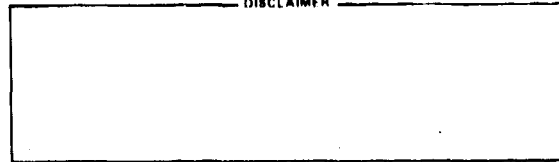$CONF - 810684 - -42$

LA-UR -81-2124

TITLE: THEORETICAL EQUATIONS OF STATE FOR METALS

MASTER

AUTHOR(S): Gerald I. Kerley

SUBMITTED TO: For proceedings of the 1981 APS Shock Wave Conference

---- DISCLAIMER ----

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663   Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

THEORETICAL EQUATIONS OF STATE FOR METALS

G. I. Kerley*
Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

Equation of state (EOS) calculations for xenon, iron, and
beryllium are described and shown to give good agreement with shock
wave experiments. The theory includes models for both solia and
fluid phases, calculation of the melting curve, and effects of
atomic shell structure on thermal electronic contributions to the
EOS.

DESCRIPTION OF THE MODELS

Two computer codes were used in our calculations. The PANDA
code [1] computes the pressure, internal energy, and Helmholtz free
energy, as functions of density and temperature, for both solid and
fluid phases; the melting line is located by matching the pressures
and Gibbs free energies of the two phases as a function of tempera-
ture. The INFERNO code of Liberman [2] computes the thermal elec-
tronic contributions to the EOS, which are input to PANDA.

The solid EOS consists of three terms. For example, the
pressure is given by

$$P_s(\rho,T) = P_c(\rho) + P_1(\rho,T) + P_e(\rho,T),\qquad(1)$$

where ρ and T are the density and temperature, respectively. P_c is
the zero Kelvin isotherm (cold curve), which we construct from band
theoretical calculations and experimental data. P_1, the lattice
vibrational term, is given by the Debye model. P_e is the thermal
electronic term from INFERNO, discussed below.

The fluid EOS consists of two terms. The pressure is written

$$P_\ell(\rho,T) = P_n(\rho,T) + P_e(\rho,T).\qquad(2)$$

P_n includes contributions from the ground electronic state and from
the motion of the nuclei. This term is computed from hard sphere
perturbation theory, using the CRIS model. [3] In this model, the
energy of a fluid atom in the cage formed by its neighbors is deter-
mined from the cold curve of the solid. Therefore, it is not neces-
sary to specify the interatomic potentials or any other parameters
in order to calculate the fluid EOS. Contributions from the elec-
tronic and nuclear degrees of freedom are strongly coupled; there-
fore, we do not separate P_n into a cold curve and a thermal term as
we do for the solid.

The INFERNO model of Liberman [2] is used to compute the thermal electronic contributions to the EOS for both solid and fluid phases. In this theory, the Dirac equation is solved to obtain wave functions and thermodynamic properties for an average atom, as a function of both density and temperature. An important feature of the theory is that it includes effects due to atomic shell structure, that are smeared out in simpler models such as Thomas-Fermi-Dirac (TFD) theory. [4]

XENON

Like all materials, xenon is expected to become metallic at high densities. Zero temperature band theoretical calculations of Ross and McMahan [5] predict the energy gap between the filled 5p band and the empty conduction band to close at a density of 12 g/cc. In shock wave experiments, where there is thermal electronic excitation, effects due to this insulator-metal transition can be observed at lower densities.

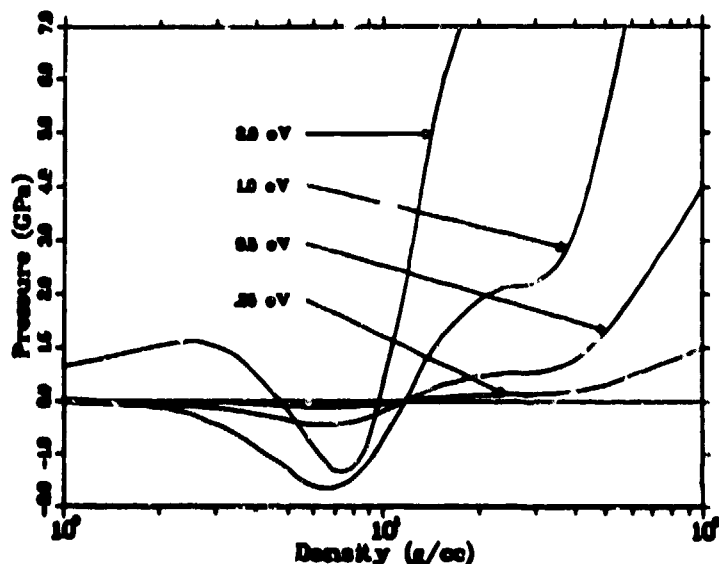The thermal electronic pressure calculated using the INFERNO model is shown in Fig. 1. At densities in the range 2-10 g/cc, narrowing of the band gap allows increased electronic excitation and also results in a negative contribution to the pressure. This result agrees with Ross's model [5] for the rare gases.

