Determination of the sequence and magnitude of charge order in LuFe_2O_4 by resonant x-ray scattering

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(Received 27 May 2014; revised manuscript received 29 July 2014; published 21 August 2014)

We have investigated the low-temperature phases of LuFe_2O_4 by resonant x-ray scattering (RXS) at the Fe K edge to determine both the ordering sequence and magnitude of charge segregation. Two successive charge ordering (CO) phases have been detected. Resonant superlattice $(1/3, 1/3, l/2)$ reflections appear below the so-called CO phase at $T_{\text{CO}} \approx 320$ K. Additionally, resonant superlattice $(1/3, 1/3, l)$ reflections are observed below 240 K concurrent with the onset of the magnetic ordering. The σ - σ' polarization dependence for all the measured superlattice reflections indicates the absence of local anisotropy of the electronic density at the Fe atom. The energy dependence of the resonant intensity for these reflections has been quantitatively analyzed following the monoclinic $C2/m$ structure in the CO phase between 320 and 240 K and the triclinic $P\bar{1}$ structure below 240 K. We find a four-modal charge segregation among the Fe atoms in the $C2/m$ phase with formal valences $\text{Fe}^{2.77+}$, $\text{Fe}^{2.63+}$, $\text{Fe}^{2.36+}$, and $\text{Fe}^{2.22+}$ whereas the simplest charge distribution that explains successfully all the RXS data in the $P\bar{1}$ phase is the trimodal $\text{Fe}^{2.8+}$, $\text{Fe}^{2.5+}$, and $\text{Fe}^{2.2+}$. Both ordering models imply the lack of charge segregation along the c axis discarding a polar configuration and thus the occurrence of ferroelectricity.

DOI: [10.1103/PhysRevB.90.085130](https://doi.org/10.1103/PhysRevB.90.085130)

PACS number(s): 61.05.C-, 71.30.+h, 75.47.Lx, 75.25.Dk

I. INTRODUCTION

Nowadays charge and orbital ordering phenomena in mixed-valence transition-metal compounds have become a very important area of research within the field of solid state physics. It is generally assumed that the mixed-valence state is unstable in the solid and that it stabilizes by localizing the charge at the transition-metal atom, which gives rise to an ordered sequence of different valence states, i.e., a charge ordered state. Moreover, owing to the localized character of the $3d$ states, it has been proposed that for some electronic configurations the occurrence of an orbital ordering is associated to the integer valence state. The charge ordering (CO) has long been considered the classical description of the metal insulator transition in magnetite [1,2]. Recently, CO has also been proposed at the origin of ferroelectricity in some mixed-valence oxides [3,4]. In particular, a ferroelectric character was ascribed to LuFe_2O_4 as a result of the ordering of the Fe^{2+} and Fe^{3+} ions [5–7]. A number of works were carried out to understand this exceptional mechanism in LuFe_2O_4 to get ferroelectricity [8–26], and this compound was categorized as the electronic ferroelectric archetypical example. Despite the widespread belief in the existence of ferroelectricity in this mixed-valence compound, very recent results on the LuFe_2O_4 intrinsic electrical properties have demonstrated that this material is not ferroelectric [27–29]. Therefore, the proposed $\text{Fe}^{2+}/\text{Fe}^{3+}$ CO [5,6] leading to a polar configuration in LuFe_2O_4 lacks experimental support.

In order to resolve the present controversy we here present a detailed resonant x-ray scattering (RXS) investigation of this compound.

The high-temperature crystal structure of LuFe_2O_4 belongs to the rhombohedral system with space group $R\bar{3}m$ [30,31] and it is usually described in the hexagonal setting where it can be seen as a stacking of $[\text{Fe}_2\text{O}_4]_\infty$ bilayers along the c axis separated by close-compact $[\text{LuO}_2]_\infty$ layers. Each $[\text{Fe}_2\text{O}_4]_\infty$ bilayer is composed by two triangular $[\text{FeO}]_\infty$ planes. LuFe_2O_4 shows two phase transitions upon cooling down: first the so-called CO transition ascribed to the ordering of the Fe^{3+} and Fe^{2+} ions at $T_{\text{CO}} \approx 320$ K [3,5,6] and secondly another transition to a ferrimagnetic ordering that takes place at $T_C \approx 240$ K [32,33]. The CO phase in LuFe_2O_4 was first characterized by the occurrence of superlattice reflections with $(1/3, 1/3, l/2)$ hexagonal Miller indices (from here on, the hexagonal setting is used). On the other hand, neutron diffraction patterns in the low-temperature phase (below T_C) show superlattice reflections with both $(1/3, 1/3, l/2)$ and $(1/3, 1/3, l)$ Miller indices which were initially ascribed to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ordering and to the magnetic ordering, respectively [16]. A recent single crystal x-ray diffraction investigation determined that the crystallographic symmetry below T_{CO} is monoclinic with space group $C2/m$ [16]. New high resolution powder diffraction (HRPD) refinements have confirmed the monoclinic $C2/m$ symmetry between 320 and 200 K but have found an additional phase transition at lower temperatures with a further symmetry reduction to the triclinic $P\bar{1}$ space group [34].

