d$, $6s$, $6p$) Period

The behavior of the elements of the ($4f$, $5d$, $6s$, $6p$) period follows the same general pattern of the previous two periods except for the rare-earth metals. The $4f$ shell lies well inside the ($5p$)⁶ closed xenon shell^{14,15} and should not be expected to have any effect on bonding, except in determining the number of outer bonding electrons.⁶²⁻⁶⁴ Thus, for europium and ytterbium, the

stability of the half-filled and filled $4f$ shell results in a divalent metal instead of the usual trivalent metal at normal pressure. The $6s$ -bonding radii were fitted to rather questionable cesium and barium isotherms from Hugoniot data, the $5d$ to hafnium, tantalum and tungsten data, and the ($5p$)⁶ xenon closed shell to xenon or CsI data. As before, the s -bonded metals are much more compressible than the d -bonded metals. The xenon core is almost as compressible as the unfilled s shell. Core hybridization should occur in a manner similar to the hybridization of the cores in the preceding periods.

At zero pressure, the trivalent rare-earth metals all fall essentially on the $5d$ curve fitted to hafnium, zirconium, and tungsten. Thus, these elements should be expected to be relatively incompressible. The divalent rare earths europium and ytterbium fall quite close to the $6s$ curve fitted to cesium and barium and should be more compressible. Experimentally, all of the rare earths measured exhibit a very high compressibility and are compressed to essentially the same interatomic spacing regardless of whether they are initially divalent or trivalent. This final interatomic spacing is actually smaller than that predicted for $6s$ bonding. However, the prediction is based on rather poorly calculated isotherms for cesium and barium, and the difference is probably not significant. As compared to the interatomic spacing predicted for $5d$ bonding, the rare earths are much too compressible, so much so in fact, that it appears necessary to conclude that at high pressure, there is no significant d bonding, and hence, that all of the rare earths are probably divalent. This would have to be accomplished by the transfer of the $5d$ electron to a $4f$ level as pressure is increased. One of the polymorphic transitions^{29,64,65} observed at low pressures may take place simultaneously with this transition. The first-order $\alpha \rightarrow \gamma$ -phase transition in cerium^{28,64-67} is thought to be the result of the reverse transfer process ($f \rightarrow d$). Apparently, at higher pressures the $d \rightarrow f$ transfer takes place, not necessarily as a first-order phase transition, in order to overcome the incompressibility characterizing d bonding at high pressure. It should be noted that the Hugoniot for cerium appears to be qualitatively different from Hugoniots for the other rare-earth metals.

At pressures of the order of 400 to 600 kbar, several of the rare earths become noticeably less compressible

⁵⁷ R. Sternheimer, *Phys. Rev.* **78**, 235 (1950).
⁵⁸ E. S. Alekseev and R. G. Arkhipov, *Fiz. Tverd. Tela* **4**, 1077 (1962) [English transl.: *Soviet Phys.—Solid State* **4**, 795 (1962)].
⁵⁹ J. Callaway and D. F. Morgan, *Phys. Rev.* **112**, 334 (1958).
⁶⁰ F. P. Bundy, *Phys. Rev.* **115**, 274 (1959); *Solid State Phys.* **13**, 81 (1962).
⁶¹ S. L. Altmann, *Proc. Roy. Soc. (London)* **A224**, 153 (1954).
⁶² K. A. Geschneider, Jr., *Rare Earth Alloys* (D. Van Nostrand, Inc., Princeton, New Jersey, 1961).
⁶³ *Rare Earth Research*, edited by E. V. Kleber (The MacMillan Company, New York, 1961); *Rare Earth Research III*, edited by L. Eyring, (Gordon & Breach Science Publishers, Inc., New York, 1964).
⁶⁴ L. F. Vereschagin and A. Jayaraman, in *Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965).

⁶⁵ H. T. Hall, J. D. Barnett, and L. Merrill, *Science* **139**, 111 (1963); A. Jayaraman, *Phys. Rev.* **139**, A690 (1965); D. R. Stephens, *J. Phys. Chem. Solids* **25**, 423 (1964); D. B. McWhan and A. L. Stephens, *Phys. Rev.* **139**, A682 (1965); D. B. McWhan, P. W. Montgomery, H. D. Stromberg and G. Jura, *J. Phys. Chem.* **67**, 2308 (1963); G. J. Piermarini and C. E. Weir, *Science* **144**, 69 (1964).

⁶⁶ E. G. Ponyatovskii, *Dokl. Akad. Nauk SSSR* **120**, 1021 (1958) [English transl.: *Soviet Phys.—Doklady* **3**, 498 (1959)]; L. D. Livshitz, Yu. S. Genshaft, and V. K. Markov, *Zh. Eksperim. i Teor. Fiz.* **43**, 1262 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 894 (1963)].
⁶⁷ A. Jayaraman, *Phys. Rev.* **137**, A179 (1965); B. L. Davis and L. H. Adams, *Solid State Commun.* **1**, 241 (1963).

on the Hugoniot, though they remain more compressible than would be the case if they were d bonded. From the present evidence, it seems most likely that this increased stiffness is probably the result of core interactions or perhaps of interactions between core electrons from one atom and valence electrons from another.

