Charge ordering dynamics under pressure in $LuFe_2O_4$

W N Sibanda[1], E Carleschi[1], G Diguet[1], C Martin[2] and G R Hearne[1]
[1]Department of Physics, University of Johannesburg, PO Box 524, 2006 Auckland Park, Johannesburg, South Africa
[2]Laboratoire CRISMAT, ENSICAEN, UMR 6508 CNRS, Caen, France

Author e-mail address: wnsibanda@gmail.com

Abstract. The pressure response of charge order behaviour in $LuFe_2O_4$ has been investigated using pressure as a perturbing thermodynamic variable up to 7 GPa in diamond anvil cell experiments at 300 K. ^{57}Fe Mössbauer spectroscopy was used as the probing technique for magneto-electronic properties. An analysis of the Mössbauer effect spectra indicates that above 3 GPa the charge order has completely collapsed, also evidenced by the change in the Mössbauer spectral line shape. Above 3 GPa the magneto-electronic phenomena can be understood in terms of electron hopping processes, which occur in the time window of the Mössbauer effect (10^{-7} s). As a consequence of this Fe^{2+} and Fe^{3+} valence states are indistinguishable and are described by an intermediate valence state, $Fe^{2.5+}$. This destabilisation of charge order is compatible with magnetic collapse seen in neutron diffraction experiments. Charge carrier confinement, $Fe^{2+} \Leftrightarrow Fe^{3+}$, prevails at these high pressures.

1. Introduction

$LuFe_2O_4$ belongs to a family of hexagonally layered metal oxides, RFe_2O_4, where R is a rare-earth metal. Recently there has been a surge of interest in $LuFe_2O_4$ because of multiferroic properties being apparently observed in this system [1]. Multiferroic compounds show a strong coupling between magnetism and ferroelectricity; hence the combination of these two ferroic orders in a material has the potential for the tailor-making of multifunctional devices. Initially $LuFe_2O_4$ was thought to be the prototypical compound for charge order (CO) based ferroelectricity, where CO refers to a localisation of charge resulting in a mixed-valence superlattice (e.g., Fe^{2+} - Fe^{3+} - Fe^{2+} - Fe^{3+}…). Properties reported in this compound due to CO-based ferroelectricity included a large magneto-dielectric response and pyroelectricity near the spin ordering temperature [1]. Recent work has cast doubt on these observations because of the hitherto unknown subtle influence of electrical contacts in generating colossal values of the magneto-dielectric response [2]. This also puts in question the mechanism of charge order driven ferroelectricity. Despite this, there is still considerable interest in $LuFe_2O_4$ because the magneto-electric coupling is still pronounced.

$LuFe_2O_4$ has a rhombohedral unit cell (space group, *R-3m*) and exhibits a layered structure at room temperature, depicted in figure 1. The structure is described by an alternating stacking of $[LuO_2]_\infty$ layers and $[Fe_2O_4]_\infty$ bi-layers along the *c*-axis (figure 1(a)). The unit cell consists of three Fe bi-layers with a 1:1 ratio of Fe^{2+} and Fe^{3+}. There is a superstructure arrangement of Fe^{2+} and Fe^{3+} ions within the triangular network of each sheet of a bilayer (figure 1(b)). This particular Fe^{2+}/Fe^{3+} CO arrangement has long been thought to lead to charge segregation along the c-axis, leading to a net dipole moment and thus the occurrence of ferroelectricity [3, 4]. Lafuerza *et. al.* [5, 6] however have contested this model of an appreciable (ionic) valence separation as well as the occurrence of ferroelectric behavior; although valence segregation does seem to occur.

The corresponding spin values are S=2 for Fe^{2+} (d^6) and S=5/2 for Fe^{3+} (d^5). The triangular network in the Fe monolayers (each layer is made up of corner sharing FeO_5 trigonal bipyramids, see figure 1(c)) presents a scenario in which the magnetic and charge order interactions are incompatible with the topology of the crystal lattice, hence geometrical CO and spin frustration occur (figure 1(b)). Geometrical frustration can result in a plenitude of degenerate ground states. For example, $LuFe_2O_4$ undergoes different phase transitions: a 3-D charge order develops at $T_{CO} \approx 320$ K with cooling, while for 320 K < T < 500 K a 2-D CO ground state occurs. 3-D ferrimagnetic ordering sets in at $T_N \approx 240$ K, and a magneto-structural transition is observed at $T \approx 175$ K. Makarova *et. al.* have reported a gradual disappearance of long range magnetic order with pressure up to 3 GPa at 50 K in neutron diffraction measurements [7]. This is thought to be linked to the destabilisation of the magnetic moment and may be correlated with the melting of the CO. The purpose of this work is to investigate the behaviour of the CO in this pressure range.

