

Effect of cobalt substitution on magnetic and transport properties of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1, 0.3$ and 0.5)

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MS received 16 February 2009

Abstract. The magnetic and transport properties of the compounds $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1, 0.3$ and 0.5), synthesized by citrate–gel route have been investigated. The spin transition in cobaltates at low temperatures affects the magnetic as well as transport properties. The irreversibility behaviour between the zero-field cooled (ZFC) and field cooled (FC) magnetization as a function of temperature becomes stronger with increasing Co content. This is understood on the basis of glassy behaviour, which becomes more robust with increasing Co substitution. The non-saturating M–H behaviour indicates strong magnetic inhomogeneities which may cause the magnetic phase separation at the nanoscopic length scale. The double exchange interaction is stronger between $\text{Mn}^{3+}\text{–O}^{2-}\text{–Mn}^{4+}$ as compared to $\text{Co}^{3+}\text{–O}^{2-}\text{–Co}^{4+}$ pairs. Co-substitution suppresses the double exchange which will lead to cluster/spin glass like behaviour as well as semiconducting features due to localization of charge carriers (mobile e_g electrons).

Keywords. Manganites; cobaltates; magnetic properties; spin state transition; charge order.

1. Introduction

The hole-doped manganites, $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$, have been studied extensively since the discovery of colossal magnetoresistance (CMR) and other interesting properties like charge order, electronic phase separation (Rao and Raveau 1998). Although extensive work has been done on the B-site substitution, work on Co substitution on Mn-site is limited (Asthana *et al* 2005 and references therein).

It is well established that cobalt exhibits different spin states (Bahadur *et al* 1979; Korotin *et al* 1996). The low spin (LS, $t_{2g}^6 e_g^0$, $S = 0$) state changes to either high spin (HS, $t_{2g}^4 e_g^2$, $S = 2$) or intermediate spin (IS, $t_{2g}^5 e_g^1$, $S = 1$) state with increasing temperature. The spin state transition has recently been demonstrated in $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ through photomagnetic studies (Bahadur *et al* 2007). However, charge order (CO) feature has been suppressed by B-site substitution in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ which is typical of CO system (Srivastava *et al* 2004). Therefore, in the present work, we have studied the effect of higher cobalt (Co) substitution on Mn-site for the series $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1, 0.3$ and 0.5) on the magnetic instabilities like charge ordering etc.

2. Experimental

The polycrystalline cobalt-substituted manganites $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1, 0.3$ and 0.5) were

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synthesized by the chemical citrate–gel route using high purity Nd_2O_3 , SrCO_3 and Mn-acetate and cobalt nitrate. The as-prepared powders were calcined at 1000°C for 2 h in air. The powders were pelletized and sintered at 1350°C for 2 h in air. X-ray diffraction (XRD) data was collected using $\text{Cu}\text{–K}\alpha$ radiation (PW 3040/60 Philips, PANalytical). A single phase for the polycrystalline samples was evidenced through the XRD measurements. All the samples crystallized in the orthorhombic structure with space group $Pnma$. The resistivity was measured using the standard four-probe d.c. method. D.C. magnetic measurements were performed on a quantum design MPMS system.

3. Results and discussion

Figure 1(a) shows temperature (T) dependence of magnetization (M) in a field of 500 Oe. Thermomagnetic irreversibility behaviour in zero-field cooled (ZFC) and field cooled (FC) is observed in all the samples. This may be attributed to the frustration caused by competing super exchange (SE) and double exchange (DE) interactions. The DE interaction is stronger for $\text{Mn}^{3+}\text{–O}^{2-}\text{–Mn}^{4+}$ in comparison to that of $\text{Co}^{3+}\text{–O}^{2-}\text{–Co}^{4+}$ (Asthana *et al* 2005). The paramagnetic (PM) to ferromagnetic (FM) transition becomes sharper with increasing x . It indicates that the sample with $x = 0.1$ is more magnetically inhomogeneous as compared to the samples with $x = 0.3$ and 0.5 (Trukhanov *et al* 2005a). The peak in the ZFC magnetization arises due to the competition between the random orientation of short range-ordered

