The magnetic properties of the hole-doped cobaltites $R_{0.5}A_{0.5}CoO_3$ (R = La, rare earth and A = Ca, Sr, Ba)

The magnetic properties of the hole-doped cobaltites $R_{0.5}A_{0.5}CoO_3$ (R = La, rare earth and A = Ca, Sr, Ba)

R Ganguly[1], A Maignan, C Martin, M Hervieu and B Raveau

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

E-mail: rajibg@magnum.barc.ernet.in (R Ganguly)

Abstract
The ac and dc magnetic properties of hole-doped cobaltites with compositions $La_{0.5}Sr_{0.5-x}A_xCoO_3$ (A = Ca, Ba) and $La_{0.5-x}R_xSr_{0.5}CoO_3$ (R = Nd, Eu) have been studied. The suppression of the cluster glass behaviour of the parent compound, $La_{0.5}Sr_{0.5}CoO_3$, by substitutions for either the lanthanum or the strontium ions is accompanied by an increase in coercive field (H_C) and thermomagnetic irreversibility. The results suggest that the large thermomagnetic irreversibility and coercive fields observed in the hole-doped perovskite cobaltites, arising due to the anisotropic nature of their ferromagnetic character, cannot be correlated with the cluster glass freezing observed in them.

1. Introduction

The discoveries of high-temperature superconductivity in the layered cuprates and colossal magnetoresistance in the perovskite manganites have created renewed interest in the transition metal-based oxides with strongly correlated electrons. The perovskite cobaltites—the evolution of their physical properties as a function of hole doping being similar to that observed in the perovskite manganites—have also been studied quite extensively [1–23]. Although, like manganites, they exhibit doping-induced ferromagnetic and metallic characters, the nature of their ferromagnetic state has been a matter of much discussion due to their unusually large thermomagnetic irreversibilities in the ferromagnetic state. Itoh *et al* [9], from their magnetic relaxation studies on $La_{1-y}Sr_yCoO_3$ ($0.0 \leqslant y \leqslant 0.5$), suggested that such large thermomagnetic irreversibilities are indicative of the absence of long-range ferromagnetic order and explained them on the basis of mictomagnetic behaviour. Mira *et al* [10], 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. Neutron diffraction studies [11, 12], however, showed that long-range ferromagnetism exists in these compounds at a Sr concentration as low as 0.1 [11] and up to $x = 0.5$ [12]. Recent studies on the

---

[1] Present address: Novel Materials and Structural Chemistry Division, BARC, Mumbai-400 085, India.

$La_{0.5}Sr_{0.5}CoO_3$ ($x = 0.5$) compound [13, 14] show that although it exhibits a transition from a paramagnetic (PM) to a magnetically ordered phase at about 250 K, it undergoes cluster glass freezing below the ferromagnetic transition temperature (T_C). This is reflected in the frequency dependence of its linear and non-linear ac magnetic susceptibility versus temperature behaviours below T_C. Anil Kumar *et al* [15], however, in view of the coercive field (H_C) versus temperature behaviour of the same compound, explain 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 was 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) [16]. The unusual properties of the cobaltites are also reflected in the observation of giant anisotropic magnetostriction [17], which has been explained on the basis of a spin state transition from LS (low spin, $t_{2g}^6 e_g^0$) Co (III) with a spherical electron cloud and zero orbital moment to the Jahn–Teller-distorted IS (intermediate spin, $t_{2g}^5 e_g^1$) Co (III) ion with finite orbital moment. Most of the studies on the spin states of the Co ions suggest that the trivalent and tetravalent Co ions remain mixtures of LS or IS states [18–22]. The presence of the IS ions with finite orbital moment, as observed from magnetic circular dichroism spectroscopy [20], and thus with spin–orbit coupling, could be the source of anisotropic exchange interaction in these compounds, as has been suggested in the literature [16].

In this paper, we report studies on the magnetic properties of the cluster glass compound $La_{0.5}Sr_{0.5}CoO_3$, with respect to La or Sr substitutions. We show that the suppression of cluster glass freezing in it as a result of such substitutions is accompanied by an increase in the thermomagnetic irreversibility and coercivity. The results clearly show that for hole-doped cobaltites, cluster glass freezing and large thermomagnetic irreversibilities are not correlated with each other.

