

## Structural effects of the spin-state crossover at high temperature in the distorted $\text{ErCoO}_3$ cobaltite

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**Abstract.** We present a neutron powder diffraction study reporting structural evidences of a spin-state crossover beginning at  $T_{SS} \approx 575$  K in the highly distorted  $\text{ErCoO}_3$  cobaltite, based on measurements in the temperature range 100 K - 1000 K. Different interrelated changes in the structural evolution upon heating have been described, which are driven by an anomalous expansion of the octahedra. The activation of IS or HS spin states brings about an expansion of the  $\text{CoO}_6$  octahedra (increase of Co-O bond lengths), and the augmentation of the Co-O distances in the  $a$ - $b$  plane respect to that along the  $c$ -axis. The spin-state crossover extends over a broad temperature interval and can be monitored by an atypical augmentation of the orthorhombic strain.

### 1. Introduction

The spin-state nature across the two electronic transitions in  $\text{LaCoO}_3$  has been matter of controversy for many years [1-8].  $\text{LaCoO}_3$  exhibits two broad transitions: there is first a spin-state crossover (SSC) at  $T_{SS}$  (between  $\sim 50$ -100 K), where a hump in the magnetic susceptibility signals the appearance of a paramagnetic semiconductor. The second one is an insulator-metal transition ( $T_{IM}$ ) between  $\sim 500$ -600 K. The stabilization of one of the three spin-states in octahedral coordination depends on the ratio between the crystal field and Hund's rule coupling. For large splitting all the electrons occupy the low energy  $t_{2g}$ -levels resulting in zero spin and orbital momentum (low spin state, LS). States with finite spin momentum arise from the transfer of one or two electrons into the higher energy  $e_g$ -orbitals and correspond to an intermediate spin (IS) or high spin (HS) state, respectively. So, the two most often investigated pictures in  $\text{LaCoO}_3$  involve the spin transition either  $LS \rightarrow (HS+LS) \rightarrow IS$  [1,2] or  $LS \rightarrow IS \rightarrow (HS+IS)$  [3-6]. However, in presence of disorder phenomena, a  $LS \rightarrow HS$  crossover at  $T_{SS}$  can not be totally ruled out [2,7].

In addition, the ground and thermally excited states of  $\text{LnCoO}_3$  perovskites ( $\text{Ln}$ :lanthanide or rare earth) with heavy rare-earths and more distorted structures are also attracting great interest [5,8-11]. So, some reports evidenced that upon increasing temperature two separate electronic transitions occur as well in the perovskites of this series with smaller volume. Decreasing the size of  $\text{Ln}$  atoms the excited states would be occupied at temperatures progressively higher. Furthermore, although there are evidences of a high temperature metallic phase in the  $\text{LnCoO}_3$  series even with lanthanides smaller than



La, Pr or Nd [8], the nature of the high temperature state is not well understood. The main purpose of the present paper was to investigate the lattice and electronic thermal evolution of  $\text{ErCoO}_3$ , a very distorted specimen of this series, putting emphasis on the structural and lattice evolution as an effective way to approach the electronic phenomena associated with the spin-state of  $\text{Co}^{3+}$  ions in the system.

