Synchrotron X-ray Study of Iron at High Pressure and Temperature

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X-ray synchrotron experiments with in situ laser heating of iron in a diamond-anvil cell show that the high-pressure ε phase, a hexagonal close-packed (hcp) structure, transforms to another phase (possibly a polytype double-layer hcp) at a pressure of about 38 gigapascals and at temperatures between 1200 and 1500 kelvin. This information has implications for the phase relations of iron in Earth's core.

Recent studies on iron (*1–3*) have led to greater understanding of the behavior of iron under the extreme pressure-temperature conditions of Earth's core. For example, the melting curve of iron is now known to a pressure of nearly 2 Mbar and it is recognized that iron may occur in additional polymorphs. The structures of four phases of iron are well known: α (body-centered-cubic, bcc), γ (face-centered-cubic, fcc), ε (hcp), and the high-temperature form δ (bcc). Boehler (*1*) and Saxena *et al.* (*2*) presented experimental evidence for the occurrence of a new iron phase, which was tentatively called β by Saxena *et al.* (Fig. 1). This determination was made by heating iron under pressure in a diamond-anvil cell with a Nd–yttrium-aluminum-garnet (YAG) laser and plotting the laser power against the corresponding temperature measured by thermal radiation spectroscopy (*2*). A change in slope on such a plot is considered to signify a phase transition or melting. Although the laser power–temperature technique may be used successfully in determining melting and phase transformations (*1, 2, 4*), structural information on the iron phase transformation is necessary to understand the state of iron in the core. Here, we report the result of an x-ray study on phase transformation of ε (hcp) iron into a new phase. The result shows that one or more new iron phases may be present in Earth's core but to recognize them, great care is needed in designing the experiments.

To obtain x-ray data, we used the synchrotron X-17C beam line at the Brookhaven National Laboratory. We loaded an iron foil (99.9% pure) in a Mao-Bell diamond-anvil cell, with predried periclase (MgO) as the pressure medium and the standard for pressure measurement, and heated the iron sample with an 18-W laser in continuous wave TEM_{000} mode. As the purpose of the study was to establish the presence of the new iron phase at any possible temperature, we made no attempt to measure the temperature. The pressure was generally between 35 and 40 GPa. At such pressures, iron should change to the γ (fcc) phase if the temperature ever exceeded 1400 K (Fig. 1). As we did not observe any fcc phase, either during heating or after the sample was quenched while maintaining pressure, the temperature in our study must not have exceeded 1500 K. Our other experiments have shown that the fcc phase can be quenched if the pressure is maintained (*5*). At pressures of ~10 GPa (Fig. 1) we could recognize the fcc phase quite clearly, both during in situ heating and in the quenched product at high pressure. At higher pressures between 35 and 40 GPa (Fig. 1), upon heating we observed phase transformation of ε (hcp) to a new phase (Figs. 2 and 3); although this new phase was not noted on unheated spots or where the laser absorption was poor, it was noted at all other spots both during in situ heating and after quenching at high pressure (*6*).

The simulation of the x-ray diffraction for the new phase is on the basis of a superlattice of hcp. We modeled the new phase as a four-layer close-packed hcp structure analogous to that of Ce and some other metals (*7*). The calculated diffraction patterns (Fig. 2) are based on the assumptions that (i) the phase mixture is ideal (that is, primary orientation of any one phase is absent), (ii) the diffraction peaks are described by pseudo-Voigt functions, and (iii) x-ray intensity does not depend on energy range. The background is taken from the experimental data. The data in the low-energy range are well simulated by this approach (Fig. 2A). At the high-energy range (Fig. 2B) the patterns are not as distinct, but when we compare the heated and unheated samples, there remains little doubt that we are looking at the transformation of ε (hcp) to a new double-layer hcp (dhcp) phase.

