Ordered oxygen deficient ‘112’ perovskites, $\text{LnBaCo}_2\text{O}_{5.50+\delta}$: complex magnetism and transport properties[#]

B RAVEAU^{1,*}, MD MOTIN SEIKH^{1,2}, V PRALONG¹ and V CAIGNAERT¹

¹Laboratoire CRISMAT, UMR 6508, CNRS-ENSICAEN, Université de Caen, 14050 Caen, Cedex, France

²Visva-Bharati University, Santiniketan 731 235, India

Abstract. The ordered oxygen deficient ‘112’ perovskites, $\text{LnBaCo}_2\text{O}_{5.50+\delta}$ (Ln = lanthanide or Y), exhibit a very flexible structure which can either uptake ($\delta > 0$) or release oxygen ($\delta < 0$) depending on the experimental conditions of synthesis and on the size of the lanthanide. These compounds exhibit remarkably complex magnetic transitions, metal–insulator transition and exceptionally high magnetoresistance. We show herein that their physics is mainly dominated by three different ferromagnetic states, depending on the cobalt valency: FM1 for $\delta = 0$ (Co^{3+}), FM2 for $\delta < 0$ ($\text{Co}^{2+}/\text{Co}^{3+}$) and FM3 for $\delta > 0$ ($\text{Co}^{3+}/\text{Co}^{4+}$). The competition between ferromagnetism and antiferromagnetism in these phases and the various transitions are discussed taking into consideration the spin state of cobalt, the issue of phase separation and the effect of cobalt coordination and disproportionation.

Keywords. Ordered oxygen deficient perovskites; ‘112’ cobaltites; ferromagnetic cobaltites; phase separation; magnetic transitions; magnetoresistive cobaltites.

1. Introduction

The discovery of an exceptionally high magnetoresistance, associated to a metal to insulator (MI) transition around room temperature in the ordered oxygen deficient ‘112’ perovskites, $\text{LnBaCo}_2\text{O}_{5.50}$ (Martin *et al* 1997), has attracted considerable interest. Soon confirmed by Troyanchuk *et al* (1998) the complex magnetic properties of this cobaltite family have been the object of many studies (Suard *et al* 2000; Respaud *et al* 2001; Baran *et al* 2003, 2005; Burley *et al* 2003; Khalyavin *et al* 2003; Taskin *et al* 2003, 2005; Soda *et al* 2003, 2004; Wu 2001, 2003; Flavell *et al* 2004; Maignan *et al* 2004; Zhou and Goodenough 2004; Chernenkov *et al* 2005; Conder *et al* 2005; Plakhty *et al* 2005; Roy *et al* 2005; Zhou and Schlottmann 2005; Hidaka *et al* 2006; Streule *et al* 2006; Gatal'skaya *et al* 2007; Podlesnyak *et al* 2007; Seikh *et al* 2008a, b, c, 2009) this last decade. The multiple magnetic transitions that appear below the MI transition, the existence of phase separation, the possibility of charge and orbital ordering and of spin state transitions, make that these oxides are still a matter of debate. In the present paper, we give an overview of the recent trends about magnetism and transport properties of these materials in connection with their complex oxygen non-stoichiometry, involving for cobalt various oxidation states (Co^{2+} , Co^{3+} and Co^{4+}) and various coordinations (octahedral, pyramidal).

2. Structure: oxygen ordering and non-stoichiometry

First determined by X-ray diffraction and electron microscopy (Maignan *et al* 1999) and then by neutron diffraction (Moritomo *et al* 2000; Akahoshi and Ueda 2001; Kusuya *et al* 2001; Fauth *et al* 2002; Frontera *et al* 2002; Khalyavin *et al* 2007), the structure of these oxides with the ideal composition, $\text{LnBaCo}_2\text{O}_{5.50}$, can be described as ordered oxygen deficient perovskites (figure 1) built up of single layers of corner-shared CoO_6 octahedra parallel to (010) interconnected through double ribbons of corner-shared CoO_5 pyramids running along $\vec{a}$.

