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THEORETICAL EQUATIONS OF STATE FOR METALS

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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 solid 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 temperature. The INFERNO code of Liberman [2] computes the thermal electronic contributions to the EOS, which are input to PANDA.

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

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

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_l, 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

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

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 determined from the cold curve of the solid. Therefore, it is not necessary to specify the interatomic potentials or any other parameters in order to calculate the fluid EOS. Contributions from the electronic and nuclear degrees of freedom are strongly coupled; therefore, we do not separate P_n into a cold curve and a thermal term as we do for the solid.

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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.

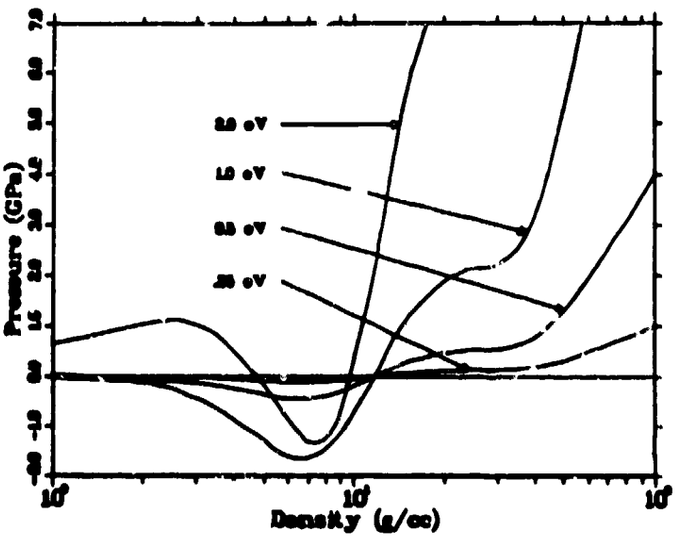

Fig. 1. Thermal electronic pressure for xenon, as a function of density, at several temperatures.

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 metallisation to occur at about 10 g/cc, in fair agreement with the band theoretical calculations.

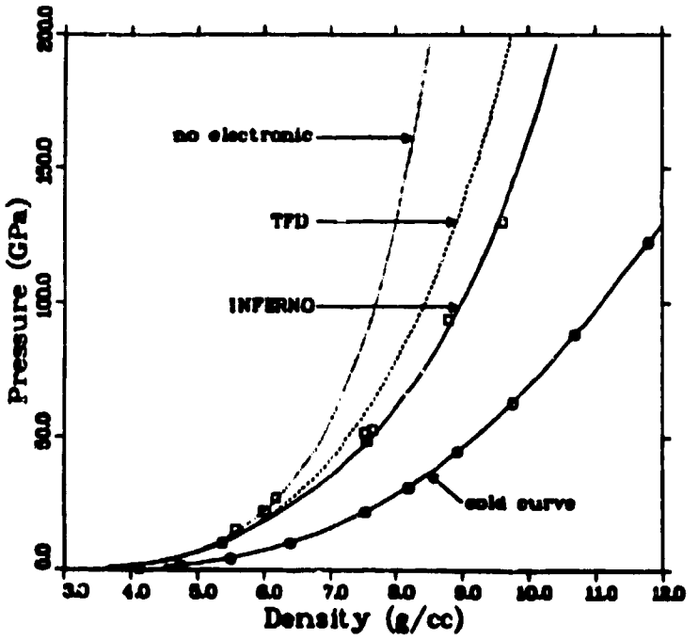

Fig. 2. Cold curve and Hugoniot for xenon.

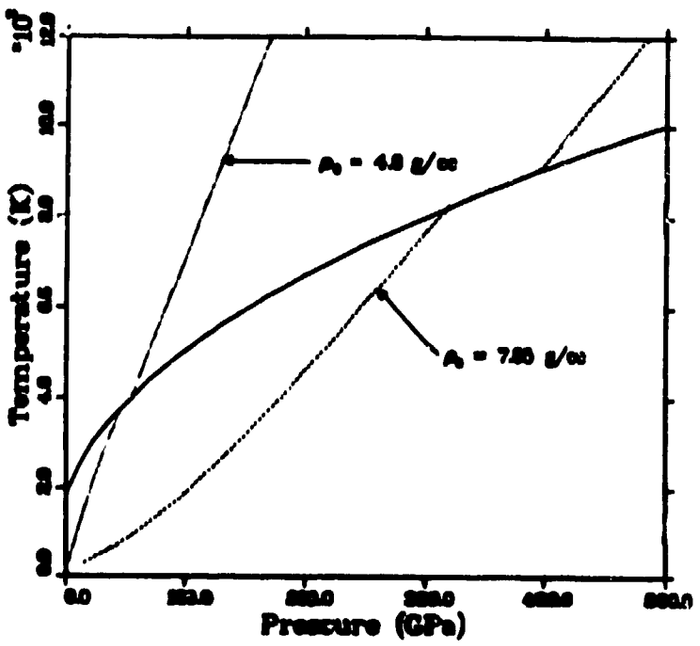

Fig. 3. Iron melting curve and Hugoniots for two initial densities.