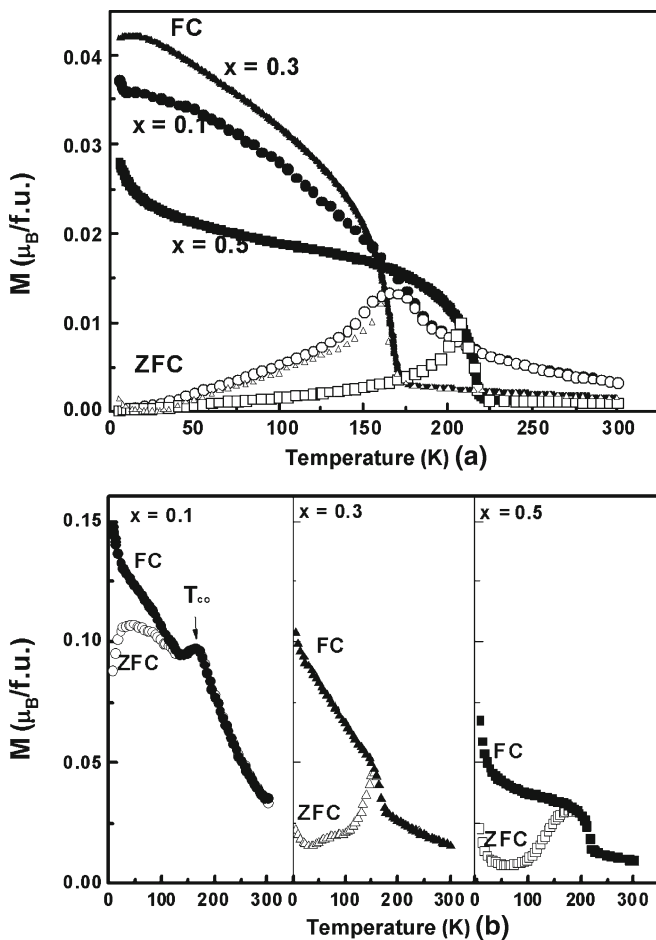


Figure 1. (a) Temperature dependence of field cooled and zero field cooled magnetization in a field of 500 Oe for $Nd_{0.5}Sr_{0.5}Mn_{1-x}Co_xO_3$ ($x = 0.1, 0.3$ and 0.5) compounds. Solid and hollow symbols show the FC and ZFC data, respectively and (b) temperature dependence of FC and ZFC magnetization in a field of 5 kOe for $Nd_{0.5}Sr_{0.5}Mn_{1-x}Co_xO_3$ ($x = 0.1, 0.3$ and 0.5) compounds.

clusters which depends on the energies of anisotropy and the external applied field (Nam *et al* 1999). Therefore, a peak in the ZFC plot can be interpreted in terms of magnetic phase separation in which FM clusters formed by DE mechanism are embedded in a nonferromagnetic matrix (Wu and Leighton 2003) and FM clusters evolve with the intensity of the field. The strong hysteretic behaviour as well as sharp peak indicates the spin/cluster glass-like phase which is characteristic of highly anisotropic compounds. A typical spin glass (SG) shows almost temperature independent M_{FC} below bifurcation point while in the present series, it rises continuously (as shown in figure 1(b)) which has been reported for cluster glass (CG) materials (Mukherjee *et al* 1996; Troyanchuk *et al* 2002; Trukhanov *et al* 2005b). This behaviour can be accounted due to the presence of Nd^{3+} ion with a large orbital angular momentum (L) value of 6 and intermediate spin (IS) state of Co^{3+} ($t_{2g}^5 e_g^1$), which is a

Jahn–Teller (JT) ion. The sharp decrease following the peak in ZFC data may also indicate transformation of the intermediate spin/high spin cobalt to the low spin state. Larger spin-orbit coupling due to these ions and JT distortion play a significant role. The magnetization behaviour at lower temperature (<25 K) especially in the sample with $x = 0.5$ is different from others. The increasing trend in the magnetization indicates the ferri/ferro-magnetic alignment of Nd-sublattice with the Co/Mn-sublattice (Asthana *et al* 2005).

Figure 1(b) shows the $M(T)$ plots for ZFC–FC measurements in a field of 5 kOe. The $Nd_{0.5}Sr_{0.5}MnO_3$ (NSMO) is a CE-type charge-ordered (CO) compound while the $Nd_{0.5}Sr_{0.5}CoO_3$ (NSCO) is an electronically phase separated system (Yoshii *et al* 2001). It is believed that the magnetic ordering can be changed from CE- to A-type in NSMO with slight variation in the Mn^{3+}/Mn^{4+} ratio (Rao and Raveau 1998). NSCO is also a well known electronically phase separated system and NSMO can also be treated as magnetically phase separated system due to the simultaneous presence of different magnetic orders depending on the external parameters like temperature and field.

The CO phase in the NSMO can be destroyed by substituting a small amount of another transition element at Mn-site which is well documented in the literature (Rao and Raveau 1998). This is also true in our case for the sample with $x = 0.1$. But our intention was to observe the effect of Co substitution in the CO system. The CO phase appears weak in the sample with $x = 0.1$ ($T_{CO} = 165$ K) but it disappears in the sample with $x = 0.3$ and 0.5 . A prominent transition from antiferromagnetic (AFM) to ferro/ferrimagnetic is observed below 20 K for the samples with $x = 0.3$ and 0.5 as observed from ZFC plots (figure 1(b)). On the other hand, only AFM transition is observed in the sample with $x = 0.1$. The magnetic behaviour can be accounted on the basis of simultaneous presence of different magnetic phases and evolution of one phase at the expense of other with temperature variation. The samples with $x = 0.3$ and 0.5 presumably contain coexisting A- and CE-type of magnetic phases which are different from the NSMO system (CE-phase only). The competition between CE-type phase and A-type phase exist in these samples due to their comparable energy scale. The presence of the phase separation is also supported by the deviation from the Curie–Weiss law which is discussed later. It is worthy to mention here, that the CO-phase is sensitive to the magnetic field. The magnetic field driven CO phase (A-, CE-type or coexisting) has been observed in a field of 5 kOe which was not observed in a field of 500 Oe. The sample with $x = 0.1$ shows a weak signature of CO phase corresponding to CE-type ordering which is similar to NSMO compound. On the other hand, the samples with $x = 0.3$ and 0.5 show the coexisting phases which could be either pure AFM phase or a combination of CO and AFM phases. It confers that the spins and charges, which are trapped in the potential well (AFM or FM) start to align themselves according to the favourable energy configuration. None of the samples follow the Curie–Weiss (C–W) behaviour in the paramagnetic regime,