In fact, such an ordering of oxygen atoms and anionic vacancies, is due to the 1:1 ordering of Ln^{3+} and Ba^{2+} cations in the form of alternating layers stacked along $\vec{c}$. As a consequence, the oxygen vacancies are located at the level of the ‘ Ln^{3+} ’ layers, forming six-sided tunnels.

This structure is very flexible, so that it can accept variable amounts of oxygen, depending on the size of the tunnels, i.e. on the size of the Ln^{3+} cations, and on the experimental conditions of synthesis. As a consequence, deviation from the ‘ $\text{O}_{5.50}$ ’ stoichiometry is often observed, changing the cobalt valency for the so obtained $\text{LnBaCo}_2\text{O}_{5.50+\delta}$ compounds. It results in the formation of long range and short-range superstructures, which most of the time cannot be detected from X-ray diffraction and require electron microscopy investigations. Such a feature is of capital importance, since a tiny variation of oxygen content in the structure, leads to dramatic variations of the magnetic properties (Akahoshi and Ueda 2001; Kusuya *et al* 2001; Burley *et al* 2003; Soda *et al* 2003; Taskin *et al*

* Author for correspondence (bernard.raveau@ensicaen.fr)

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2005; Seikh *et al* 2008a) from one sample to the other. Clearly, for $\delta=0$, cobalt is purely trivalent, with half of cobalt cations in the octahedral sites and the remaining half in the pyramidal sites, supposing absence of charge ordering. However, δ may vary between -0.50 , leading to the mixed valence $\text{Co}^{2+}/\text{Co}^{3+}$ and $+0.50$ corresponding to the mixed valence $\text{Co}^{3+}/\text{Co}^{4+}$. Such a mixed valence may correspond either to carrier delocalization or to charge ordering. Thus, the knowledge of the accurate oxygen content of these samples is absolutely necessary in order to interpret the magnetic and transport properties of the

Figure 1. Structure of $\text{LnBaCo}_2\text{O}_{5.50}$ with layers of CoO_6 octahedra interconnected with rows of CoO_5 pyramids indicating the doubling of unit cell along the b and c axes.

Figure 2. Temperature dependence of the resistivity (ρ) for the air-synthesized $\text{LnBaCo}_2\text{O}_{5+\delta}$ cobaltites. The different Ln are labeled on the graph. Inset: enlargement of the transition (Ln = Tb); the arrows indicate the cooling and heating modes. (taken from Maignan *et al* 1999).

compounds, and its omission often explains the disagreement observed between the different authors for the 'same' oxide.

3. Electron transport properties: metal–insulator transition of $\text{LnBaCo}_2\text{O}_{5.50}$ ($\delta=0$)

The evolution of the resistivity vs T (figure 2) shows that for the larger lanthanides (Pr, Nd) a metallic behaviour is observed in the whole temperature range from 100 K to 400 K, whereas for intermediate lanthanides (Ln = Sm to Dy), a metal–insulator transition takes place around room temperature. In contrast, for smaller lanthanides a semi-conducting like behaviour is only noticed. The transition temperature, T_{MI} , decreases smoothly with the size of the lanthanide from 360 K for Ln = Gd to 310 K for Ln = Dy, and correlatively a drop of the inverse magnetic susceptibility is observed in the paramagnetic state at this temperature. The origin of this MI transition is still a subject of controversy. Though it may originate from a spin state transition of the Co^{3+} cation (Martin *et al* 1997; Moritomo *et al* 2000; Kusuya *et al* 2001; Respaud *et al* 2001; Frontera *et al* 2002; Taskin *et al* 2003, 2005; Zhou and Goodenough 2004; Roy *et al* 2005; Zhou and Schlottmann 2005), there are several experimental and theoretical reports which oppose to the occurrence of a spin state transition in this system (Wu 2001, 2003; Flavell *et al* 2004; Conder *et al* 2005; Hidaka *et al* 2006; Podlesnyak *et al* 2007; Seikh *et al* 2008a, b), suggesting that it is driven by a structural transition (Akahoshi and Ueda 2001; Flavell *et al* 2004; Conder *et al* 2005; Hidaka *et al* 2006; Seikh *et al* 2008a, b) in agreement with the results obtained on detwinned single crystals of $\text{Tb}_{0.9}\text{Dy}_{0.1}\text{BaCo}_2\text{O}_{5.5}$ (Baran *et al* 2005). Studies of oxygen isotope effect of these oxides also suggest that structure changes are caused by the electron delocalization above T_{MI} (Conder *et al* 2005; Pomjakushina *et al* 2006). It is worth pointing out that these oxides do not behave as normal metals or as simple insulators or semiconductors (Maignan *et al* 1999; Suard *et al* 2000; Respaud *et al* 2001; Taskin and Ando 2005; Taskin *et al* 2005, 2006; Seikh *et al* 2008a), the resistivity showing a plateau below T_{MI} for the intermediate size lanthanides, and being almost temperature independent above T_{MI} in the metallic state.

