

Atomic-scale mechanisms for magnetostriction in CoFe_2O_4 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ oxides determined by differential x-ray absorption spectroscopy

G. Subías^{1,*}, V. Cuartero,² J. García,¹ J. Blasco,¹ and S. Pascarelli³

¹*Instituto de Ciencia de Materiales de Aragón, Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza. C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain*

²*Centro Universitario de la Defensa, Carretera de Huesca s/n, 50090 Zaragoza, Spain*

³*ESRF-The European Synchrotron, 71 Avenue des Martyrs, Grenoble, France*



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The atomic environments involved in the magnetostriction effect in CoFe_2O_4 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ polycrystalline samples have been identified by differential extended x-ray absorption fine structure (DiffEXAFS) spectroscopy. We demonstrate that cobalt atoms at octahedral sites are responsible for their magnetostriction. The analysis of DiffEXAFS data indicates that the local-site magnetostrictive strains of Co atoms are reversed in these two oxides, in agreement with the macroscopic magnetostriction. For the CoFe_2O_4 spinel, a large negative strain along the (100) direction has been determined for the CoO_6 octahedron causing a tetragonal contraction in contrast with the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ perovskite, where a positive moderate strain along the (100) direction was found resulting in a tetragonal expansion. The different local-site magnetostriction is understood in terms of the different valence and spin state of the Co atoms for the two oxides. The macroscopic magnetostriction would be explained then by the relative change in volume, either contraction in CoFe_2O_4 or expansion in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, when the tetragonal axis of the Co site is reoriented under an externally applied magnetic field.

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I. INTRODUCTION

Magnetostriction (MS) is a phenomenon observed in all ferromagnetic materials, which develop a mechanical deformation when they become magnetized by the application of an external magnetic field. It is a consequence of the magnetoelastic coupling and it pertains to the strain produced along the field direction. Functional materials with giant MS play an important role in a broad range of industrial, biomedical, and defense applications, since they can reversibly convert energy between the magnetic and elastic states [1]. Within these materials, alloys based on Fe, Ni, and Co transition metals in combination with certain rare-earth elements like Tb and Dy have been intensively studied due to their giant room temperature magnetic-field-induced strain up to thousands of parts per million [2]. In these rare-earth-based materials, the magnetostrictive strain arises from the coupling of the orbital anisotropic $4f$ charge distribution with both the $4f$ magnetic moment (via the spin-orbit coupling) and the local distortions (via the crystal field), as it has been recently determined using differential x-ray absorption spectroscopy (DiffXAS) in the TbFe_2 alloy [3].

In order to develop alternative magnetostrictive materials with reduced cost, easy manufacturing, and enhanced properties, oxide-based magnetic materials such as ferromagnetic spinels and perovskite-type oxides have been also studied for a long time, although the magnitude of MS strain is not as high as in the rare-earth compounds. In the oxide-based materials, strong electron-lattice coupling is considered as

responsible for the giant MS, but different mechanisms can apply depending on the class of magnetic oxides. Among the perovskite-type oxides, both mixed-valence magnetoresistance manganites [4] and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ cobaltites [5] show giant magnetostrictive effects. In the former, the observed volume MS at T_c is related to the quenching of the charge localization under the application of an external magnetic field, whereas in the latter, the observed anisotropic MS is thought to arise from the orbital instability of Co^{3+} ions under the applied magnetic field inducing a transition from an orbital nondegenerate low-spin state to an orbitally degenerate intermediate-spin state. However, these large strains are observed only at very low temperatures and require high magnetic fields, which restrict the use of these materials for practical applications for sensing and actuation. On the other hand, spinel structured ceramic oxides such as cobalt ferrites offer a wide range of interesting properties for application due to their large anisotropic MS of hundreds of parts per million in both single-crystal and polycrystalline samples at room temperature and low magnetic fields [6,7].

Cobalt ferrite (CoFe_2O_4) can be considered as a cobalt-substituted variant of magnetite (FeFe_2O_4). It has been recently investigated for important technological applications, both in its stoichiometric and cation-substituted forms [8,9]. It has a partially inverse spinel structure where the cobalt ions occupy the B sites (octahedral local symmetry) of the crystal lattice. The changes in the magnetic properties of magnetite due to cobalt substitution for iron, $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$, are due to the differences in the properties of Co^{2+} and Fe^{2+} (for $x \leq 1$). The high MS of cobalt ferrites has been associated with the properties of the Co^{2+} cation. It was explained within the single-ion crystal-field model [6,7,10–12], which considers

*gloria@unizar.es

that Co^{2+} cations occupy the octahedral B sites in the spinel lattice, and that the orbital angular momentum of Co^{2+} is unquenched and couples to both the spin momentum and the tetragonal distortion of the octahedral crystal field. Therefore, MS increases with the cobalt content as it was experimentally demonstrated [7].

Despite the extensive study of these ferrites, there is no direct experimental measurement of the local distortion at either of the two atom sites originated by field-induced magnetization, because this distortion is expected to be too small to be detected by conventional experimental techniques such as x-ray or neutron diffraction. As it is well known, the best technique able to determine the local structure around a specific atom in a solid is x-ray absorption spectroscopy (XAS) [13,14]. However, its sensitivity is not sufficient to determine local distortions originating from magnetostriction, though it can be improved by using a differential approach (subtraction of XAS spectra). In fact, DiffXAS [15,16] has demonstrated sensitivity to the atomic displacements of the order of femtometers, and it has made the direct assessment of local-scale MS possible, as reported for several metal alloys [17–19].

We present here a DiffXAS study of the atomic-scale MS of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ perovskite and CoFe_2O_4 spinel ferrite. $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ is a ferromagnet below 250 K [20,21], with a high anisotropic MS as large as 1000 ppm below 100 K but at relatively high magnetic field of 14 T [5]. At moderate fields of 2 T, the magnetostrictive strain has been reported to be ~ 450 ppm. On the other hand, CoFe_2O_4 is a ferrimagnet with a high Curie temperature $T_C = 793$ K, and the value of the anisotropic magnetostrictive strain varies from 200 to 400 ppm at room temperature and low magnetic fields ($\mathbf{B} < 1$ T) for polycrystalline samples [7,22,23]. We expect to extract the magnitude and sign of the changes in individual bond lengths in order to determine which atomic strains are responsible for the macroscopic MS effects in the two samples.

II. EXPERIMENTAL DETAILS

Polycrystalline powder samples of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and CoFe_2O_4 have been synthesized by a sol-gel method using the citrate route as described elsewhere [5,24]. The samples were characterized by powder x-ray diffraction (XRD) with a Rigaku D-Max system using $\text{Cu K}\alpha_{1,2}$ wavelengths. X-ray diffraction patterns collected at room temperature (Fig. S1) agreed with the formation of single-phase samples [25]. CoFe_2O_4 adopts the cubic spinel structure with the space group $Fd\bar{3}m$, whereas $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ shows a quasicubic $Pm\bar{3}m$ structure. Magnetic saturation is achieved at a magnetic field of 2 T [24,26] for CoFe_2O_4 at room temperature and for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ at low temperatures well below $T_C \approx 250$ K [5,27].

