The structural, magnetic and electrical properties of the hole-doped cobaltites La$_{0.7}$(Ca$_{1-x}$Ba$_x$)$_{0.3}$CoO$_3$ (x = 0.0, 0.5 and 1.0)

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R Ganguly, M Hervieu, N Nguyen, A Maignan, C Martin and B Raveau

Laboratoire CRISMAT, ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

Abstract
We have studied the structural, magnetic and electrical properties of hole-doped cobaltites with compositions, $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0). Due to the large difference in size between the Ca and Ba ions (size mismatch), these compounds show interesting changes in the magnetic and transport behaviours with an increase in the concentration of Ba. The distortion in the perovskite structure decreases with the substitution of Ba for Ca. Magnetic studies indicate that the anisotropy in their ferromagnetic characters, which contribute to the observations of large thermomagnetic irreversibilities and large coercive fields in these compounds, change significantly with the substitution of Ba for Ca. The unusual magnetic behaviour of the $La_{0.7}Ba_{0.3}CoO_3$ compound, as reflected in its $M–H$ behaviour, has been explained on the basis of a possible coexistence of different magnetic phases. Observations of the low-temperature resistivity minimum, and negative magnetoresistance up to 26% in the low-temperature insulating regions of these polycrystalline compounds, have been ascribed to grain boundary effects.

1. Introduction

Discoveries of high-temperature superconductivity in the layered cuprates and colossal magnetoresistance in perovskite manganites have created a renewed interest in the transition metal based oxides with strongly correlated electrons. The perovskite cobaltites, with their evolution of physical properties as a function of hole doping being similar to that observed in perovskite manganites, have also been of current interest [1–23]. Although, like manganites, they exhibit doping induced ferromagnetic and metallic characteristics, the nature of their ferromagnetic state has been much discussed due to the unusually large thermomagnetic irreversibilities exhibited by them in the ferromagnetic state. Itoh *et al* [4], from their magnetic relaxation studies on $La_{1-y}Sr_yCoO_3$ ($0.0 \leqslant y \leqslant 0.5$), suggested that the large thermomagnetic irreversibilities exhibited by these compounds is indicative of the absence of long-range ferromagnetic order, and explained these on the basis of either spin glass

behaviour ($0.0 \leqslant y \leqslant 0.18$) or cluster glass behaviour ($0.2 \leqslant y \leqslant 0.5$). Mira *et al* [5], from their dc magnetic studies on $La_{1-y}Sr_yCoO_3$ ($0.0 \leqslant y \leqslant 0.3$) also claimed that long-range ferromagnetic order cannot exist in these compounds. Separate neutron diffraction studies [6,7], however, have shown that long-range ferromagnetism exists in these compounds at a Sr concentration as low as 0.1 [6] and up to $x = 0.5$ [7]. Recent studies on the compound $La_{0.5}Sr_{0.5}CoO_3$ ($x = 0.5$) [8, 9] have shown that, although it exhibits a paramagnetic-to-ferromagnetic transition at about 250 K, it undergoes a cluster glass freezing below the ferromagnetic transition temperature (T_C), as reflected in the frequency dependence in its linear and nonlinear ac magnetic susceptibility behaviours in the low-temperature region. From the coercive field (H_C) versus temperature behaviour of the same compound, however, Kumar *et al* [10] have explained the observations of large hysteresis in its $M-H$ loop and the thermomagnetic irreversibility on the basis of the anisotropic nature of its ferromagnetic character. A similar explanation has been given for the observation of large thermomagnetic irreversibilities and large hysteresis in the $M-H$ loops in the compounds, $La_{0.7}A_{0.3}CoO_3$ (A = Ca, Sr, Ba) [11]. The unusual properties of the cobaltites are also reflected in the observation of giant anisotropic magnetostriction [12], which has been explained on the basis of a spin state transition from low spin (LS, $t_{2g}^6 e_g^0$) Co(III) with spherical electron cloud and zero orbital moment to the Jahn–Teller (J–T) distorted intermediate spin (IS, $t_{2g}^5 e_g^1$) Co(III) ion with finite orbital moment. Most of the studies on the spin states of Co ions suggest that the trivalent and tetravalent Co ions remain as a mixture of LS or IS states [13–16]. The presence of the IS ions with finite orbital moment, as observed from the magnetic circular dichroism spectroscopy [15], and thus with spin orbit coupling, could be the source of anisotropic exchange interaction in these compounds, as has been suggested in the literature [11].

A systematic study [11] of the effect of the average size of cations at the rare-earth site (r_A) of the hole-doped cobaltites at a constant level of hole doping has revealed that the hysteresis in their $M-H$ behaviours, and their thermomagnetic irreversibilities, increases as the value of the ferromagnetic transition temperature decreases, with a simultaneous increase in the distortion of the perovskite structure. X-ray diffraction patterns show that the rhombohedral distortion in the perovskite structure decreases with an increase in the average size of the ions at the rare-earth site from $La_{0.7}Ca_{0.3}CoO_3$ to $La_{0.7}Sr_{0.3}CoO_3$, and then further to $La_{0.7}Ba_{0.3}CoO_3$, which is finally cubic [11]. T_C first increases as the structural distortion decreases from $La_{0.7}Ca_{0.3}CoO_3$ to $La_{0.7}Sr_{0.3}CoO_3$, but then decreases to $La_{0.7}Ba_{0.3}CoO_3$. The decrease in the value of T_C from $La_{0.7}Sr_{0.3}CoO_3$ to $La_{0.7}Ba_{0.3}CoO_3$ has been explained on the basis of an increased distortion in the perovskite structure of $La_{0.7}Ba_{0.3}CoO_3$ due to large size mismatch of the La^{3+} and Ba^{2+} ions at the rare-earth site, similarly to the mismatch effects in the manganites [24]. Due to the random nature of that distortion, it is not reflected in the XRD patterns of the compounds but has a deteriorating effect on the ferromagnetic exchange interaction. The thermomagnetic irreversibility and the value of the coercive field (H_C) at 5 K increases in the order $La_{0.7}Sr_{0.3}CoO_3 < La_{0.7}Ba_{0.3}CoO_3 < La_{0.7}Ca_{0.3}CoO_3$, as the value of the onset temperature of the ferromagnetic order decreases in the same order. Since, in the case of the $La_{1-x}Sr_xCoO_3$ compounds, the observation of large thermomagnetic irreversibility has always been the subject of several studies, it will also be interesting to study the physical properties of the (La, Ca, Ba)CoO$_3$ system of compounds with even larger thermomagnetic irreversibilities. In this paper, we report on structural, magnetic and electrical resistivity studies of the compounds $La_{0.7}Ca_{0.3}CoO_3$, $La_{0.7}Ca_{0.15}Ba_{0.15}CoO_3$ and $La_{0.7}Ba_{0.3}CoO_3$, keeping the hole doping at constant level. Besides their large thermomagnetic irreversibilities, these compounds show interesting changes in their magnetic and transport properties as the average size of the ions at the rare-earth site varies.