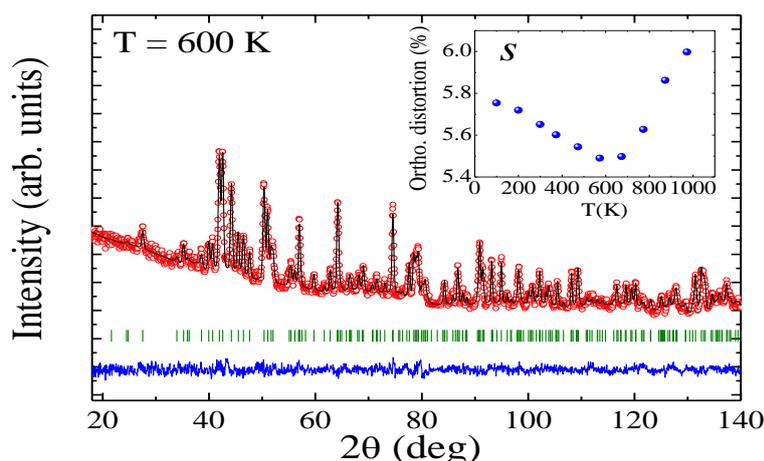
## 2. Experimental

Polycrystalline  $\text{ErCoO}_3$  was prepared by sol-gel method [12]. Stoichiometric amounts of  $\text{Er}_2\text{O}_3$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in citric acid, by adding  $\text{HNO}_3$  to favour the solution of rare-earth oxide. The solution was slowly evaporated leading to a resin, which was first dried at 393K and then slowly decomposed at temperatures up to 873 K for 12 h. Finally, the obtained precursor was heated at 1173 K under a 200 bar oxygen pressure for 12h. Then, the sample was cooled down at 5 K/min to room temperature in order to obtain a good oxygenation.

X-ray diffraction patterns at RT were recorded using a Bruker D8 diffractometer (40 kV, 30 mA) and  $\text{Cu K}\alpha$  radiation. We found the sample to be single phased and without impurities. Neutron powder-diffraction (NPD) measurements were carried out on the high-resolution D2B diffractometer of the Institute Laue-Langevin (ILL, Grenoble) at temperatures ranging from 100 K to 973 K. Above room temperature the sample was warmed in a furnace from 300 K to 973 K, while measurements at lower temperatures were performed using a CCR cryostat. Due to the relatively large absorption-cross section for neutrons of Er and Co, a narrow 5mm sample-holder was used. NPD data were recorded at the neutron wavelength  $\lambda=1.594 \text{ \AA}$  and were analyzed with the Rietveld method using the FULLPROF suite of programs [13].

## 3. Results and discussion

All the NPD diffraction patterns for  $\text{ErCoO}_3$  collected between 100 K and 973 K were successfully refined using a  $Pbnm$  (no. 62) space group with cell parameters  $a \approx \sqrt{2}a_0$ ,  $b \approx \sqrt{2}a_0$ ,  $c \approx 2 a_0$  (where  $a_0$  is the ideal cubic parameter). As an example, Figure 1 shows the refined pattern measured at 600 K. The details of the structural model obtained from the refinement at this temperature are reported in Table I, together with the agreement factors.

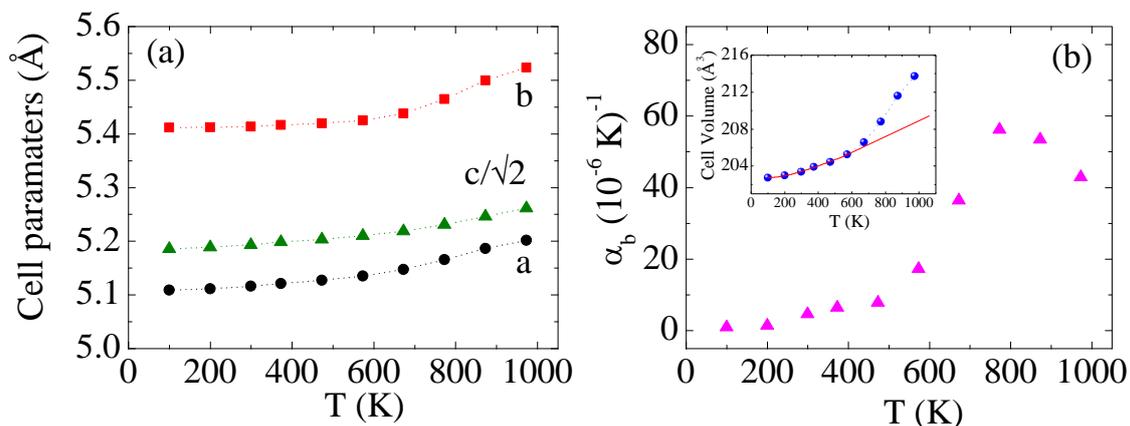


**Figure 1.** Rietveld refinement (black line) of neutron diffraction pattern from D2B (red circles, experimental points; bottom blue line, difference; green lines, Bragg reflections) for  $\text{ErCoO}_3$  at 600 K. The inset shows the temperature dependence of the orthorhombic strain ( $s$ ).