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.[7]

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.[8] 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.

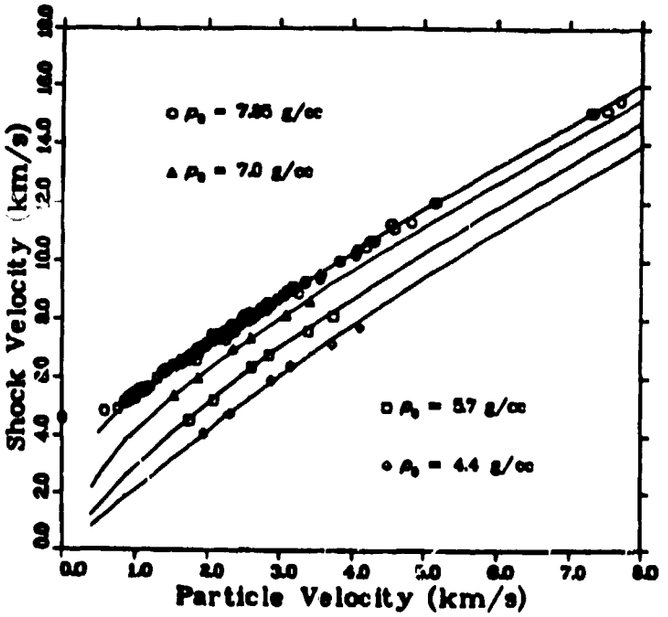

Fig. 4. Shock velocity vs. particle velocity for iron at several initial densities.

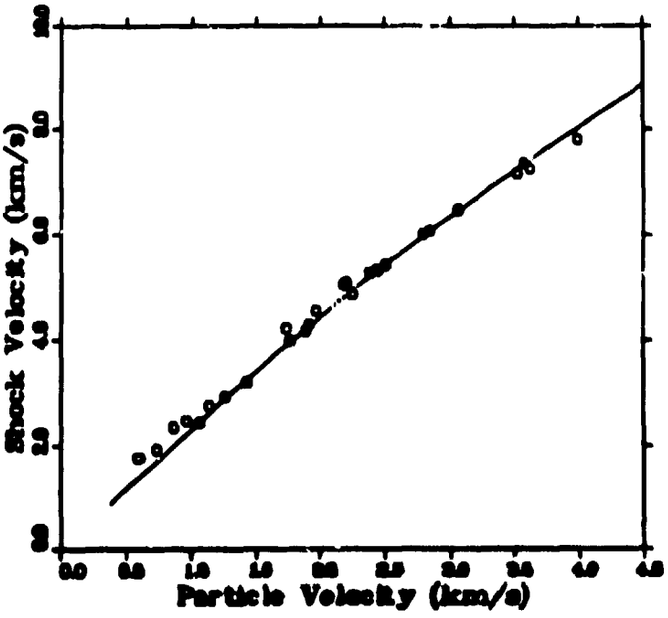

Fig. 5. Hugoniot for porous iron having an initial density of 4.8 g/cc.

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

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

which agrees with both thermodynamic data and Neal's shock wave measurements [12] to within experimental error.

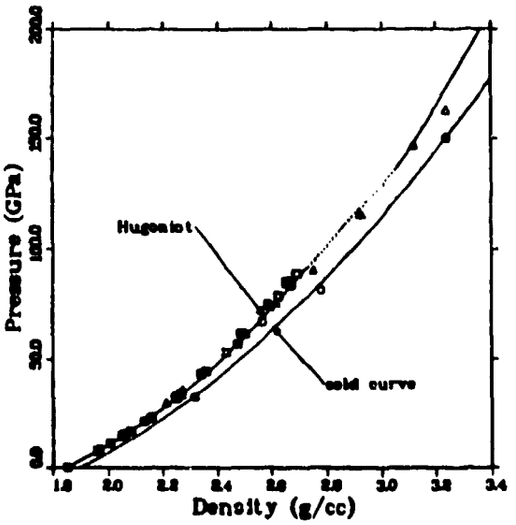

Fig. 6. Cold curve and Hugoniot for beryllium.

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.

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