

Pure Iron Compressed and Heated to Extreme Conditions

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The results of a first-principles study supported by the temperature-quenched laser-heated diamond anvil-cell experiments on the high-pressure high-temperature structural behavior of pure iron are reported. We show that in contrast to the widely accepted picture, the face-centered cubic (fcc) phase becomes as stable as the hexagonal-close-packed (hcp) phase at pressures around 300–360 GPa and temperatures around 5000–6000 K. Our temperature-quenched experiments indicate that the fcc phase of iron can exist in the pressure-temperature region above 160 GPa and 3700 K, respectively. This, in particular, means that the actual structure of the Earth's core may be a complex phase with a large number of stacking faults.

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Iron is one of the most abundant metals on Earth. It is a widely used technological material as well as a dominant component of the terrestrial planetary cores [1]. Its physical properties at high pressure and temperature have been extensively studied, leading to an extremely rich phase diagram with a presence of all three main metallic structures, the body-centered cubic (bcc), the face-centered cubic (fcc), and the hexagonal close packed (hcp). Recent advances in experimental techniques and computer modeling have made it possible to extend the Fe phase diagram up to extremely high pressures and temperatures (see Fig. 1). The presently widely accepted picture is that at ambient conditions iron stabilizes in the bcc structure (α -Fe), while the fcc phase (γ -Fe) stabilizes at temperatures above 1185 K. The reentrance into the bcc phase (δ -Fe) occurs at 1666 K, right below the melting point at 1901 K [2]. At low temperature and at a pressure higher than 12–15 GPa, Fe undergoes a bcc to hcp structural transition and remains stable in the hcp structure (ϵ -Fe) up to at least 300 GPa at room temperature [3]. The triple point among the bcc, hcp, and fcc structures is located at about 11 GPa and 750 K [4]. At further compression the double-hexagonal-close-packed (dhcp) phase (β -Fe) and the fcc phase have been reported to stabilize at intermediate temperatures [5–8] and at high temperatures below the melting point [9], respectively. Above the fcc–hcp (β phase)–liquid triple point at 60(10) GPa and 2600(100) K [7] the fcc phase has not been observed. However, in different experiments the location of the ϵ - γ -liquid triple point varies from 50 GPa and 2500 K [8,10,11] to 100 GPa and 2900 K [12]. In fact, γ -Fe was unambiguously detected *in situ* by means of x-ray diffraction at pressures up to about 70 GPa and high temperatures [9,13]. Results from different shock-wave experiments

[14,15] show that the melting temperature above the triple point increases significantly with pressure. Brown and McQueen [14] have observed two features in the Hugoniot curve indicating a post-hcp solid-solid phase transformation in the high-temperature region at pressures \sim 200–240 GPa and temperatures \sim 5000–5500 K. This possibility of an additional high-pressure solid-solid phase transition has been supported by Boehler from hydrostatic experiments [12,16], but other experiments have not detected the post-hcp solid phase [17,18].

It is quite possible that with a sufficient increase of the melting temperature with pressure, a reentrance into a solid phase could occur. It was proposed that the solid-solid phase transition could be due to development of the bcc phase [19–22] or reentrance into the fcc-phase [15]. However, according to theoretical estimations by Vocadlo *et al.* the fcc structure is less stable than both the hcp and dhcp structures at high pressure and temperature [23]. Also, the slope of the hcp \rightarrow fcc phase-transition line, deduced from the static-pressure experiments below 70 GPa (Fig. 1) and extrapolated to the very high pressure, seems to rule out a possibility of the reappearance of the fcc phase of Fe up to the Earth's core conditions. On the other hand, at ambient and low pressure magnetism of Fe is known to profoundly influence its physical properties. For instance, the stability of α -Fe is a direct consequence of magnetism. In addition to that, complex antiferromagnetic ordering states have recently been found in the fcc and hcp structures [24,25]. It has been demonstrated that even at high temperature the magnetic contribution to the free energy is essential to reproduce the hcp \rightarrow fcc transition temperature and the low-pressure part of the Fe phase diagram [26].