2. Experimental details

The samples, of compositions $La_{0.5-x}R_xSr_{0.5}CoO_3$ (R = Nd, Eu) and $La_{0.5}Sr_{0.5-x}A_xCoO_3$ (A = Ca, Ba), in the concentration range $0.0 \leqslant x \leqslant 1.0$, were prepared by solid-state reaction in air, between La_2O_3, Nd_2O_3 (dried at 1000 °C), Eu_2O_3, $CaCO_3$, $SrCO_3$, $BaCO_3$ and Co_3O_4 at 1100 °C. Room temperature x-ray powder diffraction (XRPD) patterns of the compounds were taken in a Philips Diffractometer, using Cu Kα radiation. Rietveld refinements of the XRPD patterns were carried out using the program Fullprof. Magnetic measurements (ac and dc) were carried out using Quantum Design SQUID magnetometers (5 K $\leqslant T \leqslant$ 400 K).

3. Results and discussion

Analyses of the room temperature XRPD patterns show that, except $La_{0.5}Ca_{0.5}CoO_3$, all compounds are single phase in nature. Although, in the literature, $La_{0.5}Ca_{0.5}CoO_3$ is reported to form as a single-phase compound with a rhombohedrally distorted perovskite structure [23, 24], we failed to obtain that with our synthesis conditions. The space group and the values of the lattice parameters, obtained from the Rietveld refinements of the x-ray diffraction patterns of the compounds, are shown in table 1. In agreement with the literature [7], the $La_{0.5}Sr_{0.5}CoO_3$ compound forms with rhombohedrally distorted perovskite structure. As shown by the Rietveld refinement of the XRPD data, a decrease in the average size of the ions at the rare-earth site, r_A, with increase in the substituent ion concentration, results in: change in the symmetry to orthorhombic perovskite for the $La_{0.5-x}Nd_xSr_{0.5}CoO_3$ and the $La_{0.5}Sr_{0.5-x}Ca_xCoO_3$
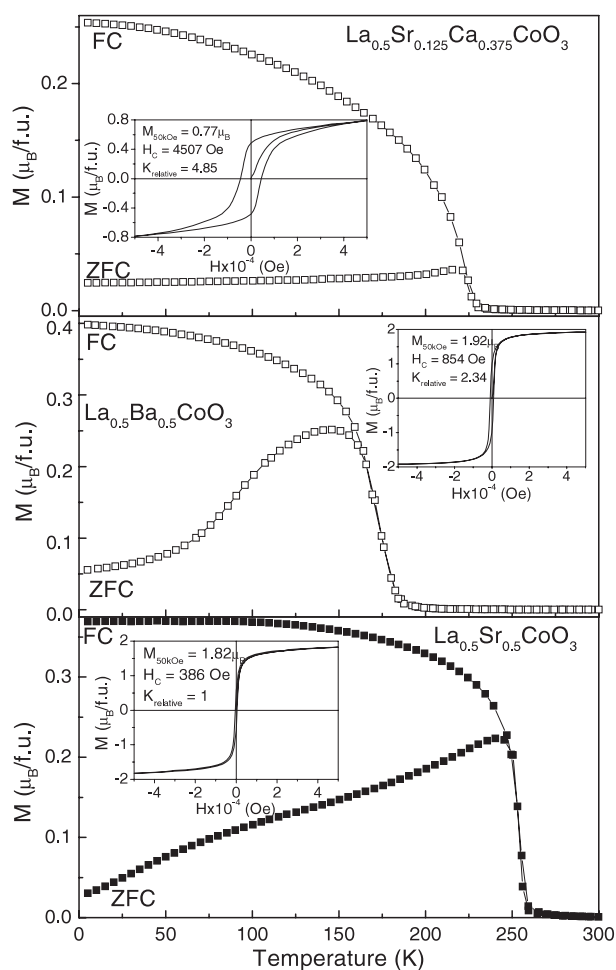
Figure 1. Plots of dc magnetization versus temperature for the $La_{0.5}Sr_{0.5}CoO_3$, $La_{0.5}Ba_{0.5}CoO_3$ and $La_{0.5}Sr_{0.125}Ca_{0.375}CoO_3$ compounds, recorded at 100 Oe, under FC and ZFC conditions. The insets show the corresponding M versus H loops.

compounds; and to monoclinic perovskite for the $La_{0.5-x}Eu_xSr_{0.5}CoO_3$ compounds. In the case of the $La_{0.5}Sr_{0.5-x}Ba_xCoO_3$ compounds, on the other hand, an increase in r_A-value with increase in Ba concentration results in change in the structure to cubic symmetry. The structures obtained for the $Nd_{0.5}Sr_{0.5}CoO_3$ and $La_{0.5}Ba_{0.5}CoO_3$ are in agreement with those reported in the literature [25, 26]. For the $Eu_{0.5}Sr_{0.5}CoO_3$ compound, however, in contrast to the literature report [25], we observe not a cubic symmetry but a monoclinic symmetry. Since the smaller size of Eu^{3+} compared to Nd^{3+} should favour the presence of a larger distortion in $Eu_{0.5}Sr_{0.5}CoO_3$ than in $Nd_{0.5}Sr_{0.5}CoO_3$, our result looks quite plausible.

