Structure analysis and stability field of β -iron at high *P* and *T*

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ABSTRACT

New synchrotron X-ray diffraction data confirm our previous report of the transformation of the hexagonal close-packed (hcp) phase of iron to the *Pbcm* orthorhombic lattice (β -iron) at high *P* and *T*. The volume differences between the ε and β , and the β and γ polymorphs are determined as 1.4 and 1.8%, respectively, indicating positive Clapeyron slopes between these polymorphs in the *P*-*T* phase diagram. All three polymorphs have a similar bulk modulus between 30 and 60 GPa.

The *Pbcm*-polymorph can be observed in a metastable state as quenched from high *T* at high *P* and also at high *T* for *P* lower than 35 GPa where β -iron is not a stable phase. Metastability is possible because the gliding of the same dense atomic layers is involved in both *T*-induced ε -hcp to γ -fcc and ε -hcp to β -*Pbcm* transformations. These observations explain why a controversy exists on the structure and *P*-*T* stability field of β -iron. From our set of experiments, we estimate that *Pbcm*-iron is stable above 35 GPa and 1500 K, and that the (γ , β , liquid-iron) triple point is located at about 55 GPa and 2400 K.

INTRODUCTION

Recent experiments on the structure of iron at very high *P* and *T* has resulted in disagreements concerning the iron phase diagram at extreme conditions. The existence of a high-*P* high-*T* polymorph (the so-called β -phase) and the determination of its structure is still debated, and this debate has hindered the study of other critical parameters such as the iron equation of state at *P* and *T* conditions appropriate to Earth's core. Numerous investigations exist concerning the iron phase diagram and possible structures. They can be classified in four categories:

(1) Experiments at moderate T using furnaces coupled with either large volume presses or diamond anvil cells (DAC): Mao et al. (1987) reported the ε - γ transition up to about 36 GPa and 1375 °C from electrical properties measurements. They did not perform any structural analysis so that a polymorphic phase transformation could have escaped detection. Funamori et al. (1996) tracked the ε -hcp to γ -fcc phase transformation by Xray diffraction in a multi-anvil press. They found the phase boundary between 1300 and 1400 K at about 31.5 GPa, thus establishing a stability field for the γ -polymorph up to this *P*. They also confirmed a positive Clapeyron slope between εhcp and γ -fcc and proposed a ΔV of less than 2% between these two iron polymorphs. Using electrically heated DAC and Xray diffraction, Dubrovinsky et al. (1998, and references therein) reported transformation to the β -phase of iron at high-T above 35 GPa.

(2) Shock wave experiments: These experiments observed a solid-solid phase boundary from sound velocity vs. shock wave Hugoniot studies just before melting at about 243 GPa (Brown and McQueen 1986). The measurement of temperature during this type of experiment has recently been reevaluated (Holland and Ahrens 1998).

(3) Theoretical calculations: Calculations based either on thermodynamics (Anderson and Duba 1997) or structure-modeling (Ross et al. 1990; Matsui and Anderson 1997) indicate that this new phase could be bcc iron. However, recent reports do not agree with a new stability field for bcc-iron at extreme P and T, and better favor hcp (Bassett and Weathers 1990; Sherman 1994; Vocadlo et al. 1997) or a tetragonal-polymorph (Stixrude and Cohen 1995) for iron in the Earth's inner core.

(4) Laser-heated diamond anvil cell experiments: These experiments have produced a large amount of the knowledge of the high-P high-T behavior of iron. Yet, the different structures proposed for iron from 30 to 200 GPa up to more than 2500 K are controversial. The occurrence of a new iron polymorph in the 50-100 GPa region was first reported by Boehler (1993) and Saxena et al. (1993). A not well-defined boundary was detected by change of the optical properties of the sample, which affects the variation of the sample *T* as a function of laser power. These studies show discrepancy for establishing the stability field for β -iron because Boehler and Saxena et al. proposed its occurring above 70-80 and 30-40 GPa, respectively. The crystallographic structure of this new phase, β-iron, was then proposed to be d-hcp, in which the hcp cell is doubled along the c axis (Saxena et al. 1995; Dubrovinsky et al. 1997). The space group for d-hcp lattices is P63/mmc, with two independent at-