Table 1. The values of the lattice parameters, average size of the ions at the rare-earth site, the Goldsmith tolerance factor (t), the size variance of the ions at the rare-earth site (σ^2), the Co–O–Co and O–Co–O bond angles and the Co–O bond lengths of the compounds of $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0).

| 'x'	a (Å)	α	r_A	't'	σ^2 (Å^2)	Co–O–Co	O–Co–O	$d_{Co–O}$ (Å)
0.0	5.383(3)	60.57(4)°	1.2052	0.9028	0.000 27	162.47(5)°	91.20(2)°	1.936(3)
0.5	5.417(2)	60.38(2)°	1.2487	0.9207	0.008 80	166.88(3)°	90.70(1)°	1.934(3)
1.0	5.457(3)	60.17(2)°	1.2922	0.9361	0.013 50	172.42(5)°	90.04(3)°	1.936(3)

2. Experimental details

The compounds of compositions, $La_{0.7}Ca_{0.3}CoO_3$, $La_{0.7}Ca_{0.15}Ba_{0.15}CoO_3$ and $La_{0.7}Ba_{0.3}CoO_3$, which will henceforth be denoted by 'Ca', 'Ca, Ba' and 'Ba', respectively, for convenience, were prepared by solid-state reaction in air between La_2O_3 (dried at 1000 °C), $CaCO_3$, $BaCO_3$ and Co_3O_4 at 1100 °C. X-ray diffraction (XRD) patterns of the compounds were taken in a Philips diffractometer, using Cu K$_\alpha$ radiation. Rietveld refinements of the XRD patterns were carried out using the program Fullprof. Four probe resistivity measurements in the temperature range from 300 to 5 K at magnetic fields of 0 and 7 T were carried out using a quantum design physical property measurement system. Magnetic measurements (ac and dc) were carried out using quantum design SQUID magnetometers ($5 \leqslant T \leqslant 400$ K). The ac susceptibility measurements at different frequencies (1.01, 9.99 and 99.99 Hz) were performed under an ac field of 3 Oe. The dc magnetic susceptibility of the compounds in the temperature region 300–600 K was measured using a Faraday balance with the sample in the He atmosphere. The data collected were corrected for atomic diamagnetism. An electron diffraction study on the 'Ba' sample was carried out at room temperature using a JEOL 200CX electron microscope, equipped with an energy dispersive spectroscopy (EDS) analyser. The sample for this purpose was prepared first by dispersing the crystallites in alcohol, and then by depositing the dispersed particles on a holey carbon film supported by a Cu grid. Numerous crystallites were characterized and analysed by reconstructing the reciprocal space and tilting them around the crystallographic axes. A high resolution electron microscopy (HREM) study was carried out with a TOPCON 002B microscope (200 kV; 1.8 Å point resolution).

3. Results and discussion

The single phase nature of the compounds was confirmed from their XRD patterns. The structural parameters of the three compounds (table 1), obtained from the Rietveld refinement of the XRD data (figure 1), show that all three compounds, i.e. the compounds 'Ca' and 'Ca, Ba' and 'Ba', form with rhombohedrally distorted perovskite structures. Although the XRD pattern of the 'Ba' compound has been indexed on the basis of a cubic structure in the literature [11], a careful analysis of its XRD pattern indicates this compound has a rhombohedral structure. To verify this, we have carried out an electron diffraction (ED) study on this compound, and a typical [001] ED pattern recorded by us is shown in figure 2(a). The visible splitting of reflections generated by the rhombohedral distortion of the cell (black arrows) confirms the rhombohedral structure of the 'Ba' compound. As shown in table 1, the rhombohedral cell angle decreases with the increase in the concentration of Ba. This behaviour is expected in a perovskite system, since the substitution of Ba^{2+} for Ca^{2+}, leads to an increase in r_A and tolerance factor (t) (table 1). For an ABO$_3$ perovskite, the rhombohedral distortion arises in the cubic perovskite structure due to the rotation of the BO$_6$-octahedra around the [111]
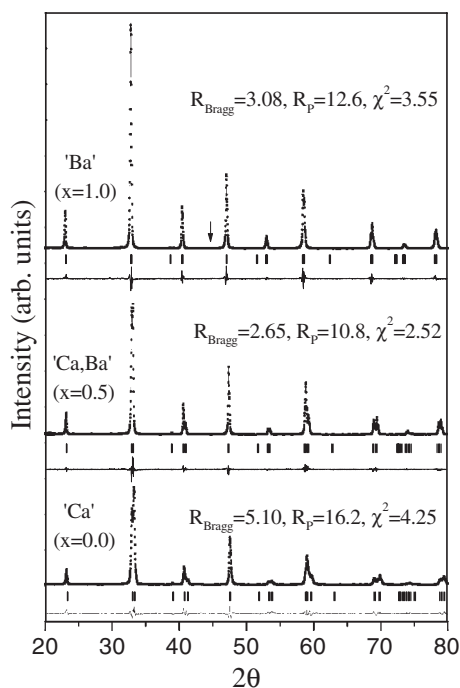
Figure 1. The observed, calculated and difference patterns of the XRD patterns of the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0, 0.5$ and 1.0). The data were fitted on the basis of the rhombohedral space group R–3 C. The agreement factors are shown in the figure.

