ESRF	**Experiment title:** Iron phase transformation to the γ phase near the α–ε–γ triple point	**Experiment number**: HC-2783
Beamline: ID27	**Date of experiment**: from: 12/11/2016 to: 15/11/2016	**Date of report**: 20/02/2017
Shifts: 9	**Local contact(s)**: V. Svitlyk	*Received at ESRF:*
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Report:

This proposal was the continuation of HC-2180. The aims of this project are: (i) to measure the equations of states of the phases and volume discontinuities for α–ε and α–γ transitions in iron near the α–ε–γ triple point; (ii) to determine the mechanism of these transformations from orientation relations between parent and child phases; (iii) to synthesize ε-Fe single crystals as samples for inelastic X-ray measurements of their single crystal elastic constants. For that purpose, we have used X-ray diffraction of a single crystal (or powder for one sample) compressed hydrostatically in a resistively-heated diamond-anvil cell.

The diamond anvil cells, loaded with iron samples embedded in neon pressure medium, were inserted in a vacuum resistive furnace which allows heating up to 850K on the samples. This device was provided by ID27. The temperature was measured by a thermocouple in contact with the back of one diamond anvil. The pressure was measured using a $SrB_4O_7:Sm^{2+}$ luminescence gauge. The phase and volume have been measured using angular-dispersive X-ray diffraction. The conditions of the experiments are summarized in **Table 1**.

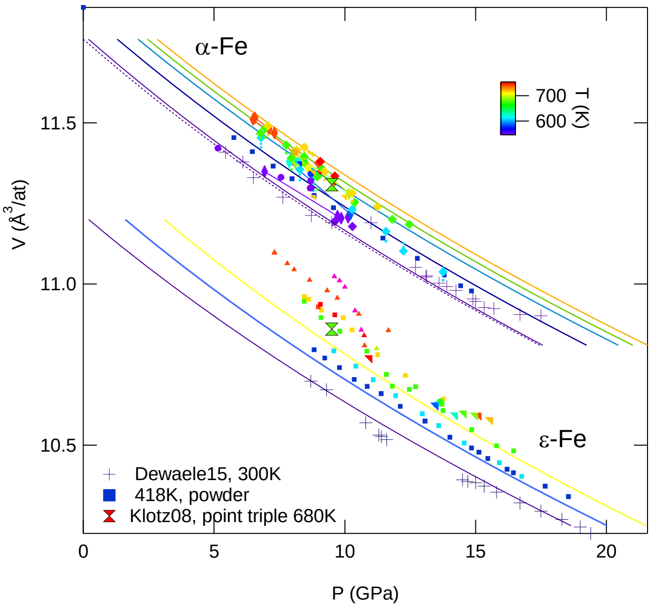
Run name	Sample	Pressure medium	Pressure range (GPa)	Temperature range (K)
FeBPHT_4	Fe single crystal	Neon	6-15	300-800
FeBPHT_5	Fe single crystal	Neon	6-15	300-800

Table 1: Conditions of the two experimental runs.

The observations we have made in this run and HC-2180 run can be summarized as follows:

- The α–ε–γ triple point has been located at 9.1±0.5 GPa and 720±30 K. The error bars are due to the hysteresis of the martensitic transformations involved.
- The Clapeyron slope of the α–ε transition line changes at high temperature, in the vicinity of the triple point.
- Thermal expansions of α-Fe and ε-Fe progressively diverge from quasi-harmonic predictions when approaching the triple point (see **Figure 1**), with an overestimate of thermal expansion in α-Fe and an underestimate in ε-Fe by these models;
- The α–ε mechanism determined from orientation relations, which was proven to be a Burgers path [3], remains unchanged up to 650 K. Concerning the γ–ε transformation, the Shoji-Nishiyama orientation relations are observed.
- An ε-Fe single crystal can be obtained following a high pressure-high temperature path (see **Figure 2**). This is very promising in the perspective of measuring the properties of this important material,

especially its elastic properties. Preliminary tests performed on ID28 showed that the acoustic phonons can be measured for the single crystal synthesized in FeBPHT_4 run.