Figures 1 and 2 show the field-cooled (FC) and zero-field-cooled (ZFC) magnetization versus temperature plots for some of the compounds recorded at 100 Oe dc field. The M versus H plots of the compounds recorded at 5 K are shown as insets with the corresponding M–T plots. As shown in these figures and in table 1, the temperatures (T_C) at which the transitions from the PM to the magnetically ordered phase occur for these compounds decrease with increase in the substituent ion concentrations. In the case of $La_{0.5-x}R_xSr_{0.5}CoO_3$ (R = Nd,
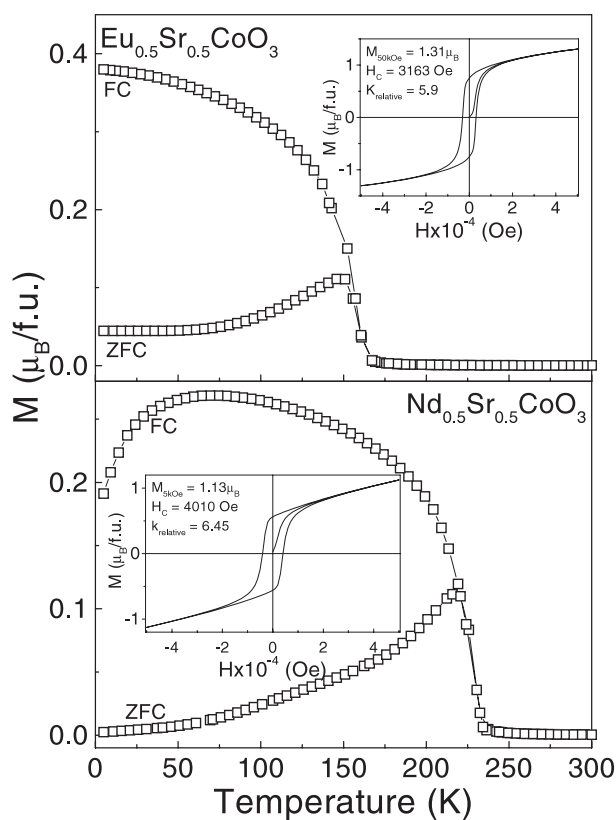
Figure 2. Plots of dc magnetization versus temperature for the $Nd_{0.5}Sr_{0.5}CoO_3$ and $Eu_{0.5}Sr_{0.5}CoO_3$ compounds, recorded at 100 Oe, under FC and ZFC conditions. The insets show the corresponding M versus H loops.

Table 1. The structural parameters and coercive field values for the $La_{0.5}Sr_{0.5-x}A_xCoO_3$ (A = Ca, Ba) and $La_{0.5-x}R_xSr_{0.5}CoO_3$ (R = Nd, Eu) compounds.

Compound	Space group	a (Å)	b (Å)	c (Å)	H_C (Oe)	T_C (K)
$La_{0.5}Sr_{0.5}CoO_3$	$R\bar{3}c$	5.4117(5)	—	13.299(1)	386	256
$La_{0.5}Sr_{0.375}Ca_{0.125}CoO_3$	$R\bar{3}c$	5.3920(7)	—	13.267(1)	703	245
$La_{0.5}Sr_{0.25}Ca_{0.25}CoO_3$	$R\bar{3}c$	5.3812(5)	—	13.230(1)	1275	235
$La_{0.5}Sr_{0.125}Ca_{0.375}CoO_3$	$Pnma$	5.367(1)	7.628(2)	5.442(1)	4507	233
$La_{0.5}Sr_{0.25}Ba_{0.25}CoO_3$	$Pm3m$	3.8577(7)	—	—	1150	227
$La_{0.5}Ba_{0.5}CoO_3$	$Pm3m$	3.8820(6)	—	—	854	185
$La_{0.25}Nd_{0.25}Sr_{0.5}CoO_3$	$R\bar{3}c$	5.3898(8)	—	13.230(3)	1251	250
$Nd_{0.5}Sr_{0.5}CoO_3$	$Pnma$	5.379(1)	7.603(2)	5.428(1)	4010	235
$La_{0.25}Eu_{0.25}Sr_{0.5}CoO_3$	$R\bar{3}c$	5.3710(7)	—	13.197(1)	1247	233
$Eu_{0.5}Sr_{0.5}CoO_3$	$P2_1/m$ $\beta = 89.39(1)$	5.369(1)	7.577(1)	5.389(2)	3163	165