RXS experiments at the Fe K -edge were reported for LuFe_2O_4 [5,35,36] and the energy and temperature

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dependence of the superlattice $(1/3, 1/3, l/2)$ reflections was used to support the occurrence of full charge segregation into Fe^{2+} and Fe^{3+} . Nevertheless, the analysis performed by either Ikeda *et al.* [5] or Mulders *et al.* [36] only used a generic structure factor with both the Thomson scattering and the resonant terms as free parameters in the fits without considering the low-temperature crystallographic structure and the CO sequence. In addition, a recent x-ray absorption spectroscopy work at the Fe K edge has discarded the full ionic Fe^{2+} - Fe^{3+} segregation in LuFe_2O_4 and has established a maximum charge disproportionation of 0.5 electrons among the different Fe sites [37].

Since RXS is the appropriate technique to investigate the charge segregation and hence the occurrence of CO, we have performed a detailed study on the energy, polarization, and temperature dependence of the scattered intensity in the neighborhood of the Fe K edge for various superlattice reflections in both the CO and magnetic phases. We have detected RXS intensity at the $(1/3, 1/3, l/2)$ reflections below T_{CO} , whose energy dependence is similar to that of those previously published [5,35,36]. In addition, RXS intensity was also observed for $(1/3, 1/3, l)$ reflections below T_{C} . Moreover, we measured reflections of the type $(0, 0, l/2)$ that do not show resonant behavior. We have carried out a quantitative analysis of the structure factor for all the superlattice reflections that have been fitted simultaneously with the chemical shift among the anomalous atomic scattering factors of the nonequivalent Fe sites in each case being the only free parameter. Our results agree with the presence of two successive orderings on cooling at $T_{\text{CO}} \approx 320$ K and $T_{\text{C}} \approx 240$ K, respectively. In neither case is the Fe charge distribution bimodal, and the maximum charge segregation is always significantly smaller than one electron.

II. EXPERIMENT

LuFe_2O_4 single crystal was grown at the Paul Scherrer Institut. The polycrystalline precursor was obtained by solid state reaction of Fe_2O_3 and Lu_2O_3 with 99.99% purity. Stoichiometric amounts of the binary oxides were mixed, pressed into pellets, and sintered at 1200 °C during 6 h in $\text{H}_2/\text{He}/\text{CO}_2$ atmosphere (H_2/CO_2 ratio 1/3) and quenched into ice water. After grinding, the obtained powder was hydrostatically pressed in a form of rods (8 mm in diameter and 70 mm in length) and sintered at the same conditions as powder during 3 h. The crystal growth was carried out by means of an optical floating zone furnace (FZ-T-10000-H-IV-VP-PC, Crystal System Corp., Japan) using four 1000 W halogen lamps as a heat source at a growth rate of 1 mm/h and 2 bars pressure of CO_2/CO mixture (5/2 ratio). Oxygen stoichiometry was determined using thermogravimetric hydrogen reduction [38] and was found as 3.94(2). The sample was also characterized by means of differential scanning calorimetry, magnetic, and electrical transport measurements. The results from all these measurements agree with the intrinsic macroscopic properties of LuFe_2O_4 reported in the literature.

RXS experiments at the Fe K -edge region (7100 to 7200 eV) were carried out at the I16 beamline [39] of Diamond Light Source (Didcot, UK) in a LuFe_2O_4 single crystal cut and polished with the [001] direction as the surface normal. The

polarization of the scattered beam (σ - σ' and σ - π' channels) was analyzed in reflection by rotating a $\text{MgO}(222)$ crystal and its intensity was detected with an avalanche photodiode. The energy and polarization dependence of the intensity of the superlattice reflections with Miller indices $(1/3, 1/3, l/2)$ $l = \text{odd}$, $(1/3, 1/3, l)$ $l = \text{integer}$, and $(0, 0, l/2)$ $l = \text{odd}$ (hexagonal setting) were measured at 17 K using a He cryostat. Additionally, the energy and polarization dependence of the intensity at selected $(1/3, 1/3, l/2)$ $l = \text{odd}$ reflections was recorded at room temperature for comparison. At fixed photon energy, the temperature evolution of representative reflections of each series was followed up to 400 K. Moreover, several Bragg reflections $(0, 0, l)$ $l = 3n$ of the hexagonal phase were also measured in order to estimate the Thomson intensity of the superlattice reflections.

III. RESULTS

Satellite reflections with indices $(1/3, 1/3, l/2)$ $l = \text{odd}$, $(1/3, 1/3, l)$ $l = \text{integer}$, and $(0, 0, l/2)$ $l = \text{odd}$ were measured at 17 K. For all the reflections the intensity was only detected in the σ - σ' channel, being the measured intensity in the σ - π' channel the corresponding to the leakage of the $\text{MgO}(222)$ crystal analyzer. Moreover, no dependence of the intensity upon rotation around the scattering vector (azimuth angle) was observed. Figure 1 shows the intensity of these reflections as a function of the x-ray energy across the Fe absorption threshold. It can be seen that the $(1/3, 1/3, l/2)$ and $(1/3, 1/3, l)$ reflections show a large nonresonant intensity (Thomson scattering contribution) and a strong self-absorption effect at the edge position since Fe is the main component in LuFe_2O_4 . We note that the intensity roughly behaves as the inverse of the x-ray absorption coefficient. In addition, the intensity for the $(0, 0, l/2)$ reflections is two orders of magnitude lower than for the $(1/3, 1/3, l/2)$ and $(1/3, 1/3, l)$ reflections and no clear resonances can be discerned.