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oms in the (000) and (1/3, 2/3, 3/4) positions (see Wyckoff 1965). Such atomic topology is required to locate the 4 atoms per d-hcp unit cell. This model leads to the absence of odd *l* for all *hkl* (or *hkil*) Bragg lines. In their X-ray diffraction experiments, Saxena et al. (1995) and Dubrovinsky et al. (1997) reported diffraction lines 101, 103, and 105 which contradicts the d-hcp model for β -iron. Previously, we verified the existence of the new β -phase but alternatively proposed an orthorhombic structure (space group *Pbcm*) for that same iron-polymorph, using angle dispersive X-ray diffraction patterns (Andrault et al. 1997).

The X-ray diffraction study of Yoo et al. (1995) also reported a new polymorph between 15 and 40 GPa, thus defining a *P* stability field at least partially overlapping that of γ -fcc iron. They proposed that this new polymorph is metastable and that its occurrence should be related to non-hydrostatic stresses. Subsequently, Yoo et al. (1996) refined the ε' experimental features, i.e., splitting of the 100 hcp-line compatible with both dhcp and *Pbcm* structural model. Shen et al. (1998) also showed no polymorph other than ε and γ -iron at high *P* from 1400 K, to the melting point (Shen et al. 1998). A d-hcp structure is proposed for *T*-quench products, and the authors state that it is a metastable iron form. We note that no crystallographic argument is given to show adequacy between the particular d-hcp model and the experimental results.

In this paper, our goal is not to reconcile all conflicting reports about the iron phase diagram but to address potentially questionable points about the determination of the stability field of this β -phase. We will first present new experimental results, where iron phases other than ϵ -hcp and γ -fcc are clearly observed at high-*P* and high-*T*. We then consider whether a β -polymorph is required from both crystallographic and thermodynamic considerations. A tentative phase diagram is proposed, which should be helpful for subsequent studies in this *P*-*T* range.

EXPERIMENTAL METHODS

The data were collected during four independent series of experiments at the ID30 beam line (European Synchrotron Radiation Facility, Grenoble, France) in the last three years. At this beam-line, two focusing mirrors provide a bright monochromatic X-ray beam in a 10.15 μ m² (FWHM) spot at the sample location from two phased undulators and a channel-cut Si 111 monochromator (Häusermann and Hanfland 1996). We took great care to clean up the X-ray profile so that the whole X-ray beam profile fits into a $25.30 \ \mu\text{m}^2$ spot (Fig. 1), thus minimizing the horizontal T gradient in the X-ray spot and avoiding contamination of the recorded patterns with diffraction from gasket material. As in our previous studies (Andrault et al. 1997; Fiquet et al. 1998), we used angle dispersive X-ray diffraction, where monochromatic radiation (λ from 0.3738 to 0.4245 Å) is combined with an imaging plate system (Fast Scan Detector) located at around 300 mm from the sample. This technique represents a major improvement in resolution as well as reliability of diffracted peak-intensities, thus enabling the investigation of subtle details of the iron structure up to 100 GPa and 2500 K. Due to the beam's great intensity, 2-D images could be recorded in time varying from 1 to 3 minutes.



FIGURE 1. Top curve, X-ray flux, transmitted through a 60 μ m diameter hole drilled in a preindented Re gasket as a function of the gasket position relative to the beam. Bottom curve, size of X-ray beam at the sample location obtained after derivation of the right upward part of the top curve. The FWHM is found to be 12 μ m with all X-rays within 25 μ m, thus providing a spatial resolution suitable to work with hot spots generated with multimode infrared lasers.

