An evidence of local structural disorder across spin-reorientation transition in DyFeO₃: an extended x-ray absorption fine structure (EXAFS) study

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Abstract

The present work is aimed at exploring the local atomic structure modifications related to the spin reorientation transition (SRT) in DyFeO₃ orthoferrite exploiting x-ray absorption fine structure (XAFS) spectroscopy. For this purpose we studied by XAFS the evolution of the local atomic structure around Fe and Dy as function of temperature (10–300 K) in a DyFeO₃ sample having the SRT around 50–100 K. For sake of comparison we studied a YFeO₃ sample having no SRT. The analysis of the extended region has revealed an anomalous trend of Fe–O nearest neighbour distribution in DFO revealing (i) a weak but significant compression with increasing temperature above the SRT and (ii) a peculiar behavior of mean square relative displacement (MSRD) [σ^2] of Fe–O bonds showing an additional static contribution in the low temperature region, below the SRT. These effects are absent in the YFO sample supporting these anomalies related to the SRT. Interestingly the analysis of Dy *L*₃-edge data also reveal anomalies in the Dy–O neighbour distribution associated to the SRT, pointing out a role of magnetic Re ions across $T_{\text{SRT,Fe}}$. These results point out micro-structural modification at both Fe and Dy sites associated to the magnetic transitions in DFO, it can be stated in general terms that such local distortions across Fe³⁺ and magnetic Re³⁺ may be present in other orthoferrites exhibiting multiferroic nature.

Keywords: rare earth ortho-ferrites, spin re-orientation transition, local structural distortions

(Some figures may appear in colour only in the online journal)

1. Introduction

Study of multiferroics/magneto-electric materials have been under extensive research because they have technological importance for device applications [1–4]. The rare-earth orthoferrite ReFeO₃ compounds with two magnetic sub-lattices

(Re³⁺ & Fe³⁺) exhibit various interesting magnetic properties arising from competing magnetic interactions between two sub-lattices viz., (i) paramagnetic to antiferromagnetic (AFM) ordering of Fe³⁺ ions (Neel transition, $T_{\text{N,Fe}}$) and rare-earth ions ($T_{\text{N,Re}}$), (ii) spin-reorientation transition (SRT) of Fe³⁺ moments ($T_{\text{SRT,Fe}}$), driven by the anisotropic exchange

interactions between Fe and Re spins, (iii) compensation temperature (T_{comp}) at which the local moments of rare-earth and Fe^{3+} are expected to be equal and opposite [5]. Around $T_{\text{N,Re}}$, due to magnetic interaction between Re^{3+} and Fe^{3+} , the Re-layers shifts towards the layers of Fe^{3+} with opposite spin directions and away from those with the same spin directions, resulting in a collective displacement of the Re^{3+} ions and producing a spontaneous ferroelectric (FE) polarization [6–8]. In some ReFeO_3 compounds the presence of FE distortion is reported only below ($T_{\text{N,Re}}$) and in some compounds it is reported around the SRT of Fe^{3+} . For example FE distortion is reported in DyFeO_3 below $T_{\text{N,Dy}}$ with applied magnetic field [8] and also in the weak ferromagnetic (WFM) state between $T_{\text{SRT,Fe}}$ and $T_{\text{N,Fe}}$ in zero magnetic field [9]. In GdFeO_3 FE distortion is reported below $T_{\text{N,Gd}}$ [10].