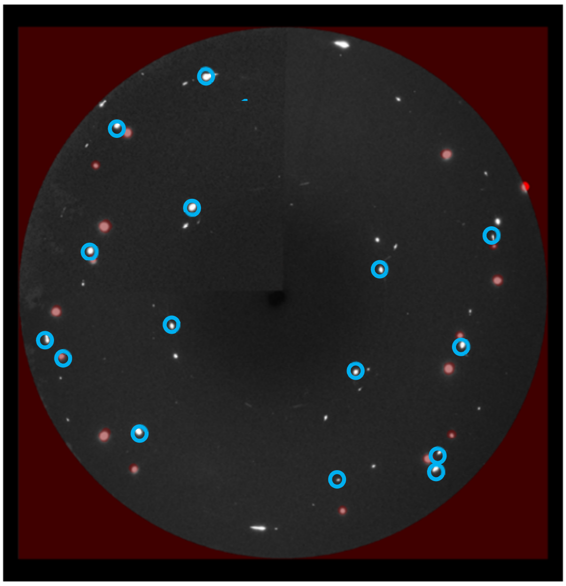


Figure 1 (left): Equations of state in ε-Fe and α-Fe near the α–ε transformation. Different symbols correspond to different experimental runs. The colors correspond to the temperature. The continuous lines are isotherms calculated using quasi-harmonic models (same T-colorscale) [1,2].

Figure 2 (right): X-ray diffraction pattern of ε-Fe synthesized in run FeBPHT_4. The ε-Fe single crystal XRD peaks are circled in blue. The pressure is 14.5 GPa.

The low thermal expansion measured in α-Fe may be due to a phonon softening and/or anharmonicity, possibly related to magnetisation and the vicinity of the α–γ transformation [4]. Anharmonic models based on ab initio modeling of both α and ε phases are likely needed to explain experimental observations represented in **Figure 1**. A better understanding of the α–γ transition mechanism in this P-T domain, which was not obtained here due to experimental difficulties, would certainly help constraining these models.

The results obtained here provide tight constraints on the phase transformation conditions and thermodynamic parameters of iron the near the triple point; as such they certainly deserve publication. They also open the following perspectives:

- Synthesis of ε-Fe single crystals in view of measuring their single crystal elastic constants by inelastic X-ray scattering between 15 and 40 GPa.
- Determination of the orientation relations between α and γ phases during the a-g transformation
- Ab initio modeling of the phonons in the α and ε phases near the transformation (performed in our laboratory).

References:

[1] S. Klotz et al., Elastic properties of α-Fe at HT by HP neutron scattering, J. Phys. D: Appl. Phys. 44, 055406, 2011
[2] A. Dewaele, P. Loubeyre, F. Occelli, M. Mezouar, P. Dorogokupets and M. Torrent, “Quasi-hydrostatic equation of state of iron above 2 Mbar”, Phys. Rev. Lett., 97, 215504, 1-4, 2006.
[3] A. Dewaele, C. Denoual, S. Anzellini, F. Occelli, M. Mezouar, P. Cordier, S. Merkel, M. Véron and E. Rausch, Mechanism of the alpha-epsilon transformation in iron, Phys. Rev. B 91, 174105, 2015
[4] L. Mauger et al., non-harmonic phonons in a-Fe at high temperatures, PRB 90, 064303, 2014

From : A. Bosak, 30.11.2016

Hcp iron at 14 GPa: ID28 IXS study 23.11.2016

17.8 keV energy, 3 meV energy resolution, KB focusing (can be 15x25 μm^2)

Multigrain sample with dominating grain with 001 axis roughly along the DAC axis

Aligned with 100, 010, 110 Bragg's reflections, measurements performed in the proximity of 110 spot

Rocking curves for 110 < 1 deg

Lattice parameters as measured at ID27 / density 9.0 g/cm^3

Phonon spectra in the proximity of 110 are very clean, further they start to get the contributions from the adjacent grains; nevertheless most of the spectra remain exploitable (example – Fig. 1).