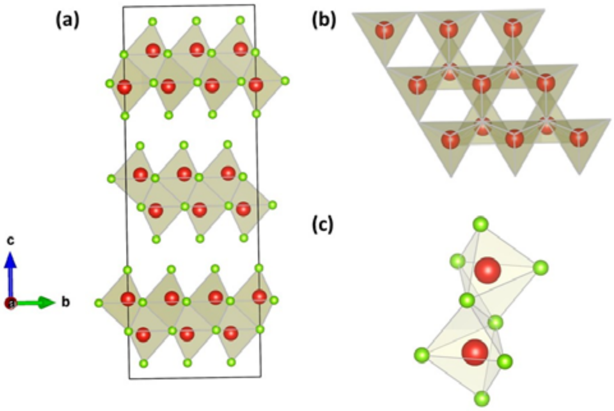


Figure 1 (Colour online): (a) Crystal structure of $LuFe_2O_4$ at room temperature, showing the *R-3m* rhombohedral layered structure atomic arrangement. The unit cell consists of three Fe bi-layers stacked along the *c*-axis. The Fe ion (in red) is coordinated in trigonal bi-pyramidal polyhedra with O ions (in green). The $[LuO_2]_\infty$ layers (not shown) are in between the bi-layers. (b) Projection of the *ab*-plane viewed along the *c*-axis showing the triangular network of Fe ions. (c) Isolated trigonal bi-pyramids sharing a corner. Structure insets generated using VESTA software [8].

To the best of our knowledge Mössbauer pressure measurements on $LuFe_2O_4$ have not yet been reported. ^{57}Fe Mössbauer spectroscopy, which is a nuclear γ-ray spectroscopy, allows probing the valence state of Fe as the only electro-magnetic active ion in the compound. To this end, a combination of high-pressure methodology and ^{57}Fe Mössbauer spectroscopy has been used in this work to investigate the magneto-electronic behaviour of a highly stoichiometric sample, $LuFe_2O_{4+\delta}$ (δ=0). In this present work we show that the CO collapses above 3 GPa in $LuFe_2O_4$ at 300 K, thereafter only dynamic charge exchange (electron hopping) are observed up to the maximum pressure, 7 GPa, reached in this study.

2. Experimental details

A polycrystalline sample of $LuFe_2O_4$ (with natural abundance of ^{57}Fe, 2%) was loaded into a Merrill-Basset diamond anvil cell (DAC). Details of its synthesis can be found elsewhere [9]. The sample and a few ruby balls for pressure calibration were loaded into a sample chamber made by drilling a 225 μm hole in a Re gasket pre-indented to 30 μm thickness. Daphne 7373 oil was used as pressure transmitting medium. A Wissel constant acceleration motor was used to scan the velocity range of interest (typically ± 5 mm/s) with a ^{57}Co (Rh) "point" source (≈ 0.5×0.5 mm, 10 mCi) at room temperature [10]. A $KrCO_2$ (1 atm) proportional counter was used to detect the 14.4 keV resonance γ-radiation.

The model used for analysis describes electron hopping relaxation within the framework of the Blume-Tjon theory [11]. In the case of electron hopping processes, the ^{57}Fe nuclei experience a Hamiltonian that relaxes between two eigenstates (with a relaxation rate of ω [rad/s]) characterised by different isomer shift (IS) and quadrupole interaction values. The Hamiltonian is described by:

$$\begin{aligned} H_1 &= \frac{\Delta_1}{6}\left(3m^2 - I(I+1)\right) + \delta_1 I \\ H_2 &= \frac{\Delta_2}{6}\left(3m^2 - I(I+1)\right) + \delta_2 I \end{aligned} \tag{1}$$