Owing the relationship between atomic structure and the magnetic response in ReFeO_3 , the careful local atomic structure characterization is a mandatory step to reliably elucidate about the origin of their peculiar magnetic properties. It is worth to mention that x-ray absorption fine structure (XAFS) spectroscopy is a very suitable experimental method that has demonstrated the capability to probe finest modifications of the local structure at atomic scale, and has been successfully applied in the field of multiferroic and strongly correlated compounds [11, 12]. However XAFS studies of ReFeO_3 compounds seem missed in the literature, except the recent work by Mahana *et al* in a similar compound, GdCrO_3 [13]. One of the reasons for such lacking of experimental data could be likely ascribed to the overlapping XAFS features of Fe K-edge and Re L_3 -edge in several ReFeO_3 compounds. However, among the ReFeO_3 compounds DyFeO_3 (DFO) specially is suitable for XAFS analysis across Fe K-edge and Dy- L_3 edges since both edges are relatively far, this minimizing the interference between the Fe and Dy fine structure features (figure 1). The DyFeO_3 crystallizes in an orthorhombic distorted perovskite structure, with space-group symmetry D_{2h} ($Pbnm$). The Fe^{3+} spin moments order AFM below $T_{\text{N,Fe}}$ (~ 645 K) with a small canting shown by Γ_4 (G_x, A_y, F_z) state in Bertaut’s representation where WFM component is along c -axis and G-type component is directed along a -axis. With lowering of temperature in the range (50–100 K), the decrease of magnetization (M) is observed due to the SRT $T_{\text{SRT,Fe}}$ where WFM component disappears and G-type component reorients towards b -axis, denoted by Γ_1 (A_x, G_y, C_z) state. On further cooling below 50 K, M again start increasing as approaching towards AFM ordering of Dy^{3+} ions ($T_{\text{N,Dy}} \sim 4$ K).

In order to shed light about micro-structural effects related to the SRT transition we have carried out detailed XAFS measurements at Fe-K and Dy- L_3 edges on a polycrystalline DyFeO_3 (DFO) sample, in the 10–300 K temperature range. For sake of comparison, in order to validate the local structure effects associated to the magnetic transition in DFO, analogous Fe-K edge XAFS data were measured also in YFeO_3 (YFO) sample, belonging to the same orthoferrite family but Y being non magnetic Re. The analysis of the XAFS data had evidenced fine structural effects associated to the SRT transition in DFO, in particular we have observed negative thermal expansion (NTE) of Fe–O bond length distribution taking

Figure 1. Example of normalized XAFS spectra measured at 10 K temperature. The Fe-K (blue) and Dy- L_3 (red) edges for DFO sample and the Fe-K (green) for YFO sample are shown. For sake of comparison DFO-Dy normalized spectrum is up-shifted by 1 and YFO-Fe normalized spectrum is down-shifted by -1 .

place above the SRT while an increasing distortion of Fe–O pair distribution is activated below T_{SRT} . A weak but significant structural effect appears by looking at the local structure around Dy, corroborating the role of Dy in the SRT.

2. Experimental details

Polycrystalline ReFeO_3 ($\text{Re} = \text{Dy}$ and Y) samples were prepared through conventional solid-state reaction method. The x-ray diffraction (XRD) patterns demonstrate single phase orthoferrites according to the literature data for DFO ($a_{\text{DFO}} = 5.5957$ Å, $b_{\text{DFO}} = 7.6288$ Å, $c_{\text{DFO}} = 5.3009$ Å) and YFO ($a_{\text{YFO}} = 5.5877$ Å, $b_{\text{YFO}} = 7.5951$ Å, $c_{\text{YFO}} = 5.2743$ Å) [15, 16]. Bulk magnetization and temperature dependent ^{57}Fe Mossbauer study have been carried out for DFO in our previous report [14]. Temperature dependent magnetization (M - T) data indicates the SRT in DFO in the 50–100 K temperature range while no such signature is observed in YFO (figures 8(a) and (b)) matching well with the known literature.

In the present work, temperature dependent XAFS experiments were carried out at beamline P65 of PETRA-III, DESY, Hamburg, Germany. The absorption spectra (XAS) were collected in transmission mode at Fe K ($E_{\text{Fe}} = 7112$ eV), and Dy L_3 ($E_{\text{Dy}} = 7790$ eV) edges on heating the sample in the temperature range 10–300 K. Samples for x-ray absorption measurements were prepared carefully by mixing about 7(8) mg of DyFeO_3 (YFeO_3) with 90mg of pure cellulose powder, mixtures were pressed (5 kbar) in solid pellets (surface area 1.3 cm^2) having a jump discontinuity around 0.7 at Fe–K and Dy- L_3 edges.