Eu) and $La_{0.5}Sr_{0.5-x}Ca_xCoO_3$ compounds, the decrease in T_C results from an increase in structural distortion with decrease in the value of r_A. A decrease in the value of r_A results in an increase in the cooperative displacement of the oxygen ion from its position in the ideal perovskite structure, and leads to an increased deviation of the Co–O–Co bond angle from 180°.
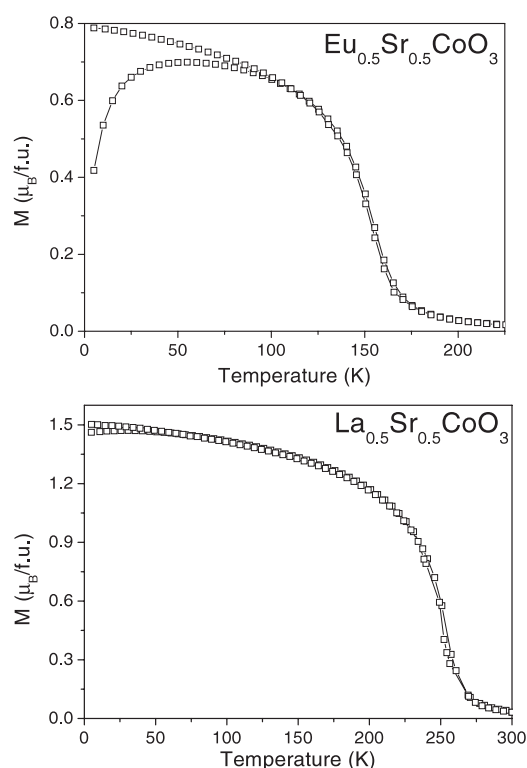
Figure 3. Plots of dc magnetization versus temperature for the $La_{0.5}Sr_{0.5}CoO_3$ and $Eu_{0.5}Sr_{0.5}CoO_3$ compounds, recorded at 3000 Oe, under FC and ZFC conditions.

Being cooperative, this distortion is reflected in the XRPD patterns and leads to a deterioration of the ferromagnetic exchange interaction between the cobalt ions and subsequently the T_C-value. In the case of the $La_{0.5}Sr_{0.5-x}Ba_xCoO_3$ compounds, on the other hand, an increase in structural distortion in the form of non-cooperative displacement of oxygen ions (random in nature, so not reflected in the XRPD patterns) with increase in the barium ion concentration causes a decrease in T_C. The effect of this non-cooperative distortion, which arises from large size mismatch between the La^{3+} and the Ba^{2+} ions, has already been observed and discussed in detail in the literature for various hole-doped cobaltites and manganites [16, 27, 28]. As shown in figures 1 and 2, all these compounds show large thermomagnetic irreversibilities at 100 Oe applied field. The observed drop in the FC magnetization versus temperature plot of the $Nd_{0.5}Sr_{0.5}CoO_3$ compound below 70 K probably arises due to an antiferromagnetic alignment between the Nd^{3+} and the Co ion moments, similar to what has recently been observed from a neutron diffraction study on $Nd_{0.67}Sr_{0.33}CoO_3$ [29]. The observed thermomagnetic irreversibility in the parent compound, $La_{0.5}Sr_{0.5}CoO_3$, has been explained in a large number of literature reports as a signature of cluster glass behaviour, in the absence of any long-range ferromagnetic character [9, 10]. Observation of the ordered moment from the neutron diffraction study [12] and the frequency independence of the PM–magnetically ordered transition [13] in this compound have, however, been explained on the basis of the presence of long-range ferromagnetic character. Some literature reports [15, 16] also suggested that the observations of large thermomagnetic irreversibility and coercive fields (H_C) in the hole-doped cobaltites arise due to the anisotropic nature of their ferromagnetic character. The large
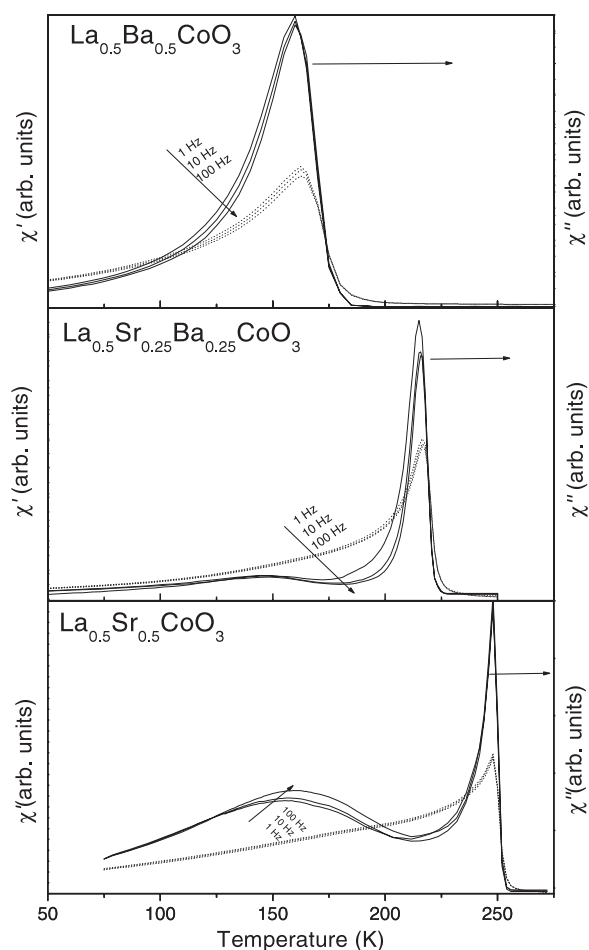
Figure 4. Plots of ac magnetization versus temperature at different frequencies for the $La_{0.5}Sr_{0.5-x}Ba_xCoO_3$ compounds ($x = 0.00$, 0.25 and 0.50), recorded at 3 Oe ac field.