direction (i.e. the threefold symmetry axis of a cubic structure), and the tolerance factor is defined as $t = r_{A-O}/1.414r_{B-O}$. The decrease in the rhombohedral distortion with increasing r_A is accompanied by an increase in the equatorial Co–O–Co bond angle (table 1 and figure 3), approaching $180°$ (the value for the bond angle in the cubic structure). The value of the O–Co–O bond angle, which is the measure of the distortion in the CoO_6-octahedra, decreases with an increase in the concentration of Ba (figure 3), approaching $90°$, the value for the undistorted perovskite structure. The Co–O bond length, however, remains almost the same for all three compounds studied. In the case of $La_{1-y}Sr_yCoO_3$ also, a decrease in the rhombohedral distortion, due to an increase in Sr concentration, is accompanied by an increase in the O–Co–O bond angle, a decrease in the O–Co–O bond angle, and a constant value of the Co–O bond length for $0.1 \leqslant y \leqslant 0.3$ [6, 7]. The values of the bond angles, O–Co–O and Co–O–Co, for 'Ca, Ba' are very close to those reported for $La_{0.7}Sr_{0.3}CoO_3$ ($r_A = 1.2442$ Å) [6], whose r_A value is close to that of 'Ca, Ba' ($r_A = 1.2487$ Å).

Figure 4 shows plots of dc magnetization versus temperature for all three compounds taken under field cooled (FC) and zero field cooled (ZFC) conditions. The ferromagnetic transition temperature increases significantly from 'Ca' to 'Ca, Ba', but thereafter decreases a little to 'Ba'. All three compounds show large thermomagnetic irreversibilities at a field as high as 3000 Oe of applied field. The observed thermomagnetic irreversibilities are much higher than that observed in $La_{0.7}Sr_{0.3}CoO_3$, which shows very little thermomagnetic irreversibility at 3000 Oe of applied field [11]. The thermomagnetic irreversibility decreases significantly as the average size of the ions at the rare-earth site increases from 'Ca' to 'Ca, Ba' and then remains almost the same with a further increase in r_A to 'Ba'. The large thermomagnetic irreversibilities in 'Ca' and 'Ba' have been explained in the literature on the basis of the anisotropic nature of the the ferromagnetic character, as reflected in their coercive field (H_C) versus temperature behaviours [11]. The very large slope observed in the FC magnetization

(a)

(b)
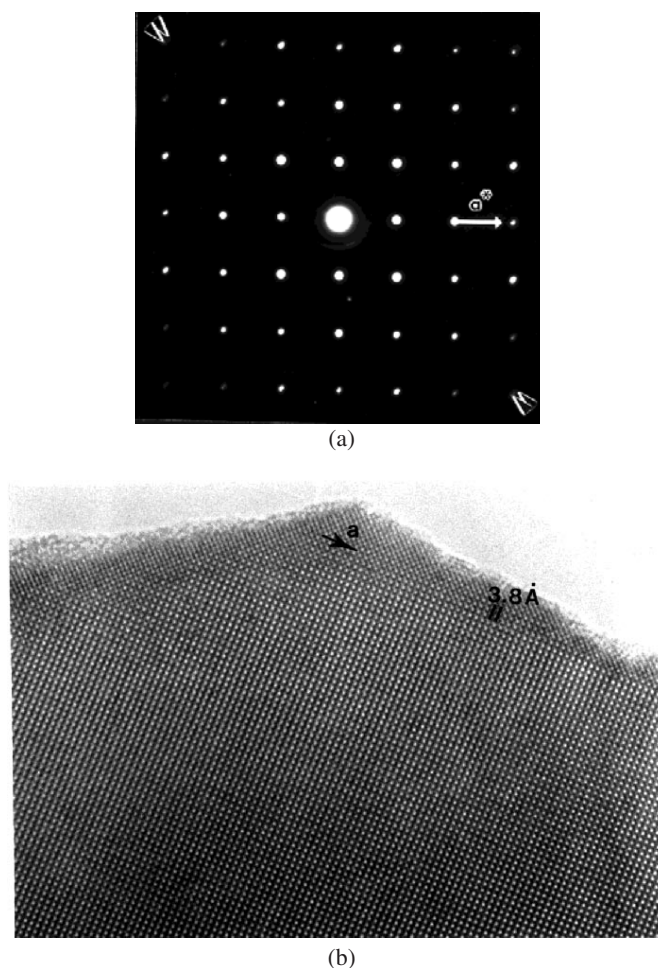
Figure 2. (a) The ED pattern, and (b) the HREM image of the compound $La_{0.7}Ba_{0.3}CoO_3$ ('Ba').