XAS and DiffXAS measurements were performed at beamline BM23 of the European Synchrotron Radiation Facility [28]. Pellets were prepared by dilution with cellulose to get a jump of about 1 at the absorption edge. Different pellets were optimized for CoFe_2O_4 at the Co and Fe K edges, respectively. For the DiffXAS experiment, pellets were inserted into a He flow cryostat that was placed at the center

of a 2-T magnetic field wheel, which is rotated in the plane perpendicular to the propagation vector of the x rays. This allows us to perform measurements from 10 K up to room temperature. The absorption coefficient $\mu(E)$ was recorded with the magnetic field direction \mathbf{B} parallel and then perpendicular, $\mu^{\parallel}(E)$ and $\mu^{\perp}(E)$, respectively, to the x-ray electric-field polarization vector \mathbf{E} . The differential absorption, $\Delta\mu(E) = \mu^{\parallel}(E) - \mu^{\perp}(E)$, averaged over a large number of cycles to improve the signal-to-noise ratio, was normalized by dividing by the edge jump. Spectra were measured in transmission in the quick-scanning mode of the monochromator. The acquisition time for each XAS spectrum was about 40 s with each pair of measurements repeated 400 times and averaged to minimize statistical noise. Error in $\Delta\mu(E)$ is estimated from DiffXAS measurements made at $+45^\circ$ and -45° angles between the magnetic field and the x-ray electric-field polarization vector. To analyze the DiffXAS signal, we first perform a standard extended x-ray absorption fine structure (EXAFS) data analysis to obtain the average local structure of Co and Fe atoms, respectively. The EXAFS analysis was performed by means of the ATHENA and ARTEMIS programs of the DEMETER package [29]. All the spectra were fitted in the k range available for the DiffXAS spectra, from 2 to 10 \AA^{-1} for CoFe_2O_4 and from 2.5 to 9.5 \AA^{-1} for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, with the free parameters being the interatomic distance R_j and the mean-square relative displacement σ_j^2 for each coordination shell. Constraints in coordination numbers are imposed by the particular crystallographic structures.

III. RESULTS

A. CoFe_2O_4

Figure 1 shows the normalized DiffXAS spectra $\Delta\mu(E)$ at both the Co K and Fe K edges at room temperature for the CoFe_2O_4 sample. The experiment was repeated, but the data acquisition was started with a 90° phase shift with respect to the first measurements. The DiffXAS signals are inverted, as shown in Fig. 1, as expected for a magnetostrictive signal. The normalized x-ray absorption spectra are also shown multiplied by 0.007 (Co K edge) and 0.001 (Fe K edge) for comparison purposes. Additional control measurements were performed with the magnetic field oriented at $\pm 45^\circ$ with respect to the x-ray electric-field polarization vector, yielding no structure and further demonstrating that the DiffXAS signals are originated by local-strain MS. As we can see, the room temperature DiffXAS signal at the Co K edge is about 8 times larger than that at the Fe K edge, indicating that the maximum local distortion occurs at the Co site. At both absorption edges, a large dichroic signal is also observed at the absorption onset, of peak-peak amplitude $|\Delta\mu| \sim 2.5 \times 10^{-2}$ at the Co K edge, and $|\Delta\mu| \sim 2 \times 10^{-3}$ at the Fe K edge. In contrast to more itinerant metallic ferromagnets [30], these large dichroic signals have been already observed at the Co and Fe $L_{2,3}$ edges in CoFe_2O_4 due to the localized nature of the magnetic moments.

Figure 2 shows Co K -edge and Fe K -edge differential extended x-ray absorption fine structure (DiffEXAFS) signals at room temperature and at 40 K. The overall shape of the DiffEXAFS signals is similar at both temperatures. However,

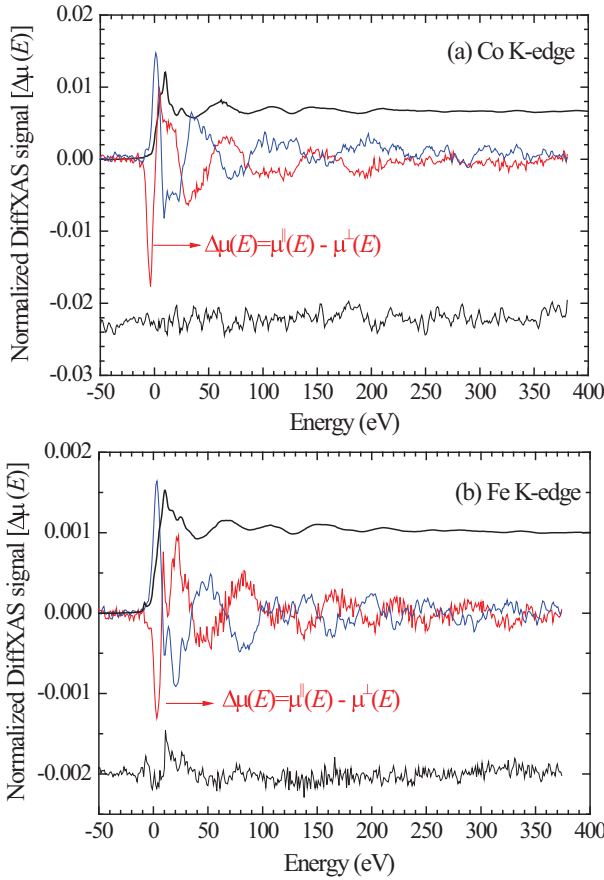


FIG. 1. (a) Normalized Co K -edge XAS $\mu(E)$ (black curve) and DiffXAS $\Delta\mu(E) = \mu^{\parallel}(E) - \mu^{\perp}(E)$ (red curve) signals at room temperature for CoFe_2O_4 . The blue curve shows the DiffXAS signal recorded with a 90° phase shift. The gray line is the DiffXAS signal measured with the magnetic field oriented at $\pm 45^\circ$ with respect to the x-ray electric-field polarization to represent the noise. The energy axis is relative to the first inflection point of the Co K edge (7718.5 eV). (b) Normalized Fe K -edge XAS $\mu(E)$ (black curve) and DiffXAS $\Delta\mu(E) = \mu^{\parallel}(E) - \mu^{\perp}(E)$ (red curve) signals at room temperature. The blue curve shows the DiffXAS signal recorded with a 90° phase shift. The gray line is the DiffXAS signal measured with the magnetic field oriented at $\pm 45^\circ$ with respect to the x-ray electric-field polarization to represent the noise. The energy axis is relative to the first inflection point of the Fe K edge (7122 eV).

the amplitude of the DiffEXAFS oscillations at the Fe K edge slightly increases at low temperatures, whereas it is independent of temperature at the Co K edge. At 40 K, the Co K -edge DiffEXAFS signal is only about 3 times larger than that at the Fe K edge.