The metal insulator transition is not only related to the size of the lanthanide but is in fact correlated to the oxygen stoichiometry (Maignan *et al* 1999; Taskin and Ando 2005; Taskin *et al* 2005; Seikh *et al* 2008a). One indeed observes that the oxides, $\text{LnBaCo}_2\text{O}_{5.50+\delta}$, exhibit a much higher conductivity when the hole concentration is increased ($\delta > 0$), and remain poor conductors when they are electron doped ($\delta < 0$). This result reflects the strong electron–hole asymmetry in those cobaltites (Taskin and Ando 2005). Note also that significant anisotropy in the transport properties of single crystals of these oxides,

were observed (Khalyavin *et al* 2003; Zhou *et al* 2004; Taskin *et al* 2003, 2005; Zhou and Schlottmann 2005) due to their layered character induced by the oxygen vacancies.

Finally it must be emphasized that the substitution of calcium for europium in the oxide, $\text{Eu}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5+\delta}$ (Seikh *et al* 2008b), does not change T_{MI} significantly, but decreases the resistivity by several orders of magnitude at low temperature, probably due to the disproportionation in this phase of Co^{3+} into Co^{4+} and Co^{2+} , introducing extra holes which enhance the carrier hopping between the mixed valence cobalt ions (Seikh *et al* 2008b). A similar decrease in resistivity has also been observed in $\text{YBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5.5}$ (Aurelio *et al* 2007).

4. Magnetism: complex magnetic transitions and crucial effect of oxygen stoichiometry

The main intriguing feature of these compounds deals with the existence, below T_{MI} , in the insulating phase, of several magnetic transitions as temperature is decreased. The latter are usually explained as paramagnetic–ferromagnetic–antiferromagnetic transitions (PM–FM–AFM). In fact, their interpretation is not straightforward and different models are proposed by the authors, so that this issue remains to date still open. For instance, for $\text{GdBaCo}_2\text{O}_{5.50}$, Taskin *et al* (2005) proposed PM–FM–AM transitions involving a magnetic structure built up of $S = 1$ Co^{3+} cations separated by non-magnetic $S = 0$ Co^{3+} cations, where the IS Co^{3+} ions are located in CoO_5 square pyramids and have a tendency to be ferromagnetically aligned along the a -axis. In contrast, for the $\text{TbBaCo}_2\text{O}_{5.50}$ phase a ferrimagnetic structure at 260 K and two antiferromagnetic structures at 230 K and 100 K were considered by Plakhty *et al* (2005). As pointed out above, the possibility of a spin transition was invoked by several authors, but there are also several evidences opposing to its occurrence (Wu 2001, 2003; Flavell *et al* 2004; Conder *et al* 2005; Hidaka *et al* 2006; Podlesnyak *et al* 2007; Seikh *et al* 2008a, b). Density functional calculations suggest that there is a strong hybridization between O-2p and Co-3d orbitals with a narrow charge transfer gap near Fermi level, which gives rise to $pd\sigma$ -hybridized hole in the O-2p valence band (Wu 2001, 2003). With increasing temperature, a gradual delocalization of the $pd\sigma$ holes in the almost HS Co^{3+} is responsible for the successive magnetic transitions, which is proposed to be accompanied by a spin reorientation in a spin-canted structure (Wu 2001, 2003). Thus the magnetic transitions in the oxides, $\text{LnBaCo}_2\text{O}_{5.50}$, can be due to competition between ferromagnetic (FM) and antiferromagnetic (AFM) interactions, leading to spin canting.

