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Hard and soft x-rays XAS characterization of charge ordered $LuFe_2O_4$

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Abstract. This work presents a thorough characterization of the mixed valence compound $LuFe_2O_4$ by means of x-ray absorption spectroscopy (XAS). Polarized XAS measurements at the Fe K-edge, Fe $L_{2,3}$-edges and O K-edge have been carried out to validate the bimodal Fe^{+2}/Fe^{+3} charge ordering (CO) proposed to give rise to ferroelectricity at $T_{CO} \approx 320$ K and also to study the anisotropy and temperature dependence of the Fe local structure. Our results discard a bimodal CO below T_{CO} and agree with the presence of a $Fe^{+2.5\pm\delta}$ distribution with $\delta \leq 0.25$. Unexpectedly, the strong anisotropy of the hexagonal crystallographic structure is not reflected in either the Fe (4*p*, 3*d*) or the O (2*p*) density of unoccupied states. Finally, the so-called CO transition is originated by the ordering of local distortions as it is revealed by the temperature evolution of the XAS spectra.

1. Introduction

The mixed valence oxide $LuFe_2O_4$ is among the most studied multiferroic candidates since a new type of ferroelectricity based on charge ordering (CO) was postulated in this compound below $T_{CO} \approx 320$ K [1]. Regarding the magnetic properties, $LuFe_2O_4$ shows ferrimagnetic ordering below $T_N \approx 240$ K and therefore both the electric and magnetic orderings would interestingly occur at high transition temperatures.

Above T_{CO}, $LuFe_2O_4$ crystallizes in a highly anisotropic hexagonal cell (*R-3m* space group) where the Fe formal valence is 2.5 and the coordination consists of a bipyramid FeO_5 with two apical (1.96 and 2.20 Å) and three equatorial (2.00 Å x 3) Fe-O distances [2]. Along the hexagonal *c* axis, the structure can be seen as an alternating stacking of $[LuO_2]\infty$ layers and $[Fe_2O_4]\infty$ bilayers with triangular geometry. According to the initially proposed CO model by Ikeda *et al.* [1], ferroelectricity is developed in this material due to a bimodal Fe^{+2}/Fe^{+3} CO that renders the triangular Fe-O bilayers polar by making one of the layers rich in Fe^{+2} and the other in Fe^{+3}. Despite this model was supported by preliminary resonant x-ray scattering and electric properties measurements [1], recent experiments have discarded the ferroelectric character of $LuFe_2O_4$ [4,5,6]. In view of these results, all the proposed phenomenology in $LuFe_2O_4$ needs to be revisited.

With the aim at validating the proposed bimodal Fe^{+2}/Fe^{+3} CO model we have carried out a complete characterization of the Fe local electronic and geometrical structure in $LuFe_2O_4$ by means of x-ray absorption spectroscopy (XAS). This investigation combines measurements in both the hard (Fe K-edge) and soft (Fe $L_{2,3}$-edges, O K-edge) x-rays energy regimes and includes the study of the anisotropy and temperature dependence of the XAS spectra.

2. Experiment details

Both polycrystalline and single crystal samples of $LuFe_2O_4$ were studied. The polycrystalline samples were obtained by solid state chemistry reaction from stoichiometric amounts of Lu_2O_3 and Fe_2O_3 and sintered at 1200 °C in a CO_2/CO (60:40) atmosphere. Powder x-ray-diffraction (XRD) measurements confirmed that the samples are single phase without noticeable impurities. On the other hand, the polycrystalline precursor for single crystal growth was prepared also by solid state reaction from Lu_2O_3 and Fe_2O_3 starting materials sintered at the same temperature in H_2/He/CO_2 atmosphere (H_2/CO_2 ratio 1:3) and quenched into ice water. The crystal growth was carried out using an Optical Floating Zone Furnace (FZ-T-10000-H-IV-VP-PC, Crystal System Corp., Japan) with four 1000-W halogen lamps as a heat source, growth rate 1 mm/h and 2 bars pressure of CO_2/CO (5:2) mixture. Phase purity was checked with XRD using a D8 Advance Bruker AXS diffractometer with Cu K_α radiation. Oxygen stoichiometry was determined using thermogravimetric hydrogen reduction and was found as 3.94(2). Two pieces were cut and polished with the surfaces perpendicular to the [001] and [110] hexagonal directions. All the samples show the expected CO ($T_{CO} \approx 320$ K) and ferrimagnetic ($T_N \approx 240$ K) transitions as confirmed by heat capacity and magnetization measurements [3].
The isostructural reference compound $LuFeCoO_4$ with formal valence Fe^{+3} [2] was also measured. $LuFeCoO_4$ powder samples were prepared in air at 1350 °C using Lu_2O_3, Fe_2O_3 and CoO as precursors. The obtained specimens were single phase as checked by XRD.

