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Thermodynamics of iron at extreme pressures and temperatures

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ABSTRACT

A thermodynamic database on all iron phases (BCC, FCC, HCP and melt) has been created using thermochemical and equations of state data from experiments and theory. The database permits the calculation of the phase diagram of iron to physical conditions of the Earth's core (pressure of 365 GPa and temperature of 6453 K). If the inner core were all iron, its upper temperature would be 6453 (500) K. The average heat capacity of a pure iron HCP inner core is calculated as 29.4 J/mol/K with an entropy of 92 J/mol/K and a gruneisen parameter of 1.81.

1. Introduction

Iron is recognized as the most suitable element to form the Earth's core; this is because of its high density and abundance in the solar chemistry. Thermodynamic database on iron phases at high pressures has been the subject of numerous publications with a general agreement on the data on solid phases. The melting of iron at high pressures still needs to be evaluated particularly in view of the recent experimental data [1,2] and the proposed BCC phase of iron at core conditions [3–9].

2. Previous work

There have been numerous studies on determining high pressure properties of iron. Melting of iron at pressures above several GPa has been accomplished by heating iron with a laser in a diamond-anvil cell [10,11], by shock wave methods [12–14] and by computations [15–17]. According to the static pressure data iron melts at temperatures that are several hundred degrees lower than those obtained in shock-wave experiments. Recently Ahrens and coworkers [14] reconciled the differences between the iron melting temperatures determined by the two techniques; the differences are not as large as previously thought. A significant development in this regard is the recent study of Ahrens et al. [14] who reported the sound speed data along the Hugoniot (the curve representing the velocity of a single shock wave and the pressure, temperature and total heat of that material, before and after the shock passes). They determined that the FCC phase melts at a temperature of 2800 K at a pressure of 70 GPa supporting the static pressure measurement of melting temperatures discussed below.

The disparity among the data from ab initio methods [15–17], shock-wave measurements [12–14], and static pressure progressively increases as we increase pressure to 200 GPa and beyond. The difference between the laser melting data and the shock-wave data of Brown and McQueen [18,19] close to 200 GPa is little over 500° (Fig. 1). This could be explained by a phase transition from HCP to another structure such as a non-magnetic BCC [4–9] or a FCC [20]. However such phase transitions have not been experimentally verified. Based on shock-compression experiments of iron, Brown and McQueen [18,19] found a solid–solid transition at 200 GPa and 4400 ± 300 K, and a solid–liquid transition at 240 GPa and about 5500 K.

The melting temperatures determined at ultra-high pressures [10,11] employed the method of visual observation of melting supplemented by the use of the power-temperature slope change. At extreme pressures, the detection of melting was difficult. The in situ X-ray data improves the detection [21] but may miss the beginning of melting. We cannot ignore the possibility of some reaction between the pressure medium and the sample [22]. The effect of stress on melting in DAC appears to be small to pressures as high as 60 GPa. The differences in the technique of iron melting detection and temperature measurements in DAC technique have led to significant uncertainties in measured temperatures but most data do lie in a band within a range of 250°. According to these data, melting of iron should occur below 4000 K at a pressure of 200 GPa. The DAC data, which extends to a pressure of 200 GPa does not permit a value greater than 4000 K for melting at that pressure. This turns out to be in stark contrast to the melting temperature measurements which combine laser heating with fast

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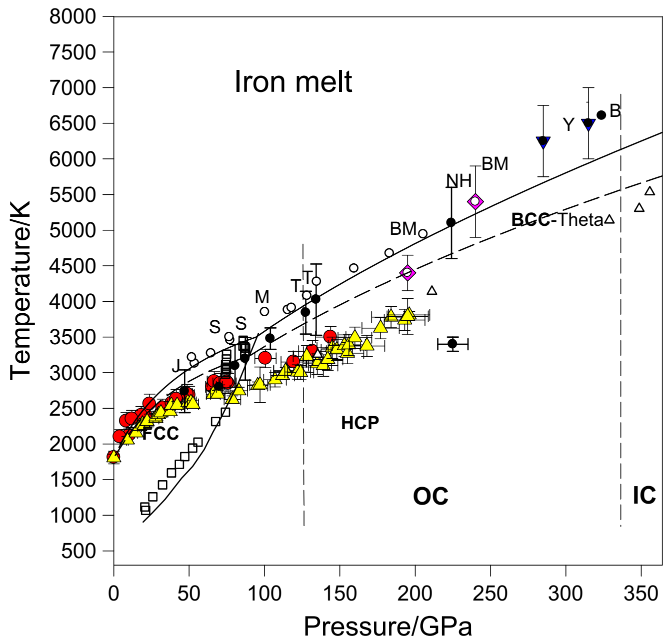

Fig. 1. The iron phase diagram as obtained by assessment of thermochemical data in the iron system. The stability field of the ab initio modeled high pressure BCC phase [4] is not included. We use the experimental data constraints as provided by [first author initial used] J [31], S [37], Ma [38], T [39], BM [19], NH [40], and Y [11] and computed data B [14]. The melting curve is very similar to the one obtained by Aitta [35] using calculations based on the Landau theory. The melting curves calculated by Belonosho et al. [14] and Alfe et al. [15] lie within 500° of the assessed melting data. The only experimental data point available for the high pressure BCC phase is from Dubrovinsky et al. [24] for a Fe–Ni alloy at 220 GPa. The open circles are melting data from Anzellini et al. [1] and open triangles are HCP iron from Tateno et al. [2]. The solid curve is our calculated curve with the assessed thermodynamic data. The FCC melting data from sources other than Anzellini et al. favor the dashed melting curve. The recent data [36] on the HCP–FCC phase transition was used to update the thermodynamic data on solid FCC or HCP phases.