For cesium, one is forced to directly confront the problem of the electronic phase transition. A number of band calculations^{31,57} as well as calculations in a Thomas-Fermi potential⁵¹ all indicate that at high pressures the d band probably falls below the Fermi level. This would result in a change from the normal s -electron bonding treated in cohesive-energy calculations^{35,36,68} and in band calculations,^{31,57,69} to bonding in which d electrons also take part. The calculations predict the transition to occur at a compression between two or threefold. Static high-pressure measurements⁷⁰ have established a 23.7-kbar phase transition from bcc to fcc and a 42.7-kbar transition from fcc to hcp. At 42.2 kbar a phase transition from one fcc structure to another fcc structure was observed with an appreciable change in volume. The phase existing between 42.2 and 42.7 kbar exhibits a high resistivity, which accounts for the resistivity cusp observed earlier.^{38,39,60} The Hugoniot is smooth at all pressures above 64 kbar, indicating no further phase transitions at high pressures. If the Hugoniot is extrapolated to zero pressure, an incorrect compressibility is obtained consistent with the idea that cesium under high pressure is somewhat different from cesium at zero pressure. Curvature of the Hugoniot in the shock-velocity-particle-velocity plane may be taken as evidence of a gradually changing character for shocked cesium. It seems most probable that the 42.2-kbar transition is the electronic transition in which the d band becomes partially populated, as predicted by theory. However, the large compressions of cesium on the Hugoniot are at variance with the relative incompressibility of d -bonded metals deduced from the present analysis. One is thus forced to the conclusion that even above the phase transition, there is only a small and probably varying amount of d bonding or population of the d band, or that there is actually a transition back to pure s bonding. Such a conclusion does not appear to be inconsistent with the band calculations.

Barium exhibits a phase transition from bcc to hcp at 59 kbar⁷¹⁻⁷³ under isothermal compression. The Hugoniot exhibits a break near 67 kbar which may be this transition or may be melting.⁷² A resistance dis-

continuity is seen by 145 kbar;⁷⁴ a transition at 15 kbar³⁹ appears to have been spurious. As for the previous alkali metals and alkaline-earth metals discussed, the d bonding present must be only a small fraction of the total bonding, because of the high compressibility of the material exhibited under shock compression.

Calculations of the band structure^{49,75} and binding⁷⁶ in tungsten indicate that the dominant contribution to binding should come from the d electrons, in agreement with the present ideas.

D. The (5*f*, 6*d*, 7*s*, 7*p*) Period

The analysis of the (5*f*, 6*d*, 7*s*, 7*p*) period is complicated by bizarre fluctuations in the calculated electronic configuration along the period^{18,77} and by fragmentary equation-of-state data. At zero pressure, the estimated radii for francium and radium fall on a 7*s* curve, while the actinium, thorium, protactinium, and uranium radii fall on a 6*d* curve calculated under the assumption that there is *no* population of the 5*f* levels. If a 5*f* level is assumed to be populated, the curve representing the Z dependence of the Hartree-Fock 6*d* radii cannot be fitted to the experimental radii. The neptunium and plutonium radii deviate from the d -electron curve in the same way as do the radii for manganese and iron or rhenium and osmium, where the population of the upper, antibonding levels in the d band causes an increased atomic radius. Shock-compression data on thorium and uranium show the low compressibility typical of d metals, tending to confirm the present analysis. The first population of the 5*f* levels in the metal appears to occur at americium. All of the preceding actinides appear to be 6*d* bonded with no significant 5*f*-level population.

E. The Early Periods

The present type of analysis has also been attempted for the earlier periods of the periodic table with little success. Probably the difficulty arises from more irregular screening effects, and the filling of antibonding states and/or p states early in the period.

5. DISCUSSION

Several authors have noted a rather smooth, monotonic correlation between the specific volume and initial compressibility of the elements.^{3,78,79} On the other hand, the present analysis has indicated that the

⁶⁸ J. Callaway, Phys. Rev. **112**, 1061 (1958); J. Callaway, R. D. Woods, and V. Sironian, *ibid.* **107**, 934 (1957).

⁶⁹ J. Callaway and E. L. Hasse, Phys. Rev. **108**, 217 (1957).

⁷⁰ H. T. Hall, L. Merrill, and J. D. Barnett, Science **146**, 1297 (1964).

⁷¹ J. D. Barnett, R. Bennion, and H. T. Hall, Science **141**, 534 (1963); Rev. Sci. Instr. **35**, 175 (1964).

⁷² A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. Letters **10**, 387 (1963).

⁷³ B. C. Deaton and D. E. Bowen, Appl. Phys. Letters **4**, 97 (1964).

⁷⁴ A. S. Balchan and H. G. Drickamer, Rev. Sci. Instr. **32**, 308 (1961).

⁷⁵ M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, 787 (1939).

⁷⁶ Y. C. Hsu, Phys. Rev. **83**, 975 (1951).