The x-ray beam energy calibration was defined measuring the XAS K-edge spectrum of Fe metal foil (Fe^0) and selecting the Fe^0 edge energy ($E_{\text{Fe}} = 7112$ eV) at the first inflection point of the absorption edge [17]. The incident (I_0) and transmitted (I_t) x-ray intensities were measured using ionization chambers and the XAS signal was calculated as $\ln(I_0/I_t)$. Data acquisition was carried out in quick EXAFS (QE) mode i.e. collecting I_0 and I_t data while monochromator moves in a continuous way and registering the energy position. The QE mode allows to collect high quality data in a shorter time with

Figure 2. Fe K-edge normalized absorption coefficient $\alpha(E)$ for DyFeO₃ sample in the temperature range from 10 K to RT, the spectra are superimposed to highlight the reproducibility and stability of the set-up. The inset illustrate the pre-edge region α and its derivative $\alpha' = d\alpha/dE$, the first derivative maximum (A) does not shift as a function of temperature, a weak raising of the pre-edge peak (arrow B) can be appreciated as a function of temperature.

respect to the conventional energy scan mode. In the present work the collection time for each spectrum was about 5 min with about 8000 energy points. Because of the large number of points in each spectrum, energy points were re-binned in a new mesh with about 2000 points integrating the I_0 and I_t intensities every four energy points, this makes the data files more suitable for data analysis programs. Two spectra were averaged up for each temperature/edge scan. Examples of normalized XAFS spectra ($\alpha(E)$) measured at the Fe-K (DFO and YFO samples) and Dy- L_3 (DFO sample) edges are presented in figure 1, the near edge region (XANES) of the Fe-K edge spectra as a function of temperature are presented for DFO sample in figure 2. The stability of the experimental set-up can be appreciated by looking at the very reproducible XANES features and energy position of the edge onset (figure 2 inset). The average statistical noise on the XAFS structural signal $\chi(k)$ was estimated [18] as $\sigma_{\chi(k)} < 2 \times 10^{-4}$ on Fe-K and $\sigma_{\chi(k)} < 1 \times 10^{-3}$ on Dy- L_3 edge spectra, the average signal to noise ratio was estimated around 100 for Fe-K and around 20 for Dy- L_3 edge spectra.

3. Results and discussions

3.1. EXAFS data extraction and modeling

The XAS data were treated using standard procedures for pre-edge background subtraction, edge jump normalization and extraction of structural EXAFS signal $\chi(k)$ using the ESTRAPROGRAM [18]. The edge energy E_0 defining the origin of the photo-electron wave-vector $k = \hbar^{-1} \sqrt{2m_e(E - E_0)}$,

(m_e = electron mass) was selected at the first inflection point of the absorption edge (maximum of the first derivative $d\alpha(E)/dE$, figure 2). The very accurate energy scale reproducibility of the experimental set-up (figure 2, (A)) is mandatory for accurate XAFS data analysis and in particular the stability of the edge energy ensure the possibility to precisely individuate finest changes of interatomic distances. The quantitative analysis of the extended (EXAFS) region of the XAS spectra were carried out using FITEXA program [18] applying a Gaussian model for neighbour shell distributions [19]. Structural data refinements were carried out in the k -space on k^w -weighted ($k^w \chi(k)$) signals, the $w = 3(1.5)$ for Fe-K(Dy- L_3) edges was selected to provide an opportune weight to the structural signals in the k -range used for the analysis. The amplitude, phase and mean free path functions used in the standard EXAFS formula [19] were calculated using FEFF 8.2 program [20]. The neighbor shells were individuated using atomic cluster models around the absorber derived from the crystallographic structures (Pbnm phase) [14].