of the 'Ca' compound extending up to 5 K shows the presence of a high degree of anisotropy in its ferromagnetic character [23]. For the 'Ca, Ba' and 'Ba' compounds, the reduced slopes of the FC magnetization plots indicate the presence of a reduced anisotropy as compared to that in the 'Ca' compound. Figure 5 shows the magnetization versus field behaviours of the compounds at 5 K. For all three compounds the magnetization is not saturated even at a field as high as 5 T. The slopes which are maintained by the magnetizations of the compounds at high field, in the virgin magnetization plots of the compounds, reflect the anisotropic nature of the ferromagnetism in them. The observation of a very large slope in the virgin plot and a large value of coercive field (H_C) of about 6500 Oe, for the 'Ca' compound, again indicates the presence of a very large degree of anisotropy in it. The 'Ca, Ba' and the 'Ba' compounds with their reduced anisotropy (as reflected in the reduced slope in the virgin magnetization plots) shows much lower values of coercive fields (table 2). In the ferromagnetic manganites and cobaltites a decrease in T_C as a result of various site selective substitutions is generally accompanied by an increase in H_C values and a decrease in the M_S values. This is not the case here, where the 'Ba' compound, which exhibits a lower T_C than the 'Ca, Ba' compound (as observed more
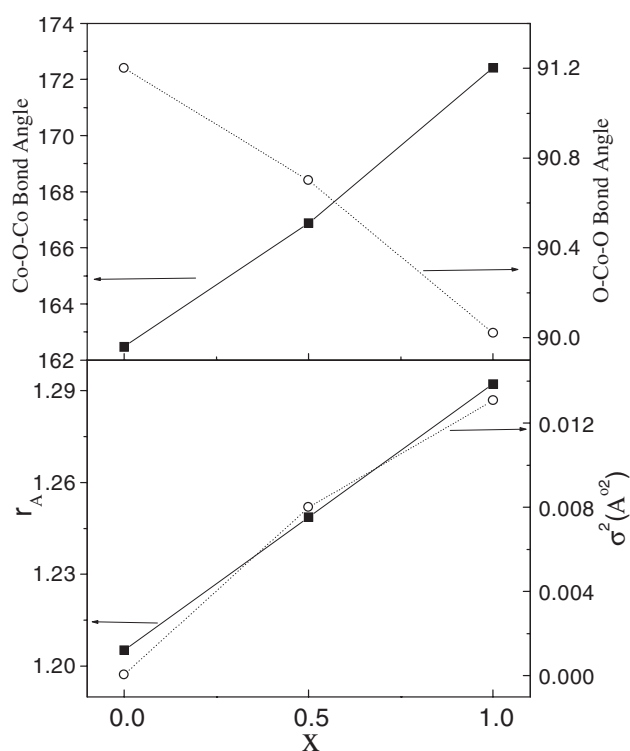
Figure 3. Plots for the Co–O–Co and O–Co–O bond angles, the average size of the ions at the rare-earth site (r_A) and the size variance of the ions at the rare-earth site (σ^2), as a function of 'x', for the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0, 0.5$ and 1.0).

clearly from the ac susceptibility behaviours, discussed later) shows a lower value of H_C and a higher value of M_S. This difference in behaviour probably arises from the change in the degree of anisotropy in the ferromagnetic character with the increase in the concentration of Ba. The source of anisotropy in the cobaltites is not clearly understood yet. It has been argued that the presence of IS Co^{4+} and Co^{3+} ions [11] with electronic configurations $t_{2g}^4 e_g^1$ and $t_{2g}^5 e_g^1$, respectively, and with spin orbit coupling could be the source of the anisotropic nature of the ferromagnetic exchange interaction in them. In the perovskite cobaltites the presence of these ions, which are J–T ions, is reflected in the observation of strong J–T distortion from the pulsed neutron diffraction studies carried out by Louca *et al* [13]. A recent study by Yoshi *et al* [15] also confirms the presence of orbital moment of the Co ions in the hole-doped perovskite cobaltites and explains them on the basis of the presence of IS Co ions. The large anisotropic magnetostriction observed in $La_{1-y}Sr_yCoO_3$ by Ibarra *et al* [12] was also explained on the basis of the conversion of LS trivalent Co ions with zero orbital moment to the IS trivalent Co ions with non-zero orbital moment. The observations of a large increase in hysteresis and thermomagnetic irreversibility upon substitution of Co for Mn in $La_{0.67}Ca_{0.33}MnO_3$ [25] and a very large coercivity in the ferrimagnetic $LaCo_{0.5}Mn_{0.5}O_3$ [26] also reflects the ability of Co ions to induce anisotropy in exchange interaction in the ferromagnetic characters of the manganites.