The important issue concerning the magnetism of the '112' cobaltites deals with the fact that their magnetic properties are strongly affected by the exact oxygen

stoichiometry. Besides the ideal ' $\text{O}_{5.50}$ ' stoichiometry involving only Co^{3+} species, a tiny variation of the oxygen content may induce dramatic variations in the magnetic properties (Burley 2003; Taskin *et al* 2005; Seikh *et al* 2008a). This is exemplified by the $\text{LnBaCo}_2\text{O}_{5.50+\delta}$ cobaltites with $\text{Ln} = \text{Sm}, \text{Eu}$ (Seikh *et al* 2008a). For $\delta \sim 0$, the $M(T)$ curves (figure 3) and the $M(H)$ curves (figure 4), clearly show a ferromagnetic component around 150 K–200 K, but the latter is complex indicating several transitions in this temperature range. Moreover, it appears that the Co^{3+} cations are antiferromagnetically coupled at low temperature, i.e. below 150 K. Thus this ferromagnetic state, named FM1, originates from the entropy driven ferromagnetic ordering of the Co^{3+} ions, but is so far not really understood. For oxygen deficient '112' cobaltites ($\delta < 0$), one clearly observes (figures 5–6) that the compounds become ferromagnetic at high temperature, i.e. close to 280 K and remain ferromagnetic in the whole temperature range down to 2 K. This new ferromagnetic state, named FM2, is associated with $\text{Co}^{2+}/\text{Co}^{3+}$ mixed valence. However, the origin of the low value of the

Figure 3. $M(T)$ curves measured at 100 Oe for (a) $\text{EuBaCo}_2\text{O}_{5.48}$, (b) $\text{EuBaCo}_2\text{O}_{5.52}$, (c) $\text{SmBaCo}_2\text{O}_{5.49}$ and (d) $\text{SmBaCo}_2\text{O}_{5.53}$. The solid (open) symbols correspond to ZFC (FC) data. The corresponding insets show H - T diagram generated from $M(H)$ curves for each composition. C-AF in insets represents canted-antiferromagnetic phase.

magnetic moment is still not elucidated. One explanation would be that a majority of Co^{3+} is in low spin state (LS) at low temperature, but this is in contradiction with the optical studies. Two other hypotheses are more likely:

- (i) the possibility of ferrimagnetic ordering which is compatible with the fact that this oxygen deficiency creates surplus of non equivalent pyramidal and octahedral sites,
- (ii) the existence of phase separation i.e. presence of FM2 domains in an AFM matrix.

In any case, the spectacular decrease of coercive field above 200 K is puzzling.

For the over oxygenated samples ($\delta > 0$), the compounds are also ferromagnetic, but the T_c is shifted towards lower temperature ($T_c \sim 110$ – 120 K) (figure 7) and the compounds remain ferromagnetic down to 5 K (figure 8). This third magnetic state, named FM3, originates from Co^{3+} – O – Co^{4+} ferromagnetic superexchange interactions, in agreement with Kanamori Goodenough rules. In summary, these results show that the $\text{LnBaCo}_2\text{O}_{5.50+\delta}$ oxides exhibit very rich phase diagrams as illustrated in figure 9. The latter shows the influence of oxygen deficiency or

excess upon the nature of ferromagnetism in those systems, the nature of the structure being only slightly affected by the displacement of one oxygen atom, probably at the level of the $\text{LnO}_{5.50+\delta}$ layers ($\delta > 0$ or < 0).

Figure 4. $M(H)$ curves of $\text{LnBaCo}_2\text{O}_{5.5+\delta}$ at a few selected temperatures. Parts b–f show the steplike feature of the $M(H)$ curve whose origins are explained.

Figure 5. Magnetization as a function of temperature measured at 100 Oe applied field for (i) $\text{EuBaCo}_2\text{O}_{5.33}$ and (ii) $\text{SmBaCo}_2\text{O}_{5.31}$. The solid (open) symbols correspond to ZFC (FC) data.