**Table I.** Structure at 600 K refined using SG *Pbnm*. Lattice parameters are  $a=5.1472(7)$  Å,  $b = 5.4379(9)$  Å,  $c = 7.3815(4)$  Å. Agreement parameters are  $\chi^2 = 1.14$  and  $R_B(\%) = 6.36$

Atom	Site	$x/a$	$y/b$	$z/c$	$B_{\text{iso}} (\text{Å}^2)$
Er	$4c$	0.9810(6)	0.0682(5)	0.2500	1.08(6)
Co	$4b$	0.5000	0.0000	0.0000	0.91(2)
O1	$4c$	0.0959(7)	0.4733(6)	0.2500	1.28(5)
O2	$8d$	0.6926(5)	0.3010(5)	0.0475(3)	1.30(5)

In Figure 2(a) we have plotted the thermal evolution of the cell parameters up to  $\sim 1000$  K. Within the resolution of the technique, we did not detect the formation of oxygen vacancies up to the maximum temperature reached. In the figure it is shown that the relation between lattice parameters  $b > c/\sqrt{2} > a$  (O type) expected for small rare-earths [8] remains in the whole temperature range. This comparison between parameters differs from the relation  $a > c/\sqrt{2} > b$  characteristic of the  $\text{LnCoO}_3$  cobaltites with larger rare-earths [9]. But the main feature to be underlined in Figure 2(a) is a remarkable extra expansion of the cell parameters starting around 575 K, which confirms a deviation on heating from the conventional thermal lattice expansion. The anomalous contribution to the lattice above that temperature is visible in the evolution of all three lattice constants represented in the Figure 2(a), but it is particularly apparent in the  $b(T)$  curve. Hence we present in Figure 2(b) the linear thermal expansion coefficient  $\alpha_b$  deduced from  $b(T)$  as  $\alpha_b = 1/b_0 \times \Delta b/\Delta T$ . In Figure 2(b) the steep enhancement of the expansion coefficient  $\alpha_b$  at  $T_{\text{SS}}$  is preceded by the regime where only phonons contribute to the thermal expansion. In this initial regime we observe a practically linear increase of the  $\alpha_b$  expansion coefficient in the interval 100-550 K. Moreover, in the inset of the same figure we have plotted the temperature evolution of the unit cell volume. The solid red line, fitting the equation  $V_0 = V_1 + V_2 \theta \coth(\theta/T)$  before  $T_{\text{SS}}$ , is a guide to the eye.