The ReFeO₃ unit cell can be considered roughly cubic, the corner linked FeO₆ octahedra are located at the cube corners while the Re ions are close to the cube center. For the data analysis we followed the procedures described in [11, 21]. In order to reduce the number of independent parameters and the correlations among them in the analysis, the single (SS) and multiple (MS) scattering contributions relevant for the data refinement were selected on the basis of their average amplitude, the signals having similar composition and geometry were grouped in a single contribution. Selected MS contributions were included for the almost collinear atomic configurations (YFO sample, see below) in which they are enhanced by the focusing effect [11, 21]. The relevance of the structural contributions were tested by statistical analysis [18]. This procedure provides the best fit agreement and allows to reproduce the main structural features up to about 4 Å around the average absorber (figures 3 and 4). After preliminary check the edge energy shift for each edge/sample was kept the same for all the structural contributions (SS and MS) and fixed in the whole temperature range to avoid spurious effect of correlation with coordination distances. The multiplicity numbers were kept fixed to their crystallographic values in the analysis to avoid the correlation with the MSRD (σ^2) parameters. Examples of data refinement in the R -space are presented in figure 3 for the different edges/samples including the partial contributions used in the data refinement.

3.2. EXAFS data analysis and results

The k -weighted experimental spectra and best fits for the DFO and YFO samples as a function of temperature are shown in figure 4 together with the moduli of the FT for experimental and best fit. The effect of temperature is weak resulting in a moderate attenuation of the structural features as a function of temperature, due to the rising thermal disorder with warming the sample. This is more evident looking at the moduli of the FT (figure 4) in which the main peaks can be associated to the

Figure 3. Examples of EXAFS data analysis at the Fe-K (DFO and YFO samples) and Dy- L_3 edges. The k -weighted Fourier transform (FT) moduli $|FT|$ and the Imaginary part of experimental data (green dots) and best fit curves (black lines) are presented. The partial contribution used in the analysis are shown (orange lines), vertically shifted for sake of clarity.

main coordination shells around the absorber (uncorrected for the phase shift).

The k^3 -weighted Fe K-edge spectra were fitted in the k range of $3\text{--}12.5\text{ \AA}^{-1}$ and $3\text{--}14.5\text{ \AA}^{-1}$ respectively for DFO and YFO sample. The Dy L_3 edge at 7790 eV determined the shorter k -range in DFO sample (figure 1). The $k^{1.5}$ -weighted Dy L_3 -edge spectra were fitted in the k range of $3\text{--}12.5\text{ \AA}^{-1}$ (figure 4). The analysis of Fe-K edge of DFO and YFO sample required five shells to fit the experimental spectra in k range of $3\text{--}12.5\text{ \AA}^{-1}$ and reproduces the main structural features up to $R \sim 4\text{ \AA}$ (figure 3). The Fe atoms are coordinated to 6 oxygen ($N_{\text{FeO}} = 6$) nearest neighbor located at about $R_{\text{FeO}} \sim 2\text{ \AA}$ from Fe, arranged in octahedral configuration (FeO₆). The coordination distances R_{FeO} , and the MSRD of Fe-O bonds

denoted by σ_{FeO}^2 as a function of temperature are shown in figures 8(c)–(f).

The crystallographic models of DFO(YFO) report 8 Dy(Y) ions broadly distributed around Fe in the $3.1\text{--}3.8\text{ \AA}$ range. After preliminary tests we were able to reproduce the Fe-Dy shells with three contributions Fe-Dy _{i} ($i = 1\text{--}3$) with $N_{\text{FeDy}_1} = 4$ at $R_{\text{FeDy}_1} \sim 3.1\text{ \AA}$, $N_{\text{FeDy}_2} = 2$ at $R_{\text{FeDy}_2} \sim 3.3\text{ \AA}$ and $N_{\text{FeDy}_3} = 2$ around $R_{\text{FeDy}_3} \sim 3.6\text{ \AA}$. We found that sharing the same σ_{FeDy}^2 for the three Fe-Dy _{i} shells provides a satisfactory best fit agreement. The same model is applied to the analysis of YFO sample, except we need to use an independent MSRD parameter for the Fe-Y₃ shell $\sigma_{\text{FeY}_3}^2$. The analysis points out quite small $\sigma_{\text{FeY}_3}^2$ that can be an artifact either due to the N_{FeY_i} that could be different from N_{FeDy_i} , or