B. $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$

Figure 3(a) shows the normalized DiffXAS spectra $\Delta\mu(E)$ at the Co K edge at $T = 25$ K. The experiment was repeated, but the data acquisition was started with a 90° phase shift with respect to the first measurements. The DiffXAS signals are inverted, as shown in Fig. 3(a), as expected for a magnetostrictive signal. The normalized x-ray absorption spectra are also shown multiplied by 0.0015 for comparison purposes.

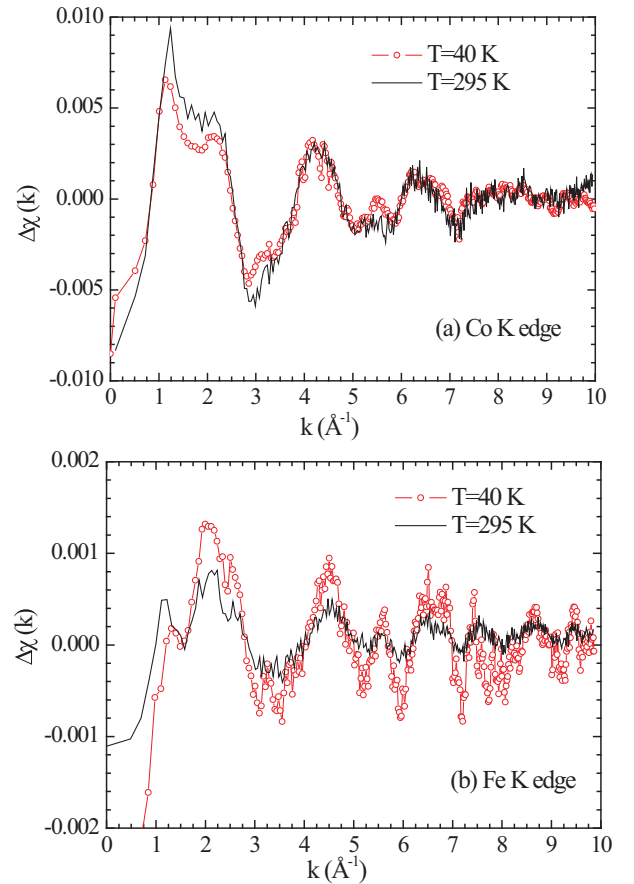


FIG. 2. DiffEXAFS spectra of the CoFe_2O_4 sample at 40 K (red line + circles) and 295 K (black solid line) at the Co K edge (a) and the Fe K edge (b).

A dichroic signal is also observed at the Co K absorption onset, $|\Delta\mu| \sim 1.8 \times 10^{-3}$, but it is smaller than for the cobalt ferrite and opposite in sign. Figure 3(b) compares Co K -edge DiffEXAFS signals at 25 and 75 K. The amplitude of the DiffEXAFS oscillations at 75 K slightly decreases (by about 20%), in agreement with the temperature dependence of the macroscopic anisotropic MS that is nearly constant below 100 K [5].

IV. THEORY AND ANALYSIS

The expression for the polarized EXAFS fine-structure function in anisotropic systems such as single crystals, oriented powders, or layered compounds is given by

$$\chi(k) = \sum_j A_j(k) \sin(ks_j + \varphi_j(k)) e^{-k^2 \sigma_j^2} 3 \cos \theta_j^2, \quad (1)$$

where $A_j(k)$ and $\varphi_j(k)$ are the scattering amplitude and phase functions of the photoelectron, s_j is the scattering path length that is equivalent to $2R_j$ (R_j being the distance between the absorbing and neighbor atoms) for single scattering, σ_j^2 is the mean-square relative displacement, and θ_j is the angle between the x-ray polarization vector \vec{E} and the R_j vectors. The DiffEXAFS spectrum obtained by the difference between two EXAFS spectra measured by applying a magnetic field

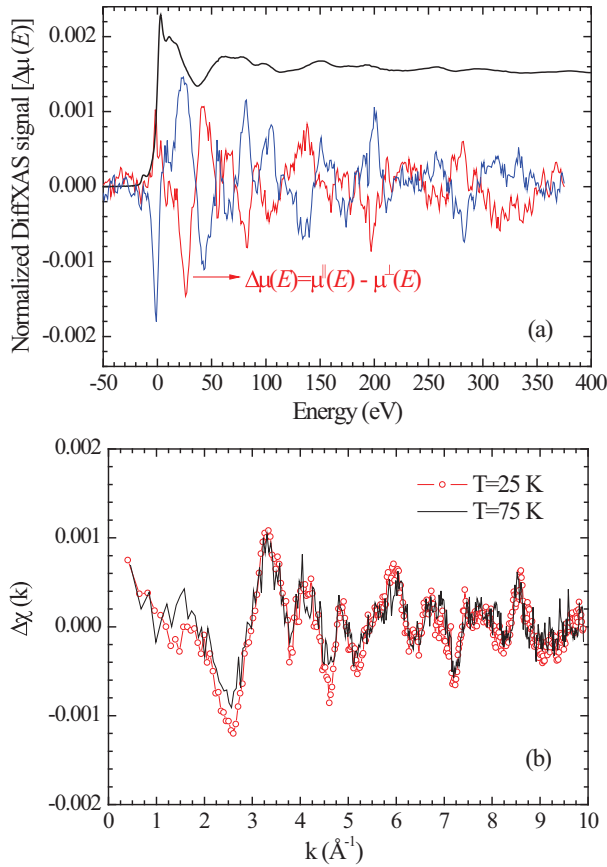


FIG. 3. (a) Normalized Co K -edge XAS $\mu(E)$ (black curve) and DiffXAS $\Delta\mu(E) = \mu^{\parallel}(E) - \mu^{\perp}(E)$ (red curve) signals at $T = 25$ K for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ compound. The blue curve shows the DiffXAS signal recorded with a 90° phase shift. The energy axis is relative to the first inflection point of the Co K edge (7725 eV). (b) DiffEXAFS spectra at the Co K edge at 25 K (red line+circles) and 75 K (black solid line).

parallel and perpendicular to the x-ray polarization vector, respectively, is small. In this case, it is possible to express the DiffEXAFS signal in terms of a first-order Taylor expansion of the x-ray fine-structure function [Eq. (1)] with respect to the modulated parameter:

$$\begin{aligned} \Delta\chi(k) = & 3 \sum_j A_j(k) e^{-k^2\sigma_j^2} [k \cos(ks_j + \varphi_j(k)) \Delta s_j \cos\theta_j^2 \\ & - 2k^2 \sin(ks_j + \varphi_j(k)) \Delta\sigma_j^2 \cos\theta_j^2 \\ & - \sin 2\theta_j \Delta\theta_j \sin(ks_j + \varphi_j(k))]. \end{aligned} \quad (2)$$