Figure 6. $M(H)$ curves of $\text{EuBaCo}_2\text{O}_{5.33}$ at (a) 2 and (b) 200 K, whereas (c) and (d) show the same curve of $\text{SmBaCo}_2\text{O}_{5.31}$ at 5 and 200 K, respectively.

Another fascinating behaviour in the magnetic properties of these oxides is developed by the substitution effect, which takes place either on A-site (Aurelio *et al* 2007; Seikh *et al* 2008b) or on B-site (Khalyavin *et al* 2004; Raveau *et al* 2006a, b). The substitution of Eu by Ca in $\text{Eu}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5}$ highly destabilizes the low tempe-

Figure 7. Magnetization curves measured at 100 Oe for (a) $\text{EuBaCo}_2\text{O}_{5.57}$, (b) $\text{EuBaCo}_2\text{O}_{5.65}$, (c) $\text{SmBaCo}_2\text{O}_{5.59}$, and (d) $\text{SmBaCo}_2\text{O}_{5.65}$. The solid (open) symbols correspond to ZFC (FC) data. The inset in (a) displays an H - T diagram generated from $M(H)$ curves for $\text{EuBaCo}_2\text{O}_{5.57}$. C-AF in insets represents the canted-antiferromagnetic phase.

Figure 8. $M(H)$ curves of (a) $\text{EuBaCo}_2\text{O}_{5.57}$ at 250 K, (b) $\text{EuBaCo}_2\text{O}_{5.65}$ at 90 and 110 K, (c) $\text{SmBaCo}_2\text{O}_{5.59}$ at 110 and 120 K and (d) $\text{SmBaCo}_2\text{O}_{5.65}$ at 5 K.

rate characteristic antiferromagnetic state of $\text{LnBaCo}_2\text{O}_{5.5\pm\delta}$ and expands the ferromagnetic state below T_C to the lowest temperatures (Seikh *et al* 2008b) as shown in figure 10. Not only that, the T_C linearly increases with the increase in calcium content. Interestingly, the calcium substitution does not change the average cobalt valence, which remains +3 due to variation in oxygen content. Consequently, the observed ferromagnetism in these substituted samples was explained on the basis of cobalt disproportionation, $2\text{Co}^{3+} \leftrightarrow \text{Co}^{4+} + \text{Co}^{2+}$, which gets facilitated in the presence of calcium due to the change in local crystal field. The resulting Co^{4+} ions are responsible for ferromagnetism via $\text{Co}^{3+}\text{--O--Co}^{4+}$ ferromagnetic superexchange interactions (Seikh *et al* 2008b). The isovalent substitution of Ba by Ca was also shown to destabilize the antiferromagnetic phase in $\text{YBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5.5}$ resulting in a ferrimagnetic ordering below 190 K (Aurelio *et al* 2007). On the other hand, for the Co-site substituted $\text{EuBaCo}_{1.92}\text{M}_{0.08}\text{O}_{5.5-\delta}$ ($\text{M} = \text{Zn}$ and Cu), profound changes in the magnetic behaviour are observed (Raveau *et al* 2006a). They suggest the formation of superparamagnetic clusters within the antiferromagnetic matrix below 40 K, which are associated with the IS Co^{3+} species. Moreover, it was reported that the substitution of Ni for Co enhances significantly the ferromagnetism in the Eu-phase (Raveau *et al* 2006b). More interestingly, ultrasharp magnetization multisteps were observed in these doped systems (figure 11), which were explained by the pinning effect of the Zn^{2+} and Cu^{2+} cations at the narrow domain walls of the ferromagnetic phase (Raveau *et al* 2006a). Such multisteps, observed in $\text{EuBaCo}_{1.85}\text{Ni}_{0.15}\text{O}_{5.57}$ below 5 K, were attributed to the domain-wall