Figure 4. (left) Experimental and best fit k^w -weighted Fe and Dy EXAFS spectra as a function of temperature. (right) Moduli of the FT ($|FT|$) of k^w -weighted Fe and Dy EXAFS spectra and best fit curves. In each frame the data is presented in increasing order of temperature as shown by $T \uparrow$.

to the correlation with the intense signal of the Fe–Fe shell superimposed (see below). We were unable to disentangle these effects but the structural information in this region are not crucial for the discussion. The structural parameters of the Fe–Dy/Y shells as a function of temperature are shown in figure 5.

The fifth shell in DFO and YFO samples corresponds to the $N_{\text{FeFe}} = 6$ neighbours at $R_{\text{FeFe}} \sim 3.9$ Å from corner linked FeO_6 octahedra connected through oxygen (Fe–O–Fe chains) along the cube edge. In DFO sample the Fe–O–Fe chains have quite small FeOFe angle (being less than 150°) resulting in weak MS contributions statistically not significant in the refinement, hence we considered only SS terms in the fifth shell of DFO sample. Whereas, the Fe K-edge spectra of YFO sample depict sharper and more intense structural features, in

particular in the region corresponding to the fifth shell (figures 3 and 4). This effect is likely due to larger MS contributions of Fe–O–Fe configurations enhanced because the larger FeOFe angle in YFO sample (focusing effect), these MS were included in the analysis of YFO sample data. The structural parameters of the fifth shells are shown in figure 6.

The local structure around Dy is made by several broadly distributed coordination shells and a quite large structural disorder, these give rise to superimposed structural signals and high correlation among the fitting parameters. After preliminary checks we were able to fit the Dy- L_3 edge spectra using seven shells (only the SS were considered) and refine the structural features up to about $R \sim 4$ Å as shown in figures 3 and 4. The Dy–O contributions, being broadly distributed in the crystallographic model, were refined using

Figure 5. Temperature dependence of Fe–Dy/Y structural parameters as a function of temperature. The coordination distances R_{FeDy_i} (red) and R_{FeY_i} (blue) ($i = 1-3$) are shown in the top panel. The MSRDs are reported in the bottom panel, the three Fe–Dy shells share the same σ^2_{FeDy} (red) while fitting the Fe–Y shells requires two independent MSRD, one for first and second shell $\sigma^2_{\text{FeY}_{1,2}}$ (blue) and one for the third shell $\sigma^2_{\text{FeY}_3}$ (light blue). The lines indicate represent fit with a Debye model trough the data.

three Dy–O_{*i*} ($i = 1-3$) shells with $N_{\text{DyO}_1} = 4$ at around $R_{\text{DyO}_1} \sim 2.25$ Å, $N_{\text{DyO}_2} = 2$ around $R_{\text{DyO}_2} \sim 2.55$ Å and $N_{\text{DyO}_3} = 2$ around $R_{\text{DyO}_3} \sim 3.1$ Å respectively. The Dy–Fe contributions were refined using two shells with $N_{\text{DyFe}_1} = 4$ at $R_{\text{DyFe}_1} \sim 3.25$ Å, and $N_{\text{DyFe}_2} = 4$ around $R_{\text{DyFe}_2} \sim 3.70$ Å and two Dy–Dy shells with $N_{\text{DyDy}_1} = 3$ at $R_{\text{DyDy}_1} \sim 3.75$ Å and $R_{\text{DyDy}_2} \sim 3.95$ Å respectively. The structural evolution around Dy ions as a function of temperature is detailed in figure 7. It may be noted that the Dy EXAFS data analysis depict the Dy–Fe shells slightly different from the structure obtained analyzing the Fe EXAFS. This could be an artifact likely due to occurrence of quite intense Dy–Dy and Dy–Fe superimposed signals which raises the correlation among the fitting parameters and hence weakens the absolute accuracy of the analysis.