The RXS intensity for all the reflections has been corrected for self-absorption on the basis of the Lambert-Beer law. For that, we have used the x-ray absorption coefficient of LuFe_2O_4 polycrystal at the Fe K edge measured in transmission mode at the CLAES beamline of the ALBA synchrotron (Cerdanyola del Vallès, Spain) [37] which was calibrated in energy with respect to the absorption spectrum measured in fluorescence at the I16 beamline. The relative units of the absorption coefficient have been converted to absolute units using the theoretical absorption cross section for LuFe_2O_4 spectra calculated by the program XCOM [40]. We have considered the reduction in the diffracted intensity due to absorption of x rays after passing through a layer of the sample of finite thickness x before being scattered. The value of x has been determined as to yield the average intensity roughly equal well above and below the absorption edge. Further details of the procedure can be found in Ref. [41]. The energy dependence of the absorption-corrected scattered intensity is given in Fig. 2 for the $(1/3, 1/3, l/2)$ and $(1/3, 1/3, l)$ reflections. The spectral shape and intensity are very similar between the two families. The energy dependence of the $(1/3, 1/3, l/2)$ reflections agrees with those given in the literature [5,35,36]. Depending on the l value, they show either a peak or a valley with similar spectral shape at the absorption edge. The intensity of the

FIG. 1. (Color online) Energy dependence of the resonant scattering intensity of the superlattice reflections without absorption correction recorded at 17 K: (a) $(1/3, 1/3, l/2)$ $l = \text{odd}$, (b) $(1/3, 1/3, l)$ $l = \text{integer}$, and (c) $(0, 0, l/2)$ $l = \text{odd}$. For the sake of comparison the intensities have been normalized to the value of the most intense reflection in each group at $E = 7100$ eV.

reflections depends on their specific structure factor. We also measured the $(0, 0, 9/2)$ and $(0, 0, 15/2)$ reflections in order to probe the existence of any charge periodicity along the c axis. However, the intensity of these reflections is two orders of magnitude lower than that of the $(1/3, 1/3, l/2)$ reflections and their spectral shape shows almost no resonances (see Fig. 2). The temperature dependence between 17 and 400 K was investigated by recording the rocking curve (i.e., intensity versus θ angle) for some representative reflections of each family at the photon energy $E = 7112$ eV (nonresonant). As shown in Fig. 3(a), $(1/3, 1/3, l/2)$ reflections disappear at a

FIG. 2. (Color online) Energy dependence of the resonant scattering intensity of the superlattice reflections corrected for self-absorption (see text): (a) $(1/3, 1/3, l/2)$ $l = \text{odd}$, (b) $(1/3, 1/3, l)$ $l = \text{integer}$, and (c) $(0, 0, l/2)$ $l = \text{odd}$ measured at 17 K.

temperature concurrent with the onset of the CO transition. On the other hand, $(1/3, 1/3, l)$ reflections disappear at about 240 K coinciding with the magnetic ordering temperature as can be seen in Fig. 3(b). The latter points to a magnetostructural character of the second transition, similar to the observed 170 K transition in some samples [16]. Overall, these results agree on the existence of two successive structural phase transitions. On cooling, the hexagonal crystal symmetry (space group $R\bar{3}m$) transforms into monoclinic (space group $C2/m$) at the critical temperature T_{CO} . Upon further cooling, a second transition occurs from monoclinic to triclinic symmetry (space group $P\bar{1}$). The energy dependence of the $(1/3, 1/3, l/2)$ reflections was also measured at room temperature and no

FIG. 3. (Color online) (a) Temperature dependence of the integrated intensity of $(1/3, 1/3, 17/2)$ (circles) and $(0, 0, 15/2)$ (squares) reflections taken at 7112 eV. The inset shows rocking curves of the $(1/3, 1/3, 17/2)$ reflection recorded below the Fe K edge as a function of temperature. (b) Temperature dependence of the integrated intensity of the $(1/3, 1/3, 12)$ reflection taken at 7112 eV. The inset shows rocking curves of this reflection recorded below the Fe K edge as a function of temperature. The temperatures of the CO (T_{CO}) and ferrimagnetic (T_C) phase transitions are indicated by arrows.

noticeable changes were observed in the spectral shape below T_{CO} . This indicates that the $(1/3, 1/3, l/2)$ reflections are the mark of the $C2/m$ phase whereas $(1/3, 1/3, l)$ reflections are associated to the magnetic transition. On the other hand, the $(0, 0, l/2)$ reflections do not show any temperature dependence and their intensity has the same order of magnitude even above T_{CO} [Fig. 3(a)]. The lack of resonances for these reflections and their very low intensity agree with the soft RXS study in Ref. [16] where the observed $(0, 0, 3/2)$ reflection only has magnetic origin as it is only observed in the σ - π' (and π - σ') channel. We also measured the intensity of the $(0, 0, l/2)$ reflections in σ - π' but we did not find any signal larger than the contribution of the leakage of the crystal analyzer. The lack of resonances for these reflections implies the absence of charge disproportionation along the c axis and challenges both the polar ordering by Ikeda *et al.* [5] and the antiferroelectric ordering proposed by J. de Groot *et al.* [19].