We used a DAC with large optical aperture (Chervin et al. 1995) mounted with diamond anvils with 300 µm culets. Rhenium gaskets were preindented to a thickness of 40 µm and drilled to a diameter of 100 µm. As samples, we used either a compacted fine powder or a 5 µm thick iron foil mounted between two 15–20 µm-thick, pure Al₂O₃ or SiO₂ polycrystalline discs. A 250 W multi-mode stabilized YAG laser was focused to a visible 50 µm hot spot at the sample. The DAC was placed in a water-cooled holder, and both DAC and cooler have a cylindrical symmetry with respect to the X-ray beam. This geometry insures a stable sample position during laser heating (the DAC temperature never exceeded 100 °C during heating). In a previous experiment, we checked that dry Al₂O₃ and SiO₂ remained chemically inert while in contact with hot iron by optical observations of the interface between a very fine iron wire and both pressure-transmitting media. Pressures were measured at room T before and after laser heating, using corundum or stishovite as the internal P standard. Sample thermal emission collection was achieved with an optical system designed for on-line measurements during the X-ray diffraction experiments (Fiquet et al. 1996) and T determined spectroradiometrically with a fit to a grey body Planck function (Boehler 1993).

The DAC loadings were designed to achieve the best sample insulation from the diamond. We used very thin iron samples (less than 5 μ m), so that the axial *T* gradient becomes negligible. As mentioned in a previous report (Andrault et al. 1998a), the fact that we clearly observe the diffraction lines of the transmitting medium (in the 15·10 FWHM μ m² X-ray spot) is evidence of the good insulation of the heated iron. This reasoning is supported by the experimental evidence of diffraction peak widths of Si during laser-heating that are comparable to those at ambient condition. Therefore, artifacts due to P or T gradients (spatial or temporal) can be monitored and corresponding data points discarded. The amount of iron grains in the X-ray spot is therefore reduced and is another reason why the 2-D imaging plate is required. This plate permits an optimum integration of intensities produced by a limited number of grains and represents a critical improvement to extract precise structural information on a mixture of phases (iron and transmitting medium).

ORTHORHOMBIC *Pbcm*-IRON

Most of the diffraction spectra recorded at high *P* and *T* show the occurrence of reflections unexpected for a hcp-structured iron. These features cannot be explained by a mixture of ε -hcp and γ -hcp iron in Al₂O₃ or SiO₂ pressure-transmitting media or by *T* gradients, chemical reaction with pressure media, and contamination by gasket diffraction lines. Instead, they point to the occurrence of a high *P* and *T* polymorph, that has already been reported after laser heating in a DAC (Boehler 1993; Saxena et al. 1993, 1995; Yoo et al. 1995; Andrault et al. 1997, 1998a); Dubrovinsky et al. 1997). We will here restrict ourselves to describe and explain the experimental features observed in our new experiments during, or after, laser heating of pure iron in the 15–100 GPa *P* range.

All new diffraction features that we observed at high T can be explained by an orthorhombic iron lattice. The space group is *Pbcm*, as extracted from the systematic absence of the 010, 001, and 011 reflections, the presence of the 100 reflection, and an atomic topology as close as possible to that found in the hcp-polymorph (see Andrault et al. 1997). We report here a Rietveld refinement of another high-T run at 36 GPa (Fig. 2) which supports the *Pbcm*-iron structure when stishovite is used



FIGURE 2. Rietveld refinement for *Pbcm* iron at 36 GPa and about 1500 K using stishovite as pressure transmitting medium. Cell parameters and iron coordinates are similar to those in our previous study (see Table 1). For this fit, most of the differences between experimental and calculated spectra are driven by difficulties in reproducing the stishovite features because its peak profile is affected by the *T* gradients between hot-iron and cold diamond anvils. Down arrows, β -Fe, up arrows γ -Fe, St, stishovite peaks. The residual is given at the bottom. Ticks indicate all peaks.

as pressure-transmitting medium instead of corundum (as in the first study). We obtain cell parameters [2.3602(5), 4.1717(6), 4.0982(20)] and atomic position for iron [0.180(2), 0.007(8), 1/4] in perfect agreement with values reported in Andrault et al. (1997, see Table 1). This perfect reproducibility eliminates any artifact due to unexpected chemical reactions with the pressure-medium, because reaction of Fe with both SiO₂ and Al₂O₃ could not produce the same material.