increase in hysteresis and thermomagnetic irreversibility upon substitution of Co for Mn in $La_{0.67}Ca_{0.33}MnO_3$ [30] and a very large coercivity in the ferrimagnetic $LaCo_{0.5}Mn_{0.5}O_3$ [31] also reflect the ability of Co ions to induce anisotropy in exchange interaction in the ferromagnetic characters of the manganites. As shown in figures 1 and 2, the values of the relative anisotropy constant, $K_{relative}$ ($K_{relative} = K_{compound}/K_{La_{0.5}Sr_{0.5}CoO_3}$, where the K-values are calculated from the formula $K = (H_C/M_S)/2$ (see [20]), considering $M_{50\ kOe}$ as M_S), and the coercive field increase with increase in the substituent ion concentration. A large increase in the coercive field with increase in x beyond $x = 0.50$ for the $La_{0.5-x}R_xSr_{0.5}CoO_3$ ($R = Nd$, Eu) and the $La_{0.5}Sr_{0.5-x}Ca_xCoO_3$ compounds is probably associated with the change in structural symmetry from rhombohedral to the more distorted ones, such as orthorhombic or monoclinic, as has been discussed in earlier paragraphs. A comparison of magnetization versus temperature plots for the $La_{0.5}Sr_{0.5}CoO_3$ and the $Eu_{0.5}Sr_{0.5}CoO_3$ compounds (figure 3) at 3000 Oe applied field shows that this increase in coercive field results in an increase in thermomagnetic irreversibility in the low-temperature region. Now, to understand the effect of an increase in thermomagnetic irreversibility on the cluster glass freezing of $La_{0.5}Sr_{0.5}CoO_3$, the ac susceptibility versus temperature behaviours of the compounds are studied.
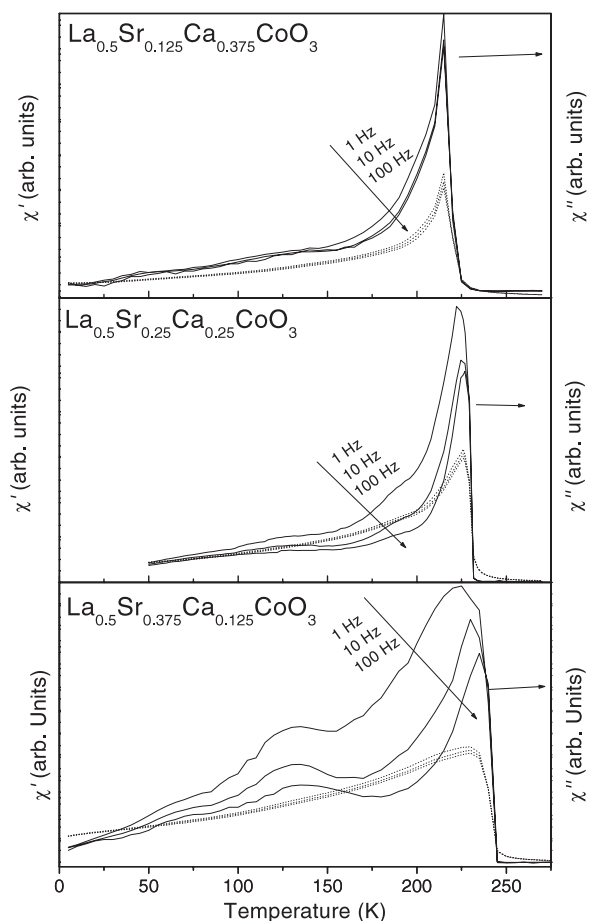
Figure 5. Plots of ac magnetization versus temperature at different frequencies for the La$_{0.5}$Sr$_{0.5-x}$Ca$_x$CoO$_3$ compounds ($x = 0.125$, 0.25 and 0.375), recorded at 3 Oe ac field.

