



	<b>Experiment title:</b> "Is there a new charge ordered state in the high pressure phase of $\text{LuFe}_2\text{O}_4$ ?"	<b>Experiment number:</b> HC-1665
<b>Beamline:</b>	<b>Date of experiment:</b> from: 23 Jan 15 to: 3 Feb 15	<b>Date of report:</b> 28 AUGUST 15
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**Report:**

The main aim was to measure the magnetic-electronic behavior of the high pressure phase (HP) of  $\text{LuFe}_2\text{O}_4$  (LFO), stabilized at  $P > 8$  GPa, by using synchrotron Mössbauer spectroscopy (MS). There is uncertainty as to whether a mixed-valence state and charge-order prevails in this HP phase [1,2]. This was to be gleaned from MS measurements of LFO at in-situ high pressure and liquid helium conditions. The high brightness tightly-focussed low-background synchrotron Mossbauer source ( SMS) at ID18 was used to probe an LFO sample pressurised in a diamond anvil cell (DAC). Such an experiment would prove impractical using in-house (home-lab)  $^{57}\text{Co}(\text{Rh})$  “point” source methodology on the well characterised highly stoichiometric, natural isotopic abundance, LFO sample obtained from Caen-France [1]. Prior Mössbauer pressure measurements to 30 GPa at 300 K had already been taken in our home-lab (~14 days data acquisition per spectrum). The HP phase is magnetic at room temperature and comprises several Fe sites. MS at liquid helium temperatures would help reveal if separate valences  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  exist.

First tests with the SMS were performed on samples pressurised to starting pressures of ~1 GPa. It took half a day to accumulate a spectrum of reasonable quality (count rate of 600 - 1000 counts per second), to discern the magnetic spectrum comprising at least four Fe sites. Both the complexity of the magnetic splittings and high absorption by the Lu constituent were contributing factors to a requirement of comparatively long acquisition times. Sample thicknesses not exceeding 25  $\mu\text{m}$  were used to mitigate the effect of the latter, electronic absorption. The transition from a low pressure structure to HP phase is irreversible and the HP phase may be recovered to ambient conditions [2]. Therefore two HP samples recovered from previous high pressure studies ( $P \geq 12$  GPa) were trapped in DAC gasket cavities and probed with the SMS at 4 K. This would also yield pertinent information on whether valence separation is existent in the HP phase. One of the LFO samples was the highly stoichiometric material mentioned above. The second was a  $^{57}\text{Fe}$ -enriched LFO sample prepared by us, but which is slightly off stoichiometric and is less well characterised. A spectrum of acceptable quality was obtained in 2-3 hours for this enriched sample at

ID18. For the unenriched recovered LFO sample a spectrum of reasonably good quality was obtained in 8-10 hours.

Plots of the data are depicted in figure 1 below. The complex nature of the magnetic spectra involving multiple Fe sites is showcased. Current analysis, using the MOSSA software, shows that there are suites of large and small magnetic hyperfine field ( $B_{hf}$ ) components in the HP phase spectrum. The large  $B_{hf}$  suite has isomer shift (spectral centroid) values of  $IS = 0.66$  mm/s and the suite of small  $B_{hf}$  components has  $IS = 0.88$  mm/s. The separation into suites of large and small  $B_{hf}$  components is considered evidence that some degree of valence separation exists. However the small IS separation of these suites, compared to ionic values of  $Fe^{2+}$  ( $IS \geq 1.2$  mm/s) and  $Fe^{3+}$  ( $IS \leq 0.5$  mm/s), is interpreted as charge delocalization. The resultant charge states are better designated as  $Fe^{(3-\Delta)+}$  and  $Fe^{(2+\Delta)+}$ , where  $0 < \Delta < 0.5$  is the delocalization coefficient signifying valence detrapping. The delocalization is considered to occur by way of minority-spin electron hopping,  $Fe^{2+} \Leftrightarrow Fe^{3+}$ , in the HP structure [3].

The combination of SMS experimental results in conjunction with our home-lab based Mössbauer pressure studies, including resistivity pressure studies, is at an advanced stage of preparation for publication. This work, primarily focused on the stoichiometric LFO sample, is to be submitted for publication in the next several weeks. A preliminary account was presented at the CORPES15 (electronic structure) conference in Paris in July 2015 (see <http://www.synchrotron-soleil.fr/Workshops/2015/CORPES2015>). The results from the off-stoichiometric LFO sample will be submitted as a separate publication.

Additional ferrite samples were measured at in-situ high pressures in the DAC at liquid helium temperatures to gain further experience at the beamline. This was to better ascertain optimum sample conditions (sample thickness and isotopic enrichment) for obtaining an acceptable magnetic spectrum in relatively short acquisition times. An example of a spectrum acquired in one hour of  $ZnFe_2O_4$  enriched to ~20%  $^{57}Fe$  is shown at in figure 1(c) below, at 62 GPa and ~3 K. Magnetic and paramagnetic/non-magnetic central components can be discerned.

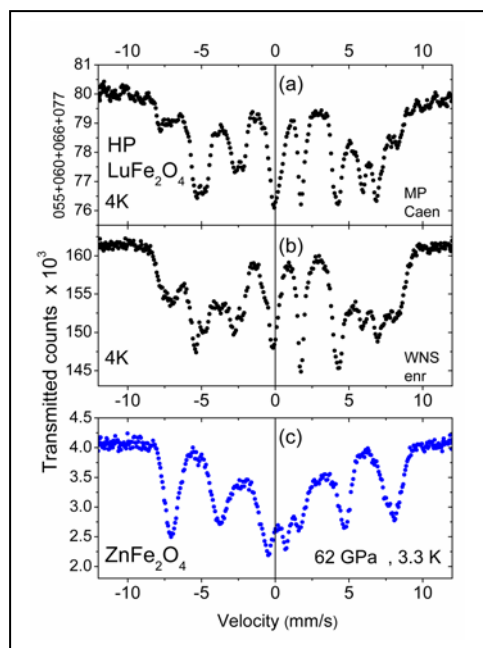


Figure 1 : HP phase of  $LuFe_2O_4$  (LFO) sample recovered to ambient pressure, measured at 4 K in the DAC. (a) Highly stoichiometric unenriched LFO sample. (b) Isotopically enriched LFO sample. (c) Enriched zinc ferrite at 62 GPa and 3.3 K.

## References

- [1] J. Rouquette, J. Haines, A. Al-Zein *et al.* Pressure-induced structural transition in  $LuFe_2O_4$ : Towards a new charge ordered state. *Phys. Rev. Lett.* **105**, 237203 (2010).
- [2] F. Damay, M. Poienar, M. Hervieu *et al.* A high-pressure polymorph of  $LuFe_2O_4$  with room temperature antiferromagnetic order. *Phys. Rev. B* **91**, 214111 (2015).
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