⁷⁷ D. B. McWhan, University of California, Lawrence Radiation Laboratory Report No. UCRL-9695, 1961, Chap. VII (unpublished).

⁷⁸ Yu. N. Ryabinin, K. P. Rodionov, and E. S. Alekseev, Zh. Tech. Fiz. **34**, 1913 (1964) [English transl.: Soviet Phys.—Tech. Phys. **9**, 1477 (1965)].

⁷⁹ C. P. Kempter, Phys. Status Solidi **8**, 161 (1965).

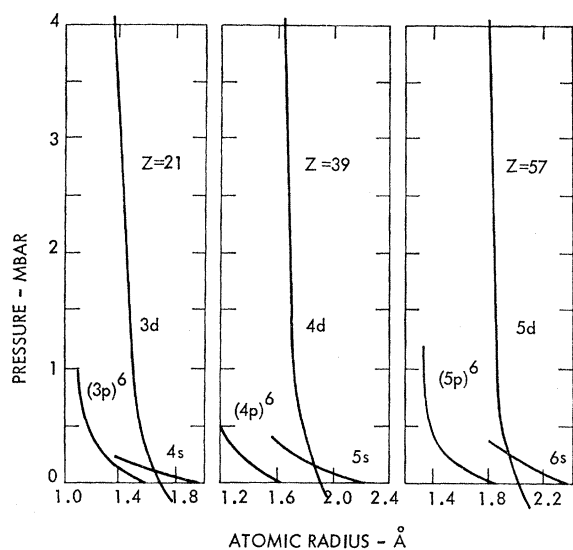


FIG. 5. Contribution to the pressure from various orbitals as functions of atomic radius. Comparisons are made at the atomic numbers indicated.

compressibilities of metals at high pressures are more properly considered to fall into groups. Both the alkali metals and alkaline-earth metals have very comparable compressibilities at high pressures, though the former exhibit significantly higher specific volumes and compressibilities at low pressure. Metals from columns IIIB (Sc, Y), IVB (Ti, Zr, Hf), VB (V, Nb, Ta), and VIB (Cr, Mo, W) of the periodic table also show comparable compressibilities at high pressure, though their compressibilities are much less than the compressibilities for the alkali metals and alkaline-earth metals. Again, compressibilities at low pressures are not as much alike for the IIIB, IVB, VB, and VIB metals as at high pressures. Presumably, the difference in compressibility between the two groups of metals is due to the presence of d -electron bonding in the IIIB, IVB, VB, and VIB metals, whereas bonding in the alkali metals and alkaline-earth metals remains dominated by s electrons at all pressures.

From the present analysis, it is possible to construct approximate universal compression curves for these various groups of metals. These curves relate metallic radius and pressure. The curve for s bonding applies to the alkali metals and alkaline-earth metals, while the curve for d bonding should apply to metals with less than half-filled d bands. For each period of the periodic table, the curves must be constructed for the same value of Z . The appropriate radii may be obtained by correcting the experimental metallic radii for their variation with Z through the use of the Z dependence $R_{ni}(Z)$ obtained from the Hartree-Fock solutions. For most shells, $R_{ni}(Z)$ is roughly proportional to Z^{-m} , where the value of m is of the order 2.2 for the $3d4s4p$ period, 3.3 for the $4d5s5p$ period, 3.0 to 4.5 for the $5d6s6p$ period outside the rare-earth region, and 0.3 for the rare-earth period. In the d -bonded metals, there is also a contribution to bonding from the s electrons and

from the closed p^6 shell, the latter contributing mainly to the repulsive potential. The p^6 cores make a similar contribution to bonding in the s -bonded metals. These various pressure contributions may be roughly separated by the subtraction of one curve of pressure versus metallic radius from another at a particular value of the radius. The results are shown in Fig. 5. The most striking feature of this figure is the fact that the pressure contribution from the $(n-1)$ d electrons is an order of magnitude more sensitive to variation in atomic radius than is the ns -electron contribution, as has been noted earlier. Furthermore, while at high pressure d -electron repulsion dominates the equation of state and makes the material incompressible, at low pressures d -electron bonding reduces the equilibrium interatomic spacing over that characterizing s bonding.

If one assumes an effective pair potential $\phi(R)$ as a function of interatomic spacing or metallic radius R and a total internal energy $U = N\phi(R)$, then the pressure at 0°K is given by the relation

$$P = \left(\frac{d(N\phi)}{dR} \right) \left(\frac{dV}{dR} \right)^{-1} = \left(\frac{d(N\phi)}{dR} \right) / 4\pi R^2 N_0. \quad (4)$$

N is the number of interacting pairs and N_0 is the number of atoms. The internal energy per atom $N\phi(R)/N_0$ may then be obtained from the experimental pressure curves by the integration

$$N(\phi - \phi_0)/N_0 = 4\pi \int_{R_0}^R R^2 P(R) dR. \quad (5)$$

Figure 6 shows this function as obtained from the integration of the pressure curves in Fig. 5. Note that the separation of the various contributions to the pressure and hence to the interaction potential ignores cross interactions between different shells and is thus rather artificial. Nevertheless, the qualitative conclusion is probably valid, namely, the conclusion that the contribution of the d electrons to the atomic interaction potential produces a very narrow minimum as a function of interatomic spacing. This minimum lies somewhat inside the minimum resulting from the s -electron contribution as one should expect from the normal radii of these shells.