This Pbcm lattice usually back-transforms to E-hcp iron during the T-quench (see Fig. 2 of Andrault et al. 1997). In some cases, however, we were able to quench a fraction of the *Pbcm* lattice, which was found to coexist with ε -hcp or γ -fcc iron. These patterns are very useful because we can extract the volume difference (ΔV) between the different iron polymorphs (Fig. 3). The scatter in Figure 3 is due to stishovite not being an ideal pressure-transmitting medium. However, the ΔV between the iron-polymorphs should be accurate because they are located in the same X-ray spot. Volume changes between ε and β iron and between β and γ -iron are found to be 1.4 and 1.8%, respectively. This leads to a 3.2% volume difference between ε and γ -iron above 20 GPa, in close agreement with that of 3.4% reported in Anderson (1995). The P-V slopes in Figure 3 also indicate very similar bulk moduli for the ε , β , and γ iron-polymorphs. In our previous study, we were able to quench Pbcm iron at about 100 GPa in the stishovite pressuremedium. A slight P release led to the Pbcm back-transformation into ε -hcp form, establishing the metastable state of the orthorhombic lattice at this very high P.

OTHER ORTHORHOMBIC LATTICES

After the laser heating, it appears that iron does not always quench back to the ε -hcp form, but rather to a different type of structure, which is therefore metastable. As for the high-*T* iron



FIGURE 3. Volumes of ε , *Pbcm*, and γ iron as a function of *P* at room *T*. We only report here data obtained for spectra where two of these three iron forms were simultaneously observed. This enables a more precise evaluation of the ΔV , found to be 1.4 and 1.8% for ($\varepsilon - \beta$) and ($\beta - \gamma$), respectively.

spectra, all unexpected diffraction features found in quenched spectra can be explained by the occurrence of another orthorhombic lattice (Fig. 4). Bragg lines are found, however, at different interplanar spacings than for the Pbcm lattice. Due to the lack of 001, 010, 012, and 021 lines, and the presence of the 100 line, both room-T patterns can correspond to the Pnmm symmetry. Note, however, that even if both spectra can be explained with the same space group, cell parameters are found much different from one lattice to another (Table 1). A tentative solution for a structure refinement (Rietveld) is proposed in Figure 4b for one of these 2 metastable lattices. Bragg-line intensities are found compatible with an iron (0.03, 1/4, 0.295)position, corresponding to "m" point group symmetry. In all orthorhombic forms, iron adopts the m-point symmetry (see Fig. 5). In the metastable orthorhombic forms, the atomic topology is similar to that of Pbcm iron, but the orientation of the m mirror in the iron lattice, and thus space group and (a,b,c) cell parameters, are found to be different (Table 1). We thus interpret the occurrence of the room T forms as an aborted backtransformation from *Pbcm* (or γ -fcc) to ε -iron lattices, where an intermediate form is quenched. This consideration explains the controversy about the structure of β -iron determined from



FIGURE 4. Metastable orthorhombic forms observed for iron after rapid quenches from high T in either corundum (**a**) or stishovite (**b**) pressure-transmitting medium. Both spectra are fitted using Pnmm space group, and lattice parameters reported in Table 1. The occurrence of these metastable forms (downward arrows) is due to an aborted back-transformation from *Pbcm* to ε -hcp iron.

either quenched or in-situ high-P and high-T experiments.

We also observed some peculiar behavior of the *Pbcm* lattice at moderate *P* (Fig. 6). The significant modification with *T* of the Bragg-line position indicates a *Pbcm* lattice with compliant (*a,b,c*) cell parameters. The 110, 020, and 002 reflections have similar *d*spacing at a maximum *T* (top spectrum of Fig. 6), where the phase transformation to the γ -iron form is also initiated. These particular *d*-spacings correspond to 2 simultaneous relations for the orthorhombic cell parameters, b = a $\sqrt{3}$ and c = a $\sqrt{3}$, so that the lattice can be defined by 1 cell parameter only. These 2 relations are normally incompatible with each other. Indeed, b = a $\sqrt{3}$ stands for an hcplattice [defined as a (*a*, a $\sqrt{3}$, *c*) pseudo-orthorhombic lattice], and is due to the presence of A₃ axes parallel to *c* axis. No space group allows two sets of A₃ axes at 90° from each other, as suggested by a second c = a $\sqrt{3}$ relation. One explanation of this is a particular dynamic behavior for this *Pbcm* lattice, discussed below.