XAS measurements in the hard (Fe K-edge) and soft (Fe $L_{2,3}$-edges and O K-edge) x-rays regimes were performed at beamlines BL22-CLAESS and BL29-BOREAS, respectively, at ALBA synchrotron (Spain). At the Fe K-edge (7712 eV) x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) were measured in transmission mode. Non-polarized spectra were recorded on isotropic powder samples while polarized spectra with the electric field of the x-rays (**E**) parallel and perpendicular to the hexagonal ***c*** axis were recorded on oriented pellets. Highly oriented pellets were obtained by mixing the polycrystalline powders with an epoxy resin and then allowing the mixture to solidify in a magnetic field of about 1 Tesla at room temperature. The degree of orientation (> 99%) was carefully checked by means of XRD and only (00*l*) peaks were seen in the oriented samples [6]. At the Fe $L_{2,3}$-edges ($L_2 \approx 720$ eV and $L_3 \approx 707$ eV) and O K-edge (543 eV) non-polarized and polarized XANES spectra were measured in total electron yield on sintered pieces and oriented single crystals, respectively. In this case, all the samples were polished in ultra high vacuum conditions ($\approx 10^{-8}$ mbar). All the XANES spectra presented have been normalized by first subtracting the linear pre-edge contribution and fixing the jump to 1 at values well above the absorption edge.

3. Results and discussion

We will start by evaluating the accuracy of the proposed bimodal Fe^{+2}/Fe^{+3} CO model in $LuFe_2O_4$ by analysing the XANES data at the Fe K-edge and $L_{2,3}$-edges at room temperature (that is below $T_{CO} \approx 320$ K). If there is coexistence of Fe^{+2} and Fe^{+3} valence states as in heterogeneous mixed valence compounds, the XANES of $LuFe_2O_4$ should agree with the 1:1 addition of the individual XANES spectra of appropriate reference compounds with the respective formal valences. $LuFeCoO_4$ is the case for Fe^{3+} while $LuFeGaO_4$ should be the case for Fe^{2+} as reported in [1]. However, we could not obtain the $LuFeGaO_4$ compound single phase not even reproducing the previously indicated synthesis route and therefore different approximations have been used to derive the XANES corresponding to the Fe^{2+} contribution.
At the Fe K-edge we have taken as reference XANES of Fe^{2+} the spectrum of $LuFeCoO_4$ shifted -4 eV according to the chemical shift (ΔE) of 4 eV found empirically between Fe^{2+} and Fe^{3+} [7]. This is justified by the fact that the main difference between XANES spectra of different ionic states with similar local structure geometry (in this case FeO_5 bipyramid) comes from the energy shift of the main