Though the normal interatomic spacings for the trivalent rare earths are in good agreement with the spacings expected for d bonding, the observation of large compressions would indicate that there is no significant d -electron contribution to bonding under compression. Hence, the $5d$ electron must be transferred to the $4f$ shell at a rather modest compression, since only in this way could the metal become characterized by s -only bonding. Of course, the metal would then be divalent. Such a transition could easily be a gradual one, though one of the first-order polymorphic transitions observed at low pressures may be associated with this electronic transition. The filling of the f shell under

pressure has been predicted by calculations.^{80,81} This behavior of the rare-earth metals is in contrast to the behavior of the actinide metals, where there is apparently no population of the $5f$ levels for the metals preceding americium. There, bonding appears to be dominated by the $6d$ band.

The metals scandium and yttrium are similar to the rare-earth metals in many of their properties and lie in the same column of the periodic table as lanthanum. However, under shock compression they show the low compressibility characteristic of d -bonded metals, indicating that they retain their one d electron at all pressures. This observation tends to support the conclusion that the large compressibility of the trivalent rare-earth metals is due to the loss of their d electron through a $5d \rightarrow 4f$ transition. Scandium and yttrium, of course, do not have the unfilled f shell available to accept their d electron, and hence, cannot exhibit such a transition.

Because of the incompressible nature of the d shells, core interactions should never be important for the d -bonded metals at experimental pressures. It appears that at least a fivefold volume compression would be needed before core interactions are observable, in agreement with the calculation mentioned earlier.⁵⁴ This would require an order-of-magnitude increase in available pressures. For the much more compressible s -bonded metals, core interactions should produce a significant contribution to the equation of state at a fourfold volume compression, only somewhat beyond the present threefold experimental compression.

The rare-earth metals appear to offer the first examples of metals where core interactions may have been observed to make an important contribution to the equation of state. The metallic radii at which this should occur are essentially the same for the alkali metals and alkaline-earth metals and for the rare-earth metals, once the appropriate scaling with Z is made. Furthermore, the equation of state of all of these metals at high pressure is apparently dominated by the same s -electron interactions. At zero pressure, however, the rare-earth interatomic spacings are smaller than the interatomic spacings for the alkali metals and alkaline-earth metals, due to the zero-pressure d bonding in the rare-earth metals. Thus, a smaller compression is needed to compress the rare-earth metals to the radii where core interactions should become noticeable. At one-and-a-half to twofold volume compression, the experimental Hugoniot for a number of rare-earth metals show a marked stiffening, and from Fig. 5 or Fig. 2, one may note that it is at just these compressions that a significant core contribution to the pressure should be expected. On the other hand, it has been suggested⁸²

⁸⁰ B. Sussholz, University of California, Lawrence Radiation Laboratory Report No. UCRL-4699, 1956 (unpublished).

⁸¹ S. V. Izmailov and G. A. Shul'man, Zh. Tech. Fiz. **35**, 1889 (1965); **36**, 405 (1966) [English transl.: Soviet Phys.—Tech. Phys. **10**, 1455 (1966); **11**, 299 (1966)].

⁸² L. V. Al'tshuler, A. A. Bakanova and I. P. Dudoladov, JETP Pis'ma v Redaktsiyu **3**, 483 (1966) [English transl.: JETP Letters **3**, 315 (1966)].

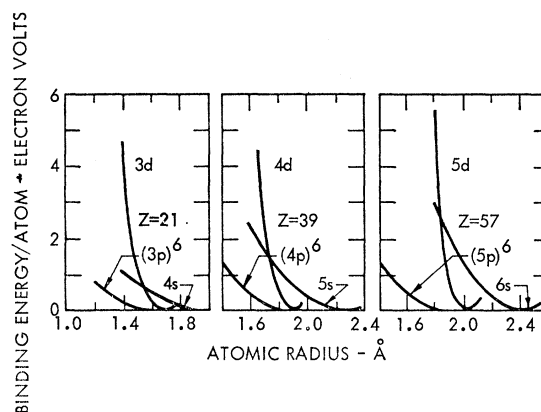


FIG. 6. Contribution to the binding energy per atom from various orbitals as functions of atomic radius. The zero of energy has arbitrarily been taken at the minimum of each interaction energy curve. Comparisons are made at the atomic numbers indicated.

that this observed stiffening of the rare-earth Hugoniot is due to a $4f$ - to $5d$ -electron transfer. However, the present analysis indicates that at high pressure there is never a large d -electron population because of the small radii and large compressions observed.