3.3. Discussions

The XANES of the EXAFS signal is very sensitive to the average coordination geometry and valence state of the

Figure 6. Temperature dependence of the structural parameters for the Fe–Fe shell in DFO and YFO samples. The Fe–Fe distances R_{FeFe} for DFO (red) and YFO (blue) are shown in the top panel while the MSRD parameters are in the bottom panel. The R_{FeFe} has only weak changes as a function of temperature while the MSRD increases with a similar behaviour for both DFO and YFO samples but DFO depicts larger static disorder (see text), the full lines represents the Debye model fit to the MSRD data.

absorber atoms [22]. The pre-edge peak centroid position of the Fe K-edge (figure 2) is found in the range 2.48–2.50 eV above the Fe⁰ foil K-edge for DFO and YFO (not shown in figure 2) samples, this confirms [23] the Fe³⁺ valence state in both the samples and in the whole temperature range, corroborating the ⁵⁷Fe Mossbauer results [14]. The pre-edge peak area (figure 2) is found within 0.095–0.103 eV, confirming the 6 oxygen co-ordination of Fe atoms in the DFO and YFO samples [23] according to their crystallographic structures.

From the EXAFS data analysis the major effects of temperature are evident at the Fe–O nearest neighbour distance. The figure 8 shows the Fe–O distances ((e) and (f) panels) and MSRD ((c) and (d) panels) as obtained on DFO and YFO samples as a function of temperature together with the bulk magnetization data ((a) and (b) panels) for the sake of comparison. The very reproducible energy scale of the experimental set-up allows very precise determination of the average nearest neighbour distances with uncertainty less than 2×10^{-3} Å, suitable to individuate weak modifications as a function of sample temperature. Comparing the Fe–O distances observed in DFO and YFO samples (figure 8) reveal a weak but significant compression of Fe–O distance in DFO with raising temperature in the 90–250 K range, whereas the Fe–O distances in YFO are almost constant in the same temperature range. This finding

Figure 7. Temperature dependence of Dy-local structure parameters: the R_{DyO_i} ($i = 1-3$) interatomic distances are shown in the bottom panel (red), the R_{DyFe_i} ($i = 1, 2$) interatomic distances are shown in the middle panel (blue) and the R_{DyDy_i} ($i = 1, 2$) interatomic distances are shown in the top panel (orange), lines are guide for the eyes.

reliably indicates that a compression of the average Fe–O distance is occurring raising the temperature in DFO and not for the YFO. The comparison of magnetic and structural data in figure 8 supports such a NTE associated to the SRT. A NTE behaviour is reported in similar compounds using either x-ray, neutron diffraction or EXAFS measurements [13, 24, 25]. High quality neutron diffraction measurements on NdFeO_3 perovskites indicated NTE of the b lattice parameter close to T_{SRT} [24]. The SRT has been reported associated to NTE in $\text{ReFe}_{1-x}\text{Cr}_x\text{O}_3$ compounds when Re is a magnetic ion (Yb and Tm) and has been explained in terms of magneto-elastic effect as a consequence of magnetic repulsion between transition metal ions [25]. Recently a temperature dependent EXAFS study on GdCrO_3 also reported signatures of NTE of Cr–O bond length across $T_M \sim 169$ K (FE and magnetic transition temperature) indicating the magnetostriction effect resulting in CrO_6 octahedra distortions associated with off-center displacement of oxygen via octahedral rotation [13]. The NTE is also observed in LaMnO_3 [26], SrRuO_3 [27] below their respective magnetic ordering temperatures. Similarly NTE is observed in other multiferroic materials and explained as a consequence of magneto-elastic volume effect, strong spin-phonon coupling, structural distortion triggered by excitations of anisotropic lattice vibrations [28, 29]. For example, the contraction of unit cell volume was observed across T_N (598–617 K) in multiferroic BiFeO_3 [29].

