Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

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To cite this article: Jessica Padilla-Pantoja *et al* 2015 *J. Phys.: Conf. Ser.* **663** 012005

Structural effects of the spin-state crossover at high temperature in the distorted $ErCoO_3$ 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}≈575 K in the highly distorted $ErCoO_3$ 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 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 $LaCoO_3$ has been matter of controversy for many years [1-8]. $LaCoO_3$ exhibits two broad transitions: there is first a spin-state crossover (SSC) at T_{SS} (between ~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 ~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 $LaCoO_3$ involve the spin transition either LS→(HS+LS)→IS [1,2] or LS→IS→(HS+IS) [3-6]. However, in presence of disorder phenomena, a LS→HS crossover at T_{SS} can not be totally ruled out [2,7].

In addition, the ground and thermally excited states of $LnCoO_3$ perovskites (*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 *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 $LnCoO_3$ 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 $ErCoO_3$, 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 Co^{3+} ions in the system.

2. Experimental

Polycrystalline $ErCoO_3$ was prepared by sol-gel method [12]. Stoichiometric amounts of Er_2O_3 and $Co(NO_3)_{2\cdot 6}H_2O$ were dissolved in citric acid, by adding 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 Brucker D8 diffractometer (40 kV, 30 mA) and Cu Kα 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 λ=1.594 Å and were analyzed with the Rietveld method using the FULLPROF suite of programs [13].

3. Results and discussion

All the NPD diffraction patterns for $ErCoO_3$ 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.

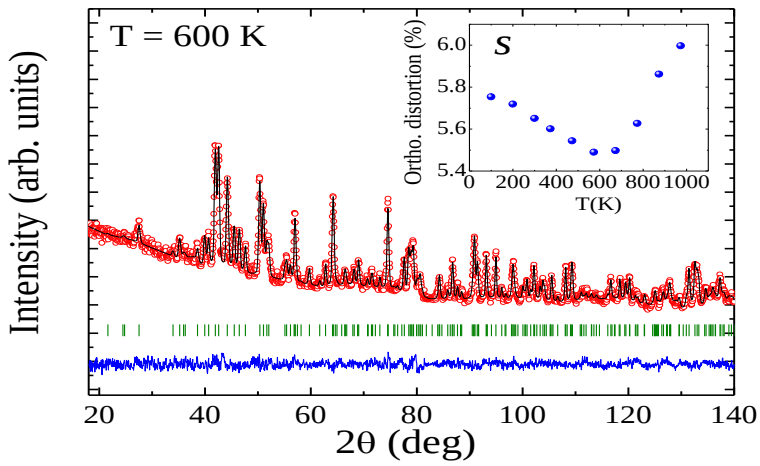

Figure 1. Rietveld refinement (black line) of neutron diffraction pattern from D2B (red circles, experimental points; bottom blue line, difference; green lines, Bragg reflections) for $ErCoO_3$ at 600 K. The inset shows the temperature dependence of the orthorhombic strain (*s*).

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 χ^2 = 1.14 and R_B (%) = 6.36

Atom	Site	*x/a*	*y/b*	*z/c*	B_{iso} (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 ~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 $LnCoO_3$ 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 α_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 α_b at T_{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 α_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_{SS}, is a guide to the eye.

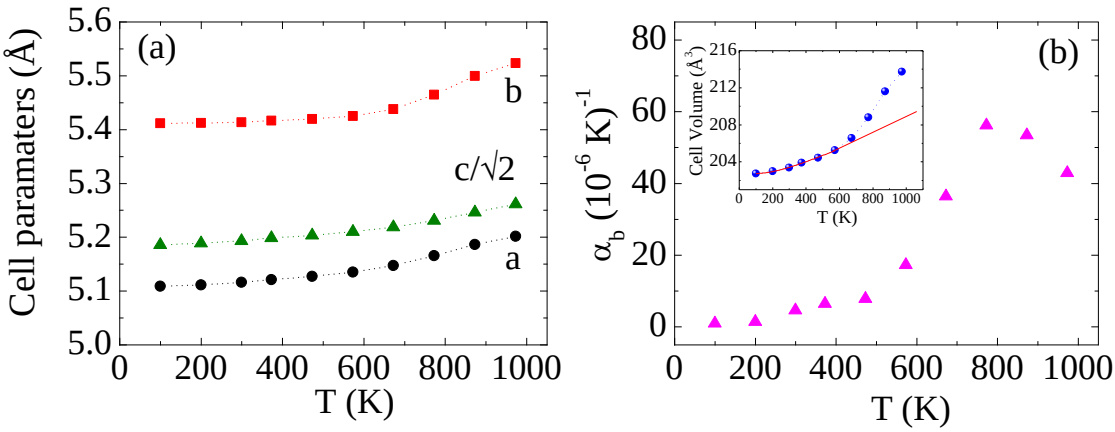

Figure 2. $ErCoO_3$: temperature dependence of (a) the lattice parameters and (b) the linear thermal expansion along *b* axis (α_b). The inset shows the temperature dependence of the cell volume for $ErCoO_3$. The solid red line, fitting the equation $V_0 = V_1 + V_2\,\Theta\coth(\Theta/T)$, is a guide to the eye.