Besides the change in H_C and M_S, the present compounds show an interesting change in the character of the M versus H loop as r_A increases. This is reflected in the position of the 'virgin'
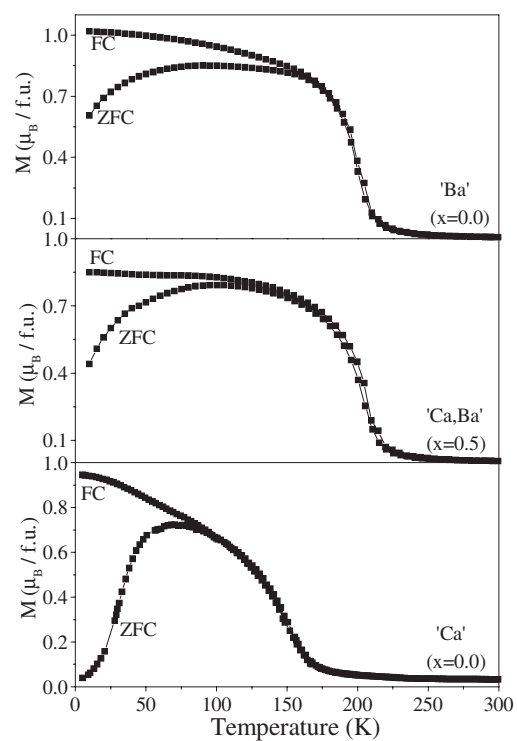
Figure 4. Plots of dc magnetization versus temperature under ZFC and FC conditions for the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0) recorded at 3000 Oe of applied field.
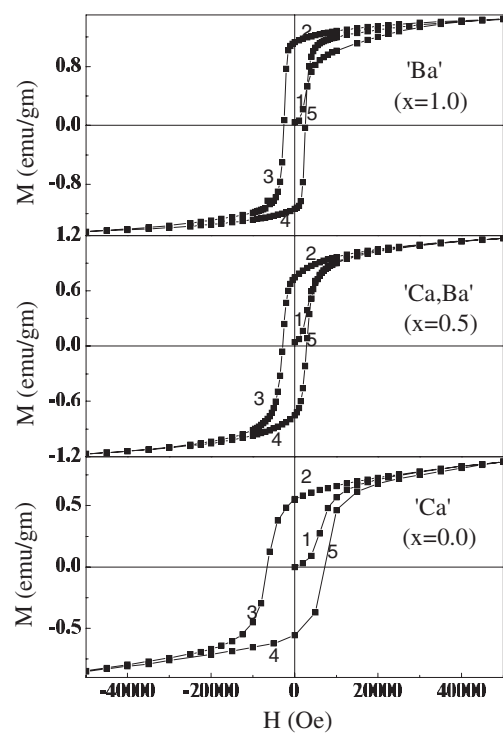
Figure 5. The M versus H loop for the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0) recorded at $T = 5$ K.

magnetization curve (marked '1') with respect to the loop area. The 'virgin' curve remains well within the loop in the case of the 'Ca' compound, but changes its position significantly with the substitution of Ba for Ca. For the 'Ca, Ba' compound, it lies at the loop boundary being very close to curve '5' and, in the case of the 'Ba' compound, it lies almost completely outside the loop. Such a behaviour, which is indicative of an irreversible transformation of the magnetic phase by the application of magnetic field, when the 'virgin' magnetic curve is recorded, has been reported in the case of the hole-doped perovskite manganite, $Pr_{0.7}Ca_{0.25}Sr_{0.05}MnO_3$, with two coexisting magnetic phases [27]. The hysteresis loops for the present compounds thus suggest that the substitution of Ba for Ca leads to magnetic phase separation with coexisting magnetic phases, the ferromagnetic phase being one of them. The other magnetic phase or phases are converted irreversibly into the ferromagnetic phase at high field leading to the observed behaviour of displacement of the virgin curve with respect to the loop. In the case of the $Ln_{1-x}Ba_xCoO_3$ systems (Ln = rare earth), the samples with $x = 0.5$, prepared by solid-state reaction, do not form with a perovskite structure [28]. Due to a large difference in the size between the rare-earth and barium ions, they form with a 112 type structure ($LnBaCo_2O_{5+\delta}$) with complete ordering of the rare-earth and barium ions [28]. These compounds also show charge ordering between Co^{2+} and Co^{3+} ions below certain temperatures. In the present case, although the 'Ba' compound forms with a perovskite structure, we have carried out a HREM study on it to see whether there is any short-range ordering of the lanthanum and barium ions in it, leading to the presence of a short-range charge-ordered phase. A typical HREM image recorded for a focus value, where the La and Ba ions appear as brightest dots, is shown in figure 2(*b*). The regular contrast of the image gives evidence of the random distribution of the lanthanum and barium ions without the presence of any local ordering even at short range, thus asserting that there is total disordering of the these two ions. This suggests that the second magnetic phase is not likely to be a charge-ordered phase. The presence of a second magnetic phase is not reflected in the magnetization versus temperature plots probably because of the presence of the ferromagnetic phase as a dominant phase, leading to a large increase in magnetization in the *M* versus *H* behaviour in the low field region. Although the coexistence of different magnetic phases is quite common in the case of hole-doped manganites, this kind of behaviour has not been observed for hole-doped cobaltites so far. Further studies are necessary to understand the magnetic nature of these Ba-substituted compounds.

From their magnetic studies on $La_{0.5}Sr_{0.5}CoO_3$, Kumar *et al* [10] have explained its large thermomagnetic irreversibility on the basis of the anisotropic nature of the ferromagnetic character. However, recent reports [8, 9] have also shown that, although this compound exhibits a paramagnetic-to-ferromagnetic transition, its magnetic domains undergo cluster glass freezing in the low-temperature region below T_C. Although its freezing phenomenon is not reflected in the frequency dependence of its χ' versus temperature behaviour, it is clearly observed in the frequency dependence of its χ'' versus temperature behaviour. So, to understand whether such freezing phenomena also occur in the present compounds with weaker ferromagnetic exchange interactions and with larger thermomagnetic irreversibilities than those observed in the $La_{1-y}Sr_yCoO_3$ compounds, we have studied the frequency dependence of the χ' and χ'' versus temperature behaviours of the compounds at 3 Oe of applied field, as shown in figure 6. Although for all three compounds a sharp drop in magnetization is observed below the ferromagnetic onset temperature, leading to the formation of cusps, no frequency dependences of the cusp temperatures are observed in both the χ' and χ'' versus temperature behaviours. This suggests that these compounds do not undergo any cluster glass freezing below the ferromagnetic transition temperature. The sharp cusp exhibited by these compounds probably results from the anisotropic nature of the ferromagnetism of these compounds, as was explained previously for the $La_{1-y}Sr_yCoO_3$ compounds [21].

Table 2. The values of the ferromagnetic transition temperature (T_C), the coercive field, (H_C), the effective magnetic moment (μ_{eff}), and the resistivities at 300 K ($\rho_{300\ K}$) and 5 K ($\rho_{5\ K}$) for the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0).