THE PHASE TRANSFORMATION BETWEEN ε AND γ-IRON: A DISCUSSION

Packing densities for fcc and hcp structures are theoretically both 0.74 if the atoms are treated as rigid spheres. The situation is complicated, however, because the hexagonal lat-



FIGURE 5. Structure model for *Pbcm* iron. Iron is located on mirror plane, perpendicular to the *c* axis. Arrows represent a slight movement of the atoms away from the particular position, as for example the n°1 atom is not located at (0.25, 0, 1/4) position, but rather at (0.22, 0.04, 1/4). Drawing the same lattice using atom 1 as a (0,0,0) position leads to diagrams usually drawn for ε -iron as reported in Andrault et al. (1997).

	ε-iron*	Fig. 5†	Fig. 2	Fig. 4a‡	Fig. 4b‡	Fig. 6
P (GPa)	15	44.6	36.	53.	34.	20-25
T(K)	300	2125 (70)	Hot*	Quench	Quench	Hot§
<i>P</i> médium		Al ₂ O ₃	SiO	AI ₂ O ₃	SiO	SiO
Space group	Pb ₃ /mmc	Pbcm	Pbcm	Pnmm	Pnmm	Pbcm
Lattice (Å) a	2.45	2.346(2)	2.360(5)	2.171	2.320	2.420
b	4.24	4.144(5)	4.172(6)	4.196	4.280	4.202
С	3.93	4.063(4)	4.098(10)	4.092	3.887	4.195
Atom x		0.220(1)	0.180(2)	0.031		
У		0.037(1)	0.007(8)	1/4		
z		1/4	1/4	0.294		

TABLE 1. Cell parameters, space groups, and atomic parameters related to the structural refinement fofeinemt Atadid T, using the GSAS program package

Note: Each column relates to a particular refinement shown in this or in a previous paper

* $\epsilon\text{-iron}$ is the hcp lattice represented using the orthorhombic/([a,c) axes.

†Andrault et al. (1997).

‡ Metastable iron lattice obtained affequench.

§ Patterns recorded during laser heating Tronot measured.



FIGURE 6. Diffraction patterns presenting the variation of the reflection positions of β -iron with *T* at moderate *P*. This effect is to relate to an easy modification of the (a,b,c) orthorhombic parameters, a sign of particular high-*T* properties for β -iron at this *P* (see text). High-*T* increases the relative γ -iron content, as required by the iron phase diagram. The spectrum recorded at the highest *T* corresponds to a special combination of β -iron interplanar spacing, where d_{110} , d_{020} , and d_{002} become equal.

tice is defined by two a-priori independent (a,c) cell parameters. The ABAB stacking sequence along the *c* axis achieves a maximum density for spherical atoms only when $c/a = \sqrt{8/3} =$ 1.633. For iron at 15 GPa and room *T*, the hcp form adopts a c/aa ratio of about 1.604 (Poirier and Price 1999). The value of their ratio and the fact that the iron hcp-lattice is denser than fcc (Fig. 3) clearly points out that the iron atoms are not spherical at high-*P*. The anisotropy is not surprising when considering that 3d orbitals only provide spherical symmetry in a 3d¹⁰ configuration; the partially filled 3d⁶ iron orbitals can certainly adopt a lower symmetry. It is possible that particular states in the electronic continuum are favored at high pressure, so that the electronic density will increase in a certain volume that should be related to a combination of some 3d orbitals (iron symmetry in ε -hcp is $\overline{6m2}$). In contrast, iron in γ -form certainly shows more degenerated 3d electronic states (atoms adopt a *mmm* point symmetry), with a lower electronic density.

