Melting, density, and anisotropy of iron at core conditions: new X-ray measurements to 150 GPa

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Abstract. Melting temperatures of iron up to 130 GPa and compressibility to 150 GPa were measured by X-ray diffraction in the double-sided laser-heated diamond cell. New experimental features are the very tightly focused X-ray beam, in situ alignment of X-ray beam and hot spot, and rapid data acquisition. The melting temperatures are in good agreement with previous optical measurements supporting “low” melting temperatures in the core. Above 70 GPa only the ε (hcp)-Fe phase is found. The measured densities of the annealed iron samples yield an accurate equation of state. The c/a ratio of iron decreases with pressure but shows an increase with temperature and at core conditions is nearly the same as at low pressure.

1. Introduction

Understanding the Earth’s thermal gradient and thermal history and the seismic density and structure of the Earth’s core requires an accurate knowledge of the phase behavior, equation of state and melting temperature of Fe at the inner-outer core boundary (IOCB) at 330 GPa. The melting curve was determined using the laser-heated diamond-anvil cell (LHDAC) by a number of laboratories up to 200 GPa[1], and shock velocity measurements have found melting between 220 and 240 GPa[2]. Theoretical melting calculations have been made to 360 GPa[3-5]. However, the extrapolated measurements and the theoretical predictions of the melting temperatures at the IOCB (330 GPa) range from 4800 K to 7000 K (see figure 1).
Figure 1- Iron melting curves. Results of LHDAC experiments [1] and shock melting experiments indicated by the arrows on the Hugoniot[2] and ab initio melting calculations[3-5] (1, 2 and 3, respectively) are shown. The melting temperatures at the inner-outer core boundary range from 4800 K to 7000 K.

At ambient temperature, iron has the bcc structure and transforms into hcp at 13 GPa[6]. The hcp phase was found to be stable up to about 300 GPa by X-ray diffraction[7]. Several years ago it was suggested, based on X-ray diffraction measurements in the laser-heated diamond cell, that the phase diagram of iron may be more complicated containing orthorhombic or dhcp phases. More recently, however, no such transitions were found[8,9]. It is highly likely that both the previously observed distortion from hcp to orthorhombic, and a change in stacking order hcp→dhcp were due to deviatoric stresses using hard pressure media in the diamond-cell. There is also a new report of the existence of a bcc-Fe phase above 230 GPa and 3400 K[10], which could be the stable structure in the Earth’s inner core. In order to clarify these earlier discrepancies on the iron phase behavior and melting, we made new measurements at the laser-heating beamline ID 27 at the ESRF using a variety of pressure media.

Most of the iron melting measurements are at pressures below 100 GPa. The results from different laboratories using six different methods in the laser-heated diamond cell and shock experiments are now in very good agreement within the experimental uncertainty of about ±100 K[1,9,11-14]. Therefore the iron melting curve to 100 GPa is probably better constrained than that for any other material. For the detection of melting a number of physical property changes between solid and liquid have been used, such as discontinuous changes in the resistivity of thin wires[15] and changes in reflectivity and laser power[1,6,16] or motion on the sample surface that can be made visible with the speckle pattern of an argon-laser beam[12,17]. These methods were compared in some experiments with the first observation of microscopic melt features on the surface of the quenched sample for iron[11] and for a number of other metals[18]. The results for iron from these different measurements are in very good agreement. Additionally, the effect of different pressure media on the melting temperatures has been thoroughly checked[1,6]. These melting results have been recently confirmed using X-ray diffraction up to 58 GPa[9].

Additional evidence for “low” iron melting temperatures below 100 GPa comes from shock velocity measurements on pre-heated iron[11]. At 71±2 GPa and 2775±160 K, a very sharp drop in the shock velocity was observed which is due to melting. Temperatures in this work were calculated and possible overshoot of the equilibrium melt conditions was not taken into account.