edge, being the spectral shape practically alike [7]. Figure 1 shows the comparison between the XANES of $LuFe_2O_4$, Fe^{+3} and Fe^{+2} with two simulations based on 1:1 additions of the Fe^{+3} and Fe^{+2} spectra with a different value of ΔE each. We note that although the small pre-peak at about 7115 eV in the $LuFe_2O_4$ spectrum cannot be reproduced by the simulations, this approach is especially accurate in the energy range close to the rising edge. On one hand, the simulation for ΔE = 4.0 eV which represents a mixture of $Fe^{+2.5-\delta}$ and $Fe^{+2.5+\delta}$ 1:1 with δ = 0.5 (i.e. a bimodal charge distribution Fe^{2+}/Fe^{3+}) and on the other hand the simulation for ΔE = 1.5 eV which represents a mixture of $Fe^{+2.5-\delta}$ and $Fe^{+2.5+\delta}$ 1:1 with δ = 0.25. As can be seen in Fig.1, the simulation for ΔE = 4.0 eV shows a shoulder at the main edge and a weak main peak that disagree with the XANES of $LuFe_2O_4$. However, the discrepancy between the simulation and the experimental spectrum of $LuFe_2O_4$ is very small for ΔE = 1.5 eV. Therefore, we can conclude that the maximum electronic disproportionation (2δ) between the different Fe ionic species in $LuFe_2O_4$ should be less than 0.5 electrons in conflict with the proposed bimodal Fe^{2+}/Fe^{3+} CO model [1].

At the Fe $L_{2,3}$-edges we have considered as reference XANES of Fe^{2+} the difference in the absorption spectra between $LuFe_2O_4$ and $LuFeCoO_4$ (that is $2\mu_{LuFe2O4} - \mu_{LuFeCoO4}$ based on the hypothesis that $\mu_{LuFe2O4}$ can be explained by the 1:1 addition of Fe^{+3} and Fe^{+2}). The latter difference spectrum nicely agrees with the XANES of Fe_2SiO_4 with Fe^{+2} formal valence [8] (see comparison in Fig.2) and thus corroborates the description of the Fe valence state in $LuFe_2O_4$ as a mix Fe^{+2}/Fe^{+3} 1:1. We note here that this description seems to contradict the results at the Fe K-edge. However one should recall that the final states probed in the two cases are different. While the XANES at the Fe K-edge is sensitive to the 4*p* states, at the Fe $L_{2,3}$-edges the 3*d* states are probed and it is impossible to distinguish between a mixture of $Fe^{+3}(3d^5)$ and $Fe^{+2}(3d^6)$ ions(configurations) and the mixed valence state $Fe^{+2.5}(3d^{5.5})$.

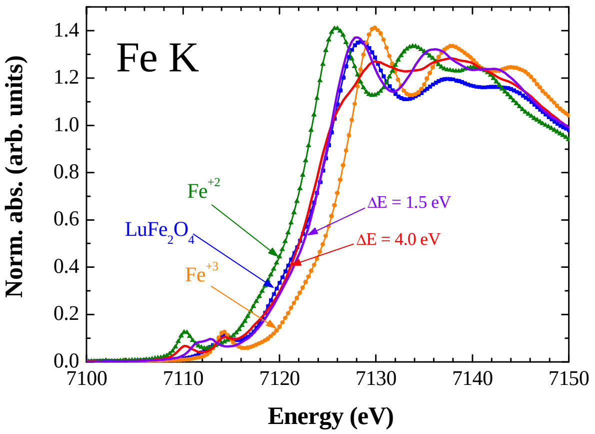

Figure 1. XANES spectra at the Fe K-edge of $LuFe_2O_4$, Fe^{+3} ($LuFeCoO_4$) and Fe^{+2} (extrapolated from the Fe^{3+} spectrum as described in the text) compared to the results of the 1:1 addition of the Fe^{+3} and Fe^{+2} spectra with different chemical shift (ΔE) among them.

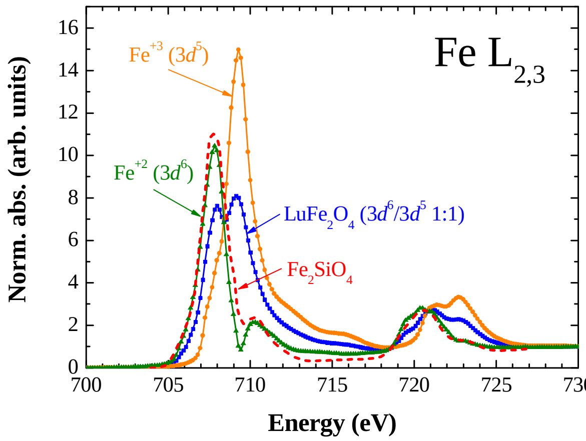

Figure 2. XANES spectra at the Fe $L_{2,3}$-edges of $LuFe_2O_4$, Fe^{+3} ($LuFeCoO_4$) and Fe^{+2} (deduced from the difference $2\mu_{LuFe2O4} - \mu_{LuFeCoO4}$). The spectra of Fe_2SiO_4 with only Fe^{+2} taken from ref. [8] is also plotted for comparison.