Similar reasoning can be used to explain the temperatureinduced ε to γ phase transformation in iron above 15 GPa (Note that we do not discuss the occurrence of the α -bcc polymorph at low P and T, partly because its physical properties are related to magnetism). The problem usually encountered when discussing phase transformations at high-T is that it is difficult to directly relate any structural evolution to an entropy increase required by the T increase. The change in vibrational state is severe. The cubic fcc lattice has three acoustic modes whereas an hcp lattice has three Raman plus three acoustic (Anne Hofmeister, personal communication). These types respond differently to both P and T (of Debye to Einstein models). Another point is the number of similar dense layers found in the two different iron lattices; fcc-iron has four equivalent (111)type, whereas hcp has a single (001) dense atomic layer. The atomic density along the three (100)-hcp layers is also high, if we consider the two sub-layers separated by $\sqrt{3}/6$ from e ach other (Fig. 7). It is not yet established that more similar dense atomic layers provides more specific entropy, but it seems logical that phonons should travel more easily in the most symmetric γ -(111) than in ε -(100) layers. These reasons could therefore explain a lower specific entropy for the hcp lattice relative to the high- $T\gamma$ -form. In fact, the structural configuration found along the 100-hcp layers might not be optimum to insure the stability of ε -iron at the enormous T involved in the Earth's core (Poirier and Shankland 1993).

STRUCTURAL PROPERTIES OF PBCM IRON

If *Pbcm* iron indeed has a stability field at high *P* and *T* in the iron phase diagram, it is at least required that the specific volume of *Pbcm* iron is lower than that of fcc-iron for a specific entropy higher than for ε -iron. The former already seems



FIGURE 7. Iron hcp lattice projected on the 001 plane. One can observe three families of (100) dense atomic layers which show special configuration because separated in two sub-layers at $a\sqrt{3}/6$ from each other.

verified because Figure 3 clearly indicates a Pbcm volume bracketed between those of ε and γ -iron. To give clues for the latter, we will discuss more the structural modifications along the ε to *Pbcm* phase transformation in iron. As mentioned previously, the main changes are the doubling of the lattice volume and the breakdown of laws related to hexagonal c-faces (a = b, A₃ axes, $\gamma = 120^{\circ}$). One also notices that some *Pbcm* interplanar d-spacings, namely 110, 020, and 002 reflections, are close to each other. These reflections are found at 2.042, 2.072, and 2.031 Å at 44.6 GPa and 2125 K, respectively, while the same atomic layers produce diffraction lines at 2.12, 2.12, and 1.965 Å in the ε -lattice at 15 GPa (see Table 1). This is important because the Pbcm 110, 020, and 002 layers correspond to the 100 and 002 dense layers of the hcp structure. It thus appears that the orthorhombic lattice produces a more symmetrical set of dense layers than found in hcp. This leads, for example, to a structural configuration where the b and c faces of the Pbcm lattice become similar, a configuration that cannot be achieved with respect to the space group for hcp-iron.

A structural interpretation of this effect is certainly related to the origin of the phase transformation; a shift of the hcp-AB layers relative to each other (Andrault et al. 1997). Such a shift in hcp will affect the nature of the 100-layers, which (as described above) are dense layers split in two close atomic sublayers. In our opinion, the occurrence of the orthorhombic lattice is mainly due to particular vibration dynamism of these double 100 hcp-layers. Reducing the gap between the two sub-layers for 1 (or 2) family of 100 dense layers would increase the gap for the other, and thus induce a loss of the hcp A_3 axes. If the gap between two sub-layers in a particular direction disappears, the 100 layer becomes similar to that along the 001 direction, trend observed experimentally. As discussed above, with respect to the ε to γ phase transformation in iron, we propose here that the formation in a set of most similar dense layers (the 110, 110, 020, and 002 *Pbcm*-layers) can be related to an entropy increase along the *T*-induced ε to *Pbcm* phase transformation.

This structural interpretation of the occurrence of *Pbcm*-iron is a clue to explaining the large variation observed for the (a,b,c) cell parameters as a function of the *T* and *P* history (see Fig. 4, Fig. 6 and Table 1). If the shift of the AB-layers between each other is affected by *T* and *P*, the orthorhombic iron will adopt cell parameters in accordance with the amount of displacement. An extreme case is illustrated in the top spectra of Figure 6, where the 110, 110, 020, and 002 *Pbcm*-layers are found equal (d_{hkl} calculated from cell parameters reported in Table 1). We believe that such a case can only be achieved if *T* is high enough at a given *P*, and it certainly relates to a most particular dynamism of the AB layer in displacement with each other.