'x'	T_C (K)	H_C (Oe)	M (5 T) (μ_B)	μ_{eff} (μ_B)	$\rho_{300\ K}$ (Ω cm)	$\rho_{5\ K}$ (Ω cm)
0.0	170	6500	0.89	3.49	0.001 63	0.001 63
0.5	212	2893	1.42	3.40	0.001 56	0.001 56
1.0	206	2544	1.37	3.34	0.001 11	0.001 11

Since these plots show sharper ferromagnetic transitions than those we have observed in the dc magnetization behaviour at high field, they give a clearer picture about the variation of the ferromagnetic transition temperature with the increase in r_A (table 2). T_C increases significantly from 'Ca' to 'Ca, Ba', as is observed from the dc magnetization behaviour but a small decrease in T_C, from 'Ca, Ba' to 'Ba', which was not clear from the dc magnetization behaviour, is clearly observed in these ac magnetization plots. These results are similar to those reported for the series of samples of compositions, $La_{0.7}Ca_{0.3}CoO_3$, $La_{0.7}Sr_{0.3}CoO_3$ and $La_{0.7}Ba_{0.3}CoO_3$, where the value of T_C does not increase monotonically with the average size of the ions at the rare-earth site, but shows a maxima at $La_{0.7}Sr_{0.3}CoO_3$ [11]. It is known that, for these perovskite cobaltites, the ferromagnetic transition temperature (T_C) depends significantly on the Co–O–Co bond angle, as the ferromagnetic exchange between the Co ions is mediated through the oxygen ions [6, 7]. The maxima in T_C at $La_{0.7}Sr_{0.3}CoO_3$, as mentioned above, results from the competitive effects of the increase in the average size of the ions at the rare-earth site, i.e. an increase in the value of tolerance factor, which reduces the cooperative distortion in the perovskite structure, and an increase in the size mismatch at the rare-earth site (r_A), which increases the local distortion in the perovskite structure in the form of random displacement of the oxygen ions around the Co ions. The size mismatch at the rare-earth site could be expressed in terms of variance of the ions at the rare-earth site (σ^2), expressed as $\Sigma y_i r_i^2 - \langle r_A \rangle^2$ [11, 24], where y_i is the fractional occupancies and r_i is radius of the ions occupying the rare-earth site. The σ^2 values along with the values of r_A of the compounds are given in table 1. Although the $La_{0.7}Sr_{0.3}CoO_3$ ($r_A = 1.244$ Å), and the compound 'CaBa' ($r_A = 1.2487$ Å) in the present case, have very close r_A values, the latter compound shows a lower T_C because of its higher σ^2 value (0.008 80 Å^2) than the $La_{0.7}Sr_{0.3}CoO_3$ ($\sigma^2 = 0.001 35$ Å^2) [11]. Similarly, the close value of T_C of the 'Ba' and the 'Ca, Ba' compounds, in spite of the fact that the tolerance factor value of the former is much higher than the latter, can be explained on the basis of the higher σ^2 value of the 'Ba' compound.

Figure 7 shows the $1/\chi$ versus temperature behaviour of the compounds in the paramagnetic region. All the compounds show a Curie–Weiss behaviour in the temperature range studied, thus suggesting that the ratio of the occurrence of different spin states remain constant in that temperature region. The μ_{eff} values, calculated from the slope of the plots, are close to those reported for the compound, $La_{0.7}Sr_{0.3}CoO_3$, with the same hole content as in the present case (table 2). Although for the present compounds, the hole concentrations remain constant, we found that μ_{eff} values show a decreasing trend in the order 'Ca' > 'Ca, Ba' > 'Ba'. Such an increase in the μ_{eff} value with a decrease in the value of r_A have very recently been reported by Paraskevopoulos *et al* [29], for the rare-earth based hole-doped perovskite cobaltites. These authors have attributed this behaviour to the polaronic effect on the μ_{eff} value, arising from the presence of dynamic J–T distortion in these cobaltites [13]. According to them, the samples with lower values of r_A are more insulating in nature and so
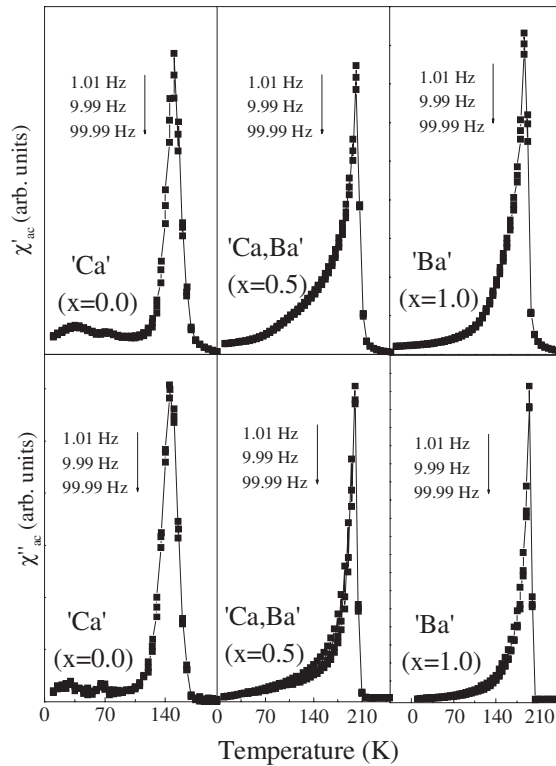
Figure 6. The real (χ') and imaginary (χ'') parts of the linear ac susceptibility versus temperature behaviours of the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0) at 1.01, 9.99 and 99.99 Hz ac frequencies.

the enhancement of the μ_{eff} value due to the polaronic effect is more effective in them. In the present case, although the resistivity of the compounds studied by us are of the same order at room temperature (300 K), the plots of resistivity versus temperature (figure 8) clearly show a decrease of the insulating character in the same order as the decrease in the μ_{eff} value, i.e. 'Ca' > 'Ca, Ba' > 'Ba'. The compound 'Ca' with the highest $\rho_{5\,K}$ value shows a maximum μ_{eff} value, whereas the compound 'Ba' with the lowest $\rho_{5\,K}$ value shows a minimum μ_{eff} value (table 2).

