**Structure of β-iron at High Temperature and Pressure**

D. Andrault et al. (1) conducted an in situ x-ray study of heated iron at high pressure (P) and found a structural transformation of $\varepsilon$-Fe (hcp) to another phase, which they assign to an orthorhombic lattice. There are two problems with this conclusion. First, their method, applying structural refinement for the purpose of "quantitative assessment of a structural model," is invalid. Second, we question whether phase analysis of collected x-ray patterns can be interpreted as a mixture of known iron phases $\varepsilon$ (hcp), or $\beta$ (dhcp, double hexagonal close packed), or both, iron oxide, and pressure medium.

X-ray data (1) are unsuitable for quantitative structural refinement because of (i) preferred orientation effects, (ii) large temperature ($T$) gradients in the sample, and (iii) stress effects. One condition for a successful application of the Rietveld refinement of crystal structures using powder x-ray diffraction data is the random distribution of the fine (small) crystallites in the sample (2). In other words, the Debye rings collected on imaging plate detector must be clear and smooth. The patterns collected at high $T$ and $P$ (figure 1 in (1), for example) demonstrate highly spotty discontinuous lines; many spots on those lines have their own shape and substructure, which means that crystallites in such samples are not small enough. The crystallites have uneven distribution, different shapes, and different orientation with respect to stress axes in the diamond anvil cell (DAC).

In diamond-anvil cell (DAC) experiments, especially with solid mediums such as those described in the report (1), samples have preferred orientations. Andrault et al. (1) do not describe how they take this effect into account (3). The preferred orientation not only decreases quality of powder diffraction data and increases uncertainty in the results of structural refinement, but also makes the reliability of the structural model doubtful. For example, they (1) stress the point that (002) $\varepsilon$-Fe (hcp-Fe) lines disappear after heating (for example, when conditions for recrystallisation were created). Such behavior of hcp metals is common and can be explained by an alignment of crystallites with the $c$ axis parallel to the load direction (4–7). Therefore, "the absence of the $010$, $001$, and $011$ reflections, and the presence of the 100 reflection" could reflect the existence of strong preferred orientation effects and does not justify a selection of possible space groups for structural models (8).

Andrault et al. (1) state in their report, “artifacts due to pressure or temperature gradient (spatial or temporal) are excluded.” Note that with Nd:YAG laser and 15$^\circ$X 2$^\circ$ FWHM X-ray beam, radial $T$ gradients of 100 to 200 K are difficult to avoid (9). But more important is the vertical (axial) $T$ gradient. Nd:YAG laser radiation is completely absorbed in the first several dozen nanometers of iron, and the rest of the metal (>99%) is heated only by thermal conduction (10). Andrault et al. (1) state that, as a result of heating diffraction, peak widths increase 1.4 to 3.5 times as compared with those of ambient conditions for Si-standard. According to the equation of state of iron ($f(T)$), this finding could be a result of a significant $T$ gradient (400 to 500 K). Moreover, the $P$ medium (corundum) next to the diamond-sample interface is cold, and $T$ gradient within corundum could be as high as 1500 to 1800 K at $\sim$2100 K. Most of the iron reflections partially overlap with corundum reflections and, as a result, structural refinement of powder data should be done for metal and $P$ medium simultaneously. The GSAS program (12) used for structural refinement in the report (1) does not include options to take into account high $T$ gradients within the samples. Resulting orthorhombic symmetry of iron obtained in the report (1) could be an artifact resulting from significant $T$ gradients in the sample.

It is important to consider deviatoric stress in interpretation of all results of DAC experiments. It was shown that in iron, the uniaxial stress component $t$ reaches a value $\sim10$ GPa at a $P$ range of 50 GPa (5, 6, 13). With the use of recently developed theory of diffraction from specimen compressed nonhydrostatically in an opposed anvil device (14) and elastic moduli (15), we calculated the positions of the diffraction lines of $\varepsilon$-Fe at 50 GPa and various $t$, from 5 to 10 GPa. We found that, as a result of deviatoric stress, ideal hexagonal hcp lattice of $\varepsilon$-Fe looked like orthorhombic, with a $b/a$ ratio of 1.74 to 1.745 (the ideal ratio for hexagonal lattice is 1.732; Andrault et al. obtained a value of 1.766). Therefore, the iron orthorhombic lattice found in the report (1) could be a result of the application of an incorrect fitting procedure for the samples under stress conditions (16–18).