X-ray resonant scattering data analysis

The structure factor of a reflection with (h, k, l) Miller indices is given by

$$F(h, k, l) = \sum_j e^{2\pi i \vec{Q} \cdot \vec{R}_j} [f_{oj} + f'_j(E) + i f''_j(E)], \quad (1)$$

where $\vec{Q}$ is the scattering vector, $\vec{R}_j$ the atomic position vector in the unit cell, f_{oj} the Thomson scattering factor, and $f'_j(E)$ and $f''_j(E)$ the real and imaginary components of the anomalous atomic scattering factor, respectively. f_{oj} is independent of the energy of the photons for energies not too different, while the anomalous terms $f'_j(E)$ and $f''_j(E)$ of the iron atoms show a strong energy dependency at the absorption edge. The anomalous atomic scattering factor is a tensor whose rank is two for dipole-dipole transitions [42]. Since the measured reflections do not show either azimuthal behavior or polarization dependence, the tensor can be approached by a scalar. Therefore, the structure factor can be written as $F(h, k, l) = F_0 + F'_Fe(E) + i F''_Fe(E)$, where $F_0 = \sum_j e^{2\pi i \vec{Q} \cdot \vec{R}_j} f_{oj}$ and the j index refers to all the atoms in the unit cell, and $F'_Fe(E) = \sum_i e^{2\pi i \vec{Q} \cdot \vec{R}_i} f'_i(E)$ and the i index only refers to the Fe atoms in nonequivalent positions (a similar expression is found for $F''_Fe(E)$). Therefore, the intensity of a reflection with (h, k, l) Miller indices is finally given by

$$\begin{aligned} I(h, k, l) &= [F_0 + F'_Fe(E) + i F''_Fe(E)]^2 \\ &= F_0^2 + 2F_0 F'_Fe(E) + F_{Fe}^2(E) + F_{Fe}^{\prime\prime 2}(E). \end{aligned} \quad (2)$$

Since in our case $F_0 \gg F'_Fe(E) + i F''_Fe(E)$, we can approximate the intensity by the lineal term only, i.e., $I(h, k, l) = F_0^2 + 2F_0 F'_Fe(E)$ (the correctness of this approach has been checked in our analysis). In this way, $I(h, k, l)$ depends on the atomic positions and CO sequence in the unit cell through the F_0 and $F'_Fe(E)$ terms.

The analysis of the energy-dependent intensity of the measured superlattice reflections was first carried out in the $C2/m$ unit cell. We have taken into account that CO breaks the threefold rotational symmetry of the R -centered hexagonal cell lowering the symmetry to monoclinic but resulting in three equivalent C -centered monoclinic domains, which are rotated by 120° with respect to each other. The observation of superlattice reflections corresponding to multiple monoclinic domains implies therefore a twinned sample. It is worth noting that superlattice reflections are forbidden in $R\bar{3}m$ but allowed in $C2/m$. The propagation vectors that transform the hexagonal cell to each monoclinic domain are $\vec{q}_A = (1/3, 1/3, 3/2)$, $\vec{q}_B = (-2/3, 1/3, 3/2)$, and $\vec{q}_C = (1/3, -2/3, 3/2)$. Table I classifies the superlattice reflections measured in the three possible monoclinic domains showing the relationship between the Miller indices in the hexagonal cell $R\bar{3}m$ and the appropriate monoclinic domain. The Fe atoms of $[\text{FeO}]_\infty$ bilayers in the $C2/m$ unit cell are placed into four nonequivalent crystallographic sites. Figure 4 shows the positions of the four different crystallographic Fe sites, denoted as Fe1(4i), Fe2(8j), Fe3(8j), and Fe4(4i). The general expressions for the structure factors of each type of superlattice reflection are

TABLE I. Measured $(1/3, 1/3, l/2)$ with $l = \text{odd}$ and $(1/3, 1/3, l)$ with $l = \text{integer}$ (hexagonal setting) superlattice reflections indexed in the $C2/m$ cell and classified into the three symmetry-equivalent monoclinic domains.

