

Effects of oxygen non-stoichiometry on the physical properties of the $\text{YBaCo}_2\text{O}_{5+\delta}$ layered cobaltites

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Abstract

We have synthesized the layered cobaltites $\text{YBaCo}_2\text{O}_{5+\delta}$ with different oxygen contents (δ_1 and δ_2), and characterized its structural and physical properties using various experimental techniques within the 80–500 K temperature range. Two superstructures have been identified due to the ordering of oxygen vacancies. One of them (corresponding to $\delta \simeq 0.50$) shows a metal–insulator transition at room temperature, while both exhibit a sequence of magnetic transitions AFM–FM–PM as the temperature is increased. We have determined the second-order nature of the FM–PM magnetic transition using the Banerjee criterion. We also show that there exist intrinsic differences between both samples in terms of the charge carriers involved, which manifest in the transport properties.

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Cobalt-oxide-based materials have attracted considerable interest in the last decade because they were expected to exhibit similar properties to those in the manganites and cuprates. The oxygen content in these compounds can be modified by the synthesis conditions ($0 \leq \delta \leq 0.8$ depending on the rare earth cation), which in turn controls the mixed valence state of Co ions [1]. The mean valence of Co varies from 2.5 for $\delta = 0$ to 3.5 for $\delta = 1$. Thus, for $\delta = 1$, Co^{3+} and Co^{4+} are present in the same amount, for $\delta = 0$, Co^{3+} and Co^{2+} are found, while for $\delta = 0.5$, only Co^{3+} is expected. Among the cobalt oxides synthesized in the last years, the compound with Y^{3+} , which is a non-magnetic ion, is a good candidate to isolate the intrinsic properties of Co in the layered perovskites. Moreover, Y is among the smallest cations which can form this compound. In the present work, we study the structural, magnetic and transport properties of cobaltites with Y, focusing on the role of oxygen non-stoichiometry.

Polycrystalline samples of $\text{YBaCo}_2\text{O}_{5+\delta}$ (hereafter named Q and SC) were prepared by solid-state reaction,

starting from high-purity powders of Y_2O_3 , BaCO_3 , SrCO_3 , CaCO_3 and Co_3O_4 , de-carbonated at 1173 K for 18 h, pressed into pellets and annealed. The sample $\text{YBaCo}_2\text{O}_{5+\delta}(\text{Q})$ was annealed for 12 h at 1273 K under oxygen flow and quenched in air from 1273 K to room temperature, while sample SC was annealed for 25 h at 1273 K and slowly cooled at $1^\circ/\text{min}$ in oxygen flow. In the latter, after a regrinding of the resulting pellets, the compression and annealing at 1273 K in oxygen processes were repeated.

We have not explicitly determined the oxygen content in the samples. However, a comparison with a detailed characterization by Akahoshi and Ueda [2,3] of samples with varying oxygen contents, reveals that our structural and magnetic data of samples Q and SC are in excellent agreement with their results, strongly suggesting that sample Q lies in the range $0.40 \leq \delta \leq 0.44$ and sample SC corresponds to $\delta \approx 0.50$. In order to study the stability of the obtained compounds, a thermogravimetric analysis was performed on sample SC. The curve was taken under a nitrogen flow of $600 \text{ cm}^3/\text{min}$ at a heating rate of $2^\circ/\text{min}$ from 298 to 773 K. We found that the oxygen loss begins at around 550–600 K. Moreover, an experiment conducted on

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a Faraday balance under heating conditions, confirmed the oxygen loss at $T > 600$ K leading to a change in the structural and magnetic properties of the heated SC sample at room temperature, which ended up similar to the Q sample.