We checked our sample for the presence

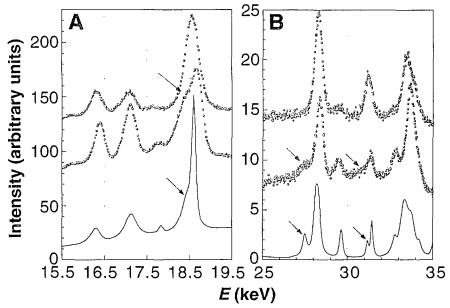

Fig. 2. Energy-dispersive x-ray data on iron. (**A**) The top curve shows the x-ray diffraction (energy-dispersive, $2\theta = 21°$) pattern for the unheated iron, which is all hcp at pressures between 35 and 40 GPa. The middle curve shows similar data for iron after laser heating, during which temperatures must have reached 1000 to 2000 K. As no fcc peaks are visible, we estimate that the average temperature was below 1500 K. The middle curve displays a clear development of a new peak below 18.5 keV (arrow). The bottom curve shows a calculated pattern for a mixture of MgO, hcp iron, and the new phase (assumed to be the dhcp phase of iron). (**B**) The data shown are similar to those in (A). The peaks are less distinctive than those in (A), but a comparison of the data for heated and unheated iron shows a clear development of the two additional peaks (arrows) in this energy range, which would belong to the dhcp phase.

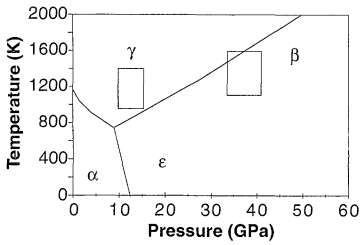

Fig. 1. Part of the iron phase diagram showing the pressure-temperature fields of our study. On laser heating, iron at lower pressures was largely converted to the fcc phase. Temperatures shown are approximate. At high pressures, the iron shows a distinct phase transformation from hcp to possibly a dhcp form of iron. According to Saxena *et al.* (*2, 4*), β iron would be stable at 1400 K between 35 and 40 GPa. The δ phase is not shown.

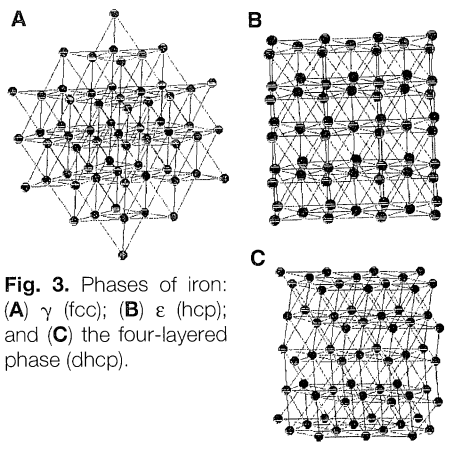

Fig. 3. Phases of iron: (**A**) γ (fcc); (**B**) ε (hcp); and (**C**) the four-layered phase (dhcp).

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of any other phase formation resulting from reaction between the iron and the pressure medium. Although the sample contained only MgO and iron, small traces of oxygen and water can never be totally ruled out. We watched the sample on the monitor and observed no visible reaction during heating. After the experiment, the pressure was released and the iron completely reverted to the bcc phase. None of the x-ray peaks in Fig. 2 correspond to any iron oxides (magnetite, hematite, or wustite). Although there are additional peaks that do not belong to ε (hcp) iron, the analysis is complicated by the fact that the x-ray pattern includes peaks from the untransformed hcp iron; this is because the laser beam heats only part of the iron while the x-rays pass through the entire thickness of the sample. Therefore, the dhcp peaks necessarily involve the peaks from the hcp iron as well.

The calculated lattice parameters (~38 GPa and 300 K) are a = 2.396 Å and c = 3.814 Å for the ε (hcp) phase and a = 2.427 Å and c = 7.66 Å for the dhcp phase (Fig. 3). The molar volumes for the ε and dhcp phases are 5.71 and 5.89 cm^3/mol, respectively (with unknown errors); these values are consistent with the thermodynamic assessment of such data (*4*) if the new phase is considered as β iron. Table 1 shows the calculated diffraction pattern of a sample (heated for 3.5 min) and after temperature quench (pressure maintained). Many of these peaks correspond to the ε hcp phase and not necessarily to the new phase. The calculated molar volume of the heated sample is 6.246 cm^3, as compared with 5.92 cm^3 for the quenched sample under a pressure of 35 to 40 GPa.