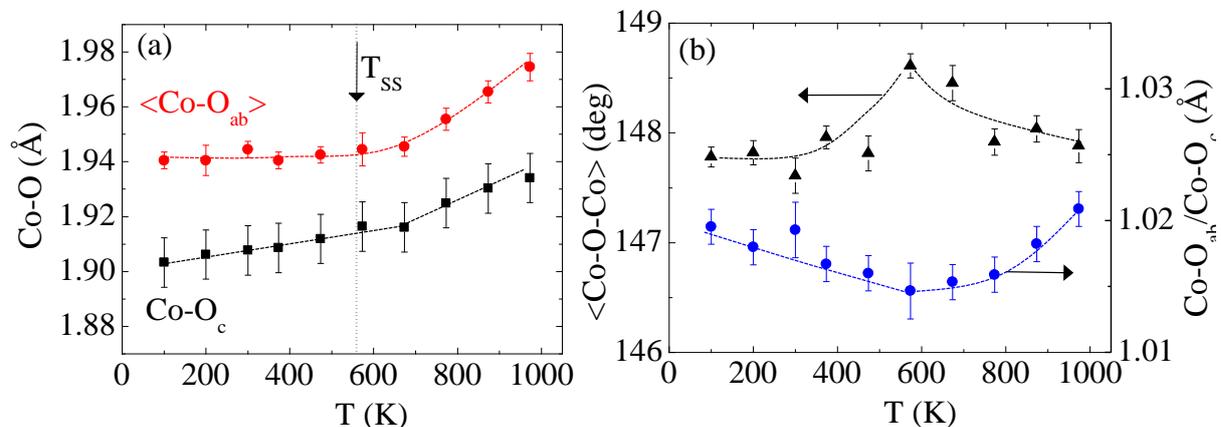


**Figure 2.**  $\text{ErCoO}_3$ : temperature dependence of (a) the lattice parameters and (b) the linear thermal expansion along  $b$  axis ( $\alpha_b$ ). The inset shows the temperature dependence of the cell volume for  $\text{ErCoO}_3$ . The solid red line, fitting the equation  $V_0 = V_1 + V_2 \theta \coth(\theta/T)$ , is a guide to the eye.

The anomalous expansion shown in these figures above  $T_{\text{SS}} \approx 575$  K is the signature of a sudden increase of populated excited magnetic states (IS or HS) in the  $\text{Co}^{3+}$  ions. The occupation of excited magnetic states is activated at  $T_{\text{SS}} \approx 575$  K but it develops progressively along the interval 575-780 K. Above  $\sim 800$  K the expansion coefficient  $\alpha_b$  starts to decrease. From the inset of Figure 2(b) a rough estimation of the anomalous volume expansion accumulated at  $\sim 1000$  K due to spin state excitations gives  $\sim 2\%$ .

The spontaneous orthorhombic strain, defined as  $s=2(b-a)/(a+b)$ , is plotted in the inset of Figure 1. It decreases on heating up to  $T_{SS}$ , where it presents a minimum. Above that temperature, the greater expansion of  $b$  (in comparison with  $c/\sqrt{2}$  or  $a$ ) preserves the relation  $b > c/\sqrt{2} > a$  and increases  $s$ . Hence, in this system the occupation of higher spin states produces an enhancement of the orthorhombic distortion. In addition, we must observe in the same figure that  $s$  is still increasing at 973 K (our highest temperature reached), indicating that the spin state change process has not come to the end at that temperature.

The same behavior has been also observed in compounds with small rare earths such as  $\text{YCoO}_3$ ,  $\text{DyCoO}_3$  and  $\text{GdCoO}_3$  [8]. The analysis of thermal expansion in the  $b$  lattice ( $\alpha_b$ ) as a function of temperature is also shown in Figure 2(b). We observe the expansion coefficient  $\alpha$  presents an inflection point just at  $T_{SS}$  and it reaches a maximum at  $T \sim 800$  K where the spin-state transition could be completed. In contrast to larger  $Ln$  in which two shoulders are visible in the expansion coefficient, here only one maximum is detected.



**Figure 3.**  $\text{ErCoO}_3$ : evolution with temperature of (a) the average  $\text{Co-O}_c$  (black squares) and  $\text{Co-O}_{ab}$  (red circles) bond lengths in the  $\text{CoO}_6$  octahedra; (b) the average  $\text{Co-O-Co}$  bond angles (black triangles, left axis) and  $\text{Co-O}_{ab}/\text{Co-O}_c$  ratio (blue circles, right axis). The dotted lines are eye-guides.