Domain A		Domain B		Domain C	
$(h, k, l)_h$	$(h, k, l)_{C2/m}$	$(h, k, l)_h$	$(h, k, l)_{C2/m}$	$(h, k, l)_h$	$(h, k, l)_{C2/m}$
$(1/3, 1/3, 2/2)$	$(0, 2, -7)$	$(1/3, 1/3, 11/2)$	$(1, -1, -4)$	$(1/3, 1/3, 7/2)$	$(-1, -1, -2)$
$(1/3, 1/3, 6)$	$(0, 2, -4)$	$(1/3, 1/3, 7)$	$(1, -1, -5)$	$(1/3, 1/3, 13/2)$	$(-1, -1, -4)$
$(1/3, 1/3, 12)$	$(0, 2, -8)$	$(1/3, 1/3, 17/2)$	$(1, -1, -6)$	$(1/3, 1/3, 8)$	$(-1, -1, -5)$
		$(1/3, 1/3, 10)$	$(1, -1, -7)$	$(1/3, 1/3, 19/2)$	$(-1, -1, -6)$

written as

$$F_{(1/3, 1/3, l/2)} = F_{0, (1/3, 1/3, l/2)} + N_{(1/3, 1/3, l/2)} \{ [f_{\text{Fe1}}(E) - f_{\text{Fe4}}(E)] + [f_{\text{Fe2}}(E) - f_{\text{Fe3}}(E)] \}, \quad (3)$$

$$F_{(1/3, 1/3, l)} = F_{0, (1/3, 1/3, l)} + N_{(1/3, 1/3, l)} \{ [f_{\text{Fe1}}(E) + f_{\text{Fe4}}(E)] - [f_{\text{Fe2}}(E) + f_{\text{Fe3}}(E)] \}, \quad (4)$$

$$F_{(0, 0, l/2)} = F_{0, (0, 0, l/2)} + N_{(0, 0, l/2)} \{ [f_{\text{Fe1}}(E) - f_{\text{Fe4}}(E)] - 2[f_{\text{Fe2}}(E) - f_{\text{Fe3}}(E)] \}, \quad (5)$$

where $f_{\text{Fe}i}(E)$ are the anomalous atomic scattering factors of the nonequivalent sites for the Fe atoms $\text{Fe}i$ ($i = 1$ to 4) and $N_{(h, k, l)} = \sum_i e^{i2\pi(hx_i + ky_i + lz_i)}$ with (h, k, l) the Miller indices of the superlattice reflections in the monoclinic setting (as appear in Table I) and (x_i, y_i, z_i) the fractional coordinates of the different $\text{Fe}i$ also expressed in the monoclinic cell.

The numerical expressions for the $N_{(h, k, l)}$ factors of the measured $(1/3, 1/3, l/2)$ reflections in the $C2/m$ model are reported in Table II together with the respective Thomson

scattering terms. We note that the $N_{(h, k, l)}$ factors are nearly insensitive to the small lattice distortions associated with the structural changes and they mainly depend on the (x_i, y_i, z_i) positions of the $\text{Fe}i$ atoms. It is clear that the resonant contribution of the Fe atoms will either add to or subtract from the Thomson scattering contribution depending on the l index and the magnitude of the resonances will depend not only on the difference among the anomalous atomic scattering factors of the Fe atoms but also on the magnitude of the Thomson scattering terms and the $N_{(h, k, l)}$ factors. Therefore, the determination of these two last terms is mandatory to reliably quantify the Fe charge segregation.

We observe that resonances will appear for $(1/3, 1/3, l/2)$ reflections if $f_{\text{Fe1}}(E) \neq f_{\text{Fe4}}(E)$ and/or $f_{\text{Fe2}}(E) \neq f_{\text{Fe3}}(E)$. The fact that $(0, 0, l/2)$ reflections are not resonant imposes additional constraints among the atomic scattering factors of the different $\text{Fe}i$ atoms. If the charge on $\text{Fe1} = \text{Fe2}$ and similarly, the charge on $\text{Fe3} = \text{Fe4}$, a charge disproportionation will occur along the c direction and consequently a resonance would appear at the $(0, 0, l/2)$ reflections. This condition implies that, within the $C2/m$ structure, the charge distribution must be four modal instead of bimodal as proposed in the literature [5,36]. Moreover, the charge disproportionation between Fe1 and Fe4 must be double that between Fe2 and Fe3 , resulting in equally charged Fe bilayers (see Fig. 4). All these constraints predict no resonances for the $(1/3, 1/3, l)$ reflections in this CO model since the average charge on

FIG. 4. (Color online) Monoclinic unit cell (space group $C2/m$) of LuFe_2O_4 for the low-temperature phase below $T_{\text{CO}} \approx 320$ K. The Lu and O atoms are shown as red and blue spheres, respectively. The different sites for the Fe atoms are shown as FeO_5 bipyramids in different colors: Fe1 site in yellow, Fe2 site in purple, Fe3 site in green, and Fe4 site in blue.

TABLE II. Thomson scattering amplitudes (F_0) and calculated $N_{(h, k, l)}$ factors for the superlattice $(1/3, 1/3, l/2)$ and $(1/3, 1/3, l)$ reflections within the $C2/m$ and $P\bar{1}$ models, respectively.

(1/3,1/3, <i>l</i> /2) reflections in the <i>C</i> 2/ <i>m</i> model				
<i>l</i> /2 index	<i>F</i> ₀ (no. of elec.)	<i>N</i> _(1/3,1/3,<i>l</i>/2)		
7/2	20	−4		
11/2	40	3.6		
13/2	−42	−2.3		
17/2	−37	3.5		
19/2	30	1.1		
21/2	−60	−4		
(1/3,1/3, <i>l</i>) reflections in the <i>P</i> $\bar{1}$ model				
<i>l</i> index	<i>F</i> ₀ (no. of elec.)	<i>N</i> ¹ _(1/3,1/3,<i>l</i>/2)	<i>N</i> ² _(1/3,1/3,<i>l</i>/2)	<i>N</i> ³ _(1/3,1/3,<i>l</i>/2)
6	20	−1	3.8	−2.8
8	38	−0.7	−3	3.7
10	25	2.3	1.7	−4

the Fe1 and Fe4 sites is the same as the average charge on the Fe2 and Fe3 sites. Therefore, the $C2/m$ superstructure describes well the occurrence of resonant scattering at the $(1/3, 1/3, l/2)$ reflections and qualitatively explains the lack of $(1/3, 1/3, l)$ reflections between 240 and 320 K but it does not account for the presence of the two types of reflections below 240 K.