X-ray measurement [1].

2.1. . BCC or HCP in the core

Theoretical studies suggest the stability of the BCC phase at core conditions [4–8] but the recent experimental work finds only HCP phase stable at the highest pressures [2]. The occurrence of the BCC-iron phase as found by Dubrovinsky et al. [5] at a pressure of 225 GPa and a temperature of 3400 K (Fig. 1) requires Ni. Anzellini et al. [1] reached the highest pressure of 200 GPa which leaves us only with the data of Tateno et al. [2] that reaches the core pressures. Dubrovinsky et al. [5] find that major part of the sample laser heated by Tateno et al. [2] was not affected by heating at reported temperatures and pressures and that the heated portion of the sample intensively reacted with carbon. Therefore it appears that we must keep the possibility that a BCC phase field may still exist.

2.2. Thermodynamic data assessment

We decided to determine the stability field of the iron phases including the melt but, for now, not of the possible BCC phase, employing the CALPHAD method [23]. This method relies on computing phase diagram by combining experimental phase equilibrium and thermochemical data. Brosh et al. [24–27] proposed a new formulation for incorporation of high pressure in the CALPHAD terminology and replaced the Birch–Murnaghan EOS by Mie–Grüneisen. We have used the quasi-harmonic model together with the Mie–Grüneisen EOS to calculate the Gibbs free energy as a function of pressure and temperature for iron. The equation of state is based on the available pressure–volume–temperature data on iron [28–31] and can be usefully extrapolated to extreme pressures. A great advantage of this formulation is that it can be used to calculate thermodynamic properties such as heat capacity and entropy to very high temperatures and pressures.

3. Thermodynamic data on iron

The thermodynamic assessment of the data in this study is done by using an optimizer with Baysian method [32] available in the FactSage package [33]. The optimizer can be used to generate a consistent set of Gibbs energy parameters from a given set of experimental data on the phase diagram using known Gibbs energy data for well established phases in a particular chemical system. Selected data as discussed below and shown in Fig. 1 on the solid–solid phase boundaries and the melting data were used to finalize the iron database [see Appendix 1].

There are numerous data available on solids [pressure–volume–temperature and phase transitions] which have been used by others [1,28–32] to model the solidus part of the phase diagram. We can add the experimental data on HCP–FCC phase transition by Tetsuya et al. [34] to the solid data base. The melt data has remained problematic and requires a selection of available experimental data.

The thermodynamic evaluation of the melting curve is based on the X-ray data of Shen et al. [21] and at increasing pressure, the data of Ma et al. [36] at 105 GPa, where all diffraction peaks disappear at $T=3510$ K. This is about 400 K higher than the previous laser heating data of Boehler [9] and Saxena et al. [10]. For data up to about 100 GPa, it would appear that we have quite a good agreement among experimental datasets whether from the shock-wave measurements or laser-heating determinations.

Here we use the following iron melting data: a) as discussed by Aitta [35], b) the experimental data of Anzellini et al. [1], c) the low temperature data [FCC melting], d) Shen et al. [21,28]. These data are shown in Fig. 1. Additionally, agreeing with Aitta [35] the following laser-heating data, some backed by X-ray diffraction data, were used [1,35,37,38]. The X-ray backed data on HCP melting are from [1] and also include the shockwave data [39,40] that lie between the Brown–McQueen points and the X-ray based data of Ma et al. [38]. These data fall quite systematically in line with the data of Anzellini et al. [1] and are included in the thermodynamic assessment. The sub-solidus HCP stability data of Tateno et al. [2] is also plotted in Fig.1. The latter study finds the HCP phase as stable to 5500 K at 365 GPa. The melting curves calculated by Belonoshko et al. [14] and Alfe et al. [15] lie close to our calculated curve in Fig.1.

4. Results and conclusions

Table 1 shows the thermodynamic data on all iron phases. With the equation of state parameters listed in Table 1, any iron property can be calculated. Table 2 contains the equations for thermal expansion and bulk modulus for the HCP phase and melt at 1 bar and a pressure of 365 GPa. The HCP properties are consistent with the calculations of Sha and Cohen [41]. A similar database was constructed by Tetsuya and Fei [42] but at that time they did not have the experimental data [1,2]. Interestingly they speculated on a possible BCC phase field. Fig. 1 shows the iron phase diagram over the pressure and temperature ranges possible in Earth. The solid line HCP melting curve relies on the combined data of Anzellini et al. [1] and the shock wave and computational data. The FCC melting is a bit problematic because the fast X-ray data [1]