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Experiment Report Form

	Experiment title: Charge-ordering and magnetic properties of iron oxides at high-pressure and low-temperature conditions	**Experiment number**: HC-5142
Beamline: ID18	**Date of experiment**: from: 27.09.2022 to: 03.10.2022	**Date of report**: 01.03.2023
Shifts: 18	**Local contact(s)**: Dimitrios Bessas	*Received at ESRF:*

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Report:

Understanding unusual transformations in iron oxides, accompanied by peculiar changes in atomic and electronic structures, is essential not only for geoscience but also for condensed matter physics and applied technologies. During the experiment, we performed the energy-domain synchrotron Mössbauer source (SMS) in membrane-driven cryogenic diamond anvil cells at ID18 up to 120 GPa and down to 10 K (Figure 1d). Thus, the aim of the experiment was partly achieved. **While we identified several magnetic and electronic transitions, we are lacking information on the high-pressure low-temperature phases.** We have performed a complementary single crystal X-ray diffraction measured at P02.2, PETRA III (Figure 1c) to identify low-temperature phases up to 24 GPa.

From our experiments, we revealed that the Fe atoms on the octahedral sites are magnetic and Fe atoms on prismatic sites are nonmagnetic at ambient conditions (Figure 1e). Under compression at room temperature, Fe on prismatic sites onset a magnetic ordering at ~4.5 GPa, accompanied by the phase transition from the *Cmcm* phase to the $P2_1/c$ phase checked by XRD (Figures 1b, c, d and f). This high-pressure structure differs from the

low-temperature structure of Fe_5O_6 observed in our data, likely due to the differences in the charge-ordering pattern. With further compression, Fe_5O_6 undergoes another phase transition from the $P2_1/c$ phase to the $C2/m$ phase at around 20 GPa (Figures 1c, d and g). This $C2/m$ phase can be preservied up to 60 GPa at room temperature. Above 60 GPa the new paramagnetic component arises, likely related to the onset of the spin crossover on the octahedral site, although another phase transition also cannot be excluded.

The SMS of the $C2/m$ phase can be well fitted by three magnetic sextets at 32 GPa, in line with the three distinct Fe sites in the structure of Fe_5O_6 (Figures 1a and g). However, when cooling down at this pressure, one sextet disappears (Figures 1f and g), which should be related to a yet undetected phase transition at this pressure-temperature range. Our SMS experiments clearly demonstrate that the phase diagram of Fe_5O_6 is much more complicated than currently assumed and further investigation is needed.

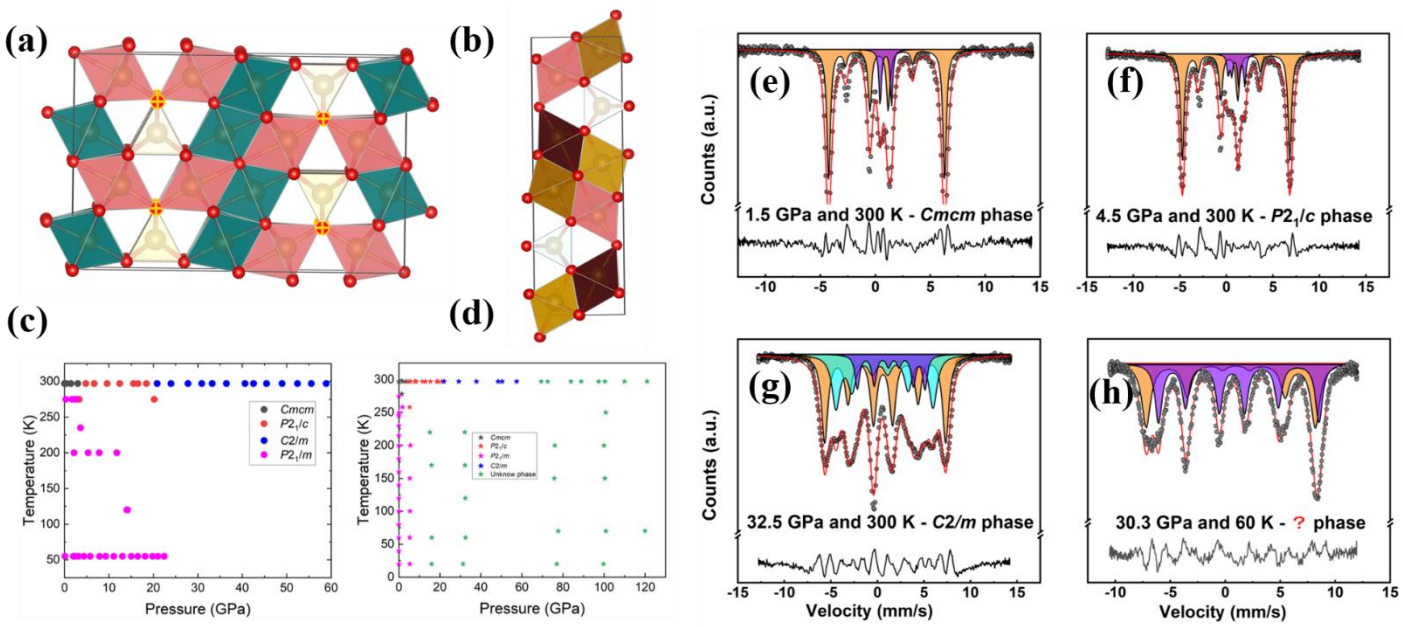

Figure 1. (a) Structure of Fe_5O_6 with Cmcm space group at ambient conditions. (b) Structure with P21/c space group at 4.5 GPa and room temperature. (c and d) Pressure-Temperature phase diagram of Fe_5O_6 coverage in our XRD and SMS experiments, respectively. (e-h) Selected SMS spectra measured at indicated pressure and temperature conditions.