The present analysis has been restricted primarily to the alkali metals and alkaline-earth metals, to the metals from columns IIIB, IVB, VB, and VIB of the periodic table, to the rare-earth metals, and to the early actinide metals. This restriction has been made, because for these metals, the electronic configuration at any pressure may be determined from the fitting of Hartree-Fock free-atom radii to the experimental atomic radii. For the succeeding d -bonded metals (columns VII B and VIII), the occupation of the upper, antibonding states in the d band⁸⁰ apparently destroys the proportionality between the Hartree-Fock free-atom radii and the atomic radii in the solids. However, the compressibility of these metals is quite similar to that for the preceding d -bonded metals. Thus, it seems reasonable to conclude that for these metals, too, the electronic configuration remains stable under pressure and that the relative compressibility of the metals is associated with the d -electron contribution to the binding.

A number of authors have proposed analytic equations of state or analytic forms for the interatomic interaction potential.^{26,79,83-94} These forms may then be

⁸³ H. Fröhlich, Proc. Roy. Soc. (London) **A158**, 97 (1937).

⁸⁴ J. Bardeen, J. Chem. Phys. **6**, 372 (1938).

⁸⁵ F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951).

⁸⁶ F. Birch, J. Geophys. Res. **57**, 227 (1952).

⁸⁷ J. J. Gilvarry, Phys. Rev. **102**, 331 (1956); J. Appl. Phys. **28**, 1253 (1957).

⁸⁸ B. I. Davydov, Izv. Acad. Nauk SSSR, Ser. Geofiz., **12**, 1411 (1956).

⁸⁹ J. S. Koehler and G. E. Duvall, Bull. Am. Phys. Soc. **6**, 132 (1961).

⁹⁰ M. A. Cook and L. A. Rogers, J. Appl. Phys. **34**, 2330 (1963).

⁹¹ N. N. Kalitkin and I. A. Govorukhina, Fiz. Tverd. Tela **7**, 355 (1965) [English transl.: Soviet Phys.—Solid State **7**, 287 (1965)].

⁹² R. H. Stokes, J. Phys. Chem. Solids **27**, 487 (1966).

⁹³ Y. K. Huang, J. Chem. Phys. **45**, 1979 (1966).

⁹⁴ J. R. MacDonald, Rev. Mod. Phys. **38**, 669 (1966).

fitted to low-pressure data and extrapolated to higher pressures, either to compare with experimental data or to obtain equation-of-state information beyond the experimental range. While such calculations may or may not be plagued by the usual uncertainties associated with extrapolation procedures, the present analysis indicates that they will certainly be incorrect at compressions greater than those where core interactions become important. At these critical compressions, given in the previous paragraphs, the nature of the repulsive interaction will undergo a qualitative change from repulsion between open shells to repulsion between closed shells. Analyses based on the assumption of a form for the repulsive interaction inappropriate to the region of compression being considered can only be misleading.

For the Thomas-Fermi model to be valid, the electronic shell structure must be unimportant in determining the equation of state. It seems unlikely that this can be true at compressions where the importance of the core interaction is changing relative to the valence-electron interaction. Thus, any agreement^{95,96} between the results of Thomas-Fermi-like equation-of-state calculations and experimentally observed equation-of-state data below a five or tenfold volume compression must be regarded as fortuitous, except possibly where closed-shell interactions dominate the equation of state at all pressures. Equations of state⁹¹ based on interpolation between the range of validity of the Thomas-Fermi model and the range of experimental data at low pressures are probably somewhat more reliable, but it must still be remembered, that because of the absence of data in the intermediate pressure region, such equations of state must ignore the sequential overlap of the inner electron shells. The core interaction treated here is the first such overlap.

Note added in proof. In a recent publication, A. A. Bakanov and I. P. Dudoladov, *JETP Pis'ma v Redaktsiyu* **5**, 322 (1967) [English transl.: *Soviet Phys.—JETP Letters* **5**, 265 (1967)], a stiffening at high pressure is exhibited in the Hugoniot for strontium and calcium. The authors suggest that this stiffening is the result of the promotion of an *s* electron to a *d* level. This is similar to the mechanism that they proposed⁸² to account for a stiffening in the Hugoniot for the rare-earth metals. Thus, it seems worthwhile to re-emphasize the conclusion reached in the preceding paragraphs from the study of the systematic behavior of metals under pressure; namely, that if these metals were *d*-electron bonded, pressures at the high densities attained experimentally would be expected to be several times larger than those observed. Thus, in either the rare-earth or the alkaline-earth metals, the *d*-electron

component in the conduction band must be small at all pressures. In the present paper, the stiffening of the rare-earth Hugoniot was attributed to a core interaction. Such an interaction is predicted to occur at just the densities where the stiffening actually is observed. On the other hand, such a core interaction should *not* be expected for strontium and calcium at the densities where *their* Hugoniot stiffen. Some other interaction appears to be needed to account for the experimental results on strontium and calcium. Comparison with the more extensive data of Larson and Wackerle [Refs. 115 and 116 in the Appendix to this paper] reveals that the results on these metals are complicated by the presence of first-order phase transitions. The Soviet work is not complete enough to properly delineate these transitions. It is suggested that first-order polymorphic transitions are the source of the observed breaks in the Hugoniot for strontium and calcium.