The second important observation of the present work is the clearly different behaviour of σ_{FeO}^2 for DFO and YFO

samples as shown in figures 8((c) and (d) panels). The σ_{FeO}^2 of both the samples progressively increase with raising temperature according to the rising of the thermally activated structural disorder, with σ_{FeO}^2 for DFO larger than YFO sample. However if we compare the σ^2 of Fe–O bonds resulting in YFO and DFO samples, it appears that the σ_{FeO}^2 (DFO) slightly increases for temperatures below $T = 100$ K while σ_{FeO}^2 (YFO) appears to decrease monotonically. Accordingly to [30, 31] the MSRD measured by EXAFS can be described as a sum of a dynamic term $\sigma^2(T)$ resulting from thermal vibrations of the inter-atomic bond, plus a constant term accounting for static structural distortion σ_S^2 , $\sigma_{\text{total}}^2(T) = \sigma^2(T) + \sigma_S^2$. The dynamic contribution can be modeled by using the correlated Debye model for the thermal vibrations [31, 32]:

$$\sigma^2(T) = \frac{3\hbar}{\omega_D^3 m_o} \int_0^{\omega_D} \omega \coth \left(\frac{\hbar\omega}{2k_B T} \left[1 - \frac{\omega_D \sin \left(\frac{\omega R_o q_D}{\omega_D} \right)}{\omega R_o q_D} \right] \right) d\omega \quad (1)$$

where m_o is the average atomic mass of the pair, R_o the inter-atomic distance and ω_D is the Debye frequency corresponding to the Debye temperature $\theta_D = \hbar\omega_D/k_B$. The quantity q_D is the radius of the Debye sphere $q_D = (6\pi^2/V_a)^{1/3}$, V_a being the real-space volume per atom. In order to get the quantitative parameters we wrote a Python-Scipy based script to calculate the $\sigma_{\text{total}}^2(T)$ and optimize the parameters (σ_S^2 and θ_D) by fitting the model to the experimental data using *Optimize.curveFit* procedure. The Debye model well reproduces the experimental data of σ_{FeO}^2 (YFO) in the whole temperature range (figure 8(d)) with $\theta_D = 270 \pm 10$ K and $\sigma_S^2 = (1.9 \pm 0.1) \times 10^{-3} \text{ \AA}^2$. On the contrary the σ_{FeO}^2 (DFO) data cannot be reproduced by the same model at the low temperatures below about 100 K (figure 8(c)) where the experimental data suggest some additional static distortion of Fe–O nearest neighbor distribution close and below the T_{SRT} , that suddenly disappears on heating the sample above a critical temperature T_o . In order to model this effect we added a step-like contribution to the Debye model having an arctangent-like shape:

$$\sigma^2(T-T_o) = -\frac{A}{\pi} \left(\arctan \left(\frac{T-T_o}{\gamma} \right) - \frac{\pi}{2} \right). \quad (2)$$

The correlation among the several parameters worsen the stability of the refinement but after preliminary tests we fixed $\gamma = 10$ K, $A = 0.05 \text{ \AA}^2$ and we obtained the fit as shown in figure 8(c) (black curve) fitting very well the σ_{FeO}^2 (DFO) experimental data in the whole temperature range with $\theta_D = 240 \pm 10$ K and $T_o = 95 \pm 5$ K and $\sigma_S^2 = (2.3 \pm 0.1) \times 10^{-3} \text{ \AA}^2$. Interestingly, the observed T_o is close to the onset of SRT (T_{SRT}) in DFO strengthening the hypothesis that such additional term $\sigma_{T_o}^2$ represents a local structure fingerprint related to the SRT transition.