The ac susceptibility versus temperature behaviours of the compounds, recorded at various frequencies, are shown in figures 4–7. The χ' and χ'' versus temperature behaviours of the parent compound, La$_{0.5}$Sr$_{0.5}$CoO$_3$ (figure 4), are similar to those reported in the literature [13, 14]. The sharp transitions observed near 250 K are frequency independent and were suggested to be PM–magnetically ordered transitions [13]. The presence of long-range ferromagnetism in this compound had earlier been confirmed by a neutron diffraction study [12]. Similar to findings already reported [13, 14], the present compound shows a second peak in its χ'' versus temperature behaviour, which is frequency dependent, with broad and non-divergent nature. In the absence of any clear frequency dependence in its χ' versus temperature behaviour, its observance for the broad non-divergent peak in the χ'' versus temperature behaviour has been explained in the literature on the basis of cluster glass behaviour [13, 14]. As has been explained [14], the frequency dependence of the ac susceptibility versus temperature behaviour arises from the relaxation behaviour of the short-range ferromagnetic clusters, which are present in the cluster glass compounds. It appears when the relaxation time of the short-range clusters along the fluctuating ac field directions increases with decrease in temperature and becomes of the order of the measurement times associated with applied frequencies (reciprocal of frequency). As shown
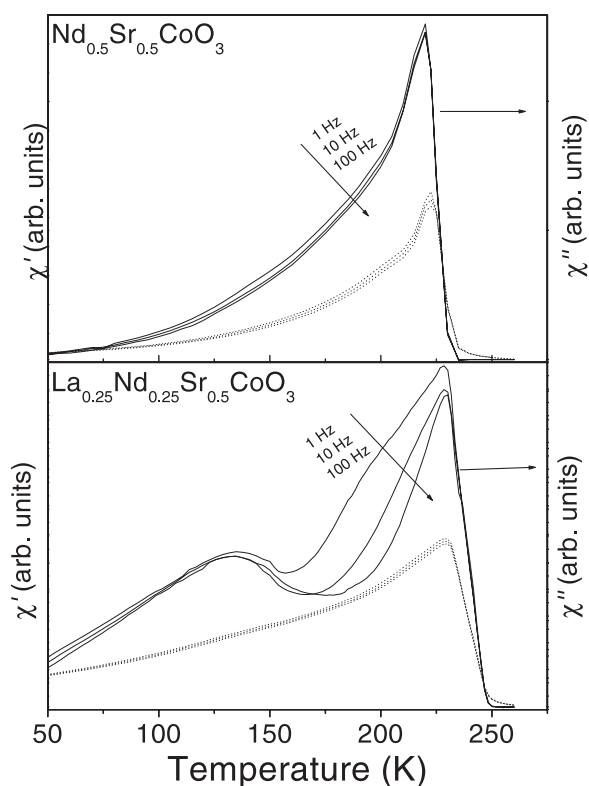
Figure 6. Plots of ac magnetization versus temperature at different frequencies for the $La_{0.5-x}Nd_xSr_{0.5}CoO_3$ compounds ($x = 0.25$ and 0.50), recorded at 3 Oe ac field.