The x-ray study confirms that iron occurs as at least four different crystallographic structures. Because the ε (hcp) iron was the only phase recognized as a suitable high-pressure phase for Earth's core, all geophysical models of the core have been based on properties of the ε iron. We must now consider that one or more additional iron phases in Earth's core are possible.

Table 1. Calculated x-ray diffraction pattern for dhcp (a = 2.427 Å, c = 7.666 Å, Mo $K_{\alpha 1}$ radiation, P = 35 to 40 GPa, T = 300 K). I, relative intensity.

hkl	*d* (Å)	*I* (%)
100	2.1018	8
101	2.0270	45
004	1.9165	33
102	1.8429	100
103	1.6233	12
104	1.4162	5
105	1.2387	9
110	1.2135	21
106	1.0918	16
021	1.0412	4
114	1.0253	22
202	1.0135	12
023	0.9719	3
107	0.9712	3
008	0.9582	3
025	0.8668	2
206	0.8116	5

Note added in proof: Recent x-ray diffraction–laser heating measurements (*8*) also provide evidence for a new phase in a pressure-temperature range similar to that studied here.

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5. J. Zhang and S. K. Saxena conducted in situ heating experiments with SAM-85 equipment [from the Center for High-Pressure Research (CHiPR), State University of New York at Stony Brook] at X-17B at the Brookhaven National Laboratory during 1993 and measured the pressure and temperature transformation of bcc to fcc.
6. The sample area studied was about 35 μm by 80 μm in size. The cold pressure variation across the sample chamber was 34 to 40 GPa. The pressure measurement was based on the [200] d-spacing of MgO. The x-ray beam was 7 μm by 15 μm in size, which was similar to the size of the laser beam (diameter 15 μm). The pressure variation within the beam-size area was less than 0.5 GPa; however, there was a significant Gaussian temperature distribution over the beam-size area.
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9. We thank J. Hu for assistance at the Brookhaven National Laboratory and colleagues at CHiPR for many useful discussions. Supported by grants from the Swedish Natural Science Research Council (NFR) and Wallenberg's Foundation.

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Excitation of Spirals and Chiral Symmetry Breaking in Rayleigh-Bénard Convection

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Spiral-defect populations in low–Prandtl number Rayleigh-Bénard convection with slow rotation about a vertical axis were measured in carbon dioxide at high pressure. The results indicate that spirals act like "thermally excited" defects and that the winding direction of a spiral is analogous to a magnetic spin. Rotation about a vertical axis, the spiral analog of the magnetic field, breaks the zero-rotation chiral symmetry between clockwise and counterclockwise spiral defects. Many properties of spiral-defect statistics are well described by an effective statistical-mechanical model.

The discovery of spiral-defect chaos (SDC) in Rayleigh-Bénard convection (*1*) was completely unexpected and challenged long-standing theoretical ideas (*2*) about the possible states and dynamics of convection. Since the initial experimental observations, numerical simulations (*3*) and experimental work (*4*, *5*) have confirmed the robust nature of the spiral state (Fig. 1A). One aspect of spiral defects that differentiates them from defects in other systems (*6*) is that they are not constrained to be created in pairs. The spiral-defect state displays individual spirals with clockwise or counterclockwise winding (Fig. 1, B and C), targets (Fig. 1D), dipoles with the same or opposite windings (Fig. 1, E and F), and multiple-armed spirals (Fig. 1, G and H). The mechanism for the creation of such a variety of forms is unknown, but, as demonstrated by numerical simulations (*3*), a crucial element is the strength of the mean-drift field, which plays an important role in low–Prandtl number convection.

In many areas of physics an external field is helpful in probing the state of a given system. For example, a magnetic field allows for a determination of magnetization and magnetic susceptibility, which are important characteristics of systems with magnetic spins. Similarly, rotation about a vertical axis is useful in probing the SDC state. Analogies between phenomena in nonequilibrium and thermodynamic systems (for example, between bifurcations and phase transitions) and concepts from condensed-matter physics (such as orientational order) have been helpful before in the analysis of nonlinear, nonequilibrium systems (*7*). We have found that a "thermal excitation" description of spiral-defect populations works very well. Rotation about a vertical axis breaks the chiral symmetry between clockwise and counterclockwise spirals, in anal-

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