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A NEW MULTIPHASE EQUATION OF STATE FOR IRON

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The PANDA code was used to develop an equation of state (EOS) for iron. Separate EOS tables were constructed for four solid phases and the fluid phase. The phase diagram and multiphase EOS table were then computed using the free energies. The results are in good agreement with thermophysical, static compression, phase boundary, and shock-wave measurements. Predicted pressures for the shock-induced ϵ - γ and γ -liquid transitions agree with those determined from sound speed measurements. The predicted melting temperatures fall in between two recent sets of experimental data which sharply disagree with one another.

INTRODUCTION

Iron and its alloys are very important materials, and there is a vast literature devoted to the study of their thermophysical properties [1]. Much of this work has been motivated by interest in models of the earth's core, which depend upon the EOS of iron at high temperatures and pressures [2]. Studies of armor penetration and high-velocity impacts are other applications for the iron EOS [3]. Finally, the complexities of the phase diagram and other intriguing properties of iron also make it a leading candidate for basic research studies.

This paper discusses an EOS model for iron that employs a more fundamental and extensive treatment of phase transitions than has been used in previous work. It is available in tabular form, covers a very wide range of densities (0-1000 g/cm³) and temperatures (0 - 1.2×10⁷K), and is suitable for use in many kinds of problems, including hydrodynamic code calculations. A more detailed discussion of this work is given in Ref. [3].

THEORETICAL MODEL

Multiphase EOS Model

The PANDA code [4] uses the following technique to construct a multiphase EOS. First, separate tables of thermodynamic properties are built for each of the solid and fluid phases, using free energy functions and thermodynamically consistent

formulas. The phase boundaries are then located using the free energies, and the separate EOS are combined into a single multiphase EOS table. The PANDA code has the capability to map out phase diagrams of arbitrary complexity.

Since the phase boundaries are not assumed in advance, but are obtained from the thermodynamic functions for the individual phases, special care must be taken with the models to achieve satisfactory results. Conversely, the method also helps to determine whether or not an expected phase diagram is consistent with reasonable assumptions about the properties of the individual phases.

Solid Phases

The Helmholtz free energy functions A for the α , γ , and ϵ phases were assumed to have the form

$$A(\rho, T) = E_c + A_l + A_m + A_e - \Delta E_b. \quad (1)$$

E_c , A_l , A_m , and A_e are contributions from the zero-Kelvin curve, lattice vibrations, magnetic excitations (α -phase only), and thermal electronic excitations, respectively. The constant ΔE_b (binding energy) gives the same energy zero for all three phases. Expressions for the pressure and internal energy follow from standard thermodynamic relations.

The zero-Kelvin curves were represented by the Birch-Murnaghan formula, smoothly joined to a high-pressure extrapolation formula [4] above ~100 GPa. Parameters for the α and ϵ phases were

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determined from static compression data and are well defined. Parameters for the γ -phase are less certain but were constrained by thermophysical data and the shock data for porous iron.

The contributions from lattice vibrations were represented using the Debye-Grüneisen model, with parameters chosen to fit heat capacity and thermal expansion data. A simple formula was used to represent the dependence of the Grüneisen function on density, which could not be inferred accurately from any experimental data.

Since the Curie temperature of α -iron is nearly independent of pressure, the magnetic term was taken as independent of density. We represented this term using Andrews' formula [5], with slightly different values for its two fit parameters.

The thermal electronic term is discussed below.

The EOS table for the high-T bcc region (δ -phase) was generated from the α -phase EOS by adding constants to the entropy and energy, chosen to match the γ - δ and δ -liquid boundaries.

Liquid Phases

The Helmholtz free energy for the fluid phase was assumed to have the form

$$A(\rho, T) = A_\phi + A_e - \Delta E_b. \quad (2)$$

A_ϕ includes the contributions from the interatomic forces and the thermal motions of the atoms, and A_e is the thermal electronic term, discussed below. The cohesive energy ΔE_b is subtracted to give the same energy zero as for the solid phases. The other thermodynamic quantities are computed from standard thermodynamic relations.

