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EQUATION OF STATE OF THE ALPHA AND EPSILON PHASES OF IRON*

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Abstract—An empirical equation of state that is thermodynamically consistent is found for the alpha (body-centered-cubic) and epsilon (hexagonal-close-packed) phases of iron. It is fit to all available types of experimental data–calorimetric, thermal expansion, acoustic, static compression, and shock data. All thermodynamic identities are satisfied, since expressions for all observables are derived from a thermodynamic potential. No specific theoretical assumptions are made, but the Helmholtz potential is formulated in terms of a number of adjustable functions of single variables by applying some general considerations of lattice vibrations, conduction electrons, and ferromagnetic exchange interaction. The effective Gruneisen parameter depends on temperature as well as volume. Ultrasonic and shock data for the alpha phase are found to be consistent with X-ray determinations of compression based on the sodium chloride standard. The Slater and Dugdale–MacDonald relations are tested against the fit at low pressure and are found to be in error. At high pressure not enough different types of data exist to establish a unique fit without theoretical assumptions.

1. INTRODUCTION

THIS work was undertaken to find an equation of state to be used in a calculation reported elsewhere [1] of shock wave propagation with a phase transformation. A thermodynamically consistent equation of state based on all types of available experimental data was desired, for earlier work was lacking in these respects. The inversion of experimental data to find a thermodynamic potential turned out to be a large task in itself. We hope that the work has value, not only as an empirical fit for iron, but as a review of experimental data, as a test of consistency of different kinds of data, and as an indication of what theoretical predictions are required to establish the equation of state of iron uniquely.

Thermodynamic consistency is guaranteed by deriving all thermodynamic quantities from a Helmholtz potential. Contributions to the potential from lattice vibrations, conduction electrons, and magnetic exchange interactions are included. Expressions for these contributions are derived, initially, in terms of general functions of single variables. For the purpose of applying the equation of state, specific functional forms are then assumed, and data are fit by adjusting parameters occurring in these functional forms. The object of this work is restricted to determining a consistent empirical fit and not to draw conclusions about atomistic processes.

The phase diagram is shown in Fig. 1. Boundaries between the alpha (body centered-cubic), gamma (face-centered-cubic), and epsilon (hexagonal-close-packed) phases are taken from Bundy [2]. The melting curve is from Strong [3], and the Curie transition is from Leger *et al.* [4]. The projection of the Hugoniot onto the P–T plane is from the present work.

Many empirical equations of state have been formulated to fit limited classes of experimental data. The equation of state for-

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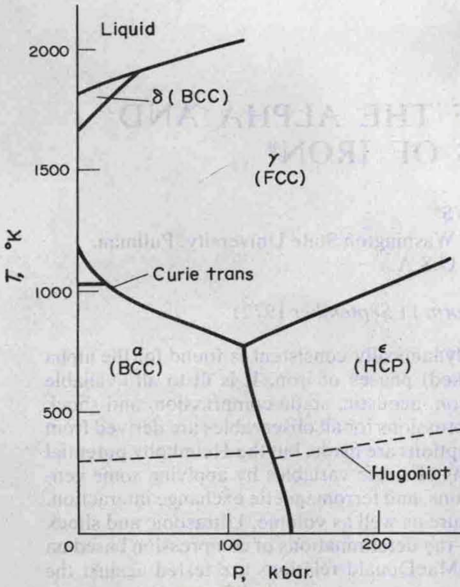

Fig. 1. Phase diagram of iron. The alpha, gamma and epsilon phase boundaries are from Bundy [2]. The melting curve is from Strong [3]. The Curie transition is from Leger [4].

mulations of Soviet shock wave researchers have been reviewed by Al'tshuler *et al.*[5]. Independent terms for the lattice and electrons were used. They assumed a Grüneisen equation of state for the lattice and determined the Grüneisen parameter from the Dugdale–MacDonald relation. Only shock data were used to determine the fit.

The Gibbs potential of iron has been considered by metallurgists investigating the phase stability of iron and iron rich alloys. The heat capacities of the α and γ phases have been extrapolated from the stability field of each phase into the other by separating the heat capacities into lattice, exchange, and electronic components [6, 7].

The difference between the Gibbs potential of α and γ iron was later formulated as a function of pressure as well as of temperature [8], and potential difference between the α and ϵ phases of pure iron was estimated by extrapolating from data on iron-ruthenium alloys [9–11].

The objective of the theoretical metallurgists was only to determine approximate values of the Gibbs potential, not to determine a function from which all other functions could be determined accurately.

In the present work a potential is formulated from which accurate pressure-volume isotherms may be derived. Also, care is taken with the anharmonic effect (Grüneisen parameter, or, equivalently, thermal expansivity), so that the difference between isotherms, isentropes, and Hugoniot curves are accurate.

2. SEMI-EMPIRICAL EQUATION OF STATE

Assume that the Hamiltonian for an assembly of iron atoms is the sum of independent terms for the lattice, the exchange interaction, and the conduction electrons,

$$H = H_1 + H_x + H_e. \tag{1}$$

This assumption of independent terms is not rigorously correct, for both the lattice potential and the exchange interaction are affected by the conduction electrons. Then, the assembly partition function is a product of independent factors

$$Q = Q_1 Q_x Q_e = \sum \exp(-H/kT) \tag{2}$$

where the summation is over all states, and k is Boltzmann's constant. The Helmholtz potential is a sum of independent terms,

$$A = A_1 + A_x + A_e = -kT \ln Q. \tag{3}$$

All extensive thermodynamic variables are defined for one mole. The number of atoms, N, is Avogadro's number.

The lattice Helmholtz potential is developed for a quasiharmonic model. It is assumed that the internal degrees of freedom of the lattice (the normal modes) are independent oscillators and that the temperature is low enough that the thermal motion of the oscillators is harmonic. However, the macroscopic compression of the solid may be large enough that the nonlinearity of the interatomic