Recently we made several improvements in order to increase the accuracy of melting measurements: Two new 40 Watt diode-pumped Nd:vanadate lasers (INAZUMA, Spectra-Physics) with perfect TEM00 mode and very high power stability, resulted in larger hot spots and reduced temperature fluctuations to less than 10 degrees. A more stable gasket, consisting of tungsten and
diamond powder provided a larger cell volume resulting in a more efficient thermal insulation of the sample from the diamonds and thus, a reduction in the temperature gradients. This gasket also allowed the use of argon as a pressure medium to over 100 GPa. Moreover, we significantly improved the optical resolution by replacing the previous reflecting objective with achromatic lenses with variable numerical aperture to minimize chromatic aberration.

The only diamond cell measurements above 100 GPa are from Boehler[1] to 200 GPa and Saxena et al.[13] to 140 GPa. These two sets of measurements using similar methods to detect melting are in good agreement and well within the experimental uncertainty, suggesting a melting temperature at 200 GPa near 4000 ±200 K. However, both the theoretical estimates and shock data predict higher melting temperatures.

Above 100 GPa melting measurements in the diamond cell become exceedingly difficult and the detection of melting is limited to the observation of an increase in the reflectivity upon melting. We therefore started to systematically investigate the melting behavior of iron above 100 GPa by X-ray diffraction.

2. Experiment

The data reported here are from 20 different runs. Disks of high-purity iron with dimensions of 10-20 μm in diameter and 5-10 μm in thickness were loaded into a newly designed DAC with conical anvils[19] using tungsten gaskets. Culets varied from 200 to 300 μm. Ar, Xe, KCl and Al₂O₃ were used as pressure transmitting media. For the solid pressure media the high-pressure cells were dried under vacuum and subsequently flushed with Ar, prior to pressurizing. In the experiments with noble gases as pressure media, ruby plates with 10 μm thickness were used to thermally insulate the sample from the diamonds. Pressure was measured by the ruby fluorescence method[20]. These pressures were in good agreement with those obtained from the EOS of Ar, Xe, and Al₂O₃. The samples were heated from both sides with two 40 W Nd:YVO₄ lasers (λ= 1.06 μm wavelength). The laser beams were defocused to create the largest possible hotspot. At the highest pressures of this study temperature gradients in an area with 10 μm in diameter within this hotspot were within 100 K. Using the laser focusing, temperatures on both sides were adjusted to within 100 K. Emission spectra were measured from areas of 2 μm diameter in the spectral range 550 – 800 nm. The Planck’s radiation function was fitted to the spectra assuming wavelength-independent emissivities. The measurements were performed at the ID-27 beamline of the European synchrotron radiation facility (ESRF) using X-ray wavelengths of 0.26472 and 0.3738 Å and beam diameters of 3 μm (FWHM) were used. Diffraction images were recorded every two seconds with a Mar345 CCD detector, while the power of the lasers was gradually increased.

Ideally, at melting, all diffraction lines of the sample should disappear and a diffuse scattering halo should appear. However, the determination of melting by X-ray diffraction is not that straightforward because at melting the absorption properties of the sample change, leading to instabilities. Additionally, the molten sample tends to disperse into the pressure medium. Therefore, sample confinement in a suitable pressure medium and rapid recording of the X-ray patterns are essential. We observed two different types of changes in the X-ray patterns when the melting temperature was reached: The first are fast changes in the position and intensity of the spots in the diffraction pattern (see figure 2). We interpret this as recrystallization in a partially molten sample caused by temperature instabilities, which are due to changes in the absorption. This phenomenon is observed every time melting is reached. The second is the expected halo, or diffuse scattering ring. This observation, however, is not always reproducible because it requires a larger of melt fraction the mobile, recrystallizing sample probed by the X-ray beam. The appearance of a diffuse scattering ring is accompanied by the disappearance of all iron peaks (see figure 3), indicating complete melting of the sample. After cooling the iron diffraction peaks reappear and the ring disappears.
Figure 2 – Effect of recrystallization during melting of iron at 116 GPa. Top: Laser power, middle: maximum sample temperature, bottom: peak intensity fluctuation versus time. When the sample starts to melt (3160 K), large fluctuations in the peak intensities are observed and the temperatures remain nearly constant with increasing laser power.