The anomalous expansion shown in these figures above $T_{SS} \approx 575$ K is the signature of a sudden increase of populated excited magnetic states (IS or HS) in the Co^{3+} ions. The occupation of excited magnetic states is activated at $T_{SS} \approx 575$ K but it develops progressively along the interval 575-780 K. Above ~800 K the expansion coefficient α_b starts to decrease. From the inset of Figure 2(b) a rough estimation of the anomalous volume expansion accumulated at ~1000 K due to spin state excitations gives ~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 $YCoO_3$, $DyCoO_3$ and $GdCoO_3$ [8]. The analysis of thermal expansion in the *b* lattice (α_b) as a function of temperature is also shown in Figure 2(b). We observe the expansion coefficient α presents an inflection point just at T_{SS} and it reaches a maximum at T~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.

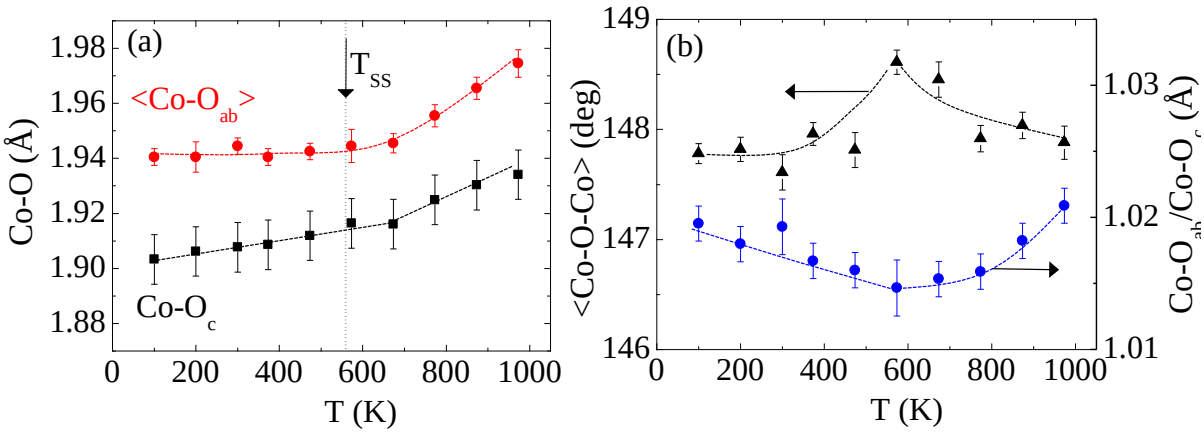

Figure 3. $ErCoO_3$: evolution with temperature of (a) the average Co-O_c (black squares) and Co-O_{ab} (red circles) bond lengths in the CoO_6 octahedra; (b) the average Co-O-Co bond angles (black triangles, left axis) and Co-O_{ab}/Co-O_c ratio (blue circles, right axis). The dotted lines are eye-guides.

The refined Co-O bond lengths in the equatorial plane (<Co-O_{ab}>) and apical axis of the CoO_6 octahedra are plotted in Figure 3(a). The average <Co-O-Co> bond angle for $ErCoO_3$ up to ~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 (Co-O_c) in the wide temperature range below 1000 K. However, the difference between them does not show a monotonous evolution: it is ~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 ~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 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 <Co-O_{ab}>/Co-O_c ratio due to the phonon (lattice) contribution.

On the other hand, the temperature evolution of the average <Co-O-Co> bond angle (see Figure 3(b), left axis) also reveals a non monotonous evolution. This angle displays a maximum around ~580 K coinciding with T_{SS}. The maximum value of the average bond angle (~148.5º) 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 <Co-O-Co> 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 CoO_6 octahedra observed upon heating above T_{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 $LnCoO_3$ perovskites (*Ln* =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 Co^{3+} ions through the characterization of the structural and lattice evolution up to very high temperatures. To our knowledge, $ErCoO_3$ is the smallest Co^{3+} simple perovskite investigated so far in a broad temperature range up to ~1000K. 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 $T_{SS}\approx575$ K in this highly distorted cobaltite. Several interrelated structural changes above T_{SS} are driven by the anomalous expansion of the octahedra. The activation of IS or HS spin states brings about an expansion of the 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 $LnCoO_3$ 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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