The effect of temperature on the Fe next neighbour shells is generally weak on both DFO and YFO samples (figures 5 and 6), the Fe–Dy interatomic distances R_{FeDy/Y_i} are roughly constant as a function of temperature while the MSRDs increase, roughly accordingly to the correlated Debye model. The MSRD of the first two Fe–Dy/ $Y_{1,2}$ shells are found similar in DFO

Figure 8. (top panels) Temperature dependence of magnetization DyFeO₃ (a) and YFeO₃ (b) respectively. (middle panels) Temperature evolution of σ_{FeO}^2 for DFO (c) and YFO (d) respectively. Symbols are the experimental data points and the solid lines are best fit to the data. Fitting of DFO data with a Debye model (orange line) does not match the experimental data below 100 K and requires an additional term (black line) accounting for the raising disorder below and around the SRT (see text for discussion). (bottom panels) Temperature evolution of the average Fe–O bond length $R_{\text{Fe-O}}$ for DFO (e) and YFO (f) respectively. The lines are linear fit to the low/high temperature regions (e) and to the whole temperature range (f). Note the signatures of NTE of Fe–O average bond length above T_{SRT} in the 90–250 K range for DFO.

and YFO while for the third Fe–Dy/Y₃ shells the YFO sample depicts much lower MSR likely being an artifact as discussed above. Also the R_{FeFe} interatomic distance does not change significantly as a function of temperature in both DFO and YFO samples while the Fe–Fe MSR measured in DFO sample is systematically larger than for YFO sample. The Debye model suggests similar T_{D} temperature while the static contribution is $\sim 2 \times 10^{-3} \text{ \AA}^2$ larger in DFO with respect to YFO. Looking careful at the data (figure 6) suggests a weak upturn of σ_{FeFe}^2 in DFO sample occurring at low temperatures ($< 100 \text{ K}$) but it is a weak effect, within the experimental uncertainty.

The effect of the temperature on Dy local structure is also generally weak and partially masked by the complex local structure around Dy absorber. However from the data in figure 7 it is evident discontinuous behaviour of the R_{DyO_1} and R_{DyO_2} interatomic distances around the T_{SRT} as shown in figure 8. This effect depicts a microstructural counterpart of the magnetic transition also active around the magnetic Re in DFO. The next neighbour shell distances (figure 7) are roughly constant as a function of temperature, as already found at the Fe edges. Usually it is believed that in this type of compounds the Re^{3+} play a role only at very low temperatures. However, we have seen recently from temperature dependent Raman spectroscopy measurements that the correlation between the Re^{3+} vibration modes and Fe^{3+} spin ordering exists even up to $T_{\text{N,Fe}}$ in GdFeO_3 [33], which is similar to the studied

compound in the present work. Therefore, the observed results indicates that Re^{3+} indeed is correlated with SRT. In GdCrO_3 [13], individual Gd–O, Gd–Cr bond lengths and MSR show anomalous behavior across T_{M} suggesting Gd displacement caused by magnetostriction effect associated with Gd–Cr interaction. The absence of the observed structural changes in YFO as compared to DFO implies that the interaction between Dy and Fe play important role in inducing NTE and FeO_6 octahedral distortion in DFO. In similar compound GdCrO_3 , anomalies are observed in MSR and interatomic distances involving Gd and Cr absorber, around the transition temperature $T_{\text{M}} \approx 169 \text{ K}$ pointing out a structural effect associated to the ferroic transition. It is noticeable that in this work the local structural effects observed around Fe and Dy magnetic ions in DFO sample are limited to the nearest neighbour Fe/Dy–O shells pointing out the relevance of very local scale interactions related to the magnetic response of these compounds.

4. Conclusion

We present accurate temperature dependent xray absorption fine structure (XAFS) analysis on polycrystalline DyFeO₃ at Fe–K and Dy–L₃ edges. The results reveal fine local structural modifications associated to SRT in DyFeO₃. In particular we report a NTE of Fe–O bond length above SRT and activation of static distortion of Fe–O bonds below SRT. For sake of

comparison we performed an analogous Fe–K edge XAFS on a structurally similar system YFeO_3 , having different magnetic properties and, in particular not the SRT. The absence of these structural features in YFeO_3 strength the hypothesis that the fine local structure modifications around Fe atoms in DyFeO_3 are related to the SRT. Furthermore the EXAFS results also point out some weak but significant structural effect around Dy close to SRT, pointing out a role of Dy local structure as well.

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