6. CONCLUSIONS

The alkali metals and alkaline-earth metals remain essentially *s*-electron bonded at all experimental pressures, the interactions of these electrons determining the equation of state. For metals with less than half-filled *d*-electron bands, and probably for metals with more than half-filled *d*-electron bands as well, the equation of state is determined almost completely by the *d* electrons. These electrons contribute a very narrow and deep minimum to the effective interatomic potential, and the *d*-bonded metals are much less compressible than the *s*-bonded metals. The high compressibility of the normally trivalent rare-earth metals indicates that under compression only *s* bonding is important, and hence, that the metals become divalent through a $5d \rightarrow 4f$ electronic transition. This behavior is in contrast to the behavior of metals from the first part of the actinide sequence, where there does not appear to be any significant *5f*-shell population at any pressure.

Interactions between the closed-electron-shell cores should not be important to the equation of state of the *s*-bonded or *d*-bonded metals with less than half-filled shells at volume compressions below four or fivefold, respectively. At less than a twofold volume compression, core effects are predicted and observed to become important to the equation of state of the rare-earth metals.

Agreement between experimental data and simple Thomas-Fermi-like equation-of-state calculations is probably fortuitous at compressions below five or tenfold, except possibly for materials where the interaction is between closed-shell atoms.

ACKNOWLEDGMENTS

I thank W. H. Gust, D. B. Larson, and J. Wackerle for the extensive use of their unpublished data. This work has profited from conversations with E. Teller,

⁹⁵ R. L. Rosenberg and B. J. Alder, in *Metallurgy at High Pressures and High Temperatures*, edited by K. A. Gschneider, (Gordon and Breach Science Publishers, Inc., New York, 1964), p. 302.

⁹⁶ W. G. McMillan, *Phys. Rev.* **111**, 479 (1958).

R. E. Duff, R. N. Keeler, D. B. Larson, R. Grover, and M. Ross.

APPENDIX

Equation-of-State Data

Table V lists equation-of-state data for the elements as used in this work. The initial density ρ_0 is given in g/cm³, the pressure in Mbar, the molar volume,

$V=A/\rho$, in cm³/mole, and the atomic radius in the metal $R_m=(3/4\pi N_0)^{1/3}V^{1/3}$, in angstroms. All quantities are on the 0°K isotherms calculated from Hugoniot data. In tracking down shock work on the various materials, I have been assisted by a compendium of shock-wave data edited by M. van Thiel.⁹⁷ Much of the data are also referred to in the review articles on shock work mentioned earlier.¹⁻⁷

TABLE V. Summary of equation-of-state data.

Z	Initial density (g/cc) ρ_0	Molar volume (cc/mole) at specified pressure				Atomic radius (Å) at specified pressure				
		0	0.25 Mbar	1.0 Mbar	4.0 Mbar	0	0.25 Mbar	1.0 Mbar	4.0 Mbar	
Li	3	0.53	13.1	{6.4 6.9}	1.73	{1.37 1.40}
Be	4	1.85	4.9	4.2	1.25	1.19
B	5	2.34	4.6	1.22
C	6	{2.25 3.51}	{5.3 3.4}	{4.2 3.2}	{1.28 1.11}	{1.19 1.09}
N	7	1.14	12.3	1.7
O	8	1.57	10.2	1.6
F	9	1.5	12.6	1.7
{NaF	(10)	2.79	7.5	5.5	1.44	1.30
{Ne	10	1.55	13.0	1.73
{Na	11	0.97	24.0	{(10.7) (11.3)}	2.12	{(1.62) (1.65)}
Mg	12	1.74	14.0	9.8	6.8	...	1.75	1.57	1.39	...
Al	13	2.70	10.0	8.2	6.2	...	1.58	1.48	1.35	...
Si	14	2.42	11.6	1.66
P	15	{1.82 2.20}	{17.0 14.1}	{1.89 1.77}
S	16	2.07	15.5	1.83
Cl	17	2.2	16.1	1.8
{KCl	(18)	1.98	18.9	11.0	(7.5)	...	1.96	1.63	(1.44)	...
{Ar	18	1.75	22.3	11.4	2.07	1.65
{K	19	0.86	45.5	{(17.3) (14.1)}	2.62	{(1.90) (1.78)}
Ca	20	1.52	26.3	(10.4)	2.19	(1.60)
Sc	21	3.02	14.9	11.1	1.81	1.64
Ti	22	4.51	10.8	9.0	6.8	(4.4)	1.62	1.53	1.39	(1.20)
V	23	6.1	8.4	7.4	5.9	...	1.49	1.43	1.33	...
Cr	24	7.10	7.3	6.6	5.6	...	1.43	1.38	1.30	...
Mn	25	7.20	7.6	1.45
Fe	26	7.86	7.1	(6.0)	5.0	3.8	1.61	(1.34)	1.26	1.15
Co	27	8.82	6.7	6.1	5.0	...	1.39	1.34	1.26	...
Ni	28	8.86	6.6	6.0	5.0	3.9	1.38	1.34	1.26	1.16
Cu	29	8.90	7.1	6.2	5.2	3.8	1.41	1.35	1.27	1.15
Zn	30	7.14	9.2	7.3	5.8	4.1	1.54	1.43	1.32	1.18
Ga	31	5.90	11.8	1.67
Ge	32	5.32	13.6	8.3	1.75	1.49
As	33	5.73	13.1	1.73
Se	34	4.82	16.4	1.87
Br	35	4.2	19.0	2.0
{RbBr	(36)	3.35	24.7	13.6	2.14	1.75
{Kr	36	3.12	26.8	2.20
Rb	37	1.48	56.0	(20.2)	2.81	(2.00)
Sr	38	2.6	33.7	14.5	2.40	1.79
Y	39	4.51	21.4	14.4	2.04	1.79
Zr	40	6.49	14.0	11.4	8.4	...	1.77	1.66	1.50	...
Cb,Nb	41	8.60	10.8	9.5	7.8	...	1.63	1.56	1.46	...
Mo	42	10.20	9.4	8.7	7.3	5.6	1.55	1.51	1.43	1.31
Tc	43
Ru	44	12.2	8.3	1.49
Rh	45	12.42	8.3	7.6	(6.6)	...	1.49	1.44	(1.38)	...
Pd	46	11.95	9.0	8.0	6.8	...	1.53	1.47	1.39	...
Ag	47	10.49	10.3	8.7	7.2	...	1.60	1.51	1.42	...
Cd	48	8.64	13.0	10.1	8.0	5.7	1.73	1.59	1.47	1.31
In	49	7.27	15.9	12.0	8.9	...	1.85	1.68	1.52	...
Sn	50	7.28	16.4	12.4	9.5	6.7	1.87	1.70	1.56	1.39
Sb	51	6.68	18.3	12.6	1.94	1.71
Te	52	6.25	20.5	2.01
I	53	4.88	26.1	14.0	2.18	1.77
{CsI	(54)	4.51	28.9	17.2	(11.8)	...	2.26	1.90	(1.67)	...
{Xe	54	3.59	35.5	18.3	2.42	1.94