Fig. 1. Thermal electronic pressure for xenon, as a function of density, at several temperatures.

In this work, the cold curve was taken from the band calculations of Ross and McMahan, [5] shown as circles in Fig. 2. This result, together with the CRIS model and the INFERNO model, completely define the fluid EOS a priori. Our predictions of the Hugoniot are compared with experiment [6] in

Fig. 2. If no electronic excitation is allowed, the calculations deviate sharply from experiment at high pressures. When the TFD model is used to describe the electronic excitations, the results are better but still not satisfactory. Calculations using the INFERNO model are in excellent agreement with the experimental data. INFERNO predicts metallization to occur at about 10 g/cc, in fair agreement with the band theoretical calculations.
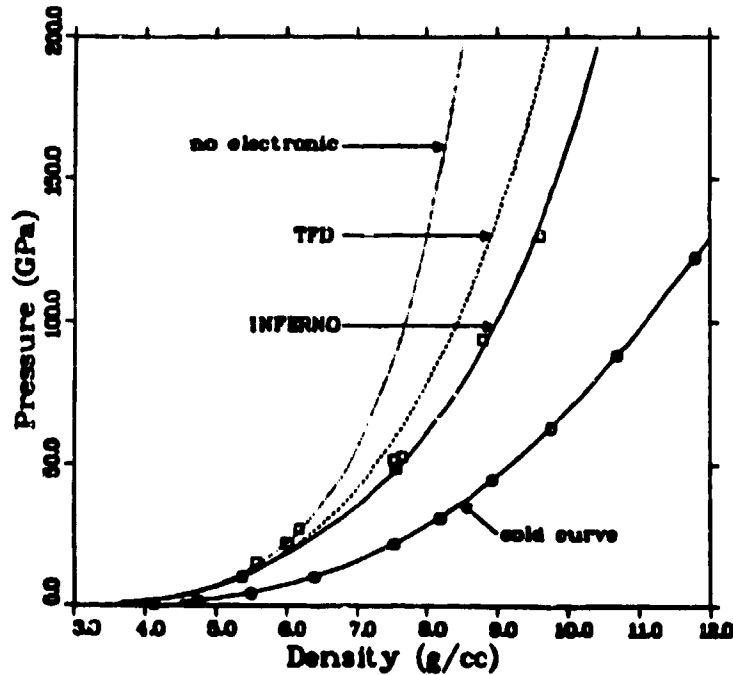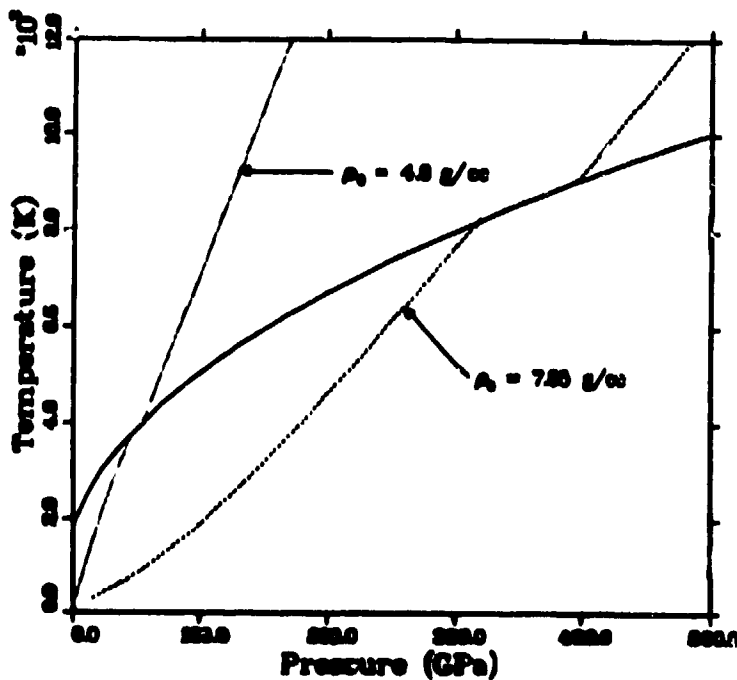
Fig. 2. Cold curve and Hugoniot for xenon.

