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# Ferromagnetic clusters in polycrystalline BaCoO<sub>3</sub>

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## Abstract

Polycrystalline  $BaCoO_3$  was synthesized by a citrate technique using thermal treatments at high oxygen pressure. Magnetic susceptibility measurements on the compound were carried out under AC conditions. The magnetic properties of the material at low temperatures were found to be determined by the appearance of nanoscale ferromagnetic (FM) regions and not by a true magnetic phase transition. These clusters have a mean size of about 1 nm in diameter and obey an Arrhenius-like thermal relaxation. (C) 2007 Elsevier B.V. All rights reserved.

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# 1. Introduction

Cobalt oxides have drawn considerable attention in the last few years due to their interesting electronic structure and magnetic properties [1–4]. In particular, the behavior of BaCoO<sub>3</sub> has been thoroughly analyzed recently. The first studies on the material showed that its ground state was a long-range antiferromagnet [5–7]. However, more recent works indicate that its magnetic properties are more complicated and a competition between antiferromagnetic (AF) and ferromagnetic (FM) interactions was observed [8]. On the other hand, electronic structure calculations [9] yield that the ground state of the material is a long-range ferromagnet with an alternating orbital order along the CoO<sub>6</sub> chains (the material has a quasi-one-dimensional structure).

In a recent paper [10], it was shown by an analysis of the susceptibility measurements performed by Yamaura et al. [8] combined with ab initio electronic structure calculations, that the magnetic properties of  $BaCoO_3$  can be explained assuming the material is formed by FM regions

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of a nanometric size embedded in a nonferromagnetic matrix. Similar phase separation on a nanometric scale has been thoroughly studied for the case of manganites [11,12]. However, it is still under debate whether these FM droplets occur in BaCoO<sub>3</sub> or not. Recent studies conclude that the low-temperature (T < 14 K) magnetic phase of the material and other related compounds is a two-dimensional AF long-range ordering [13].

In this paper, we present ac magnetic measurements with the aim of bringing more experimental evidence to the occurrence of a magnetic phase separation in this system.

#### 2. Experimental

BaCoO<sub>3</sub> material was obtained in powder form by a citrate technique. Stoichiometric amounts of analytical grade Ba(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6H<sub>2</sub>O were dissolved in citric acid. The solution was slowly evaporated, leading to an organic resin, which was dried at 120 °C and slowly decomposed at temperatures up to 600 °C for 12 h. The black precursor powders, very reactive, after an intermediate treatment at 900 °C, in air, were heated at 900 °C under a 200-bar oxygen pressure for 10 h. Then, the sample

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was cooled at  $300 \,^{\circ}\text{C} \,\text{h}^{-1}$  down to room temperature (RT) in order to favor the oxygenation of the products.

The reaction product was characterized by X-ray diffraction (XRD) for phase identification and to asses phase purity. XRD patterns were analyzed by the Rietveld method [14], using the FULLPROF refinement program [15]. No regions were excluded in the refinement. Magnetization (M) between 5 and 100 K was measured in a SQUID magnetometer (Quantum Design) under ZFC ac conditions. An applied field amplitude of 8 Oe at frequencies of 1, 3 and 10 kHz were employed. Also, curves of magnetization as a function of the applied field (H) at several temperatures were recorded.

#### 3. Results and discussion

The XRD pattern of BaCoO<sub>3</sub> compound is characteristic of a perovskite showing well-defined reflections corresponding to a hexagonal structure. No impurity phases were detected. The crystal structure refinement was performed from XRD data collected at RT. The structure was defined in the hexagonal space group P6<sub>3</sub>/mmc (No. 194). The lattice parameters are a = b = 5.6525(2) Å, c = 4.7629(3) Å and V = 131.79(1) Å<sup>3</sup>. Ba, Co and O atoms were located at 2*d*, 2*a* and 6*h* positions, respectively. A good fit between the observed and the calculated profiles was obtained. Table 1 lists the refined structural and thermal parameters, together with unit-cell parameters refined from XRD data at RT.

BaCoO<sub>3</sub> presents a 2H-type perovskite structure, consisting of infinite chains of CoO<sub>6</sub> face-sharing octahedra, running along the *c*-direction. The sharing of faces is associated with short metal–metal distances (in this case, Co–Co, 2.381(4) Å) accounting for abnormal magnetic or electrical properties. From a purely ionic point of view, we should expect strong repulsion between Co<sup>4+</sup> ions at this short distance. However, the O–O distance in shared faces is only 2.543(2) Å, suggesting that the Co<sup>4+</sup> ions are shielded from one another along the *c*-direction.

Fig. 1 shows the ac magnetic susceptibility as a function of temperature. A cusp at temperature close to 30 K is observed in both real and imaginary parts of the magnetic susceptibility ( $\chi'$  and  $\chi''$ ). For increasing frequencies, this peak appears at higher temperatures. Also, all the  $\chi'$  curves below and above 30 K collapse. At 12 K, a second peak can

Table 1

Structural parameters for  $BaCoO_3$  refined in the hexagonal  $P6_3/mmc$  space group from XRD data at RT

Atom	Site	X	у	Ζ	$f_{\rm occ}$	$B(\text{\AA})^2$
Ba	2d	1/3	2/3	3/4	1.0	0.39(9)
Co	2a	0	0	0	1.0	0.23(7)
0	6 <i>h</i>	0.1505(4)	-0.1505(4)	1/4	1.0	0.11(5)

Lattice parameters: a = b = 5.6525 Å, c = 4.7629 Å and V = 131.79 Å<sup>3</sup>. Reliability factors:  $\chi^2 = 1.70$  and  $R_{\text{Bragg}}\% = 6.24$ .