TABLE V. (continued)

Z	Initial density (g/cc) ρ_0	Molar volume (cc/mole) at specified pressure				Atomic radius (\AA) at specified pressure				
		0	0.25 Mbar	1.0 Mbar	4.0 Mbar	0	0.25 Mbar	1.0 Mbar	4.0 Mbar	
Cs	55	1.83	73.0	(24)	3.07	2.12
Ba	56	3.5	39.3	(20.0)	2.50	(2.00)
La	57	6.15	22.6	14.4	(9.6)	...	2.08	1.79	(1.56)	...
Ce	58	6.77	20.7	(11.4)	2.01	(1.65)
Pr	59	6.77	20.6	12.5	(8.3)	...	2.01	1.71	(1.49)	...
Nd	60	7.01	20.5	12.7	(8.5)	...	2.01	1.71	(1.50)	...
Pm	61
Sm	62	7.54	19.9	13.2	8.3	...	1.99	1.74	1.48	...
Eu	63	5.17	29.4	12.3	2.27	1.69
Gd	64	7.87	19.9	13.4	(8.5)	...	1.99	1.75	(1.50)	...
Tb	65	8.25	19.3	1.97
Dy	66	8.56	18.9	12.9	8.1	...	1.96	1.72	1.47	...
Ho	67	8.80	18.8	1.95
Er	68	9.06	18.5	13.2	8.4	...	1.94	1.74	1.49	...
Tm	69	9.32	18.1	1.93
Yb	70	6.96	24.9	12.2	2.15	1.69
Lu	71	9.85	17.8	1.92
Hf	72	13.3	13.4	11.6	1.75	1.66
Ta	73	16.6	10.9	9.7	8.2	5.9	1.63	1.57	1.48	1.33
W	74	19.17	9.6	8.9	7.8	(6.0)	1.56	1.52	1.46	1.34
Re	75	20.53	9.0	1.53
Os	76	22.48	8.4	1.49
Ir	77	22.42	8.6	1.51
Pt	78	21.45	9.1	8.4	7.4	...	1.53	1.49	1.43	...
Au	79	19.24	10.2	9.1	7.7	...	1.59	1.53	1.45	...
Hg	80	13.53-L	14.9-L	11.1-L	(1.81)	(1.64)
Tl	81	11.84	17.2	12.8	9.7	...	1.90	1.72	1.57	...
Pb	82	11.34	18.2	13.8	10.4	7.5	1.93	1.76	1.60	1.44
Bi	83	9.80	21.3	15.1	11.4	...	2.04	1.82	1.67	...
Po	84	9.32	22.5	2.08
At	85
{FrAt	(86)
Rn	86	(4)	(56)	(2.8)
Fr	87
Ra	88	(5)	(45)	(2.6)
Ac	89	10.0	22.7	2.08
Th	90	11.7	19.9	15.1	10.9	...	1.99	1.82	1.63	...
Pa	91	15.4	15.0	1.81
U	92	18.9	12.6	10.8	8.9	6.7	1.71	1.63	1.52	1.39
Np	93	20.4	11.7	1.67
Pu	94	19.8	12.2	1.69
Am	95	13.6	17.8	1.92

Notes on Equation-of-State Data

V, Cr, Co, Au, Tl: 0.25 Mbar, Ref. 98; 1 Mbar, Ref. 99.