Turning now to the second problem with this report, Andrault et al. (1) do not present clear hcp-Fe patterns. Bottom lines in figure 2 in the report (1) already contain at least two additional features at 1.85 and 2.03 Å. They mention that those reflections "are due to initiation of the transformation of $\varepsilon$ hcp iron toward a high-temperature polymorph" and incomplete transition to a new phase. At 100 GPa (Fig. 1A), there are even more unexplained features on the pattern that Andrault et al. have marked as "hcp-iron" (19, 20), which raises the question whether Andrault et al. (1) had pure hcp-Fe at any $P$; they do not present any data on the unheated samples. The additional features are quenchable at high $P$ (see figures 2 and 4 in (1)). The corundum lines, for example, (104) ($\sim$2.44 Å), (110) ($\sim$2.27 Å), and (113) ($\sim$1.99 Å), are much broader after heating and look almost like doublets. Moreover, according to Andrault et al. (1) "the features are mostly unquenchable." We would not expect the high-$P$, $T$ phase to remain the same after decompression. So, if the new features on diffraction patterns are only "mostly" unquenchable (meaning that some high-$P$, $T$ reflections continue to show after quenching), we have to question whether the sample has changed by possible chemical reactions.

Three of four new lines (1.44, 2.03, and 2.35 Å) appeared at high $T$ (Table 1) at 44.6 GPa (cold $P$ according to the report (1)) correspond to iron oxide FeO with B1 structure [lattice parameter $a = 4.070$ Å (3) corresponds to 48 GPa cold $P$, according to (11)]. At $P$ higher than 16 GPa and room temperature, wustite transforms to a phase with rhombohedral lattice (21). The reflections of this rhombohedral phase (Fig. 1B) shows almost completely overlap with corundum (104), (110), (113), and (108) lines. Therefore, appearance and disappearance of lines at 1.44, 2.03, and 2.35 Å during heating and cooling at 44.6 GPa [figure 2 in (1)] is just a result of the transformation of rhombohedral FeO to cubic and vice versa (22) and not a result of the presence of an orthorhombic iron phase. That leaves us with only one reflection (1.85 Å) (or, equally, shoulder [see Figure 2 and 5 in (1)], as it was observed in our laboratory (23)) unexplained in terms of Table 1. Possible indexing of the diffraction lines recorded at 44.6 GPa and 2125(70) K and described as iron lines by Andrault et al. (Table 1 in [1]). Columns with $\varepsilon$-Fe and dhcp-Fe taken from the report (1) and with the sign "\*" indicate some experimental features which cannot be explained by the occurrence of $\varepsilon$-Fe.