The refined Co-O bond lengths in the equatorial plane ( $\langle\text{Co-O}_{ab}\rangle$ ) and apical axis of the  $\text{CoO}_6$  octahedra are plotted in Figure 3(a). The average  $\langle\text{Co-O-Co}\rangle$  bond angle for  $\text{ErCoO}_3$  up to  $\sim 1000$  K are displayed in Figure 3(b). The average of the Co-O distances in the  $a$ - $b$  plane is larger than along the  $c$ -axis ( $\text{Co-O}_c$ ) in the wide temperature range below 1000 K. However, the difference between them does not show a monotonous evolution: it is  $\sim 1.9\%$  at 100 K, decreases under heating, reaches a minimum value of 1.5% around 575-600 K, and then increases again upon heating up to 2.1% at  $\sim 1000$  K. Both distances exhibit a sudden enhancement at  $T_{SS}$  but it is steeper for the Co-O equatorial bonds. Therefore, the activation of IS or HS spin states brings about: (i) an expansion of the  $\text{CoO}_6$  octahedra (increase of Co-O bond lengths) and (ii) the augmentation of the Co-O distances in the  $a$ - $b$  plane respect to that along the  $c$ -axis. This resultant flattening of the octahedra due to spin state excitations is superimposed to the expected thermal diminution of the  $\langle\text{Co-O}_{ab}\rangle/\text{Co-O}_c$  ratio due to the phonon (lattice) contribution.

On the other hand, the temperature evolution of the average  $\langle\text{Co-O-Co}\rangle$  bond angle (see Figure 3(b), left axis) also reveals a non monotonous evolution. This angle displays a maximum around  $\sim 580$  K coinciding with  $T_{SS}$ . The maximum value of the average bond angle ( $\sim 148.5^\circ$ ) is very small due to the small size of the Er atoms. Contrarily to the conventional lattice evolution of distorted perovskites, we have observed a drop of the  $\langle\text{Co-O-Co}\rangle$  bond angle in the range where the excitation to a higher spin state takes place. This unusual evolution must be considered as another expression of the enhancement

of the orthorhombic distortion concomitant to the spin state change previously described. It is driven by the expansion in the  $\text{CoO}_6$  octahedra observed upon heating above  $T_{\text{SS}}$ . To be noted is that the evolution becomes almost flat above 800 K. This evolution presents similarities with the evolution of the average bond angle previously reported in large  $\text{LnCoO}_3$  perovskites ( $\text{Ln} = \text{La, Pr, Nd}$ ) above the second SSC [9]. The drop is much more pronounced for Er (small rare-earth) and hardly perceptible for La (the largest lanthanide).

#### 4. Conclusion

The main purpose of this paper was to obtain experimental evidence of the electronic phenomena associated with the spin-state of  $\text{Co}^{3+}$  ions through the characterization of the structural and lattice evolution up to very high temperatures. To our knowledge,  $\text{ErCoO}_3$  is the smallest  $\text{Co}^{3+}$  simple perovskite investigated so far in a broad temperature range up to  $\sim 1000\text{K}$ . We have observed one shoulder or clear maxima in the thermal evolution of the linear expansion coefficient resulting from the activation of a broad spin-state crossover from LS to IS or HS states that begins at  $T_{\text{SS}} \approx 575\text{K}$  in this highly distorted cobaltite. Several interrelated structural changes above  $T_{\text{SS}}$  are driven by the anomalous expansion of the octahedra. The activation of IS or HS spin states brings about an expansion of the  $\text{CoO}_6$  octahedra, and the augmentation of the Co-O distances in the  $a$ - $b$  plane respect to that along the  $c$ -axis. The spin-state crossover extends over a broad temperature interval and can be monitored by an atypical augmentation of the orthorhombic strain. Further experimental work is needed to clarify the nature of the spin transitions in  $\text{LnCoO}_3$  cobaltites with, respectively, heavy and light lanthanides.

#### Acknowledgements

We thank financial support from MINECO (Spanish government) under projects MAT2009-09308, MAT2012-38213-C02-02 and MAT2013-41099-R, and to the ILL for granting beamtime. J. P.-P. thanks the CSIC for a JAE-Predoc contract.

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