We note that according to theoretical estimations, at pressures above 60 GPa both the fcc and hcp structures

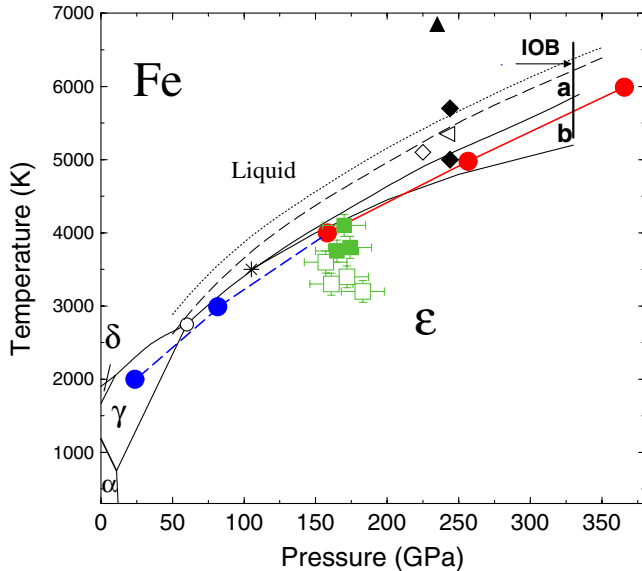


FIG. 1 (color online). Phase diagram of Fe. The phase diagram is based on the work by Ma *et al.* [11]. The open circle corresponds to ϵ - γ -liquid triple point, the star to the melting point; (a) corresponds to the melting curve calculated from the Lindeman's law, (b) to the melting curve calculated using the Kraut-Kennedy law, filled diamonds to the melting points from the shock-wave data, filled triangle to the melting point from Yoo *et al.* [8]; the long-dashed and dotted curves correspond to the theoretical estimation of the melting temperature from molecular-dynamics study with and without free-energy correction, respectively, from Alfe *et al.* [32]. The conditions in the Earth's core are indicated with a vertical solid line marked as IOB (inner-core-outer-core boundary). The filled circles connected by a solid line represent the fcc-hcp phase boundary obtained theoretically in this Letter. In the low-pressure region the theoretical curve is shown as a long-dashed line with filled circles. Note that in that region the neglect of the magnetic contribution to the free energy of Fe leads to an overestimation of the fcc-hcp transition temperature [28]; the opaque and filled squares correspond to the present experimental points for homogeneous hcp-Fe phase and the fcc-hcp phase mixture, respectively.

should become nonmagnetic [25]. Therefore, the boundary curves between the hcp and fcc phases in low-pressure magnetic and high-pressure nonmagnetic regions must behave differently. Consequently, extrapolations usually made from the low-pressure region might be inadequate for the description of the high-pressure region. In this Letter we present new insight into the structural behavior of pure iron at extremely high pressure and temperature by means of first-principles calculations, supported by the experimental results obtained at multimegabar pressure. Though our simulations cover both the low- and the high-pressure regions, we focus on the behavior of Fe at extremely high pressures and temperatures. We therefore suppress the magnetic effects in our simulations and restrict ourselves to nonmagnetic solutions only. We have studied electron and vibration spectra and thermodynamical properties of the fcc and hcp phases of pure iron over

wide pressure and temperature ranges, up to 400 GPa and 6600 K, respectively. We reexamine the stability of the fcc structure with respect to the hcp structure and show that at the Earth's core conditions the energy difference between the fcc and hcp structures is so subtle on the temperature scale that the presence of neither of them can be ruled out. Our theoretical results are supported by our temperature-quenched laser-heated diamond anvil-cell experiments, revealing the fcc-Fe in the pressure-temperature region above 160 GPa and 3700 K, respectively.

The details of the theoretical calculations of the electronic and phonon spectra are described in the supplementary materials [27].

In Fig. 1 we assemble the hcp-fcc boundary line, obtained in our free-energy calculations. The pressure dependence of the Gibbs energy difference between the fcc and hcp structures (ΔG) of pure Fe at different temperatures is shown in Fig. 2. At pressures below the fcc-hcp-liquid triple point, the calculated phase-transition points for the nonmagnetic case lie somewhat higher than the experimental data [11] (see Fig. 1). Here the experimental information is reliable, while our calculations neglect the effect of magnetism [28]. However, at pressures above 80–100 GPa the calculated boundary line is more reliable than the extrapolated one, as the magnetic moments in both the fcc and hcp phases are quenched.