The structure of $\text{YBaCo}_2\text{O}_{5+\delta}$ is formed by a stacking sequence of $[\text{CoO}_2]-[\text{BaO}]-[\text{CoO}_2]-[\text{YO}_\delta]$ planes along the c -axis [4–6], usually called “112” structure derived from the $a_p x a_p x 2 a_p$ perovskite cell. The oxygen vacancies have a strong tendency to become ordered, which results in several superstructures. Indeed, our preliminar indexation of X-ray diffraction data indicate that sample Q corresponds to a tetragonal cell with lattice parameters $a = b = 3 \times 3.873 \text{ \AA}$ and $c = 7.503 \text{ \AA}$, in agreement with the “332” superstructure reported in Ref. [2] for samples with $0.25 \leq \delta \leq 0.44$. On the other hand, sample SC shows the characteristic doubling of the b -axis (“122” superstructure in the orthorhombic $Pmmm$ space group) due to the alternate ordering of oxygen pyramids and octahedra coordinating the Co ions, consistent with $\delta \simeq 0.5$. In this case, the crystal lattice consists of alternating $[\text{CoO}_6]$ octahedra chains along the c -axis and corner-sharing $[\text{CoO}_5]$ pyramids along the b -axis, resulting in alternating octahedral and pyramidal layers in the a - c plane, as shown in Fig. 1.

Low-field magnetization versus temperature was first measured for samples Q and SC (Fig. 2) using a vibrating sample magnetometer for $80 \text{ K} \leq T \leq 300 \text{ K}$. Two characteristic temperatures are observed, indicated as T_C and T^* , associated with magnetic transitions. At $T = T_C$ a paramagnetic (PM) to ferromagnetic (FM) transition occurs, whereas at $T = T^*$ the magnetization abruptly drops to zero. To understand the nature of this second transition we measured the paramagnetic susceptibility at high temperature ($300 \text{ K} \leq T \leq 470 \text{ K}$) using a Faraday balance under a 0.5 T field in a 1 Torr air atmosphere. The inset in Fig. 2

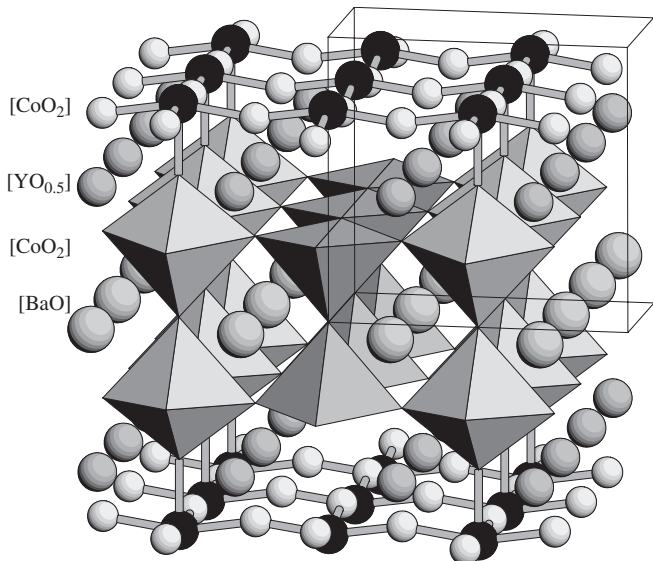


Fig. 1. The structure of $\text{YBaCo}_2\text{O}_{5.50}$. Half Co atoms are in square-pyramidal coordination and the other half in octahedral coordination.

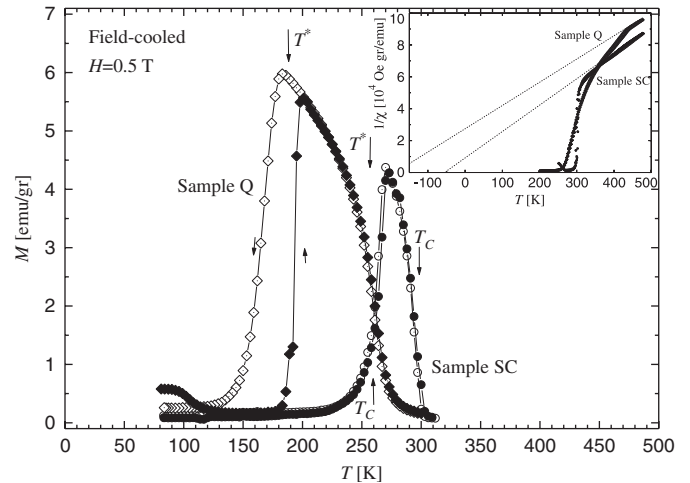


Fig. 2. Temperature dependence of magnetization for the quenched $\text{YBaCo}_2\text{O}_{5+\delta}$ sample (Q) and the slowly cooled sample (SC) under cooling (open symbols) and warming (solid symbols) conditions in a field of 0.5 T. Inset: temperature variation of the inverse susceptibility of samples Q and SC. High-temperature data was collected using a Faraday balance.