Therefore, $\Delta\chi(k)$ contains three contributions. The first corresponds to the strain acting on each interatomic distance Δs_j and shows a cosine phase dependence so it is in quadrature with the EXAFS signal. The second term retains the sine phase dependence of the original EXAFS signal and describes changes to the disorder $\Delta\sigma_j^2$. In our particular case where we have performed the measurements at fixed temperature and always under an applied magnetic field, we can consider that the contribution from the disorder term is negligible. Moreover, we have also considered that there is no change on the bond angle $\Delta\theta_j$ induced by the magnetic field so the third

term is discarded too. Then we analyze the DiffEXAFS data by considering exclusively the strain term so Eq. (2) results in

$$\Delta\chi(k) = \sum_j A_j(k) e^{-k^2\sigma_j^2} k \cos(ks_j + \varphi_j(k)) \Delta s_j 3 \cos\theta_j^2. \quad (3)$$

We note here that (1) for each individual j th coordination shell, the related DiffEXAFS signal is in quadrature with its respective EXAFS signal, and (2) Δs_j is 2 times the difference in the interatomic distance between the absorbing atom and an atom in the j th coordination shell for the two orientations of the applied magnetic field, parallel and perpendicular to the x-ray polarization vector, so it depends on the angle between the scattering path s_j and the magnetic field. For a polycrystalline sample, the DiffEXAFS spectrum will be

$$\Delta\chi(k) = \sum_j A_j(k) e^{-k^2\sigma_j^2} k \cos(ks_j + \varphi_j(k)) \Delta s'_j, \quad (4)$$

where $\Delta s'_j = \langle 3 \cos\theta_j^2 \Delta s_j \rangle = \frac{1}{4\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} 3 \cos\theta_j^2 \Delta s_j^{\phi,\theta} \sin\theta d\theta d\phi$ is averaged over all the possible orientations of the scattering path s_j in the several crystallites with respect to the magnetic field and thus the x-ray polarization vector.

A combined analysis of the EXAFS and DiffEXAFS data has been carried out for all samples. The analysis procedure was as follows: First, the experimental EXAFS spectrum is conventionally fitted using the FEFF8.10 program [31] to determine which scattering paths in the sample are significant and to generate their amplitude $A_j(k)$ and phase $\varphi_j(k)$ information. Once a good conventional EXAFS fit was obtained, the only remaining parameters for the DiffEXAFS analysis are the structural strains $\Delta s'_j$ that were fitted to the experimental DiffEXAFS spectra. We also performed an empirical analysis of the DiffEXAFS data using experimental backscattering $A_j(k)$ and $\varphi_j(k)$ for the isolated first- and second-coordination single shells retrieved by Fourier filtering its related EXAFS spectra. Both methods of analysis gave consistent results, so we present only the results from the first, more accurate analysis.

Since the dependence of the change in s_j with the magnetic field is not known, we can either directly compare the local magnetostriction strains determined by the DiffEXAFS analysis with the macroscopic magnetostriction values measured in the polycrystalline samples or, following the approach used by Díaz *et al.* in Ref. [18], we can associate a specific j th coordination shell in EXAFS with a specific crystal direction. Then, we can define a magnetostriction coefficient λ_{Dj} measured by DiffEXAFS as

$$\lambda_{Dj} = \frac{\Delta s'_j}{s_j}. \quad (5)$$

For instance, in the case of CoFe_2O_4 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ samples, the first oxygen coordination shell around the octahedral Co atoms is related to the (100) direction, so the magnetostriction strain of the Co-O bond from the DiffEXAFS analysis will allow us to extract the λ_{D100} to be compared to the macroscopic λ_{100} one.

In the comparison with the macroscopic magnetostriction coefficient λ_j along a crystal direction, it is important to remember that, for a polycrystal, DiffEXAFS gives the magnetostriction coefficient λ_{Dj} of a specific crystal direction but

TABLE I. Structural parameters of the dominant contributing coordination shells used for the fit of the EXAFS spectrum at the Co K edge of the CoFe_2O_4 sample. The shells are numbered in increasing distance from the absorber. $s_j = 2R_j$ is the scattering path length between the absorbing Co atom and an atom in the j coordination shell, and σ_j^2 is its mean-square relative displacement. The symmetry point groups O_h and T_d are also indicated for the Fe and Co atoms. $\Delta s'_j$ is the average change in the j scattering path length for the two orientations of the applied magnetic field used for the fit of the DiffEXAFS spectrum.

Shell j	s_j (Å)	$\Delta s'_j$ (Å)	σ_j^2 (Å ²)	Number of legs	Scattering path ^a
1	4.132(26)	-0.008	0.009(1)	2	O atom at (1/4, 0, 0)
2	5.920(22)	-0.0015	0.0045(7)	2	Co/Fe O_h atom at (1/4, 1/4, 0)
3	7.018(30)	-0.004	0.004(1)	2	Fe T_d atom at (-3/8, 1/8, 1/8)
4	10.264(32)	-0.004	0.0025(11)	2	Co/Fe O_h atom at (-1/4, 1/2, 1/4)

^aRelative to the Co O_h atom at the origin of the cubic $Fd\bar{3}m$ cell. The number in parentheses indicates the error in the last significant decimal.

averaged over all the possible orientations of the crystal with respect to the magnetic field direction and the polarization of the beam [see Eqs. (4) and (5)]. Díaz *et al.* [18] have calculated the relationship between the strain $\Delta s'_j$ measured by DiffEXAFS for the (100) and (111) directions of a cubic polycrystal [Eq. (5)] and the strain measured in a cubic single crystal when it changes from the demagnetized state to saturation by applying a magnetic field parallel to the (100) or (111) directions, respectively. For that, it is assumed that λ_{Dj} can be calculated by the same expression used for the macroscopic magnetostriction coefficient λ_j [32]:

$$\lambda_j = \frac{3}{2}\lambda_{100}(\alpha_1^2\beta_1^2 + \alpha_2^2\beta_2^2 + \alpha_3^2\beta_3^2 - \frac{1}{3}) + 3\lambda_{111}(\alpha_1\alpha_2\beta_1\beta_2 + \alpha_2\alpha_3\beta_2\beta_3 + \alpha_1\alpha_3\beta_1\beta_3), \quad (6)$$

where α_i and β_i are the cosines that define the magnetic field and the measurement direction, respectively, relative to the cubic crystal axes in spherical coordinates. They found $\lambda_{D111} = \frac{2}{3}\lambda_{111}$ and $\lambda_{D100} = 0.675\lambda_{100}$. By this approach we have compared our local magnetostriction with the macroscopic one.