Secondly, we will deal with the polarization dependent XAS spectra. Figure 3 compares the XANES spectra of $LuFe_2O_4$ polarized for the two configurations **E** // **c** and **E** ⊥ **c** and non-polarized measured at the Fe K-edge, Fe $L_{2,3}$-edges and O K-edge. Overall only small intensity changes in some of the spectral features are observed between the two polarizations while the non-polarized data shows an intermediate behaviour (we note that the weighted addition 2:1 of the **E** // **c** and **E** ⊥ **c** spectra agrees reasonably with the non-polarized spectrum). It is noteworthy that despite the strong crystallographic anisotropy between the direction of the hexagonal *c* axis and the *ab* plane the XANES spectra show very weak electronic anisotropy in the Fe 4*p*- and 3*d*- and O 2*p*-projected density of unoccupied states. We would like to add that the lack of strong anisotropy at the Fe and O K-edges is well reproduced by means of multiple scattering calculations [6,9].

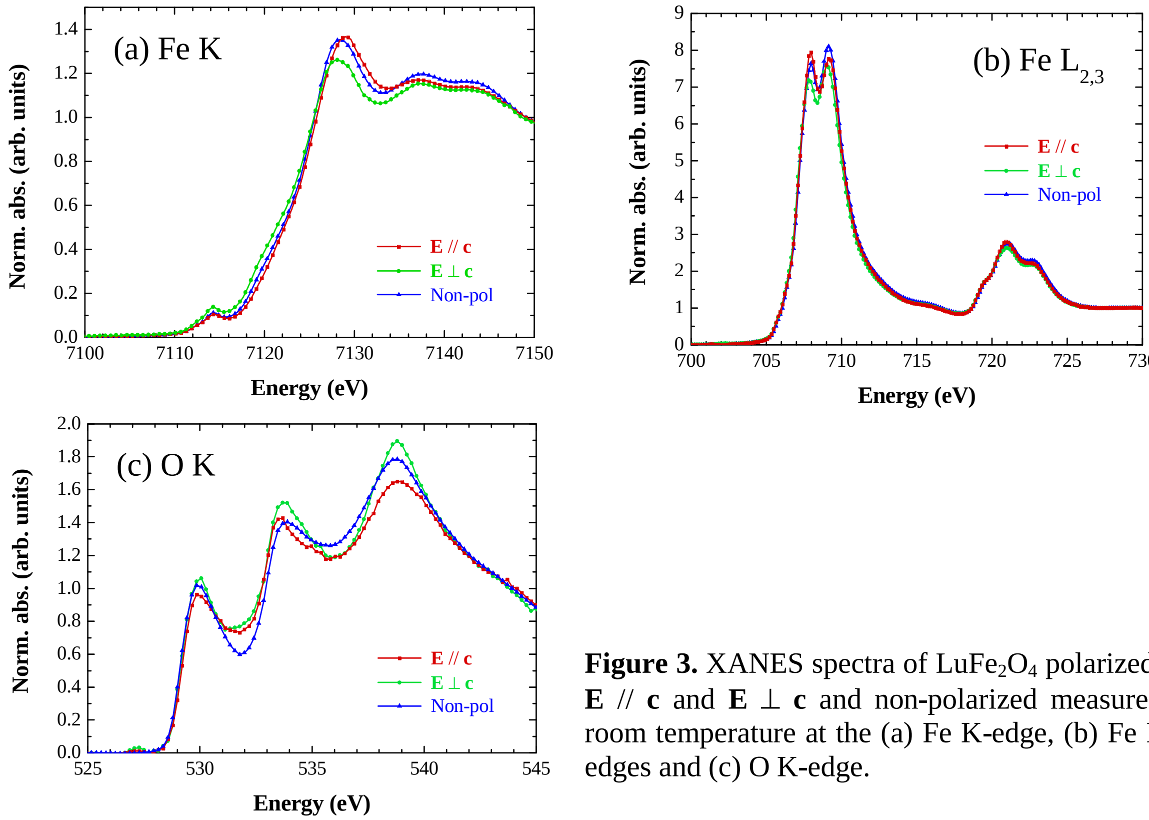

Figure 3. XANES spectra of $LuFe_2O_4$ polarized for **E** // **c** and **E** ⊥ **c** and non-polarized measured at room temperature at the (a) Fe K-edge, (b) Fe $L_{2,3}$-edges and (c) O K-edge.

Regarding the EXAFS spectra at the Fe K-edge, the polarized data (not shown) have allowed discriminating the strongest contributions in each direction. For the FeO_5 bipyramid a nearly equal Fe-O distance along the *c* axis (1.96 ± 0.03 Å) and in the *ab* plane (1.96 ± 0.01 Å) was obtained [6] which is in agreement with the lack of anisotropy reflected in the XANES results. Moreover the Fe-O distances show large Debye-Waller factors compared to $LuFeCoO_4$ especially in the *ab* plane indicating a high degree of distortion.