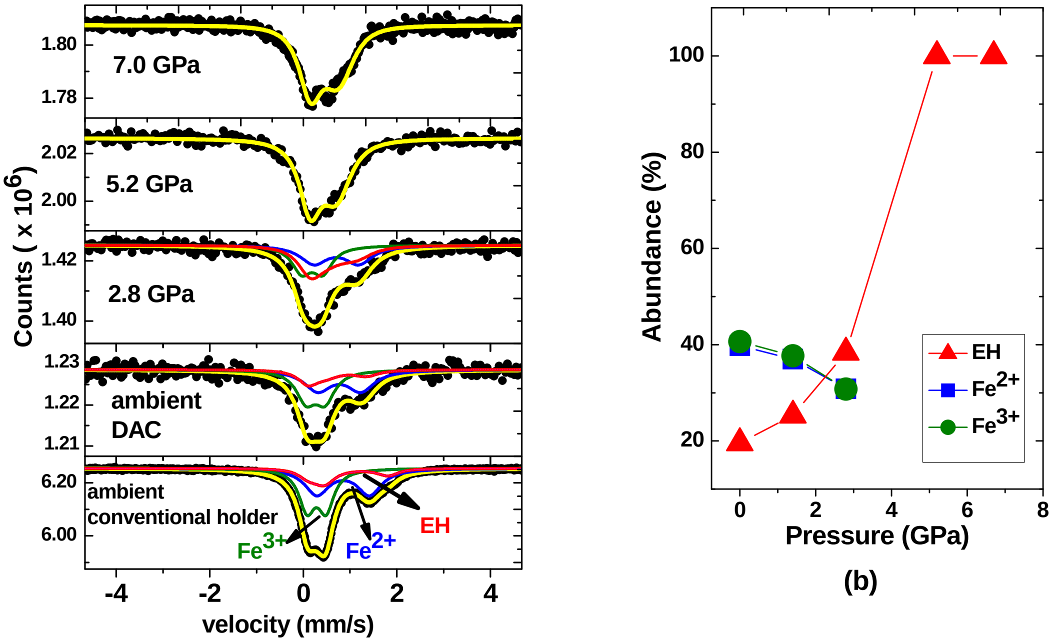
where H_1 and H_2 are the different eigenstates experienced by the ^{57}Fe nuclei. Each eigenstate gives rise to a characteristic quadrupole split doublet with associated isomer shift, quadrupole splitting, QS (Δ) and IS (δ) respectively. Thus H_1 gives rise to Δ_1 and δ_1, and H_2 to Δ_2 and δ_2. I and m are the nuclear spin quantum number and magnetic quantum number respectively. The IS and QS values fluctuate simultaneously between characteristic values for Fe^{2+} and Fe^{3+} (i.e. the average valence state is $Fe^{2.5+}$). The relaxation rate in [rad/s] is involved in the lineshape profile which is derived from a solution of a time dependent Hamiltonian characterizing the fluctuation between the two states (profiles) in Equation 1 [11, 12]. It is therefore obtained as one of the fitting parameters of the spectral profile and then converted to electron hopping frequency [Hz].

The spectra were analyzed using an appropriate Mössbauer spectra fitting program from which the hyperfine interaction parameters and the corresponding relative abundances of spectral components were derived [13]. Thickness broadening, pressure gradients and geometrical effects were taken into account in this analysis. The spectra were evaluated assuming Lorenztian line shapes for the resonant absorption patterns. The reported IS values are relative to α-Fe at 300 K.

3. Results and discussion

Figure 2 below shows a selection of Mössbauer spectra measured at various pressure runs up to 7 GPa at 300 K. The model used in the analysis was first implemented in the ambient spectra measured with the $LuFe_2O_4$ sample loaded in a conventional 1.7 cm^2 copper clamp holder and a 20 mCi ^{57}Co (Rh) conventional source. This ensures better counting statistics, high signal-to-noise ratio and high resolution obtained by using a conventional source with a narrower line-width; hence reliable hyperfine parameters could be extracted (see figure 2 (a) for comparison). The parameters obtained were then used as the starting values for the compression measurements.

The fitting model adopted for the sample at ambient pressure and temperature incorporates a fluctuating valence state; a markedly different approach from previous works [14, 15]. The observed Mössbauer spectra were analysed with three sub-spectra; two distinct quadrupole doublets describing Fe^{2+} (in blue) and Fe^{3+} (in green) sites with intensity ratio 1:1 describing the static CO. A third component was added to describe electron hopping between Fe^{2+} and Fe^{3+} (Fe^{2+} $\Leftrightarrow$ Fe^{3+}) (in red). This originates at CO nano-domain boundaries or is a result of the geometrical charge frustration [16-18]. The presence of the right most absorption peaks (higher velocity side) in figure 2 (a) are a signature of Fe^{2+}. Hence we deduce that the CO is already present at room temperature. The disappearance of this absorption peak would therefore indicate CO collapse.