in the figures, in all cases, increase in the substituent ion concentration results in suppression of this frequency-dependent second peak. The χ'' versus temperature plots show frequency dependence for the compounds in the intermediate concentration range, but not for the end compounds, $La_{0.5}Ba_{0.5}CoO_3$, $La_{0.5}Sr_{0.125}Ca_{0.375}CoO_3$, $Nd_{0.5}Sr_{0.5}CoO_3$ and $Eu_{0.5}Sr_{0.5}CoO_3$. The frequency dependence in the $La_{0.5}Sr_{0.375}Ca_{0.125}CoO_3$, $La_{0.5}Sr_{0.25}Ca_{0.25}CoO_3$ and $Nd_{0.25}La_{0.25}Sr_{0.5}CoO_3$ compounds is observed over larger temperature ranges than in the parent compound, including the peak, which is supposed to arise due to a PM– magnetically ordered transition. The absence of frequency dependence in the $La_{0.5}Ba_{0.5}CoO_3$, $La_{0.5}Sr_{0.125}Ca_{0.375}CoO_3$, $Nd_{0.5}Sr_{0.5}CoO_3$ and $Eu_{0.5}Sr_{0.5}CoO_3$ compounds with higher H_C (table 1) and supposedly larger thermomagnetic irreversibilities (as has been discussed in the last paragraph) than in $La_{0.5}Sr_{0.5}CoO_3$ clearly shows that the cluster glass behaviour observed in these hole-doped cobaltites is not related to their large thermomagnetic irreversibilities. This result is in agreement with the literature reports of the absence of any frequency dependence in the ac susceptibility versus temperature behaviours of the $La_{0.7}A_{0.3}CoO_3$ ($A = Ca$, Ba) compounds, with much larger thermomagnetic irreversibilities than that of the $La_{0.7}Sr_{0.3}CoO_3$ compound [16, 32], which is considered to be a cluster glass [9]. This behaviour is opposite to those observed in the case of the hole-doped perovskite manganites. A decrease in the average size of the ions and an increase in size mismatch of the ions at the rare-earth site induce mictomagnetic behaviours in them, with a simultaneous enhancement of thermomagnetic irreversibilities [33– 35]. In the present case, the observed increase in thermomagnetic irreversibility with increase
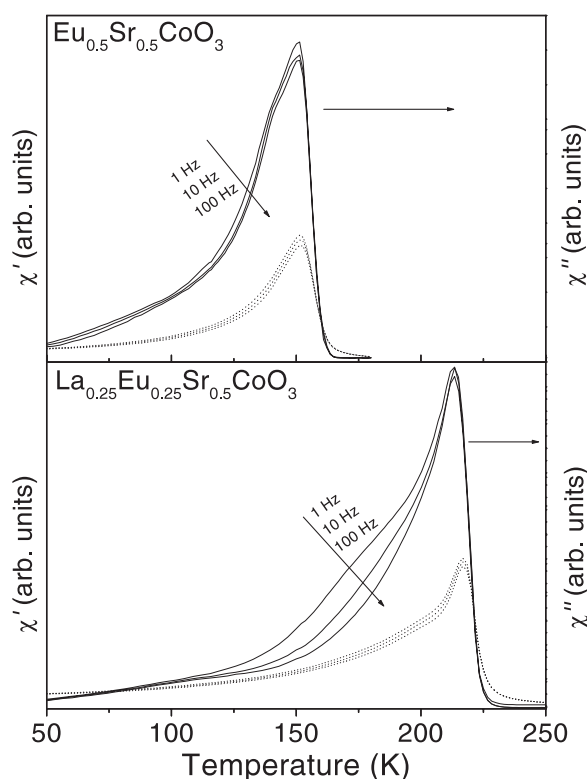
Figure 7. Plots of ac magnetization versus temperature at different frequencies for the $La_{0.5-x}Eu_xSr_{0.5}CoO_3$ compounds ($x = 0.25$ and 0.50), recorded at 3 Oe ac field.

in the dopant ion concentration is related to an increase in the coercive field (figures 1–3), arising probably due to an increase in the anisotropic nature of the ferromagnetic character.

In conclusion, our studies on the $La_{0.5-x}R_xSr_{0.5}CoO_3$ (R = Nd, Eu), $La_{0.5}Sr_{0.5-x}Ca_xCoO_3$ and $La_{0.5}Sr_{0.5-x}Ca_xCoO_3$ compounds show that the cluster glass behaviour of the parent compound ($x = 0.0$) is suppressed with increase in the substituent ion concentrations. Since such suppression of the cluster glass behaviour is accompanied by an increase in the thermomagnetic irreversibilities, the results clearly suggest that in the hole-doped cobaltites, the cluster glass behaviour and the thermomagnetic irreversibilities are not correlated with each other.