The $P\bar{1}$ crystal symmetry of the low-temperature phase imposes the existence of six nonequivalent crystallographic Fe sites, which corresponds to the four sites of the $C2/m$ symmetry with Fe2 and Fe3 sites split into two groups that we call Fe21, Fe22, Fe31, and Fe32. The general expression for the structure factor of the $(1/3, 1/3, l)$ reflections in this triclinic model is then given by

$$\begin{aligned} F_{(1/3, 1/3, l)} = & F_{0, (1/3, 1/3, l)} + N_{(1/3, 1/3, l)}^1 (f_{\text{Fe1}} + f_{\text{Fe4}}) \\ & + N_{(1/3, 1/3, l)}^2 (f_{\text{Fe21}} + f_{\text{Fe32}}) \\ & + N_{(1/3, 1/3, l)}^3 (f_{\text{Fe22}} + f_{\text{Fe31}}), \end{aligned} \quad (6)$$

where N^x are the partial $e^{i2\pi(hx_i + ky_i + lz_i)}$ terms of each type of the six Fe sites.

Since the $(1/3, 1/3, l/2)$ charge periodicity must remain almost unaltered between the two phases, the atomic scattering factor of Fe2 would be the average of Fe21 and Fe22 and similarly, that of Fe3 would correspond to the average of Fe31 and Fe32. In terms of localized charge, the charge disproportionation of the Fe2 into Fe21 and the Fe22 and Fe3 into the Fe31 and Fe32 atoms should be symmetric. The numerical expressions for the $N_{(h,k,l)}^x$ factors of the measured $(1/3, 1/3, l)$ reflections in the $P\bar{1}$ model are also reported in Table II. Although this model imposes a six-modal charge distribution, we propose a simpler approach to account for this constraint by considering the charge on Fe1 = Fe21 = Fe_x, Fe22 = Fe32 = Fe_y, and Fe31 = Fe4 = Fe_z. Within this model, the structure factor of the $(1/3, 1/3, l/2)$ reflections is not changed and resonances will appear at $(1/3, 1/3, l)$ reflections due to the disproportionation of the Fe2 and Fe3 sites. The structure factors of these l integer reflections include then differences among three valence states: Fe_x, Fe_y, and Fe_z. For example, $F_{(1/3, 1/3, 6)} = F_{0, (1/3, 1/3, 6)} + 2.8(f_{\text{Fe}_x} - f_{\text{Fe}_z}) + (f_{\text{Fe}_y} - f_{\text{Fe}_z})$.

In order to fit the experimental RXS spectra having the charge disproportionations as the only adjustable parameters, we have independently determined the Thomson scattering terms F_0 of the superlattice reflections by normalization to three intense Bragg reflections $(0,0,6)$, $(0,0,15)$, and $(0,0,21)$. The conversion to electron units (e) was made using the Bragg reflection's structure factors calculated from FULLPROF [43]. The resulting Thomson intensities (see Table II) reasonably agree with the values deduced from the HRPD experiment [34]. The sign of F_0 was assigned according to the structural model. In any case, the error in F_0 was estimated to be about 30%. The anomalous atomic scattering factor for the Fe atom was obtained from the x-ray absorption spectrum of LuFe₂O₄ measured in transmission mode [37]. The imaginary part $f''(E)$ is proportional to the linear x-ray absorption coefficient, whereas the real part $f'(E)$ is obtained from the imaginary one by Kramers-Kronig transformation. In order to get $f'(E)$ and $f''(E)$ in electron units, the normalized absorption spectrum

FIG. 5. (Color online) Real $f'(E)$ and imaginary $f''(E)$ components of the anomalous atomic scattering factor of the Fe atom in LuFe₂O₄ (circles). The respective components corresponding to the isolated Fe atom are also shown for comparison (solid lines).

was scaled to the theoretical values of the atomic Fe taken from the Cromer-Liberman tables. Figure 5 shows the real and imaginary components of LuFe₂O₄ at the Fe K edge compared with those of an isolated Fe atom. Due to the experimental correlation between the energy position of the absorption edge (chemical shift) and the charge state of the absorbing atom, the anomalous atomic scattering factor of a Fe atom with valence $\text{Fe}^{+(2.5 \pm \delta)}$ will be $f(\text{Fe}^{+(2.5 \pm \delta)})(E) = f(\text{Fe}^{+2.5})(E \pm 4\delta)$ with the energy in eV since the chemical shift between Fe³⁺ and Fe²⁺ ions is about 4 eV [44]. We note that the chemical shift at the Fe K edge between LuFe₂O₄ (Fe^{2.5+}) and LuFeCoO₄ (Fe³⁺) was found to be 2 eV [37]. Therefore, resonances in the RXS spectra will mainly occur at the Fe K edge due to differences between the anomalous atomic scattering factors of the nonequivalent crystallographic Fe sites originated by the shifting of the energy position of the absorption edge.