(a)

(b)

Figure 2 (Colour online): (a) Selected ^{57}Fe Mössbauer spectra of the pressure response of LuFe$_2$O$_4$ at 300 K plotted on a restricted velocity scale. The black circles are the data points and the solid line through the data points is the overall fit to the data. With an increase in pressure, at ≈ 3 GPa, the Fe^{2+} signature is no longer easily discernable, indicating the initiation of CO collapse. At P > 3 GPa (see 7 GPa spectrum), the Mössbauer line shape is fitted with a component consistent with electron hopping processes only in the MHz regime (indicated by EH). (b) A plot of the EH component abundances as a function of pressure. The increase in the abundance of the EH component is readily apparent. Solid lines through the data points are to guide the eye.

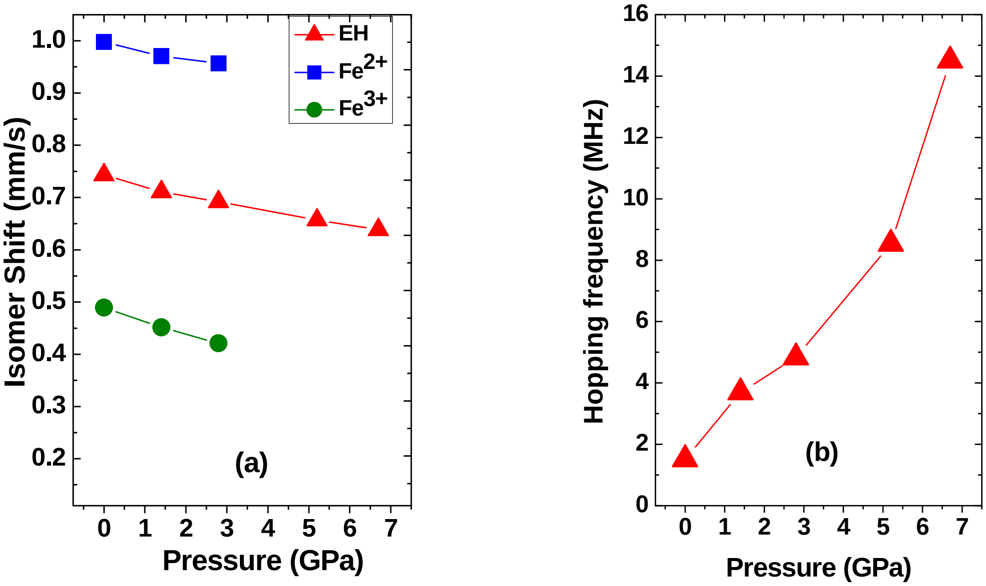


Figure 3 (Colour online): (a) Pressure dependence of the IS. The IS of EH (red triangle) is an average of the corresponding values of the fitted components, Fe^{2+} and Fe^{3+} in equation (1). The IS decreases with increasing pressure. (b) The pressure dependence of the hopping frequency as deduced from the fitting of the MS spectra. Solid lines are to guide the eye in (a) and (b).

The fit results of the ambient pressure spectrum reveal the co-existence of static CO (site-centered CO) of Fe^{2+} and Fe^{3+} in a 1:1 ratio and ≈ 20 % abundant sites where electron hopping is occurring (as explained above), in which the hopping frequency is 1.5 MHz, see figure 2 (b) and figure 3 (b). As the pressure increases, the Fe^{2+} signature becomes less discernable, indicating the beginning of CO collapse (see the Mössbauer spectrum at 3 GPa in figure 2 (a)). This is also confirmed by the increase in the abundance of the EH component with pressure (see figure 2(b)). Rouquette *et al*. observed a progressive rhombohedral to orthorhombic structural phase transition of the unit cell from 4–8 GPa [9]. Our Mössbauer analysis therefore infers that the CO collapse and structural phase transition are concomitant. In the range 5–7 GPa the Mössbauer line shape is consistent with electron hopping *only on* a nanosecond time scale (MHz regime), which is within the time (sensing) window of the Mössbauer effect of 100 ns [12, 16].

Figure 3 (a) shows the obtained values of the IS as a function of pressure. The plotted values of the IS (in red) for the EH component are the average of that of the individual components (Fe^{2+} and Fe^{3+}) describing the electron hopping model in equation (1). For all components, the IS decreases with pressure, which is attributed to the *s*-electron density increasing near the Fe nucleus. In fact, the IS is related to *s*-electron density, ρ_s, at the nuclear site. The quadrupole splitting (QS) of the components is observed to increase with pressure as expected (not shown). QS reflects deviation from cubic symmetry, an increase in QS is therefore attributed to increased site distortion around the Fe ion when pressure increases.