References

[1] Jonker G H and van Santen J H 1953 *Physica* **19** 120
[2] Raccah P M and Goodenough J B 1968 *J. Appl. Phys.* **39** 1209
[3] Rao C N R, Prakash O M, Bahadur D, Ganguly P and Nagabhusana S 1977 *J. Solid State Chem.* **22** 353
[4] Ganguly P, Anil Kumar P S, Santhen P N and Mulla I S 1995 *J. Phys.: Condens. Matter* **6** 533
[5] Senaris-Rodriguez M A and Goodenough J B 1995 *J. Solid State Chem.* **118** 323
[6] Yamaguchi S, Taniguchi H, Takagi H, Arima T and Tokura Y 1995 *J. Phys. Soc. Japan* **64** 1885
[7] Mahendiran R and Raychaudhuri A K 1996 *Phys. Rev.* B **54** 16 044
[8] Golovanov V, Mihaly L and Moodenbaugh A R 1996 *Phys. Rev.* B **53** 8207
[9] Itoh M, Natori I, Kubota S and Motoya K 1994 *J. Phys. Soc. Japan* **63** 1486

[10] Mira J, Rivas J, Vazquez M, Garcia-Beneytez J M, Arcas J, Sanchez R D and Senaris-Rodriguez M A 1999 *Phys. Rev.* B **59** 123

[11] Caciuffo R, Rinaldi D, Barucca G, Mira J, Rivas J, Senaris-Rodriguez M A, Radaelli P D, Fiorani D and Goodenough J B 1999 *Phys. Rev.* B **59** 1068

[12] Sathe V G, Pimpale A V, Siruguri V and Paranjape S K 1996 *J. Phys.: Condens. Matter* **8** 3889

[13] Nam D N H, Jonason K, Nordblad P, Khiem N V and Phuc N X 1999 *Phys. Rev.* B **59** 4189

[14] Mukherjee S, Ranganathan R, Anil Kumar P S and Joy P A 1996 *Phys. Rev.* B **54** 9267

[15] Anil Kumar P S, Joy P A and Date S K 1998 *J. Phys.: Condens. Matter* **10** L487

[16] Ganguly R, Gopalakrishnan I K and Yakhmi J V 1999 *Physica* B **271** 116

[17] Ibarra M R, Mahendiran R, Marquina C, Garcia-Landau B and Blasco J 1998 *Phys. Rev.* B **57** R3217

[18] Louca D, Sarrao J L, Thompson J D, Roder H and Kwei G H 1999 *Phys. Rev.* B **60** 10 378

[19] Saitoh T, Mizokawa T, Fujimori A, Abbate M, Takeda Y and Takano M 1997 *Phys. Rev.* B **56** 1290

[20] Yoshi K, Mizumaki M, Saitoh Y and Nakamura A 2000 *J. Solid State Chem.* **152** 577

[21] Potze R H, Sawatzky G A and Abbate M 1995 *Phys. Rev.* B **51** 11 501

[22] Yamaguchi S, Okimoto Y and Tokura Y 1997 *Phys. Rev.* B **55** R8666

[23] Taguchi H, Shimada M and Koizumi M 1982 *J. Solid State Chem.* **41** 329

[24] Samilov A V, Beach G, Fu C C, Yeh N-C and Vasquez R P 1998 *Phys. Rev.* B **57** 14 032

[25] Yoshi K and Nakamura A 2001 *Mater. Res. Bull.* **36** 1447

[26] Suard E, Fauth F and Caignart V 2000 *Physica* B **276** 254

[27] Ganguly R, Maignan A, Hervieu M, Martin C and Raveau B 2002 *Solid State Commun.* **121** 537

[28] Rodriguez-Martinez J, Lide M and Attfield P 1996 *Phys. Rev.* B **54** R15 622

[29] Paraskevopoulos M, Hemberger J, Krimmel A and Loidl A 2001 *Phys. Rev.* B **63** 224416

[30] Ganguly R, Gopalakrishnan I K and Yakhmi J V 1999 *Physica* B **266** 332

[31] Mahendiran R, Bréard Y, Hervieu M and Raveau B 2001 unpublished

[32] Ganguly R, Hervieu M, Nguyen N, Maignan A, Martin C and Raveau B 2001 *J. Phys.: Condens. Matter* **13** 10 911

[33] Freitas R S, Ghivelder L, Damay F, Dias F and Cohen L F 2001 *Phys. Rev.* B **64** 144404

[34] Maignan A, Varadaraju U V, Millange F and Raveau B 1997 *J. Magn. Magn. Mater.* **168** L237

[35] Maignan A, Martin C, Van Tendeloo G, Hervieu and Raveau B 1999 *Phys. Rev.* B **60** 15 214