Plot labels: no electronic, TFD, INFERNO, cold curve; axes Pressure (GPa) vs Density (g/cc).

Fig. 3. Iron melting curve and Hugoniots for two initial densities.

Plot labels: $\rho_o = 4.8$ g/cc, $\rho_o = 7.85$ g/cc; axes Temperature (K) vs Pressure (GPa).

IRON

Application of the theory to iron is complicated by the existence of several solid phases. In this work, we considered only the close packed ε-phase, which is stable at pressures above 13 GPa. The cold curve was taken from the static high pressure experimental data of Mao and Bell.

Our theoretical melting curve for iron is shown in Fig. 3. In this calculation, we forced agreement with the experimental melting point at zero pressure by subtracting an empirically-determined constant from the free energy of the fluid. (This correction was about 4% of the solid binding energy.) Calculated Hugoniots for two initial densities are also shown in Fig. 3. Alpha-phase iron, having a density of 7.85 g/cc, is predicted to begin melting at about 300 GPa, in fair agreement with the value of 250 GPa obtained by Brown and McQueen. Porous α-phase iron, having a density of 4.8 g/cc, is predicted to begin melting at 45 GPa.

Shock velocity vs. particle velocity curves for iron of various initial densities are shown in Fig. 4. Agreement between the theory and the experimental data [8-10] is very good for both solid and fluid phases over the entire range, which extends to 1000 GPa. More detail can be seen in Fig. 5, showing the shock data [8,10] for an initial density of 4.8 g/cc. In the calculated Hugoniot, the mixed phase region is shown by a dashed line. Agreement with the experimental data is excellent except at the lowest pressures, for which the shocked state is in the α-phase.
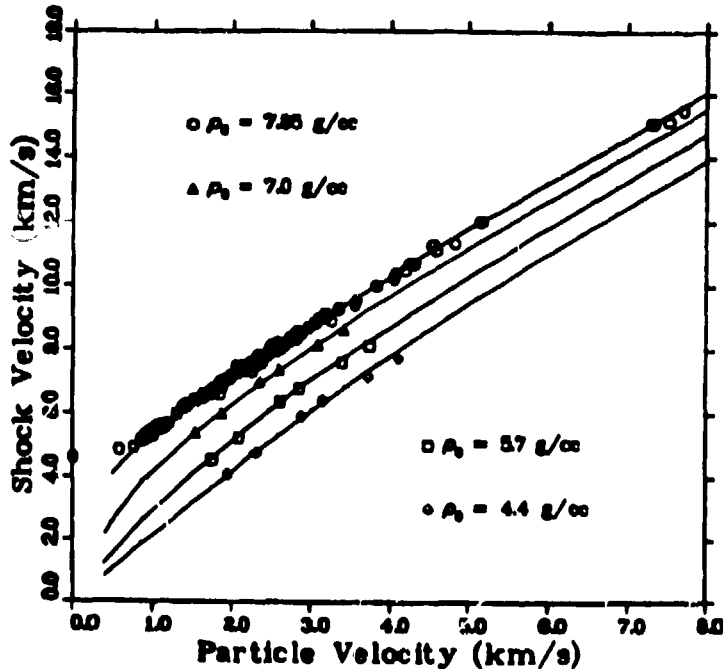

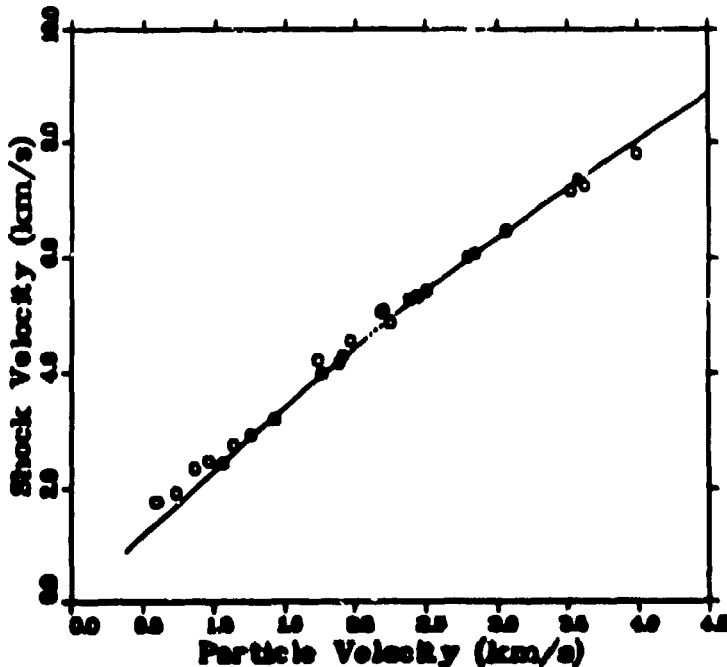Fig. 4. Shock velocity vs. particle velocity for iron at several initial densities.