Plots of resistivity versus temperature of the compounds are shown in figure 8. The effect of the average size of the ions at the rare-earth site does not have much effect on the room temperature resistivity ($\rho_{300\,K}$) values of the compounds, as they are of the same order. The room temperature semiconductor-like behaviour ($d\rho/dT < 0$) of the 'Ca' compound changes to a metal-like behaviour ($d\rho/dT > 0$) below the ferromagnetic transition temperature. In the literature, a report [30] shows that, in the epitaxial thin-film form, the 'Ca' compound shows a much lower room temperature resistivity and shows a metal-like behaviour from room temperature down to low temperature. A similar difference in behaviour in the single-crystal and polycrystalline forms has been observed in $Sm_2Mo_2O_7$, which has been explained on the basis of additional carrier scattering in the grain boundaries in the polycrystalline form [31]. The 'CaBa' and 'Ba' compounds exhibit metal-like behaviour at room temperature and show a faster decrease in ρ below T_C due to the reduction of the spin disorder scattering. All three compounds, however, show a resistivity minimum with a decrease in temperature below the
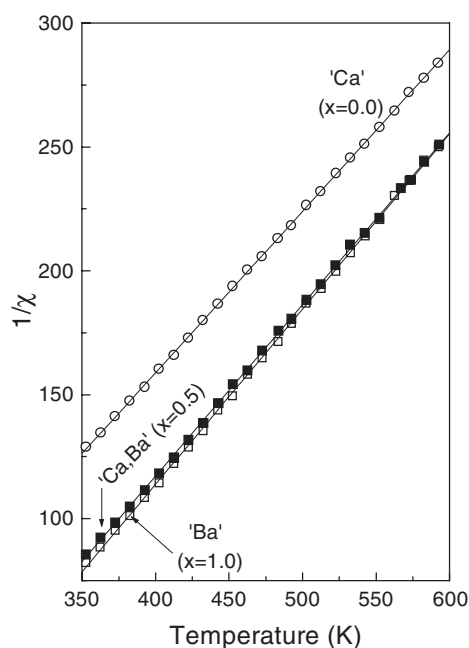
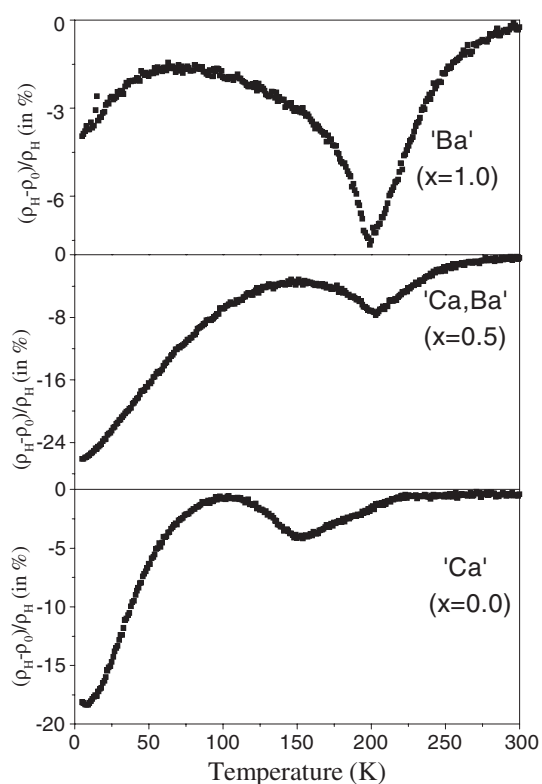**Figure 7.** Plots of $1/\chi$ versus temperature for the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0).
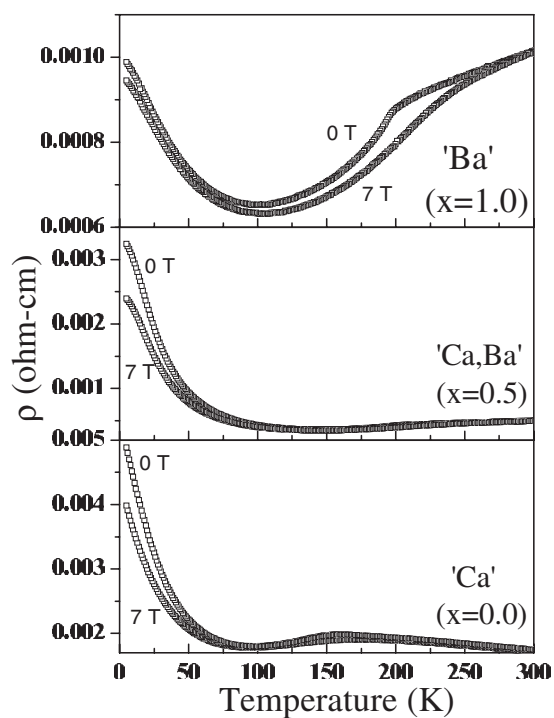
Figure 8. Plots of resistivity versus temperature for the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0) at 0 and 7 T magnetic fields.