Finally, we would like to discuss the evolution with temperature of both the XANES and EXAFS spectra when crossing the CO transition at $T_{CO} \approx 320$ K. The XANES spectra (Fe K-edge, Fe $L_{2,3}$-edges and O K-edge) remain the same above and below T_{CO} (not shown). This means that the Fe electronic state can be described as $Fe^{+2.5}(3d^{5.5})$ in the hexagonal phase ($T > T_{CO}$) while in the distorted phase at $T < T_{CO}$ there is a distribution of $Fe^{+2.5-\delta}$ and $Fe^{+2.5+\delta}$ with $\delta \leq 0.25$ and not necessarily bimodal (the 3*d* population remains the same in average and being $\alpha 3d^5 + \beta 3d^6$ with $\alpha + \beta = 1$ for each $Fe^{+2.5\pm\delta}$). In the EXAFS spectra at the Fe K-edge, the most significant change with temperature is a small evolution in the intensity of the second coordination shell. Figure 4 shows the temperature dependence of the modulus of the Fourier Transform of the *k*-weighted EXAFS spectra (*k*-range: 1.5 – 12 $Å^{-1}$) for the two sets of polarized data **E** // **c** and **E** ⊥ **c**. The Debye-Waller factors of the second coordination shell (Fe-Fe distances) decrease continuously upon cooling down as expected from thermal vibrations contributions and they do not show any anomaly at T_{CO} (see inset of Fig. 4). However, changes are much smaller in the first coordination shell upon cooling. This result also reveals the disorder in the Fe-O bonds previously mentioned.