shows the inverse susceptibility for samples Q and SC. Following a simple Curie–Weiss model, the high-temperature data extrapolate linearly to negative θ values, viz., $\theta = -162 \text{ K}$ and -30 K for samples Q and SC, respectively. This result indicates that the main magnetic interactions between the Co spins are antiferromagnetic (AFM), which accounts for the transition observed at T^* (FM \rightarrow AFM). The effective magnetic moment μ_{eff} for the SC sample in this model yields $3.2\mu_B$, which could be compatible with a mixture of Co^{3+} in high spin and low spin configurations. Several cobaltites actually exhibit the coexistence of different spin states related to the different oxygen coordination of the Co ions.

In the Q sample a remarkable hysteresis is observed between the magnetization measured on cooling and warming around T^* . This behaviour suggests a first-order transition and the possibility of phase coexistence. In the SC sample, on the other hand, such hysteresis is barely appreciable. In the vicinity of T_C no hysteresis was detected. To study the nature of this transition we have used the Banerjee criterion [7]. Fig. 3(a) shows the results for sample Q. In Fig. 3(b) we plot the H/M versus M^2 curves where a positive slope is clearly seen in all the M^2 range, indicating that the FM–PM phase transition is second order [7]. In order to assess T_C we have employed the Arrott plot M^2 versus (H/M) . The magnetization values M_0 were obtained by extrapolating to $H/M = 0$ the data in the high-field region. From the relation of M_0^2 and T in the Arrott plot, we obtain $T_C = 259 \pm 1 \text{ K}$ for sample Q ($T_C = 293 \pm 1 \text{ K}$ for sample SC), which is shown in the bottom panel of Fig. 3.

The resistivity of samples Q and SC is shown with solid lines in Fig. 4(a) and (b) for the temperature range $80 \text{ K} \leq T \leq 300 \text{ K}$. The resistivity of the quenched sample does not show any change at T_C , but at 190 K there is a clear jump, which coincides with the temperature at which

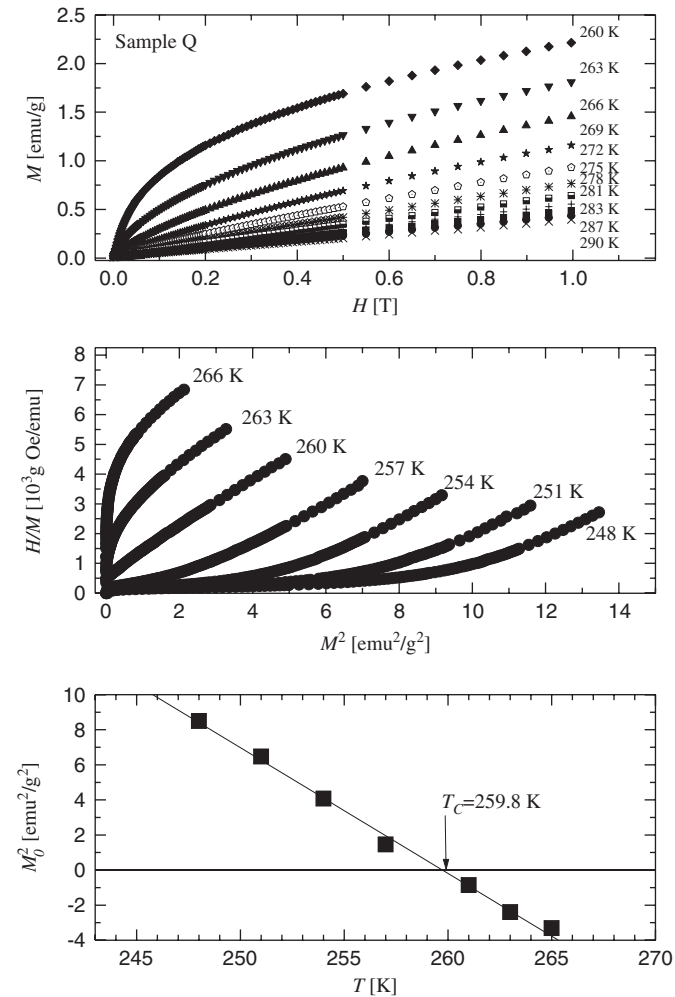


Fig. 3. (a) Magnetization versus magnetic-field isotherms for $\text{YBaCo}_2\text{O}_{5+\delta}$ (sample Q) in the vicinity of its T_C . (b) H/M versus M^2 plots of isotherms in the vicinity of the Curie point. (c) Temperature dependence of the M_0 magnetization derived from the Arrott plot (b).