A. CoFe_2O_4

The Co K -edge EXAFS spectrum at 40 K has been fitted assuming that Co atom is located at the octahedral site of the cubic spinel structure (space group $Fd\bar{3}m$) as it is well known [33]. The fit that better adjusted the data in the k range available for the DiffEXAFS spectra, from 2 to 10 \AA^{-1} , included single scattering paths up to the fourth coordination shell assuming a cubic $Fd\bar{3}m$ lattice. The parameters obtained from the best fit are shown in Table I, and the comparison between the EXAFS spectrum at the Co K edge and this best fit is reported in Fig. S2 [25].

The Fourier transform (FT) of the DiffEXAFS signal at the Co K edge, weighted in k^2 , for the CoFe_2O_4 sample at 40 K shows almost the same features as its related EXAFS spectrum, both compared in Fig. 4. The most important difference between them is that the peaks related to the scattering of further coordination shells in the FT of the DiffEXAFS spectrum are much less intense than the first coordination shell peak. According to Eq. (4), this results in a larger strain Δs_j for the first oxygen coordination shell around the octahedral Co atom, that is, along the (100) direction. This result suggests that the oxygen environment of Co detected by DiffEXAFS is

tetragonally distorted. The position of the peaks is very similar in both FT spectra, so we used the same four shells as in the EXAFS analysis (see Table I) to fit the DiffEXAFS data.

The best fit for the Co K -edge DiffEXAFS signal is shown in Fig. 5, and the individual contributions of the fitted strains for the different coordination shells included in the fit are shown in Fig. S3(b) [25]. The signal from the oxygen first shell is clearly larger in amplitude than those of the higher-order shells, resulting in a strain value $\Delta R_{\text{CoO}}/R_{\text{CoO}} \approx -1900 \times 10^{-6}$. The magnetostrictive strain for the Co - Fe_{Td} scattering path is $\Delta R_{\text{CoFeTd}}/R_{\text{CoFeTd}} \approx -600 \times 10^{-6}$, larger than that of the Co-Co(Fe) O_h one, $\Delta R_{\text{CoCo(Fe)O}_h}/R_{\text{CoCo(Fe)O}_h} \approx -250 \times 10^{-6}$. This result agrees with the fact that the magnetostrictive second-shell peak of the DiffEXAFS $|\chi(R)|$ spectrum [shown in Fig. 4(a)] corresponds to the longer interatomic distance detected by EXAFS, that is, the Co- Fe_{Td} one (Table I). Moreover, the sign of all the magnetostrictive strains is negative, in agreement with that of the macroscopic measurements [22,23].

A multisite-multishell analysis has been performed to fit the Fe K -edge EXAFS spectrum at 40 K due to the presence of two nonequivalent Fe atoms at the tetrahedral (T_d) and octahedral (O_h) sites of the spinel structure. The fit that better adjusted the data in the k range available for the DiffEXAFS

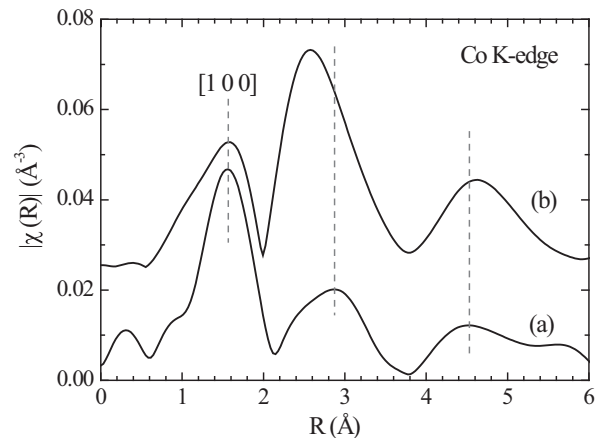


FIG. 4. (a) Fourier transform of the DiffEXAFS signal of CoFe_2O_4 weighted in k^2 ($k : [2, 9.5 \text{ \AA}^{-1}]$) at $T = 40 \text{ K}$ compared to (b) its Fourier-transformed EXAFS spectrum at the Co K edge, which was reduced in amplitude and shifted in the y axis for comparison. The brackets at the first peak indicate the dominant strain direction.

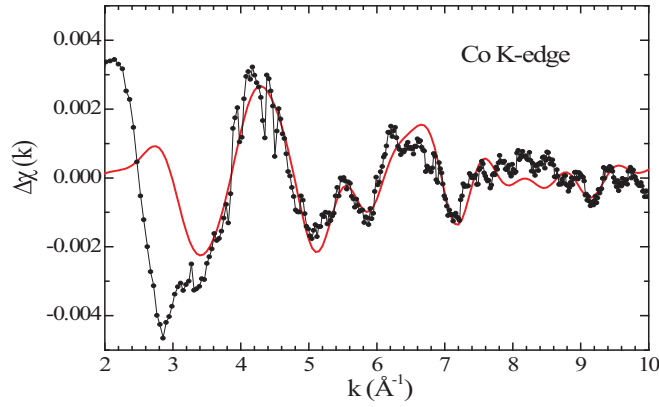


FIG. 5. DiffEXAFS spectrum obtained at the Co K edge of the CoFe_2O_4 sample at 40 K. The fit of the spectrum (red line) was done in between the k limits $k = 2$ and 10 \AA^{-1} using Eq. (4) and the parameters in Table I.

spectra, from 2 to 10 \AA^{-1} , included two single scattering paths ($\text{Fe}_{\text{Td}}\text{-O}$ and $\text{Fe}_{\text{Oh}}\text{-O}$) for the first coordination shell, considering that one-half of the Fe atoms in CoFe_2O_4 occupy the octahedral site and the other half the tetrahedral site and two single scattering paths [$\text{Fe}_{\text{Oh}}\text{-Fe}_{\text{Td}}$ and $\text{Fe}_{\text{Oh}}\text{-(Fe/Co)}_{\text{Oh}}$] for the second and third coordination shells. The contribution from the $\text{Fe}_{\text{Td}}\text{-Fe}_{\text{Td}}$ scattering path was found to be negligible. The parameters obtained from the best fit are shown in Table II, and the comparison between the EXAFS spectrum at the Fe K edge and this best fit is reported in Fig. S4 [25].

The Fourier transform of the DiffEXAFS signal at the Fe K edge, weighted in k^2 , for the CoFe_2O_4 sample at 40 K shows almost the same features as its related EXAFS spectrum, both compared in Fig. 6. In this case, the peaks related to the scattering of further coordination shells in the FT of the DiffEXAFS spectrum are not largely reduced with respect to the first coordination shell, indicating a more homogeneous strain around the Fe atoms. Furthermore, the magnetostrictive peaks for the second and third shells correspond to the longer interatomic distances detected by EXAFS, which are the $\text{Fe}_{\text{Oh}}\text{-Fe}_{\text{Td}}$ ones (Table II), similar to the result found at the Co K edge.