The term A_ϕ depends upon the potential energy ϕ of an atom in the field of its neighbors. It was calculated using the CRIS model [6], in which the free energy is expanded about the properties of a fluid of hard spheres having diameter σ , as follows:

$$A_\phi(\rho, T) = A_0(\rho, T, \sigma) + N\langle\phi\rangle_0 + \Delta A. \quad (3)$$

A_0 is the free energy for the hard sphere fluid, and $\langle\phi\rangle_0$, the first-order correction, is an average of ϕ over all configurations of the hard sphere fluid. ΔA

includes all corrections to the first two terms, and N is Avogadro's number.

In the CRIS model, the hard-sphere diameter is defined by a variational principle that minimizes $|\Delta A|$, and the potential energy function ϕ is computed from the approximate formula

$$\phi \approx (\rho/\rho_s) E_c(\rho_s). \quad (4)$$

Here ρ is the actual density of the fluid, and ρ_s is the solid density having the same nearest neighbor distance as that of each configuration in the average. When the function E_c for ϵ -iron is used, the model gives very good predictions of the liquid properties, including the structure factor and viscosity [6]. Small adjustments were made to certain parameters in the CRIS model to refine the predicted density and melting point [3].

Figure 1. Zero pressure density vs. temperature for iron

Thermal Electronic Contributions

The thermal electronic term A_e was found to be quite important at temperatures above ~ 500 K. It was computed by combining results from two theories. The INFERNO code [7], used for densities $\rho > 6$ g/cm³, agrees well with the experimental electronic specific heat of iron and has been shown to give good results for compressed matter [6]. The PANDA ionization equilibrium model [4] was used for $\rho < 1$ g/cm³, where INFERNO becomes cumbersome and less accurate. These two models were

averaged at intermediate densities. The data were combined to form a smooth table of the electronic entropy, and the other thermodynamic functions were numerically computed from the entropy [4].

The calculated density vs. temperature is compared to experimental data [8] [9] in Fig. 1. Calculations with and without the thermal electronic term show that it has a large effect on the density as well as on the energy (as expected from the large electronic coefficient of specific heat [3]). This result is due to the insulator-metal transition, which contributes to the pressure for $\rho \approx 4\text{--}10 \text{ g/cm}^3$.

SHOCK DATA AND PHASE TRANSITIONS

Figure 2 shows the calculated phase diagram and pressure-temperature Hugoniot loci for iron shocked from initial densities ranging from 3.4 to 7.85 g/cm^3 . The shock wave measurements sample the phase diagram over a wide range of temperatures and pressures. The calculated Hugoniots agree very well with experimental data [10] in the shock velocity-particle velocity plane, as shown in Fig. 3. Applications of the new EOS in calculations of other shock problems are discussed in Ref. [3].

The melting curve and the γ - ϵ phase boundary at high pressures are of considerable interest but are not yet well known, experimentally. Our calculated melting curve agrees with measurements up to 20 GPa [11][12]. At higher pressures, our predictions fall in between the two recent sets of measurements that are in stark disagreement [13][14].

We note that the model does not predict any ϵ - γ -liquid triple point, as has been assumed in other theoretical treatments; instead, the temperature on the ϵ - γ phase line reaches a maximum at a pressure of about 1×10^4 GPa. This result is due primarily to the fact that our zero-Kelvin curves for the ϵ - and γ -phases approach one another at high pressures.

Additional insight into the behavior of the melting and ϵ - γ phase boundaries can be obtained from the experiments of Brown and McQueen [15], who measured the rarefaction wave velocities for iron, shock compressed to pressures between 77 and 400 GPa. They detected two discontinuities that they interpret as due to the ϵ - γ transition (200 ± 2 GPa,) and melting (243 ± 2 GPa). The model correlates quite well

with those results, shown by arrows in Fig. 3.

The phase boundaries and EOS predicted by our model are in satisfactory agreement with the experimental data available, especially in view of presently unresolved uncertainties. However, the existence of other high-pressure phases, which we have not considered here, cannot be ruled out.

Figure 2. Hugoniots and phase boundaries for iron. Solid lines are Hugoniots, dotted lines are phase boundaries; circles [13], squares [14] are experimental melting curves.

Figure 3. Hugoniots for iron at various initial densities.

IMPLICATIONS FOR THE EARTH'S CORE

Geophysical data show that the Earth's core consists of an inner solid region (radius 1220 km) and an outer liquid region (radius 3500 km), both

of which are composed primarily of iron [2][16]. The pressure and wave velocity profiles as functions of depth are fairly well known, while the density profile, as determined from different models [16], has an uncertainty of ~4%. The composition and temperature cannot be determined directly.