The pressure dependence of the hopping frequency is plotted in figure 3 (b) and shows a substantial ten-fold increase in the measured pressure range. Pressure decreases the inter-atomic distance and therefore the hopping between Fe sites is expected to be enhanced, consistently with what is observed here. The presence of *only* electron hopping and IS values intermediate between that of Fe^{2+} and Fe^{3+} above 3 GPa infer that the electrons are still confined, perhaps in some sort of dimerised bond between

Fe-Fe pairs in the *ab*-plane of the bi-layers. This would therefore suggest that the compound is still an insulator in this pressure regime, even though the CO is destabilized [19].

4. Conclusions

In summary, we have investigated the stability of the CO in a highly stoichiometric sample of $LuFe_2O_4$. The CO is destabilised at 3–7 GPa at room temperature. The Mössbauer spectra above 3 GPa indicate *only* electron hopping processes with relaxation rates on the nano-second time scale (2–16 MHz). The presence of electron hopping and IS values intermediate to that of Fe^{2+} and Fe^{3+} suggests charge confinement in the triangular network of the *ab*-plane of the crystal lattice (e.g. formation of dimers, $Fe^{2+} \Leftrightarrow Fe^{3+}$). Even though CO has been destabilised at pressure, there still appears to be confinement of the charge carriers. This will have implications for the electrical-transport behaviour. The destabilisation of CO is compatible with the collapse of magnetic order seen in neutron diffraction studies [7].

Acknowledgements

This work was supported by funding from the UJ-URC and NRF (SA), and supply of the sample used in this study from M. Poienar (Caen) is also acknowledged with gratitude.

References

[1] Subramanian M A, He T, Chen J, Rogado N S, Calvarese T G and Sleight A W 2006 *Adv. Mater.* **18** 1737
[2] Lafuerza S, Garcia J, Subias G, Blasco J, Conder K and Pomjakushina E 2013 *Phys. Rev. B* **88** 085130
[3] Ikeda N 2008 *J. Phys.: Condens Matter.* **20** 434218
[4] Ikeda N, Ohsumi H, Ohwada K, Ishii K, Inami T, Kakurai K, Murakami Y, Yoshii K, Mori S, Horibe Y and Kito H 2005 *Nature* **436** 1136
[5] Lafuerza S, Subías G, Blasco J, García J, Nisbet G, Conder K and Pomjakushina E 2014 *EPL* **107** 47002
[6] Lafuerza S, Subías G, García J, Blasco J, G. Nisbet, Conder K and Pomjakushina E 2014 *Phys. Rev. B* **90** 085130
[7] Makarova O L, Bourgeois J, Poienar M, Mirebeau I, Kichanov S E, André G, Elkaim E, Hanfland M, Hervieu M, Maignan A, Haines J, Rouquette J, Martin C and Damay F 2013 *Appl. Phys. Lett.* **103** 082907
[8] Momma K and Izumi F 2011 *J. Appl. Crystallogr.* **44** 5
[9] Rouquette J, Haines J, Al-Zein A, Papet P, Damay F, Bourgeois J, Hammouda T, Doré F, Maignan A, Hervieu M and Martin C 2010 *Phys. Rev. Lett.* **105** 237203
[10] Takele S and Hearne G R 2001 *Nucl. Instrum. Meth. B* **183** 413
[11] Tjon J A and Blume M 1968 *Phys. Rev* **165** 456
[12] Herber R H and Eckert H 1985 *Phys. Rev. B* **31** 34
[13] Klencsar Z, MossWinn 4.0Pre Manual, 2013.
[14] Patankar S, Pandey S K, Reddy V R, Gupta A, Banerjee A and Chaddah P 2010 *EPL* **90** 57007
[15] Bang B K, Kim S B, Cheong S-W and Kim C S 2007 *Phys. Status Solidi (B)* **244** 4566
[16] Hearne G R, Sibanda W N, Carleschi E, Pischedda V and Attfield J P 2012 *Phys. Rev. B* **86** 195134
[17] Angst M, Khalifah P, Hermann R P, Xiang H J, Whangbo M-H, Varadarajan V, Brill J W, Sales B C and Mandrus D 2007 *Phys. Rev. Lett.* **99** 086403
[18] Litterst F J and Amthauer G 1984 *Phys Chem Minerals* **10** 250
[19] Diguet G, Hearne G R, Sibanda W N, Carleschi E, Musyimi P, Pischedda V and Attfield J P 2014 *Phys. Rev. B* **89** 035132