TABLE II. Structural parameters of the dominant contributing coordination shells used for the fit of the EXAFS spectrum at the Fe K edge of the CoFe_2O_4 sample at 40 K. The shells are numbered in increasing distance from the absorber. $s_j = 2R_j$ is the scattering path length between the absorbing Co atom and an atom in the j coordination shell and σ_j^2 is its mean-square relative displacement. The symmetry point groups O_h and T_d are also indicated for the Fe and Co atoms. $\Delta s'_j$ is the average change in the j scattering path length for the two orientations of the applied magnetic field used for the fit of the DiffEXAFS spectrum.

Shell j	s_j (Å)	$\Delta s'_j$ (Å)	σ_j^2 (Å ²)	Number of legs	Scattering path Fe_{Td}^a - X
1	3.884(20)	-0.0025	0.007(1)	2	O atom at (1/8, 1/8, 1/8)
2	6.924(10)	-0.003	0.007(1)	2	$\text{Fe}(\text{Co})_{\text{Oh}}$ atom at (-3/8, 1/8, 1/8)
3	10.868(10)	-0.0042	0.007(1)	2	$\text{Fe}(\text{Co})_{\text{Oh}}$ atom at (-5/8, 1/8, 1/8)
Shell j	s_j (Å)	$\Delta s'_j$ (Å)	σ_j^2 (Å ²)	Number of legs	Scattering Path Fe_{Oh}^a - X
1'	3.916(28)	-0.0025	0.015(3)	2	O atom at (1/4, 0, 0)
2'	5.910(14)	-0.0014	0.006(1)	2	$\text{Fe}(\text{Co})_{\text{Oh}}$ atom at (1/4, 1/4, 0)
3'	10.262(22)	-0.003	0.004(1)	2	$\text{Fe}(\text{Co})_{\text{Oh}}$ atom at (-1/4, 1/2, 1/4)

^aRelative to the Fe atom at the origin of the cubic $Fd\bar{3}m$ cell. The number in parentheses indicates the error in the last significant decimal.

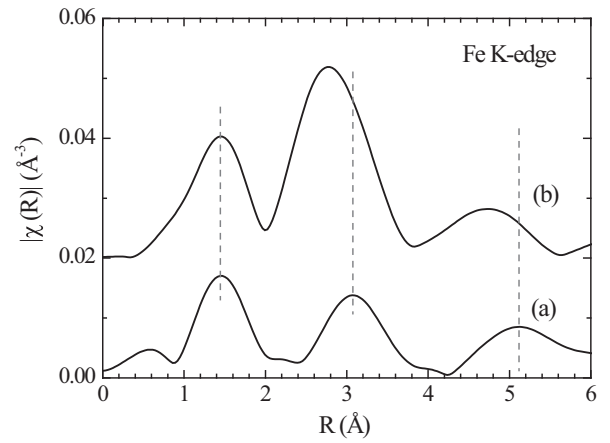


FIG. 6. (a) Fourier transform of the DiffEXAFS signal of CoFe_2O_4 weighted in k^2 ($k : [2, 9.5 \text{ \AA}^{-1}]$) at $T = 40 \text{ K}$ compared to (b) its Fourier-transformed EXAFS spectrum at the Fe K edge, which was reduced in amplitude and shifted in the y axis for comparison.

We have fitted the DiffEXAFS spectra of CoFe_2O_4 at the Fe K edge using the same contributing shells as for the related EXAFS spectrum. The best fit for the Fe K edge DiffEXAFS is shown in Fig. 7, and the individual contributions of the fitted strains for the different coordination shells included in the fit are shown in Fig. S5(b) [25]. The resulting magnetostrictive strains for the Fe atoms at 40 K are $\Delta R_{\text{FeTdO}}/R_{\text{FeTdO}} = \Delta R_{\text{FeOhO}}/R_{\text{FeOhO}} \approx -600 \times 10^{-6}$, $\Delta R_{\text{FeTdFe}(\text{Co})_{\text{Oh}}}/R_{\text{FeTdFe}(\text{Co})_{\text{Oh}}} \approx -400 \times 10^{-6}$, and $\Delta R_{\text{FeOhCo}(\text{Fe})_{\text{Oh}}}/R_{\text{FeOhCo}(\text{Fe})_{\text{Oh}}} \approx -200 \times 10^{-6}$. The sign of all the magnetostrictive strains is also negative, in agreement with that of the Co atom and the macroscopic measurements [22,23]. At room temperature, the magnitude of the magnetostrictive strains for the Fe atoms is reduced by a factor of around 2.2.

Another model can be used to fit the DiffEXAFS data at the Fe K edge giving the same quality of the fit (see dashed line in Fig. 7). Based on the macroscopic magnetostriction constants measured in a single crystal of cobalt ferrite, the ratio $\lambda_{100}/\lambda_{111}$ is large, namely, ~ 10 , with $\lambda_{100} < 0$ and $\lambda_{111} > 0$ [34,35]. Therefore, we can assume that only the

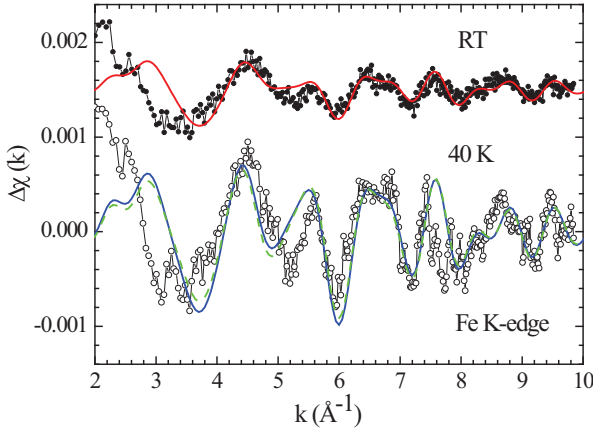


FIG. 7. DiffEXAFS spectra at the Fe K edge for CoFe_2O_4 . The fit of the spectra (red line room temperature (RT), and blue and green lines 40 K) was done in between the k limits $k = 2$ and 10 \AA^{-1} using Eq. (4). The associated fit parameters are shown in Table II. The green dashed line is the best fit considering only the octahedral Fe contribution (1') for the first oxygen coordination shell.

octahedral Fe is magnetostrictive, which results in a strain for the first oxygen coordination shell of $\Delta s'_j = -0.004 \text{ \AA}$ at 40 K, i.e., $\Delta R_{\text{FeO}_6}/R_{\text{FeO}_6} \approx -1000 \times 10^{-6}$.