THE IRON PHASE DIAGRAM

In some runs at moderate *T*, we have observed the orthorhombic *Pbcm*-phase at *P* below 30 GPa, a *P* range where only ε -hcp and γ -fcc are known to be stable (Mao et al. 1987; Funamori et al. 1996). This observation perfectly agrees with Yoo et al. (1995), who proposed the occurrence of a metastable ε' polymorph. In these cases, *T* was certainly too low to achieve the phase transformation to the γ -form, which would require the ABA to ABC modification for the dense layer stacking. In fact, as *Pbcm*-iron certainly occurs due to a slight modification in the ABA stacking, nothing restricts *Pbcm* iron to be observed at moderate *T* as an intermediate structure before the phase transformation from ε -hcp to γ -fcc. Still, the question remains: Does the *Pbcm* lattice become a stable lattice for iron at certain *P* and *T*?

To insure a stability field for Pbcm-iron, one should confirm that sufficient thermal energy has been provided to iron so that energy barriers between ε and γ polymorphs are overcome. High-T also relaxes stresses that might be encountered upon compression in the DAC and that may favor the occurrence of a distorted iron-form. This is certainly achieved if Treaches a value close to the melting point for a particular P. We present in Figure 8 diffraction spectra recorded as a function of T, where we achieved the melting of iron at about 2400 K for 55 GPa. At the melting T, we have clearly observed a rapid time-dependent variation of the black body emission that can be attributed to the melting onset, resulting in a mixture of solid and liquid iron phases of varying proportions. The high-T diffraction pattern can therefore hardly be analyzed using a crystalline-iron structural model only. The 100-line of the Pbcm orthorhombic lattice, however, is clearly present. This line's occurrence indicates a stability field for the Pbcm iron considering that T is too high there for deviatonic stresses and the energy barrier not to be overcome. These results also show that the γ -iron stability field does not extend above 55–60 GPa. Note that P for high-T spectra in Figure 8 might be slightly higher than 55 GPa due to thermal pressure effects in the laser-heated DAC (see Andrault et al. 1998b).

Our new information includes the location of the β - γ -liquid triple point at around 55 GPa and 2400 K, a positive Clapeyron



FIGURE 8. Sequence of laser heating showing the melting of iron at about 2400 K and 55 GPa. Top and bottom patterns correspond to quenched iron in a metastable orthorhombic form (as in Fig. 4). A transformation to *Pbcm* iron starts at moderate *T*, as illustrated by the occurrence of the 100 peak located at about 2.35 Å at 2375 K. The iron diffraction pattern loses much intensity, due to the onset of melting. Still, some iron lines remain clear, in particular, the 100 *Pbcm* line which evidences a stability field for this structure at extremely high-*T*. A small feature at about 1.8 Å can correspond to the 200 line of γ -iron. This high-*T* pattern certainly corresponds to *T*-*P* conditions very close to the γ - β -liquid triple point.

slope between ε and β -iron (as evidenced in Fig. 3), and also the stability of ε -iron at 100 GPa and room T. Our experimental set-up, however, does not provide an accurate position for the β - γ - ϵ triple point due to uncertainties concerning the lower pressure at which Pbcm iron is stable. We note that this triple point is certainly higher than 30 GPa, because no β -phase was observed in the multi-anvil study performed by Funamori et al. (1996). From our whole set of data at various P-T conditions, we estimate that the P-T stability field of Pbcm iron begins at about 35 GPa (Fig. 9). Considering that the volume difference between all iron polymorphs is believed to decrease with increasing P (Anderson 1995), it is likely that the Clapeyron slope between ε and β -forms will decrease with P so as to approach horizontal in the P-T diagram at around 330 GPa. Unless there is another polymorph of iron stable at high temperatures and pressures above 330 GPa, Pbcm iron is the phase of pure iron that is stable at inner core conditions.

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FIGURE 9. The iron phase diagram revisited. Modified after Saxena et al. (1995).

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