the magnetization of this sample abruptly drops (Fig. 2). In the slowly cooled sample, the resistivity shows an abrupt increase below 294 K and a slight increase at 270 K. The step at 294 K corresponds to a metal–insulator transition, which in this compound accidentally coincides with the T_C .

Fig. 4 also shows in symbols the thermoelectric power measurements (right axis) for samples Q and SC. Similar to what has been observed in the Dy cobaltite [8], the $\delta = 0.50$ phase is a p-type conductor, and the addition of oxygen vacancies in the octahedral sites can completely suppress the metal–insulator transition and turn this compound a n-type conductor. It is also interesting to note that the hysteretic behaviour found in the magnetization measurements for sample Q around T^* is clearly observed in the thermoelectric power data, again suggesting the coexistence of different electronic phases. This is probably related to the possibility of finding Co ions in different oxidation states (2+, 3+), whereas for the $\delta = 0.5$ cobaltites only Co^{3+} ions are expected.

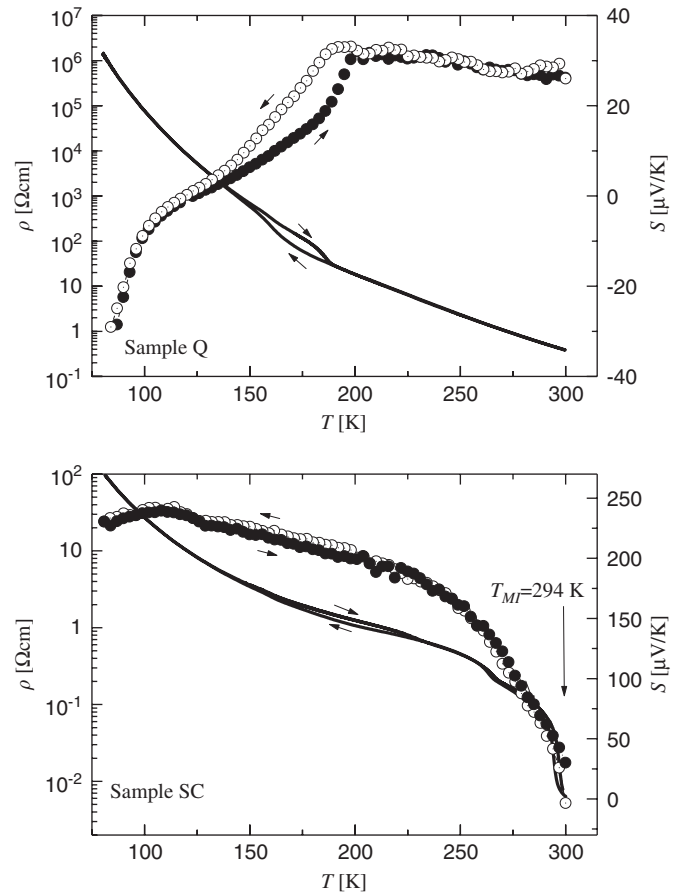


Fig. 4. Resistivity (solid lines, left axis) and thermoelectric power (symbols, right axis) for the quenched (Q) and slowly cooled (SC) $\text{YBaCo}_2\text{O}_{5+\delta}$ samples.

In summary, we have presented our preliminary results on the structural, magnetic and transport properties of the cobaltites $\text{YBaCo}_2\text{O}_{5+\delta}$ obtained under different synthesis conditions. New experiments are under way to study the relation between the oxygen vacancies configuration and the spin state of the Co atoms, as well as the transport mechanisms and the possibility of finding phase separation phenomena in these oxides.

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