At the onset of fast recrystallization, the temperature raises slower with increasing laser power. This phenomenon has been frequently observed in previous melting experiments. It is likely due to change in absorption in the liquid and a gradual increase in the melt fraction of the sample.

In order to study the first of these phenomena, the recrystallization process, the observed intensities on the CCD detector were integrated as a function of $2\theta$ in order to give conventional, one-dimensional diffraction profiles. The area under every peak of iron was calculated for each diagram (i.e. Peaks of $\varepsilon$-hcp-Fe at $t = 2$ seconds: $I_{(100)}$, $I_{(002)}$, $I_{(101)}$, $I_{(102)}$ and $I_{(110)}$; at $t = 4$ s: $I'_{(100)}$, $I'_{(002)}$, $I'_{(101)}$, $I'_{(102)}$ and $I'_{(110)}$, etc…). If the total sum of all area changes of the iron peaks in consecutive diffractograms ($|I_{(100)} - I'_{(100)}| + |I_{(002)} - I'_{(002)}| + ...$) is plotted versus time, large fluctuations are observed when the melting point is reached (see Fig. 2). The melting temperature is then taken at the onset of these strong fluctuations assuming that the fast reorientation of crystallites is only possible in a partially molten sample. These melting temperatures are in agreement with those obtained from the disappearance of diffraction peaks and the occurrence of diffuse scattering described above (both phenomena take place on the temperature plateau).
Figure 3 – A) Diffraction patterns of a 10 micron iron sample before (148 GPa), during and after (130 GPa) heating. The pressure medium was MgSiO$_3$ dry gel, which converted to the post-perovskite phase during heating. At 3136 K all hcp iron peaks disappear completely and a diffuse ring associated with liquid iron appears (clearly visible in the original spectrum). When the sample is cooled down, hcp-Fe peaks reappear and diffuse scattering disappears. In the present case, the intensities of the Fe peaks after heating are significantly smaller than before heating, most likely due to a thinning of the sample. B) Diffraction image at 3196 K. At this temperature only peaks belonging to the post-perovskite phase are present [21] and the diffuse ring is due to the fully molten iron sample. We did not detect any chemical reaction between iron and the pressure transmitting media from the diffraction patterns.
3. Results and discussion

3.1. Fcc – hcp boundary and melting

Figure 4 shows the new phase diagram of iron obtained from our experiments in comparison with previous X-ray and optical measurements[1,9,22]. The only phases observed for iron were \(\varepsilon\) hcp and \(\gamma\) fcc. Only in those experiments at conditions close to the \(\varepsilon\) - \(\gamma\) boundary peaks both phases coexist. The \(\gamma\)-\(\varepsilon\)-liquid triple point is at a pressure between that reported in reference [1] and [8] at 70 GPa and 2700 K.

Figure 4 – Phase diagram of iron. The solid lines correspond to the present data (solid symbols) and the dashed lines are taken from Boehler[1]. X-ray data by Ma et al.[22] (empty symbols) and Shen et al.[9] (crossed symbols) are also shown.

Our data confirm that iron at high P-T conditions has the hcp structure and that the melting slope is small above 100 GPa. Compared to our previously published phase diagram [1] both the melting curve and the fcc-hcp boundary are shifted to slightly higher temperatures and lower pressures. This is most likely due to two factors: X-ray measurements tend to overestimate the temperature, because the heated surface of the sample is always slightly higher than the average sample probed by the X-ray beam. Second, the pressure measured optically in stiff pressure media was most likely overestimated due to annealing effects in close vicinity of the heated sample.
3.2. Equation of state of $\varepsilon$-Fe and its anisotropy

Volume measurements of the $\varepsilon$-Fe are presented in Fig. 5. Our pressure-volume data were fitted using a third-order Birch-Murnagahan EOS. The best-fit values for the characteristic parameters were $V_0 = 11.23(2) \text{ Å}^3$/atom, $B_0 = 160(6) \text{ GPa}$ and $B_0' = 5.6(2)$. The bulk modulus obtained from our data is only slightly smaller than that recently reported by Dewaele et al.[23] at room temperature with helium as pressure transmitting medium, but in general the compression measurements shown in figure 5 are in good agreement. The small discrepancy between the different EOS reported could be qualitatively explained by the effect of nonhydrostatic stresses in the sample (different pressure media) and the experimental uncertainty in the pressure measurements (different pressure gauges and pressure gradients).