B. $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$

The Co K -edge EXAFS spectrum at 130 K has been fitted in the k range available for the DiffEXAFS spectra, from 2 to 10 \AA^{-1} , including single scattering paths up to the fourth coordination shell and the multiple-scattering path Co-O-Co, assuming the quasicubic $Pm\bar{3}m$ crystal structure. The parameters obtained from the best fit are shown in Table III, and the comparison between the EXAFS spectrum at the Fe K edge and this best fit is reported in Fig. S6 [25].

The FT of the DiffEXAFS signal at the Co K edge, weighted in k^2 , for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ sample at 25 K shows almost the same features as its related EXAFS spectrum, both compared in Fig. 8. In this case, the peaks related to the scattering from second-neighbor shells in the FT of the DiffEXAFS spectrum are almost as intense as the first coordination shell. On the other hand, the position of the peaks is similar in both FT spectra, though the Co magnetostrictive

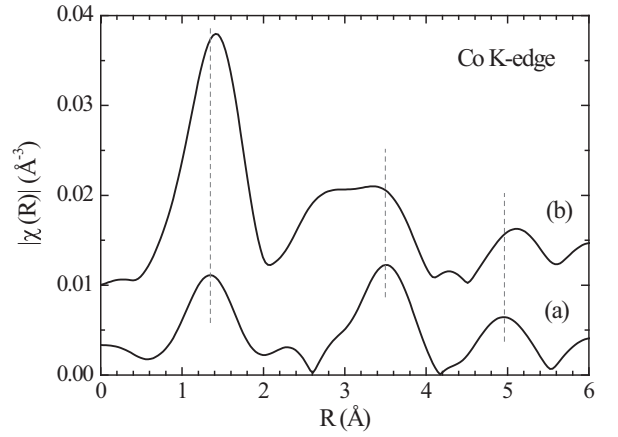


FIG. 8. (a) Fourier transform of the DiffEXAFS signal of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ weighted in k^2 ($k : [2, 9.5 \text{ \AA}^{-1}]$) at $T = 25 \text{ K}$ compared to (b) its Fourier-transformed EXAFS spectrum at the Co K edge, which was reduced in amplitude and shifted in the y axis for comparison.

second-ordination shell mostly corresponds to the longer interatomic distance determined by EXAFS that is the Co-Co scattering path (Table III).

To fit the DiffEXAFS data we have used five shells, the same as in the EXAFS. The best fit is shown in Fig. 9, and the individual contributions of the fitted strains for the different coordination shells included in the fit are shown in Fig. S7(b) [25]. The resulting magnetostrictive strains for the Co atoms at 25 K are $\Delta R_{\text{CoO}}/R_{\text{CoO}} \approx 450 \times 10^{-6}$, $\Delta R_{\text{CoLa(Sr)}}/R_{\text{CoLa(Sr)}} \approx 200 \times 10^{-6}$, $\Delta R_{\text{CoOC}_6}/R_{\text{CoOC}_6} \approx 460 \times 10^{-6}$, and $\Delta R_{\text{CoCo}_2}/R_{\text{CoCo}_2} \approx 300 \times 10^{-6}$. The sign of all the magnetostrictive strains is positive, in agreement with that of the macroscopic measurements [5]. We note that the main contributions come from the O first shell and the Co second shell, in particular from the multiple-scattering path 3 in Table III. This means that the main strain occurs along the [100] direction.

V. DISCUSSION AND CONCLUSIONS

We have shown that the main effect induced by the magnetic field is a strain in the local environment of either the Co atom in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ or the Co/Fe atoms in CoFe_2O_4 .

TABLE III. Structural parameters of the dominant contributing coordination shells used for the fit of the EXAFS spectrum at the Co K edge of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ sample. The shells are numbered in increasing distance from the absorber. $s_j = 2R_j$ is the scattering path length between the absorbing Co atom and an atom in the j coordination shell, and σ_j^2 is its mean-square relative displacement. $\Delta s'_j$ is the average change in the j scattering path length for the two orientations of the applied magnetic field used for the fit of the DiffEXAFS spectrum.

Shell j	s_j (\AA)	$\Delta s'_j$ (\AA)	σ_j^2 (\AA^2)	Number of legs	Scattering path ^a
1	3.84(5)	0.00175	0.010(2)	2	O atom at (1/2, 0, 0)
2	6.70(9)	0.0015	0.005(7)	2	La/Sr atom at (1/2, 1/2, 1/2)
3	7.64(6)	0.0035	0.013(3)	3, 4	Co atom at (1, 0, 0) multiple scattering Co-O-Co
4	10.75(10)	0.003	0.009(5)	2	Co atom at (1, 1, 0)

^a Relative to the Co atom at the origin of the cubic $Pm\bar{3}m$ cell. The number in parentheses indicates the error in the last significant decimal.

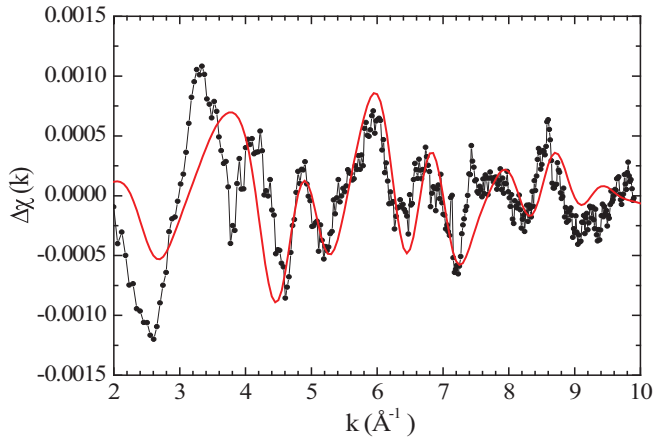


FIG. 9. DiffEXAFS spectra at the Co K edge for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ at 25 K. The fit of the spectra (red line) was done in between the k limits $k = 2$ and 10 \AA^{-1} using Eq. (4). The associated fit parameters are shown in Table III.

Local magnetostriction at the Co and Fe environments in CoFe_2O_4 is negative, i.e., the magnetostrictive lattice shrunk in the direction of the magnetic field as for the macroscopic magnetostriction [22,23]. The strains at the Co and Fe local environments are larger for the first oxygen shell than for higher-order shells. Besides, they are clearly different for the two atomic environments. The larger strain measured by DiffEXAFS corresponds to the first oxygen coordination shell around the Co atom, being about 2–3 times larger than the one around the Fe atom at low temperatures (40 K). We also note that the strain around the Fe atoms decreases at room temperature, whereas the Co site remains almost unaltered. Therefore, the larger strain of the Co-O shell indicates that the atom responsible for the large magnetostriction in CoFe_2O_4 is cobalt.