Let us analyze the results of our simulations in more detail. At 1000 K (not shown in Fig. 2) ΔG is positive in the whole considered pressure range, meaning that at this temperature the hcp structure is more stable than the fcc structure. The increase of temperature results in a reduction of ΔG and, consequently, in stabilization of the fcc structure. At 2000 K ΔG is already negative at low pressures

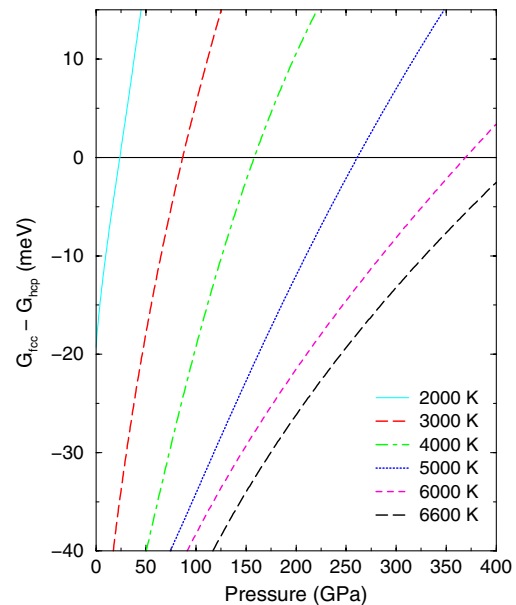


FIG. 2 (color online). Calculated Gibbs energy difference between the fcc and the hcp phases of Fe (ΔG) as a function of pressure at different temperatures.

and, consequently, the fcc structure appears in the calculated phase diagram. At the same time, under compression ΔG increases and eventually becomes positive indicating a stabilization of the hcp structure.

At higher temperatures the pressure of the fcc \rightarrow hcp transition increases even further. At 4000 K the hcp \rightarrow fcc transition temperature is higher than the melting temperature. However, at 5000 K the hcp-fcc transition line lies below the solid-liquid boundary and essentially coincides with the region of the solid-solid phase transition reported by Brown and McQueen [14]. Moreover, one can see that at the Earth's core conditions, indicated in Fig. 1 by the vertical line ($P \approx 330\text{--}360$ GPa and $T \approx 6000\text{--}6600$ K), the fcc structure becomes more stable than hcp according to our calculations. We notice, however, that the Gibbs energy difference is of order 3–5 meV/atom (35–60 K), i.e., extremely small, indicating that the fcc and hcp structures are energetically virtually degenerate. We notice also that our theoretical simulations neglect the anharmonic effects. Definitely, at extreme temperature they could be important [20,21,29]. However, as both the fcc and hcp structures are dynamically stable and have similar close packing, we do not expect the anharmonic contribution to qualitatively influence the Gibbs energy differences obtained in the present work.

Most importantly, the Gibbs energy difference between the fcc and hcp structures at the conditions of the Earth's core is very small and cannot be claimed within the method used in the present work. It urges highly accurate applications of molecular dynamics and quantum Monte Carlo methods. Nevertheless, the effect of the temperature on the stabilization of the fcc phase with respect to the hcp phase is substantial. According to our calculations, the energy difference changes by 60–70 meV between 0 K and 6000–6600 K in favor of the fcc phase.

We should also mention that in Ref. [23] it has been suggested that the thermal pressure of the fcc structure in the high-temperature region essentially exceeds that of the hcp and dhcp phases, and therefore the positive PV contribution has to destabilize the fcc structure at extreme conditions. However, in those calculations the forces used to calculate the phonon frequencies have been obtained at zero temperature. In our study, we see that the electronic entropy contribution itself increases stability of the fcc structure with respect to the hcp structure. In addition, calculation of forces that includes the Fermi smearing changes the vibrational contribution to the free energy at high temperatures in favor of the fcc phase.

γ -Fe is a temperature-quenchable phase (e.g., once synthesized at high pressure and temperature it remains if temperature is reduced to ambient), at least at pressures below 70 GPa [6,7,13]. However, at pressures above 100 GPa iron γ phase has not been observed so far either by *in situ* or by temperature-quenched experiments [6,11,30,31]. In the course of the studies of the behavior of iron and its chemical properties in the multimegabar pressure range, we conducted a series of experiments in