<table>
<thead>
<tr>
<th>Experiment ($I$)</th>
<th>$\varepsilon$-Fe (hcp)</th>
<th>$\beta$-Fe (dhcp)</th>
<th>FeO (B1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.347</td>
<td>+</td>
<td>+</td>
<td>111</td>
</tr>
<tr>
<td>2.072</td>
<td>+</td>
<td>+</td>
<td>100</td>
</tr>
<tr>
<td>2.031</td>
<td>+</td>
<td>004</td>
<td>100</td>
</tr>
<tr>
<td>1.846</td>
<td>+</td>
<td>102</td>
<td>200</td>
</tr>
<tr>
<td>1.824</td>
<td>101</td>
<td>+</td>
<td>200</td>
</tr>
<tr>
<td>1.440</td>
<td>+</td>
<td>104</td>
<td>220</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>2.393</td>
<td>2.393</td>
<td>4.070(3)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>3.845</td>
<td>8.126</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. (A) Diffraction spectra of iron and silica collected before (bottom line) and after laser heating [reproduced from figure 4 in (1)]. Values of d-spacing taken from table 2 in (1). Square marks the area where one could expect the exclusive (100) orthorhombic iron reflection. Circles denote features that were not explained by Andrault et al. (1). Silica reflections (for example, around 2.1 Å) are quite broad and appear not to be single peaks. Arbitrary units, a.u. (B) Calculated diffraction pattern of a mixture of corundum at 45 GPa (upper marks, a = 4.5453 Å, c = 12.4197 Å) and rhombohedral FeO (a = 2.7545, c = 7.3045 Å). Positions of corundum and FeO reflections are close; they are broad and may even be split reflections as seen on the top line in figure 2 of (1) (iron and corundum sample after laser heating at 44.6 GPa), which could be a result of partial oxidation of iron and presence of rhombohedral FeO in the sample. (C) Calculated diffraction pattern of a mixture of hcp-Fe (bottom marks), dhcp-Fe (middle marks), and silica with CaCl2-like structure (top marks) (19). Major features in Fig. 1A, including small reflections −1.93 Å and −1.53 Å, could be explained by this model. (D) Calculated diffraction patterns of mixture of α-Fe (hcp) at P = 98 (bottom marks) and 72 (top marks) GPa (11), and silica with CaCl2-like structure (middle marks) (19). Difference in P could be a result of a drop in P locally at the laser heated spot, or a result of phase transition in silica, or both. This model explains major lines presented in figure 1 and Table 2 in (1), but cannot explain, for example, small lines −1.93 Å and −1.53 Å.
mixture of corundum, e-Fe and iron oxide. This line was observed in our previous experiments with iron (23–25) and has been explained as the most intensive (102) dhcp-Fe (double hexagonal close packed) line, which could appear alone in the case of an incomplete transformation from hcp to dhcp structures, or which could be a result of effects of preferred orientation (26).

An analysis of the pattern collected at 100 GPa (I) is more difficult because (i) the quality of the data from the quenched sample is not precise; (ii) the description of the data in the report is schematic [for example, see the position of the silica reflections; some reflections on the pattern are not described or not explained, see figure 1a in (I)]; and (iii) crystal chemistry of silica and Fe-O system at extremely high P, T is poorly known. But the “exclusive orthorhombic” (100) reflection (near ~2.3 Å) is absent (Fig. 1A) (27), and most of the features could be qualitatively explained by the mixing of hcp-Fe, dhcp-Fe, and silica with CaCl2-like structure (Fig. 1C). A less preferred alternative is that P dropped on the locally heated spot and the x-ray pattern is for dhcp-Fe at different P in the sample (Fig. 1D) (28). Note that the model with a mixture of dhcp-Fe could explain, for example, the reflection ~1.93 Å [dhcp-Fe (101)], which was not explained by orthorhombic iron structural model.

On the basis of discussion above and our interpretation of the data, we conclude that data of Andrault et al. (1) do not provide evidence of the existence of iron with orthorhombic structure, but instead support the existing data on the transition from e-Fe to β-Fe, which probably has a dhcp structure (23–25, 29).

Response: Dubrovinsky et al. do not agree with our interpretations (1) of iron at high P and T. We favor an orthorhombic-iron explanation of the experimental features, which seems to us the most parsimonious. Dubrovinsky et al. state that we encountered several artifacts including: (i) stress at 2125 K that would make e-iron look like an orthorhombic lattice; (ii) P as different as 72 and 96 GPa in the same 15 to 8 μm² area after the sample annealing; and (iii) a severe oxidation in a new unquenchable Fe-O-polymorph (2). Their criticism might be viewed as a defense of the “d-hcp” model of iron at high P and T (3). We answer each of their criticisms in turn.

1) Powder statistics. Dubrovinsky et al. state that with reduced powder statistics the reliability of the observed intensities is not sufficient for an assessment of a crystallographic model. The data show, however, that even if our iron diffraction lines are somehow spotty, they do correspond to hundreds of crystallites over the 29 rings (Fig. 1) [Figure 1 in (I)]. It is because there is a reduced number of iron grains in the x-ray spot that angle dispersive diffraction with use of a 2-dimensional detector is required. For such small samples, the use of energy dispersive diffraction is prohibited because of the limited reciprocal space covered by the 0-dimensional Ge-detector. In an energy-dispersive experiment, the occurrence or absence of particular diffraction peaks is often not reproducible (4).