Since in CoFe_2O_4 the oxygen atoms coordinated to Co are located at the lattice sites along the (100) crystallographic directions in the cubic crystal (Table I), we can calculate an atomic magnetostriction coefficient $\lambda_{100}^{\text{Co}}$ by applying the relationship $\lambda_{D100} = 0.675 \lambda_{100}$, where $\lambda_{D100}^{\text{Co}} = \frac{\Delta R_{\text{Co-O}}}{R_{\text{Co-O}}}$, resulting in $\lambda_{100}^{\text{Co}} \approx -2800$ ppm. This value is markedly higher than those obtained from the macroscopic measurement in single crystals either at room temperature $\lambda_{100} \approx -500$ ppm or at 2 K, $\lambda_{100} \approx -730$ ppm [7]. However, the values of the DiffEXAFS strains $\Delta R/R$ for higher-order coordination shells around Co decrease with increasing the interatomic distance, yielding values much more comparable to the macroscopic magnetostriction for polycrystalline CoFe_2O_4 , which is reported to vary between -200 and -400 ppm [22,23].

Another important point to be discussed is the role of the Fe atoms in the magnetostrictive properties of CoFe_2O_4 . In this case, we have two different Fe sites: (1) the octahedral Fe site, where the oxygen atoms are located at the lattice sites along the (1, 0, 0) crystallographic directions, and (2) the tetrahedral Fe sites, where the oxygen atoms are located at the lattice sites along the (1, 1, 1) direction. Therefore, applying the same procedure as for the analysis of the Co DiffEXAFS data, we deduce the atomic magnetostriction coefficients $\lambda_{100}^{\text{Fe}}$ and $\lambda_{111}^{\text{Fe}}$ from the measured strain around the octahedral and

tetrahedral Fe sites, respectively. Our analysis was not able to differentiate between a model where both Fe sites were magnetostrictive with comparable strain and a model where only the octahedral Fe sites are considered to contribute to the magnetostriction. The latter model is better supported by the macroscopic measurements [34,35] and results in $\lambda_{100}^{\text{Fe}} = (\frac{\Delta R_{\text{FeOh-O}}}{R_{\text{FeOh-O}}})/0.675 \approx -1500$ ppm at 40 K and $\lambda_{100}^{\text{Fe}} = (\frac{\Delta R_{\text{FeOh-O}}}{R_{\text{FeOh-O}}})/0.675 \approx -600$ ppm at room temperature. The magnetostriction coefficient for the Fe atoms is also higher than the macroscopic coefficient along the (100) direction, but it approaches it more than the one for the Co atoms. Moreover, the temperature dependence reported for the macroscopic λ_{100} coefficient [7] is due to the magnetostrictive environments of the Fe atoms.

From the above comparison we can reach several conclusions. First, locally, the strain displacement produced by the magnetic field is not uniform in the cobalt ferrite, challenging the application of the conventional theory of magnetostriction based on the crystal elastic constants for this system. This could explain the difference in magnitude of the atomic magnetostriction coefficients obtained by DiffEXAFS compared to the macroscopic measurements, particularly for the Co atoms. Second, the magnetostriction in CoFe_2O_4 is mainly conducted by the presence of high-spin Co^{2+} ($3d^7, t_{2g}^5 e_g^2$, $S = 3/2$) in the octahedral sites. For Co^{2+} , the distortion is expected to be tetragonal with $c/a < 1$, characteristic of a t_{2g} degeneracy, which will produce large negative magnetostrictive effects through spin-orbit-lattice interactions with an axially distorted cubic crystal field [11]. This distortion propagates to second neighbors (including the Fe sites) but reducing their value and approaching the macroscopic coefficient [22,23].

On the other hand, the sign of the Co magnetostrictive coefficient, detected by DiffEXAFS, in the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ sample is positive, indeed opposite to that found in CoFe_2O_4 , but in agreement with the macroscopic anisotropic magnetostriction [3]. The detected bond strain values at 25 K are $\frac{\Delta R_{\text{Co-O}}}{R_{\text{Co-O}}} \approx 450$ ppm and $\frac{\Delta R_{\text{Co-O-Co}}}{R_{\text{Co-O-Co}}} \approx 460$ ppm so the largest magnetostriction effect is observed along the Co-O-Co bond direction, i.e., the (100) direction. Thus, the related atomic magnetostriction coefficient $\lambda_{100}^{\text{Co}}$ is $\lambda_{100}^{\text{Co}} = (\frac{\Delta R_{\text{Co-O}}}{R_{\text{Co-O}}})/0.675 \approx 700$ ppm. This value of the magnetostrictive coefficient of the oxygen environment around the Co atom in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ is much smaller than that found in CoFe_2O_4 , but in this case, Co is in a mixed-valence state ($\text{Co}^{3+}/\text{Co}^{4+}$), and this multi-valence condition must be discussed in the interpretation of the local magnetostriction results. The positive magnetostriction indicates tetragonally distorted octahedral sites with a c -axis expansion ($c/a > 1$) characteristic for an e_g degeneracy [36,37]. Thus, Co^{3+} and Co^{4+} seem to be in an intermediate-spin state, confirming the proposed model from macroscopic measurements [5]. From the Co-La/Sr bond strain, we can obtain the atomic magnetostriction coefficient along the (111) direction, which is $\lambda_{111}^{\text{Co}} = (\frac{\Delta R_{\text{Co-La(Sr)}}}{R_{\text{Co-La(Sr)}}})/0.667 \approx 340$ ppm. The macroscopic coefficient for the polycrystalline sample can be then calculated from $\lambda_{111}^{\text{Co}}$ and $\lambda_{100}^{\text{Co}}$ using Eq. (7), which yields $\lambda_M = 470$ ppm:

$$\lambda_M = \frac{2\lambda_{100} + 3\lambda_{111}}{5}. \quad (7)$$

This value is close to the macroscopic measurements at 25 K and 2 T applied magnetic field [5]. This indicates that for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, the mechanical response to the strain produced by the magnetic field is uniform.

In summary, we have determined the atomic environments responsible for the magnetostrictive properties of polycrystalline CoFe_2O_4 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ferromagnetic oxides by means of the DiffEXAFS technique. The analysis of the DiffEXAFS spectra shows that the magnetostriction effect in these cobalt oxides is governed by the magnetostrictive environments around the octahedral Co atoms. The different magnetostrictive environment of Co for the two oxides is explained in terms of the different valence and spin state of the Co atom. For the CoFe_2O_4 spinel, high-spin Co^{2+} sites are tetragonally distorted, with a c -axis contraction giving rise to a large negative magnetostriction strain for the first oxygen coordination shell along the (100) direction that is independent of the temperature. This distortion is not uniform in the sample. It propagates to the neighboring Fe

atoms, but it is reduced in magnitude and decreases with increasing temperature. On the other hand, a c -axis expanded tetragonal distortion is found for the octahedral mixed-valent intermediate-spin $\text{Co}^{3+}/\text{Co}^{4+}$ atom in the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ perovskite, resulting in a positive magnetostriction strain along the Co-O-Co direction that is uniform in the sample in this case.

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