Sine fit applied to reasonably well defined phonons to get the sound velocities

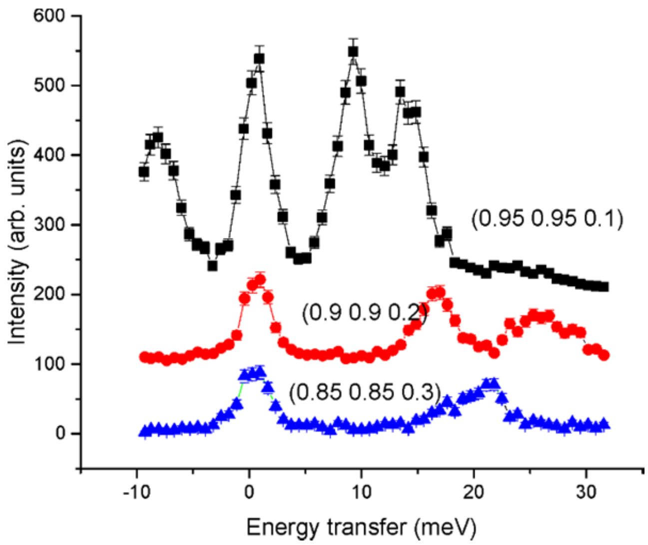


Fig. 1. IXS spectra taken for q//112

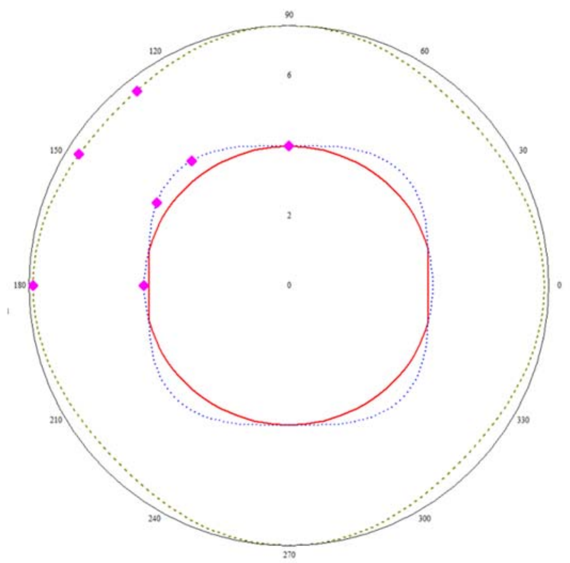


Fig. 2. Measured and fitted sound velocities

While for the fitted moduli the error bar can be quite large, we can state the absence of the agreement with some DFT calcualtions [Sha and Cohen PRB 2010, as illustrated in Fig. 3. NB: Experimental point, corresponding to the in-plane experimental transverse wave is sitting on the sheet with different polarization.

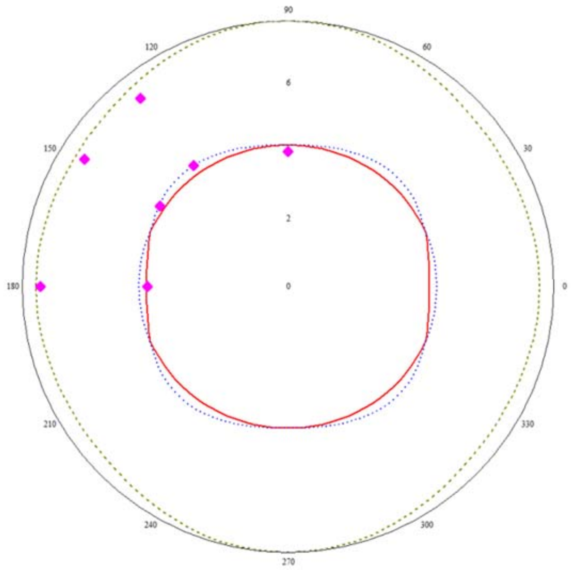


Fig. 2. Measured and calculated [Sha and Cohen PRB 2010] sound velocities

Conclusion:

- hcp iron single crystal grains are already suitable for the study of elasticity
- isolated single crystal grain is needed for the complete study of lattice dynamics
- c-axis orientation perpendicular to the cell axis is highly desirable
- we have solid ideas about hcp iron elasticity just above the transition
- at least some ab initio calcualtions are off in absolute values and in the ratios between the moduli