![Figure 5 – Room temperature compression of iron in comparison with other recent measurements. The samples in this study are fully annealed due to several melting-freezing cycles but the compressibility is smaller than in the study by Dewaele et al.[23] in a helium pressure medium. All the data shown[7,23,24] are in agreement within the uncertainty of the pressure measurements.](image)

Apart from the compressibility of $\varepsilon$-Fe the variation of the axial ratio $c/a$ of hexagonal iron has gained renewed interest due to the observation that compressional seismic waves in the inner core travel faster along the Earth’s rotation axis than in the equatorial plane[25], implying that the
solid inner core is anisotropic. From the data plotted in Fig. 6, it can be seen that the compression of ε-Fe at room temperature is anisotropic, the relation c/a decreasing with pressure. The data were fitted using a Boltzmann sigmoidal function, giving the following pressure dependence of the axial ratio c/a:

\[ \frac{c}{a} = 1.5963(1) + \frac{0.0131}{1 + \exp((P-26(6))/47(2)))} \]

Figure 6 – Axial compression of ε-Fe at room temperature. Our results (solid symbols) are fully consistent with those of Dewaele et al.[23] using helium as a pressure medium.

In comparison with other experimental and theoretical studies, Ma et al.[22] and Mao et al.[7] found no systematic variation in c/a with pressure. Fig. 6 shows the large data dispersion in these studies. Lattice dynamics and thermodynamic calculations at high-pressure found that the equilibrium axial ratio of ε-hcp-Fe increases slightly as a function of pressure at ambient temperature[26]. However, our results are consistent with a recent study of Dewaele et al.[23], where the pressure effect led to a decrease in the c/a axial ratio.

The c/a variation in ε-Fe with temperature was also studied. Figure 7 allows us to compare our results with previous experimental data and with results from theoretical calculations. Both, experiments and theoretical calculations find that there is an increase of the c/a ratio with temperature at high-pressure. Previous experimental data initially shows an increasing trend with temperature, but at temperatures above 2300 K a slight decrease is observed. However, this decrease is not found in the theoretical prediction. Here, we report experimental data up to 3300 K at three different pressures: 84, 106 and 140 GPa. We find that the axis ratio increases
continuously with temperature in all the cases, using linear fitting showing a linear decrease with pressure. Our results are in good qualitative agreement with Sha et al.[26] and Modak et al.[27].

![Figure 7 – Axial ratio of $\varepsilon$-Fe as a function of temperature for different pressures. The pressures of the present work are 84, 106 and 140 GPa and the data are represented by solid symbols. Empty symbols correspond to the experimental work of Ma et al.[22] Dashed lines are theoretical calculations: Sha et al.[26], Steinle-Neumann[28], Belonoshko et al.[5] and Modak et al.[27].](image)

4. Conclusions.

The new measured melting curve of iron using X-ray diffraction agrees with previous optical measurements within the error bars but is systematically shifted to lower pressures. The fcc-hcp-liquid triple point is at 70 GPa and 2700 K. Our experiments confirm that the hcp ($\varepsilon$)-Fe is the only phase found at high pressures and high temperatures. The EOS of hcp-Fe yields the following parameters: $V_0 = 11.23(2)$ Å$^3$/atom, $B_0 = 160(6)$ GPa and $B_0' = 5.6(2)$. Our results show that the compressibility of the lattice parameters is anisotropic at room temperature, the $c/a$ ratio decreasing with pressure, in agreement with recent hydrostatic measurements[23]. Other conclusion from this work is that $c/a$ increases with temperature but at the P-T conditions of the core the $c/a$ ratio is close to that at low pressures.

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