Figure 9. Phase diagram of (a) $\text{SmBaCo}_2\text{O}_{5.50+\delta}$ and (b) $\text{EuBaCo}_2\text{O}_{5.50+\delta}$ showing different regions including FM1, FM2 and FM3, paramagnetic insulator (PMI), paramagnetic metal (PMM), canted antiferromagnetic (CAF) and antiferromagnetic insulator (AFI).

motion in a 'strong pinning' ferromagnetic system, which is very different from any metamagnetic transition previously observed in manganites. The Ni^{2+} species change the local crystal field dramatically and induce a very effective pinning of the narrow domain walls at low temperature, responsible for the very sharp and large steps observed for the oxide $\text{EuBaCo}_{1.85}\text{Ni}_{0.15}\text{O}_{5.57}$ (Raveau *et al* 2006b).

5. Magnetoresistance

After the discovery of giant magnetoresistance in $\text{LnBaCo}_2\text{O}_{5.50}$ oxides (Martin *et al* 1997), several studies were devoted to the study of this property (Maignan *et al* 1997; Respaud *et al* 2001; Khalyavin *et al* 2003; Taskin *et al* 2003, 2005; Zhou *et al* 2004; Zhou and Schlottmann 2005; Aurelio *et al* 2006; Seikh *et al* 2008b). The origin of this effect may be linked to the competition between ferromagnetism and antiferromagnetism that appears in these systems. In the systems with competing magnetic orders, a magnetic field that favours one kind of ordering often causes also a large magnetoresistance. Consequently, the charge transport in the system turns out to be very sensitive to both, the ferromagnetic and antiferromagnetic

ordering, and magnetic fields readily induce a giant magnetoresistance by affecting the subtle antiferromagnetic–ferromagnetic balance (Respaud *et al* 2001; Taskin *et al* 2003, 2005). In spite of the apparent similarity with manganites, the origin of magnetoresistance in cobaltites must be very different, since there is no insulator to metal transition by applying a magnetic field, indicating that double exchange cannot be the driving force for magnetoresistance in cobaltites. Similarly it was shown that spin-valence effects, i.e. tunnelling between spin polarized metallic regions could not be at the origin of magnetoresistance in these compounds (Taskin *et al* 2005). The different activation energy in the antiferromagnetic and ferromagnetic phase is at the origin of the MR effect in these cobaltites (Taskin *et al* 2005). At a temperature lower than T_{IM} , the resistivity curves start to exhibit a negative magnetoresistance which is related to the establishment of an antiferromagnetic state (Maignan *et al* 2005).

A large negative MR was found for the field applied along the easy axis, which is believed to arise from the destruction of the long-range order of the t_{2g} orbitals via spin-orbit coupling (Zhou and Schlottmann 2005). The latter appears through the sequence of antiferromagnetic to ferromagnetic transition via a spin flop mechanism. Since in this layered system, anisotropic transport properties are manifested in the single crystals, anisotropy can be expected in the MR effect as well (Khalyavin *et al* 2003; Zhou *et al* 2004; Taskin *et al* 2005; Zhou and Schlottmann 2005). Considerable anisotropy in the isothermal magnetoresistance with regard to the field direction has indeed been observed in $\text{GdBaCo}_2\text{O}_{5.5}$ (Zhou *et al* 2004).

Very recently, it was shown that the substitution of Eu by Ca in $\text{Eu}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.5}$ results in a drastic decrease

Figure 10. $M(T)$ curves of $\text{Eu}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_{5.50\pm\delta}$ registered at 0.3 T: (a) $\text{EuBaCo}_2\text{O}_{5.49}$, (b) $\text{Eu}_{0.95}\text{Ca}_{0.05}\text{BaCo}_2\text{O}_{5.48}$, (c) $\text{Eu}_{0.9}\text{Ca}_{0.1}\text{BaCo}_2\text{O}_{5.44}$ and (d) $\text{Eu}_{0.8}\text{Ca}_{0.2}\text{BaCo}_2\text{O}_{5.41}$. The open (solid) symbols correspond to ZFC (FC) data (taken from Seikh *et al* 2008b).