ferromagnetic transition temperature, similar to the behaviours exhibited by the disordered metallic systems. The low-temperature insulator-like behaviour of these compounds is not governed by an Arrhenius-type or any other activated hopping behaviour. A similar behaviour observed in perovskite manganites has been explained on the basis of quantum correction to

the electrical resistivity behaviour arising out of electron–electron interaction in a disordered metallic system [32]. The insulating behaviour of the present compounds cannot be fitted to the equation also governing that behaviour. In the literature, similar occurrences of the resistivity minimum in polycrystalline $La_{1-y}Sr_yCoO_3$ ($0.2 \leqslant y \leqslant 0.3$) compounds have been explained on the basis of spin state transitions of the Co^{3+} ions from higher spin states (HS or IS) to the LS state in the weakly conducting hole-poor matrix regions, which separate the highly conducting hole-rich regions [6, 19, 21]. According to Senaris-Rodriguez and Goodenough [19], since the IS Co^{3+} ions of the hole-poor matrix regions mediate the electrical conductivity between the hole-rich regions, their progressive conversion to the LS state with a decrease in temperature, destroys the metallic character below a certain temperature. Since in the case of the $La_{1-y}Sr_yCoO_3$ ($0.2 \leqslant y \leqslant 0.3$) compounds the onset of the insulating characteristics are observed near or below the temperature of the spin state transition in the undoped $LaCoO_3$ (≈ 100 K), Mahendiran and Raychaudhuri [21] ascribed them to HS–LS transitions of the Co ions. However, the observation of the resistivity minimum at about 150 K for the 'Ca, Ba' compound indicates that it may arise due to such spin state transition. For the compounds, $La_{1-y}Sr_yCoO_3$, in the composition range $0.2 \leqslant y \leqslant 0.3$ [19, 21], an increase in hole concentration (y) results in a decrease in the temperature of the onset of the insulating characteristic and an increase in the value of T_C. In the present case, however, the 'Ca, Ba' compound, with higher T_C than the 'Ba' compound, shows the onset of the insulating characteristic at a much higher temperature. This also indicates that the temperature of the resistivity minimum is not correlated with the value of the ferromagnetic transition temperature. Interestingly, the occurrences of the above-mentioned resistivity minimum are limited only to the polycrystalline forms of the hole-doped cobaltites. The compounds of compositions, $La_{1-y}Sr_yCoO_3$ ($y = 0.2, 0.3$) and $La_{0.7}Ca_{0.3}CoO_3$, do not show similar behaviour in their resistivity versus temperature plots, in single-crystal form, and remain metallic up to the lowest temperature studied [20, 30]. This suggests that, for the hole-doped cobaltites, the onset of insulating characteristics at low temperature are not their intrinsic properties, but probably arise from the carrier scattering processes at the grain boundaries in the polycrystalline forms [31]. In the present case, the resistivity minimum for the 'Ca, Ba' compound occurs at a higher temperature (≈ 150 K) than for the 'Ca' and the 'Ba' compounds (≈ 100 K). This could probably arise from the presence of more defects in the grain boundaries of 'Ca, Ba' in the presence of two divalent ions with widely different sizes.

A comparison of the resistivity versus temperature behaviours measured at 0 and 7 T magnetic fields (figure 9) shows that, like $La_{1-y}Sr_yCoO_3$ compounds, these compounds also exhibit a peak in negative magnetoresistance near the ferromagnetic transition temperature. This can be attributed to suppression of spin disorder scattering under the influence of the magnetic field, which is maximum near T_C. For all three compounds, the negative magnetoresistance, after its peak near the ferromagnetic transition temperature, again starts to increase in the insulating region, reaching as high as about 26% at $T = 5$ K for the 'Ca, Ba' compound. The $La_{1-y}Sr_yCoO_3$ ($0.2 \leqslant y \leqslant 0.3$) ceramics also show negative magnetoresistance in the low-temperature insulating region [21], but with a much lower value than we observed for the 'Ca, Ba' compound. For hole-doped perovskite cobaltites, a higher negative magnetoresistance than in the present case is observed only in the insulating $La_{1-y}Sr_yCoO_3$ compounds with low doping level ($0.0 < y \leqslant 0.1$) [21] and in the Ga-doped $La_{1-y}Sr_yCoO_3$ compounds [33]. In both these systems, which were considered to be cluster glasses, the observed magnetoresistance shows a peak at low temperature, represented as the temperature of cluster glass freezing. In the present case, the ac susceptibility behaviours of the compounds do not show any freezing in the low-temperature region and no peak in the magnetoresistance is observed at low temperature. The increase in magnetoresistance with a

Figure 9. Plots of magnetoresistance in percentage values $[100(\rho H - \rho 0)/\rho 0]$ versus temperature for the compounds $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}CoO_3$ ($x = 0.0$, 0.5 and 1.0).

decrease in temperature in the insulating region of these compounds is very similar to what is observed for the compound $Sm_2Mo_2O_7$ [31], indicating that the magnetic field has a significant influence on the carrier scattering processes at the grain boundaries in the polycrystalline forms of these cobaltites. Besides $Sm_2Mo_2O_7$, such a low-temperature magnetoresistance behaviour has also been observed in polycrystalline hole-doped manganites, and has been explained on the basis of inter-grain tunnelling of spin polarized carriers under the influence of the magnetic field [34, 35].

In conclusion, our studies of the hole-doped cobaltites of compositions, $La_{0.7}(Ca_{1-x}Ba_x)_{0.3}O_3$ ($x = 0.0$, 0.5 and 1.0), have shown that the anisotropy in the exchange interaction, which gives rise to large thermomagnetic irreversibilities and large hysteresis in the $M-H$ loops of these compounds, changes significantly with the average size of the ions at the rare-earth site. The unusual magnetic behaviour of the $La_{0.7}Ba_{0.3}CoO_3$ compound, as reflected in its $M-H$ behaviour, has been explained on the basis of a possible coexistence of different magnetic phases. Observations of the low-temperature resistivity minimum, and negative magnetoresistance up to 26% in the low-temperature insulating regions of these polycrystalline compounds, have been ascribed to grain boundary effects.

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