The dependence of the scattered intensity with the photon energy was then fitted using the structural models previously described. We have fixed the scattering Thomson terms determined as described above for each reflection and the anomalous atomic scattering factors were varied through the chemical shift of the absorption edge. We recall that the local charge and consequently, the energy chemical shift (ΔE) with respect to the average Fe^{2.5} are not independent for all the nonequivalent Fe atoms. For the $C2/m$ symmetry, $\Delta E_{\text{Fe1}} = -\Delta E_{\text{Fe4}}$ and $\Delta E_{\text{Fe2}} = -\Delta E_{\text{Fe3}} = \Delta E_{\text{Fe1}}/2$ to preserve the electroneutrality and to fulfill the condition of the lack of charge disproportionation along the c axis. On the other hand, for the $P\bar{1}$ symmetry and the proposed trimodal distribution, $\Delta E_{\text{Fe1}} = \Delta E_{\text{Fe21}} = \Delta E_{\text{Fe}_x}$, $\Delta E_{\text{Fe4}} = \Delta E_{\text{Fe31}} = \Delta E_{\text{Fe}_z}$ with $\Delta E_{\text{Fe}_z} = -\Delta E_{\text{Fe}_x}$ and $\Delta E_{\text{Fe22}} = \Delta E_{\text{Fe32}} = \Delta E_{\text{Fe}_y} = 0$.

Figure 6 shows the energy dependence of the $(1/3, 1/3, l/2)$ reflections taken at 17 K compared with the best-fit results for the $C2/m$ structure. We can note the good agreement between best-fit simulation and experimental spectra in what refers to both the spectral shape and the sign and magnitude of the resonances. The larger apparent discrepancy occurs for the $(1/3, 1/3, 19/2)$ reflection due to the weak contribution

FIG. 6. (Color online) Experimental energy dependence of RXS intensity (symbols) of the superlattice reflections $(1/3, 1/3, l/2)$ $l = 7, 11, 13, 17, 19$, and 21 and best-fit simulations using the four-modal Fe valence distribution based on the $C2/m$ symmetry (red solid lines) and the trimodal Fe valence distribution based on the $P\bar{1}$ symmetry (blue dashed lines).

of the resonant part (see Table II). The same chemical shift was used for all the reflections. The values obtained are $\Delta E_{\text{Fe1-Fe4}} = 2.2 \pm 0.1$ eV and $\Delta E_{\text{Fe2-Fe3}} = 1.1 \pm 0.1$ eV, which corresponds to a charge segregation of $\delta E_{\text{Fe1-Fe4}} = 0.55 \pm 0.05$ e and $\delta E_{\text{Fe2-Fe3}} = 0.27 \pm 0.05$ e. The same quality of fit was obtained for these half-integer reflections using the trimodal $P\bar{1}$ model (see also Fig. 6) since the chemical shift between Fe1 and Fe4 remains the same as expected and the chemical shift between Fe2 and Fe3 corresponds to $\Delta E_{\text{Fe2-Fe3}} = 1/2[(\Delta E_{\text{Fe21}} + \Delta E_{\text{Fe22}}) - (\Delta E_{\text{Fe31}} + \Delta E_{\text{Fe32}})] = 1/2(\Delta E_{\text{Fe1-Fe4}})$. On the other hand, the $C2/m$ four-modal distribution does not give any resonances for the $(1/3, 1/3, l)$ reflections with l integer (Fig. 7). Consequently, the $C2/m$ model only accounts for the ordering taking place at $T_{\text{CO}} = 320$ K. Therefore, reflections of the type $(1/3, 1/3, l)$ have been fitted using the trimodal $P\bar{1}$ model. Figure 7 shows the best-fit simulations for the studied reflections. As can be observed, the agreement between theory and experiment is good

enough, indicating the successive charge disproportionation of the monoclinic Fe2 and Fe3 atoms into Fe21/Fe22 and Fe31/Fe32, respectively, taking place in the neighborhood of the magnetic ordering transition.

IV. DISCUSSION AND CONCLUSIONS

Our RXS study shows the presence of two families of resonant reflections which have been studied. On one hand, $(1/3, 1/3, l/2)$ $l = \text{odd}$ reflections appear below $T_{\text{CO}} = 320$ K. The energy dependence of the absorption-corrected RXS intensity for these reflections is identical to that already published by Ikeda *et al.* [5] and Mulders *et al.* [35]. On the other hand, new $(1/3, 1/3, l)$ $l = \text{integer}$ resonant reflections were recorded and studied for the first time. These new reflections seem to be coupled to the magnetic order transition at $T_{\text{C}} = 240$ K. We note that these reflections were already observed by neutron diffraction but they were ascribed to