2) Preferred orientation. Preferred orientations of the crystallites are likely to happen on compression, especially for anisotropic structures such as dhcp.
We suggest that the d-hcp structure corresponds to a model that makes the occurrence of the d-hcp Bragg-lines has not been quenched spectra. We therefore exclude artifacts resulting from large thermal gradients because it is located between the laser-heated iron and the cold diamonds. The generation of stress during cold compression (8) or T quenching is the main reason why we used high-T spectra to test our structural model. Stress is lowest at high T because the iron shear modulus decreases with increasing T. Dubrovinsky et al. appear to agree with this concept, but do not question the previous d-hcp iron determined with the use of quenched spectra (3).

5) Purity of our starting material. Dubrovinsky et al. state that the new peaks observed at high T for iron [figure 2 of (1)] are those of a hypothetical B1-cubic high-T polymorph of FeO. This polymorph would (in their opinion) be unquenchable, but if it were, we would not have observed the diffraction lines of the low T FeO rhombohedral phase (9), which overlap with the corundum spectrum. Their criticism is answered by the fact that we did not observe the FeO-rhombohedral lines at any P performed in our study (1) with the use of Al2O3 [10] and with SiO2 as the P medium. The SiO2 diffusion pattern does not overlap with that of FeO (Fig. 2).

Still, the quality of diffraction spectra recorded at extreme conditions of pressure and temperature might not be sufficient for a full Rietveld structure refinement. We used the GSAS package to test our structural model by comparing calculated with observed intensities. The fact that we obtained such a good agreement [figure 5 of (1)] is a strong corroboration of the validity of the Pbnm-model for iron.

It is this agreement between experiments and a structural model that makes the difference between the Pbnm and d-hcp models for iron at high P and T. The d-hcp model does not provide a definite crystallographical model, and previous studies did not propose a space group related to an atomic topology. Also, there is no Lebail refinement available that would support the validity of the d-hcp model to explain experimental features (11). It seems that the occurrence of the d-hcp Bragg-lines has not been reproduced, although attempts have been made, and thus these lines should not be used to determine extinction rules (12). We suggest that the d-hcp structure corresponds to an intermediate iron structure that occurs at moderate T.
References and Notes

4. The d-hcp lattice was proposed on the basis of results using energy dispersive diffraction [see (3), and L. S. Dubrovinsky, S. K. Saxena, P. Lazor, Eur. J. Mineral. 10, 43 (1998)].
5. At a nominal pressure of 44.6 GPa [Figure 2 of (1)], the iron peak located around 2.06 Å show a FWHM of 6.6, 5.3, and 5.6 10^-3 for temperature of 300, 1965, and 2125 K, respectively.
6. In a previous study in 1996, Saxena et al. deliberately produced a huge thermal gradient and argued for the occurrence of d-hcp lattice [fig 2 in (3)]. This is the best way to develop strong thermal stresses, thus promoting formation of nonequilibrium phases.
10. Corundum peaks cannot mask the FeO features from 30 to 65 GPa because FeO [K_T = 142 to 182 GPa [9]] is significantly more compressible than corundum [K_T = 253 GPa; P. Richet, J. A. Xu, H. K. Mao, Phys. Chem. Minerals 16, 207 (1988)].
11. L. S. Dubrovinsky, presentation at a meeting of the American Geophysical Union, San Francisco, USA, 8–12 December 1998.
12. Dubrovinsky et al. recently reported a first quantitative assessment of the experimental lines using the d-hcp lattice [table 1 in (13)]. Two characteristic lines (004 and 103) are single spots on the reported pattern [fig. 2 in (13)] that disappear on prolonged heating. The occurrence of the 100, 102, and 104 d-hcp lines could correspond to that of ε-hcp (100, 101, 102). Thus, they report only 1 stable new line located at 2.0009 Å, a line that is expected for orthorhombic iron [110-line; see table 2 of (1)].
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Editor's Summary