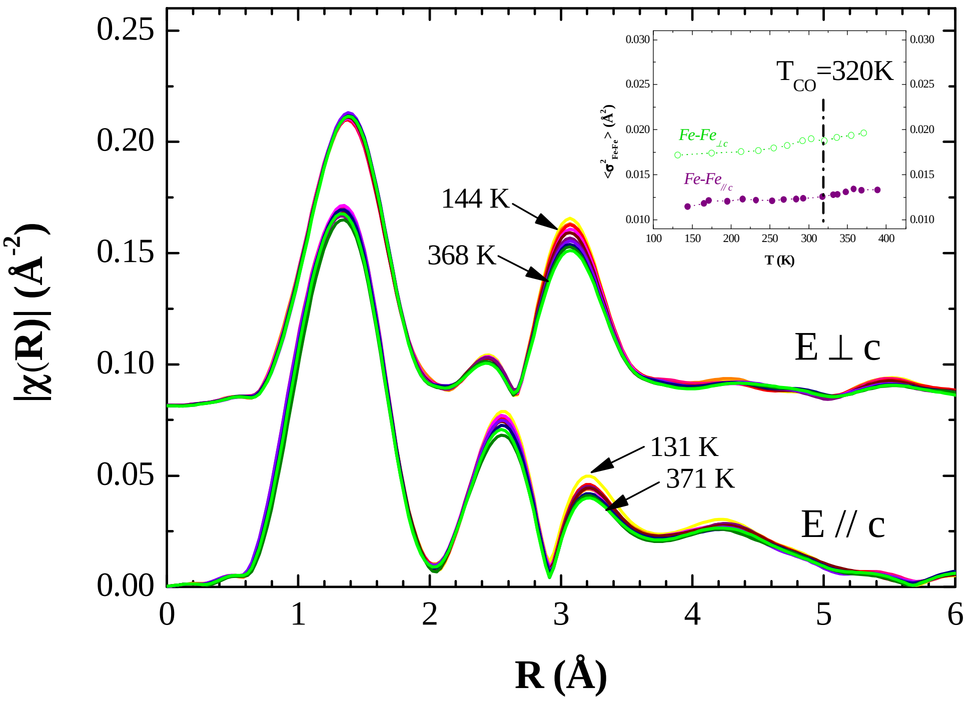

Figure 4. Temperature dependence of the moduli of the FTs of the *k*-weighted EXAFS signals at the Fe K-edge of $LuFe_2O_4$ for the two polarizations **E** // **c** and **E** ⊥ **c**. Inset: Thermal dependence of the refined Debye-Waller factors (σ^2) for the Fe-$Fe_{//\mathbf{c}}$ and Fe-$Fe_{\perp\mathbf{c}}$ distances. The temperature of the CO transition is indicated.

4. Conclusions

Our results demonstrate the lack of pure ionic charge segregation Fe^{+2}/Fe^{+3} below T_{CO} that was initially proposed as a new mechanism leading to the appearance of ferroelectricity in $LuFe_2O_4$ [1]. As deduced from our analysis of the XANES spectra at the Fe K- and $L_{2,3}$-edges the Fe formal valence above T_{CO} is $Fe^{+2.5}(3d^{5.5})$ while below T_{CO} the data agree with a valence distribution of $Fe^{+2.5-\delta}/Fe^{+2.5+\delta}$ with $\delta \leq 0.25$ and not necessarily bimodal. In the simplest case of a bimodal distribution the valence states would be $Fe^{+2.25}$ and $Fe^{+2.75}$. Regarding the 3*d* configuration, it can be expressed below T_{CO} for each $Fe^{+2.5\pm\delta}$ as $\alpha 3d^5 + \beta 3d^6$ with $\alpha + \beta = 1$. For example, if the two species $Fe^{+2.25}(0.25{\cdot}3d^5 + 0.75{\cdot}3d^6)$ and $Fe^{+2.75}(0.75{\cdot}3d^5 + 0.25{\cdot}3d^6)$ were present, the 3*d* population would remain the same as above T_{CO} in average. This picture for the Fe electronic state is in agreement with recent works in $LuFe_2O_4$ by means of resonant x-ray scattering and high resolution powder diffraction [10,11].

On the other hand, the electronic anisotropy in the XANES at the Fe K-edge (Fe 4*p* states), Fe $L_{2,3}$-edges (Fe 3*d* states) and O K-edge (O 2*p* states) has been found to be unexpectedly weak considering the strong anisotropy of the hexagonal crystal structure and the FeO_5 bipyramid coordination. Along these lines, the polarized EXAFS data at the Fe K-edge yield Fe-O distances along the direction of the *c* axis and in the *ab* plane almost alike (≈ 1.96 Å) despite the difference between the apical (1.96 and 2.20 Å) and equatorial (2.00 Å x 3) Fe-O distances deduced from crystallography [2]. Taking into account the large Debye-Waller factors obtained for the Fe-O distances compared to the reference compound $LuFeCoO_4$, a possible explanation could be the presence of various Fe sites with different distortions that result in a reduced average local distortion [6].

The XANES spectra do not show any evolution when crossing T_{CO} and the EXAFS spectra temperature dependence confirms the presence of local distortions even above T_{CO}. Therefore, the so-called CO transition has an order-disorder character. That is, dynamically distorted FeO_5 bipyramids in the symmetric hexagonal phase freeze upon cooling down and the charge disproportionation results from the freezing of local distortions [6].

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