Zr, Cb, Pd, In, Pt: 0.25 Mbar, Ref. 98; 1 Mbar, Ref. 100. Isotherms calculated.

Rh: 0.25 Mbar, Ref. 98. Isotherm extrapolated to 1 Mbar.

Th: 0.25 Mbar and 1 Mbar, Ref. 99.

Ag: 0.25 Mbar, Ref. 98; 1 Mbar, Refs. 99, 101.

Ti, Mo: 0.25 Mbar, Ref. 98; 1 Mbar, Refs. 99, 102; 4 Mbar, Ref. 102.

Ta: 0.25 Mbar, Ref. 98; 4 Mbar, Ref. 102.

Fe: 0.25 Mbar, Ref. 98; 1 Mbar, Refs. 103, 104; 4 Mbar, Ref. 104.

Ni: 0.25 Mbar, Ref. 98; 1 Mbar, Refs. 99, 104, 105; 4 Mbar, Ref. 104.

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Cu:	0.25 Mbar, Ref. 98; 1 Mbar, Refs. 99, 104, 105, 106; 4 Mbar, Ref. 104.		comparison of offset between isotherm and Hugoniot for Rb.
Zn, Cd, Sn:	0.25 Mbar, Ref. 98; 1 Mbar, Refs. 99, 104; 4 Mbar, Ref. 104.	Sr, Ba:	0.25 Mbar, Ref. 115. Isotherm calculated using extrapolation of high-pressure Hugoniot to low pressures.
W:	0.25 Mbar, Ref. 99; 1 Mbar, Refs. 99, 107. Extrapolated isotherm to 4 Mbar.	Ca:	0.25 Mbar, Refs. 115, 116. Isotherm calculated using extrapolation of high-pressure Hugoniot to low pressures.
Pb:	0.25 Mbar, Ref. 98; 1 Mbar, Refs. 99, 104, 105, 106; 4 Mbar, Ref. 104.	Sc, Y:	0.25 Mbar, Ref. 117. Isotherms calculated, preliminary data.
U:	0.25 and 1 Mbar, Ref. 108. Isotherm calculated.	La, Sm, Dy:	0.25 and 1 Mbar, Refs. 117, 118. Isotherms calculated.
Sb:	0.25 Mbar, Ref. 99. Isotherm calculated using extrapolation of high-pressure Hugoniot to low pressures.	Ce:	0.25 Mbar, Refs. 117, 118. Isotherm calculated.
Bi:	0.25 and 1 Mbar, Ref. 99. Isotherm calculated using extrapolation of high-pressure Hugoniot to low pressures.	Pr, Nd, Gd:	0.25 and 1 Mbar, Ref. 117. Isotherms calculated.
Hg:	0.25 Mbar, Ref. 109. Isotherm calculated.	Eu, Yb:	0.25 Mbar, Ref. 117. Isotherm calculated.
Ge:	0.25 Mbar, Refs. 97, 110. Isotherm calculated using extrapolation of high-pressure Hugoniot to low pressures.	Er:	0.25 and 1 Mbar, Ref. 118. Isotherm calculated.
C:	0.25 Mbar, Refs. 110, 111, 112.	Hf:	0.25 Mbar, Ref. 117 (preliminary data). Isotherm calculated.
Be:	0.25 Mbar, Refs. 98, 100.	I:	0.25 Mbar, Refs. 97, 119. Isotherm calculated.
Mg:	0.25 Mbar, Refs. 98, 100, 108; 1 Mbar, Ref. 108. Isotherm calculated.	Ar:	0.25 Mbar, Ref. 120. See text.
Al:	0.25 Mbar, Refs. 98, 105, 106, 108; 1 Mbar, Refs. 105, 106, 108.	Xe:	0.25 Mbar, Ref. 121. See text.
Li, Na, K:	0.25 Mbar, Refs. 113, 114. The discrepancy is due partly to different methods of calculating the isotherms, and partly to different Hugoniot. See text.	NaF:	0.25 Mbar, Refs. 97, 122.
Rb:	0.25 Mbar, Ref. 113.	KCl:	0.25 Mbar, Refs. 122, 123, ¹²⁴ Isotherm calculated; 1 Mbar, Ref. 124. Isotherm calculated.
Cs:	0.25 Mbar, Ref. 113. Isotherm estimated from Hugoniot and	RbBr:	0.25 Mbar, Ref. 122.
		CsI:	0.25 Mbar, Refs. 122, 123, 125. Isotherm calculated; 1 Mbar, Ref. 125.

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