laser-heated diamond anvil cells (DAC's) (see details of the experimental procedure and the setup in [27] and Refs. [30,31]). Most of the diffraction patterns of the quenched samples contain only diffraction lines of ε -Fe. An example of a diffraction pattern, obtained by quenching at pressure 157(15) GPa from 3600(150) K, is shown in Fig. 3, upper panel (see also Fig. S1 in Ref. [27], upper panel). Nevertheless, some diffraction patterns, collected from samples heated at temperatures above 3700 K and pressures above 160 GPa, show a presence of a mixture of both ε -Fe and γ -Fe (Fig. 3, lower panel, see also Fig. S1, lower panel). The location of our experimental runs on the phase diagram is depicted in Fig. 1 with opaque and solid squares, corresponding to the samples consisting of the homogeneous hcp phase and to the mixture of the hcp and fcc phases, respectively. Note that only several of the hcp-Fe points (above 150 GPa) are shown. The region of existence of the fcc phase, obtained in this study, is much lower than it could be expected from an extrapolation of the fcc-hcp boundary curve, known for the pressures below 70 GPa. This strongly indicates that the slope of the fcc-hcp boundary is essentially different in the high-pressure and low-pressure regimes; this confirms our expectations.

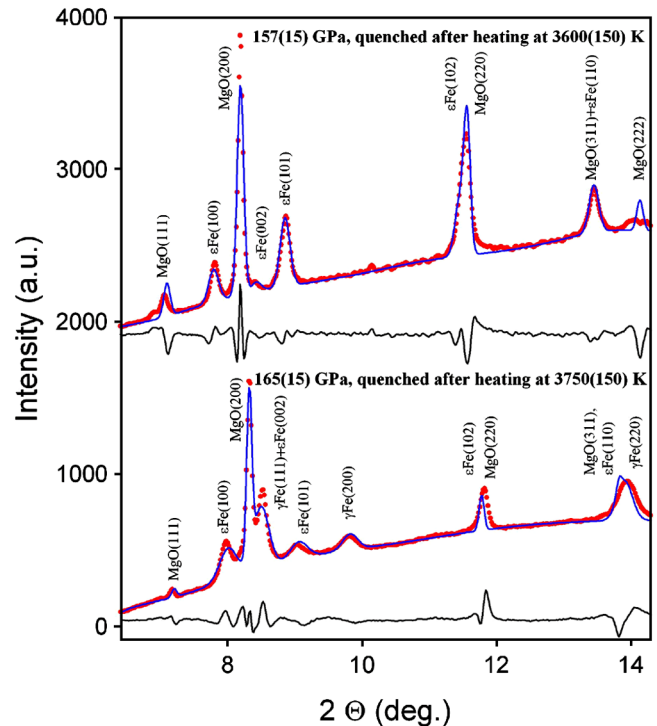


FIG. 3 (color online). Examples of the full-profile model-based general structure analysis system processed x-ray (wavelength 0.2647 Å) diffraction patterns of iron heated in MgO pressure transmitting media at 157(15) GPa and 3600(150) K (upper panel) and at 165(15) GPa and 3750(150) K (lower panel). At 165(15) the molar volumes of ε -Fe and γ -Fe are 4.65(3) and 4.66(3) cm^3/mol , respectively. Red dots correspond to experimental points, blue line to the calculated diffraction profile, black lines to the differences between the experimental and predicted intensities.

Though the conditions of our temperature-quenched experiments do not allow us to discuss the aspects of the thermodynamical stability of the fcc phase, our experimental observations unambiguously point out that γ -Fe can exist, at least as a metastable phase, at pressures above 160 GPa. Further, the presence of the phase mixture between the fcc and hcp phase at high temperatures and pressures indicates that the energies of the fcc and hcp phases should be very close, in accord with our theoretical predictions. Moreover, stabilization of the fcc phase happens in the P - T region, which is very close to our theoretical prediction of the fcc-hcp phase boundary.

It should be mentioned that the energetic degeneration between the fcc and hcp phases under the Earth's core conditions differs from the previously widely accepted picture. At the same time, it has recently been demonstrated [20,21] that the bcc phase of Fe, not considered in this study, can be stabilized at the Earth's core conditions by the anharmonic effects. However, the energy difference between the bcc and hcp phases, reported in Refs. [20,21], is of the same order, as the fcc-hcp energy difference obtained in the present study. Therefore, none of the bcc, fcc, and hcp phases can be ruled out from structural competition at high pressure and temperature. Moreover, the subtle energy difference between the phases at such temperature may lead to a coexistence of several phases, for instance, in a way of formation of the hcp-fcc structural matrix with random or cluster distribution of stacking faults, corresponding to the inclusions of the other phase. This, in particular, means that the actual structure of the Earth's core may be a complex phase with a large number of stacking faults.

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