FIG. 7. (Color online) Experimental energy dependence of RXS intensity (symbols) of the superlattice reflections $(1/3, 1/3, l)$ $l = 6, 8$, and 10 and best-fit simulations using the four-modal Fe valence distribution based on the $C2/m$ symmetry (red solid lines) and the trimodal Fe valence distribution based on the $P\bar{1}$ symmetry (blue dashed lines).

have a purely magnetic origin [16]. With the present work we have shown the structural origin of these reflections and their resonant character. In addition, aiming at detecting any charge disproportionation ordering along the c axis, we also studied $(0,0,l/2)$ reflections. From this family, both $(0,0,9/2)$ and $(0,0,15/2)$ were measured but they are very weak, their Thomson intensities being about 1% of the $(1/3,1/3,l/2)$ reflections. Moreover, they are not resonant and the intensity remains constant with temperatures up to 400 K (therefore, they are probably related to any minor impurity). All these RXS results allow us to establish an almost complete transformation sequence of the charge disproportionations in LuFe_2O_4 on cooling.

The origin of the superlattice reflections has been satisfactorily explained in terms of the structural distortions derived from

FIG. 8. (Color online) Multimodal Fe valence distributions in the two low-temperature phases of LuFe_2O_4 corresponding to the $C2/m$ (four-modal) and $P\bar{1}$ (trimodal) phases illustrated in the two Fe bilayers that compose the $C2/m$ monoclinic unit cell for simplicity.

the reduced crystal symmetry from $R\bar{3}m$ to $C2/m$ at 320 K and from $C2/m$ to $P\bar{1}$ at 240 K. The symmetry changes split the unique Fe site of the high-temperature hexagonal phase into four and six in the $C2/m$ and $P\bar{1}$ phases, respectively. Due to this differentiation, the local charge at each of the Fe sites is different giving rise to charge disproportionations among them. The quantitative analysis of the RXS intensity of these superlattice reflections by the calculation of the structure factor following the two structural $C2/m$ and $P\bar{1}$ models have allowed us to determine the formal valence state of each of the nonequivalent crystallographic Fe sites. We note that the unique free parameter in the fitting procedure was the chemical shift among the anomalous atomic scattering factors of the different Fe atoms. Therefore, the charge distribution of the Fe atoms in the $C2/m$ phase (240 to 320 K) characterized by the $(1/3,1/3,l/2)$ reflections is nicely explained by a four-modal distribution of formal valences: $+2.77$, $+2.63$, $+2.36$, and $+2.23$ (see Fig. 8, left panel). This distribution is similar to that found by de Groot *et al.* [16] but in opposition to the first reports in the literature [5,36] shows the lack of any charge disproportionation along the c axis direction. Reflections with Miller indices $(1/3,1/3,l)$ $l = \text{integer}$ are not resonant in this four-modal charge distribution. The sensitivity of the present RXS study cannot resolve the six distinct formal valence states for the Fe atoms in the $P\bar{1}$ phase. Taking into account that the charge distribution in $P\bar{1}$ must be compatible with the one in $C2/m$ since the $(1/3,1/3,l/2)$ reflections remain unaltered, the simplest plausible distribution that agrees with the experimental data is a trimodal distribution in which one-third of the Fe atoms remain in the intermediate $+2.5$ valence state and the other two-thirds disproportionate in $\text{Fe}^{2.8+}$ and $\text{Fe}^{2.2+}$, respectively (see Fig. 8, right panel).

These findings joined to the results obtained from our previous x-ray absorption study [37] suggest the following mechanism for the reported phase transitions in LuFe_2O_4 : The Fe atoms are segregated in the low-temperature $P\bar{1}$ crystal symmetry into six nonequivalent atoms whose oxidation states can be grouped in three different charges, i.e., $\text{Fe1} = \text{Fe21} = \text{Fe}_x(+2.8)$, $\text{Fe4} = \text{Fe31} = \text{Fe}_z(+2.2)$, and $\text{Fe22} = \text{Fe32} = \text{Fe}_y(+2.5)$. Upon heating there is a transition from $P\bar{1}$ to $C2/m$ symmetry; the Fe1 and Fe4 preserve the charge disproportionation but the Fe2 atoms fluctuate between the +2.8 and +2.5 valence states and the Fe3 atoms are fluctuating between the +2.5 and +2.2 valence states of the $P\bar{1}$ phase in such a way that the charge disproportionation between the average valences of these sites is half of that between Fe1 and Fe4. Finally, all local distortions (valences) are dynamic above 320 K being +2.5 the average valence on the single Fe site of the hexagonal phase.

The detailed study of the mixed-valence LuFe_2O_4 compound has shown that similarly to other mixed-valence transition-metal compounds, the CO phase transitions originate from a strong electron-phonon coupling which gives rise to associated local distortions and charge segregation at the different crystallographic metal sites. In conclusion, the description of the CO transitions in LuFe_2O_4 as due to ionic $\text{Fe}^{2+}/\text{Fe}^{3+}$ ordering is far from reality.

ACKNOWLEDGMENTS

The authors thank Diamond Light Source for granting beam time and the I16 beamline staff for technical support during the experiment. Financial support from the Spanish MINECO (Project No. MAT2012-38213-C02-01) and DGA (CAMRADS) is acknowledged.

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