Using our EOS, the temperature at the Earth's center can be estimated from the pressure (~365 GPa) and the density (13.1-13.6 g/cm³) obtained from different models [16]. Using the PREM model, the temperature at the Earth's core is found to be ~8000K, which is well above the melting point and inconsistent with the geophysical data (unless iron is alloyed with lighter elements). However, the CAL-8 Earth model gives a temperature of ~5600K, on or slightly below our calculated melting curve. Thus for CAL-8, our predicted conditions for melting coincide nicely with the existence of a solid-liquid transition in the Earth's core.

Figure 4. Sound speed vs. pressure, Earth's core conditions

Figure 4 compares the measured bulk sound velocity vs. pressure through the Earth's core (the geotherm) with our calculated results along both an adiabat and an isotherm. (The adiabat follows the melting curve over the entire range.) Both curves agree fairly well with the measurements, the isothermal calculation giving especially good results. (As in other models, the calculated densities are ~10% below the measurements for the outer core, suggesting the presence of lighter elements [2][16].) Our EOS may be a good starting point for

further analyses.

REFERENCES

- [1] T. J. Shankland, O. L. Anderson, and D. Young, "Ironworkers Convention I: Workshop on Physics of Iron," *J. Geophys. Res.* 95, 21,689-21,690 (1990), and subsequent papers from the workshop.
- [2] R. Jeanloz, "The Nature of the Earth's Core," *Annu. Rev. Earth Planet Sci.* 18, 357-386 (1990).
- [3] G. I. Kerley, "Multiphase Equation of State for Iron," Sandia National Laboratories report SAND93-0027, 1993.
- [4] G. I. Kerley, "User's Manual for PANDA II: A Computer Code for Calculating Equations of State," Sandia National Laboratories report SAND88-2291, 1991.
- [5] D. J. Andrews, "Equation of State of the Alpha and Epsilon Phases of Iron," *J. Phys. Chem. Solids* 34, 825 (1973).
- [6] G. I. Kerley, "A Model for the Calculation of Thermodynamic Properties of a Fluid Using Hard-Sphere Perturbation Theory and the Zero-Kelvin Isotherm of the Solid," in *Molecular Based Study of Fluids*, J. M. Haile and G. A. Mansoori (Eds.), Washington, DC: Am. Chem. Soc., 1983, pp 107-138.
- [7] D. A. Liberman, "Self-Consistent Field Model for Condensed Matter," *Phys. Rev. B* 20, 4981-4989 (1979).
- [8] Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, *Thermophysical Properties of Matter*, New York: IFI/Plenum, Vol. 12, pg. 2.
- [9] A. V. Grosse and A. D. Kershenbaum, "The Densities of Liquid Iron and Nickel and An Estimate of Their Critical Temperature," *J. Inorg. Nucl. Chem.* 25, 331-334 (1963).
- [10] See Ref. [3] for a complete list of references to the Hugoniot and phase transition data shown in Figs. 2 and 3.
- [11] H. M. Strong, R. E. Tuft, and E. E. Hanneman, "The Iron Fusion Curve and γ - δ -1 Triple Point," *Metall. Trans.* 4, 2657 (1973).
- [12] L.-G. Liu and W. A. Bassett, "The Melting of Iron up to 200 kbar," *J. Geophys. Res.* 80, 3777-3782 (1975).
- [13] R. Boehler, N. von Bagen, and A. Chopelas, "Melting, Thermal Expansion, and Phase Transitions of Iron at High Pressures," *J. Geophys. Res.* 95, 21,731-21,736 (1990).
- [14] Q. Williams, R. Jeanloz, J. Bass, B. Svendsen, and T. J. Ahrens, "The Melting Curve of Iron to 250 Gigapascals: A Constraint of the Temperature of the Earth's Core," *Science* 236, 181-182 (1987).
- [15] J. M. Brown and R. G. McQueen, "Phase Transitions, Grüneisen Parameter, and Elasticity for Shocked Iron Between 77 GPa and 400 GPa," *J. Geophys. Res.* 91, 7485-7494 (1986), and earlier references cited therein.
- [16] B. A. Bolt, *Inside the Earth*, San Francisco: W. H. Freeman and Company, 1982.

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