Figure 11. Magnetic field dependence of the magnetization of $\text{EuBaCo}_{1.85}\text{Ni}_{0.15}\text{O}_{5.57}$ registered at 2 K for three sweep rates of (a) $5 \times 10^{-3} \text{ T s}^{-1}$, (b) 10^{-2} T s^{-1} and (c) $2.5 \times 10^{-2} \text{ T s}^{-1}$ (taken from Raveau *et al* 2006b).

Figure 12. Scenario of the magnetic phase separation vs magnetic field in the '112' cobaltites (a) before applying the magnetic field, (b) as the field is progressively increased, with alignment of the superparamagnetic droplets, (c) FM domain wall motion and (d) alignment of all the spins.

in MR effect, though the system turns into the ferromagnetic state (Seikh *et al* 2008b). In the Ca-doped samples the development of local ferromagnetic states facilitates the carrier hopping, which in turn brings local spin polarization. Such an already spin polarized state could be responsible for lower MR effect with the increase in x .

6. Phase separation

Like many other strongly correlated systems, the $\text{LnBaCo}_2\text{O}_{5.50+\delta}$ cobaltites exhibit phase separation, as reported by many authors (Akahoshi and Ueda 2001; Taskin *et al* 2005; Aurelio *et al* 2006; Raveau *et al* 2006a, b; Seikh *et al* 2008a, b). Generally phase separation takes place at lower temperatures, due to the instability of homogeneous carrier distribution. In this complex magnetic system there exists competing ferromagnetic and antiferromagnetic interactions and the delicate balance between these two states is strongly affected by temperature, doping or magnetic field. It was suggested that the $\text{GdBaCo}_2\text{O}_{5+\delta}$ system exhibits interesting nanoscopic phase separation into two insulating phases in the electron-doped regime, whereas an insulating and a metallic phase is marked in the hole-doped region (Taskin *et al* 2005). The variation in oxygen content plays a significant role to drive the phase separation in this system (Akahoshi and Ueda 2001; Taskin *et al* 2005). The relaxation of the lattice distortion caused by the charge ordering triggers phase separation (Akahoshi and Ueda 2001). To explain the magnetic data of the Sm- and Eu-phases, a phase separation scenario was proposed (Seikh *et al* 2001a), where the ferromagnetic domains are implanted within the antiferromagnetic matrix.

The study of the phases $\text{EuBaCo}_{1.92}\text{M}_{0.08}\text{O}_{5.5+\delta}$ doped with $\text{M} = \text{Co}, \text{Ni}$ or Cu (Raveau *et al* 2006a, b) allows a pictorial presentation of the phase separation and its dependence on magnetic field to be proposed (figure 12).

In this scenario, superparamagnetic droplets and small compensated ferromagnetic regions are first embedded in an antiferromagnetic matrix (figures 9a–b), and the displacement of the domain walls within the FM domains (figures 9c–d) is then considered, explaining the appearance of ferromagnetism with a magnetic moment much smaller than the one expected. In Ca-doped $\text{EuBaCo}_2\text{O}_{5.50+\delta}$, the divergence of zero field cooled and field cooled magnetization data and a large thermomagnetic hysteresis loop below T_C were attributed to the existence of phase separation, i.e. the presence of independent ferromagnetic regions in an antiferromagnetic matrix (Seikh *et al* 2008b). A possible phase separation scenario, involving the formation of canted antiferromagnetic domains in the high temperature paramagnetic phase was also proposed.

7. Conclusions

The investigation of ordered oxygen deficient '112' cobaltites, $\text{LnBaCo}_2\text{O}_{5.50+\delta}$, shows great potential of these systems for the generation of new magnetic transitions and new ferromagnetic states which are so far not com-

pletely understood. These results emphasize the crucial influence of oxygen stoichiometry upon such properties, which make that the control of oxygen content in these phases is absolutely necessary for the interpretation of their physical properties. The distribution of the oxygen vacancies or excess with respect to the ideal formula, $\text{LnBaCo}_2\text{O}_{5.5}$, is also a very important issue, which should be explored carefully using neutron diffraction and electron microscopy, in order to understand the existence of local structural distortions and their influence upon the complex magnetic transitions. The issues of phase separation and spin transitions in these systems are still a matter of debate.

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