Fig. 5. Hugoniot for porous iron having an initial density of 4.8 g/cc.

BERYLLIUM

The cold curve for beryllium was taken from the band theoretical calculations of Perrot,[11] shown as circles in Fig. 6. The solid EOS is fairly sensitive to the form of the Grüneisen parameter. We used the expression

$$\gamma = 1.3/\rho + 2/3 \qquad (3)$$

which agrees with both thermodynamic data and Neal's shock wave measurements[12] to within experimental error.
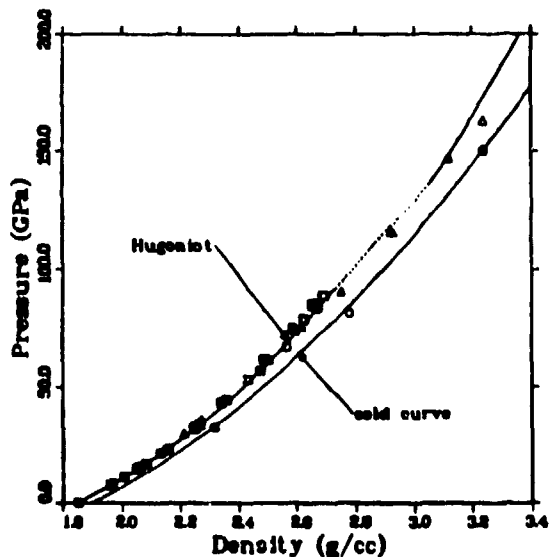
Fig. 6. Cold curve and Hugoniot for beryllium.

The calculated melting point at zero pressure is 1545 K, in good agreement with experiment. The theoretical melting curve has a small negative slope over the pressure range 10-160 GPa, and melting is predicted to begin at about 90 GPa, under shock loading.

The theoretical Hugoniot is compared with experiment [10,13] in Fig. 6. The mixed phase region is depicted by a dashed line. Our theory predicts a significant softening of the Hugoniot due to melting. These calculations are in very good agreement with the data of Isbell, et. al., [13] shown by triangles. New measurements in this high pressure region would be useful.

REFERENCES

1. G. I. Kerley, "Users Manual for PANDA: A Computer Code for Calculating Equations of State," Los Alamos National Laboratory report LA-8833-M (1981).
2. D. A. Liberman, Phys. Rev. B20, 4891 (1979).
3. G. I. Kerley, J. Chem. Phys. 73, 469 (1980); 73, 478 (1980).
4. R. D. Cowan and J. Ashkin, Phys. Rev. 10l, 144 (1957).
5. M. Ross and A. K. McMahan, Phys. Rev. B21, 1658 (1980).
6. W. Nellis, M. van Thiel, A. C. Mitchell, and M. Ross, "The Equation of State of D_2 and Xe in the Megabar Region," presented at the Eighth International Thermophysical Properties Conference, National Bureau of Standards, Wash. D.C., 1981.
7. H. K. Mao and P. M. Bell, J. Geophys. Res. 84, 4533 (1977).
8. J. M. Brown, and R. G. McQueen, J. Geophys. Res., to be published.
9. L. Y. Al'tshuler, N. N. Kalitkin, L. V. Kuz'mina, and B. S. Chekin, Sov. Phys. JETP 45, 167 (1977).
10. S. P. Marsh, LASL Shock Hugoniot Data (University of California, Berkeley, 1980).
11. F. Perrot, Phys. Rev. B21, 3167 (1980).
12. T. Neal, "Determination of the Grüneisen γ for Beryllium at 1.2 to 1.9 Times Standard Density," in High Pressure Science and Technology, Sixth AIRAPT Conference, edited by K. D. Timmerhaus and M. S. Barber (Plenum Press, NY, 1979) pg. 80.
13. W. M. Isbell, F. H. Shipman, and A. H. Jones, "Hugoniot Equation of State of Eleven Elements to Five Mbars," Materials Science Laboratory report MSL-68-13.