Fig. 1. ac magnetic susceptibility as a function of temperature at several frequencies.

be noticed. In a recent study [13] by muon rotation and relaxation techniques, a transition at 14 K has been registered, which is attributed to a two-dimensional AF ordering.

Previously reported dc measurements [8] reveal a behavior similar to an assembly of ultrafine magnetic particles. ZFC curves show a maximum in  $\gamma$  at higher temperatures for decreasing applied fields. Moreover, at this temperature ZFC traces separate from FC ones, especially at very low fields. This response can be understood considering a phase separation scenario for BaCoO<sub>3</sub>, in which FM nanoscale regions are immersed in a nonferromagnetic matrix, as described by Wolfahrth's model [16]. Sugiyama et al. [13] have reported the presence of 1D FM interactions between 14 and 53 K, which is consistent with our scenario of FM clusters developing in the system. At low enough temperature (the so-called blocking temperature,  $T_{\rm B}$ ), these clusters undergo a blocking evidenced by a peak in the ZFC curves and a splitting of the ZFC and FC curves below  $T_{\rm B}$ . It is worth noting that no chemical phase segregation has been observed in the sample, i.e., the inhomogeneous regions have a pure magnetic or electronic origin. At temperatures higher than  $T_{\rm B}$ , FM interactions among the clusters disappear, giving rise to a superparamagnetic state. This is supported by calculations of the effective magnetic moment from experimental data [8,13] that give a higher value than that expected for a low-spin Co<sup>4+</sup> ion. Also, in Ref. [10], a superparamagnetic region at 50 < T(K) < 250 is described for this cobaltite.

Fig. 2 shows M vs. H curves measured at temperatures lower and higher than  $T_{\rm B}$ . At 100 K, a linear dependence can be observed, consistent with the presence of a superparamagnetic behavior. In contrast, at temperatures below  $T_{\rm B}$ , the curves tend to saturate at the highest applied fields (above some  $3 \times 10^4$  Oe), providing more evidence of the existence of a blocked state.



Fig. 2. Magnetization as a function of applied field at selected temperatures. The curve at T = 20 K (below  $T_{\rm B}$ ) exhibits a clear deviation from linearity.

Thermal relaxation of the FM clusters can be described by an Arrhenius-like equation

$$\tau = \tau_0 \times \exp\left(\frac{Q}{kT}\right),\tag{1}$$

where  $\tau$  is the relaxation time at temperature T,  $\tau_0$  is the relaxation time at infinite temperature, Q is the energy barrier and k is the Boltzmann constant. This energy barrier for the thermal relaxation of the clusters can be estimated to be due to the anisotropy energy associated to each cluster, KV, where K is the magnetic anisotropy energy. Considering the highly anisotropic structure of BaCoO<sub>3</sub>, the constant K can be considered to be due mainly to the magnetocrystalline anisotropy energy.

From the experimental data measured in ac experiments, it is possible to obtain the relaxation time (through the employed frequency, v, that is  $v = 1/2\pi\tau$ ) for each  $T_{\rm B}$ . A very good linear fit was obtained for the measured data, supporting the validity of our hypotheses. The energy barrier can be calculated from the slope of the straight line, giving  $Q = 7.9 \times 10^{-14}$  erg (0.05 eV), that is a reasonable value if we consider those reported for magnetic nanoparticles [16].

To estimate the mean volume of the clusters, we will use the value of the anisotropy constant that comes out of the magnetocrystalline anisotropy energy calculated ab initio using the LDA+U approximation including spin-orbit effects in Ref. [10]:  $K = 2 \times 10^8 \text{ erg cm}^{-3}$ . This gives a mean volume of the cluster of about  $4 \times 10^{-22} \text{ cm}^3$ , i.e., a typical diameter of each cluster of approximately 1 nm, assuming spherical geometry for them (i.e., 10–12 Co ions).

The mean size obtained for clusters is in very good agreement with the results reported recently by some of us (1.2 nm), where the experimental dc data from Yamaura et al. [8] were analyzed. In that case, no measurements of the relaxation times were available and the size was calculated

through the following equation that is valid for superparamagnetic particles:

$$KV = 25kT_B,\tag{2}$$

where the factor 25 is associated with the measuring time [17], assumed with a time constant of 100 s for both ZFC and FC experiments.

The relaxation data measured in ac experiments gives also an estimation of  $\tau_0$ , being about  $10^{-13}$  s. This value is very small compared to those reported by Dormann et al. [18], that are on the order of  $10^{-11}$  s. However, these higher values are obtained for noninteracting nanoparticles of a much bigger size than our clusters (composed by only a few Co atoms). It looks reasonable to obtain longer relaxation times for those particles than for our nanometric clusters.

# 4. Conclusions

In this paper, we present solid evidences that support the hypothesis of a phase separation in BaCoO<sub>3</sub>. This is characterized by the appearance of single-domain FM clusters of a nanometric size developing in a nonferromagnetic matrix. ac magnetic measurements conclude that at 14 < T(K) < 30, the properties of the material are determined by a relaxation phenomenon and not by a true magnetic phase transition. Also, we were able to estimate the size of these regions, being about 1 nm in diameter. Thermal relaxation of the assembly of clusters was found to be governed by an Arrhenius-like law, with an energy barrier of 0.05 eV.

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