which indicates the presence of microscopic magnetic inhomogeneities. The deviation from the linearity in the inverse susceptibility versus temperature plot suggests that the cobalt HS (or IS) state changes to LS state below a critical temperature in cobaltates, e.g. $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ (Asthana *et al* 2005). The charge ordered manganites (like NSMO) exhibit the more complex behaviour as compared to type-I manganites. Therefore, only the deviation in C–W law cannot be taken as an evidence for HS/IS to LS transition. The variation in magnetic moment in ZFC data in all cases indicates the possibility of mixed spin state of Co^{3+} and Co^{4+} as a ground state and their transformation as a function of temperature. Therefore, it is more logical to attribute magnetic behaviour in terms of electronic phase separation and gradual population of favourable spin states. It is also conferred from the non-saturating and low magnetic moments at 5 K.

Figure 2 shows the isothermal magnetization plots for the samples with $x = 0.1, 0.3$ and 0.5 at 5 K. None of these samples shows saturation even up to a field of 80 kOe and maximum moment is still very small. The nonsaturation behaviour arises due to the competing AFM and FM interactions. The small value of moments and nonsaturation behaviour again suggest the possibility of phase separation. The hysteretic behaviour is observed in all the cases but a large coercivity (~ 5 kOe) has been observed in the sample with $x = 0.5$ as shown in figure 2 (inset). This can be accounted due to the higher magneto-crystalline anisotropy of the cobalt ion and its presence in the form of IS state. It is interesting to note that the sample with $x = 0.5$ shows a sharp jump in the M–H behaviour around 40 kOe field which is similar to the metamagnetic transition due to the presence of magnetic inhomogeneities. It indicates the simultaneous presence of different AFM magnetic phases (A-, C- and CE-type) at particular temperatures and which get transformed into the FM phase at the expense of AFM phase.

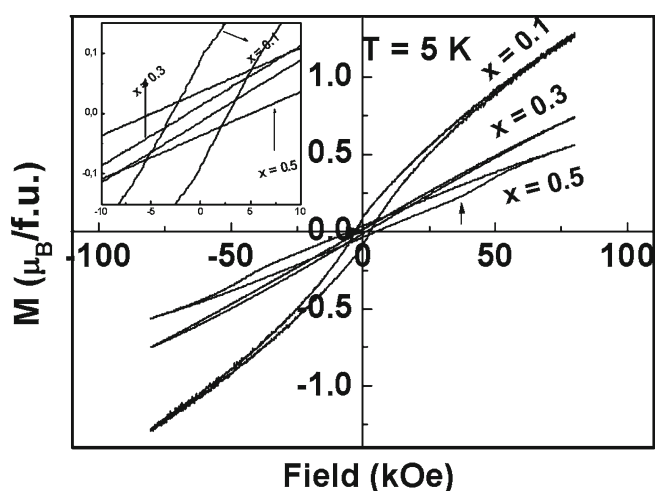


Figure 2. Isothermal magnetization plots for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.1, 0.3$ and 0.5) compounds at 5 K. Inset shows hysteretic behaviour.

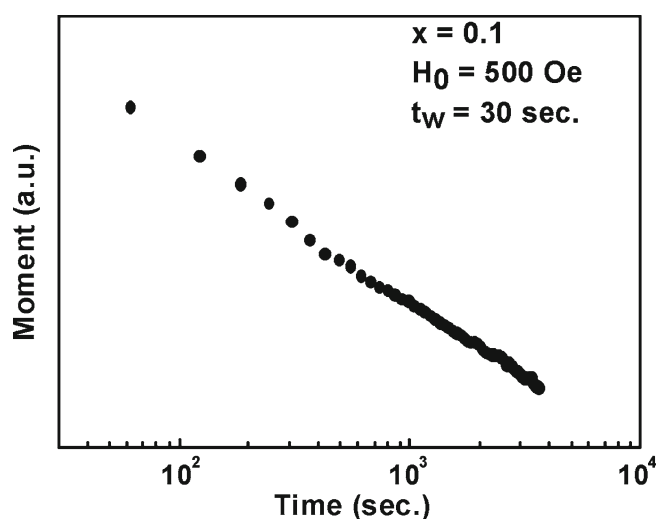


Figure 3. Magnetic relaxation with time for sample with $x = 0.1$ using a probing field of 500 Oe at 5 K.

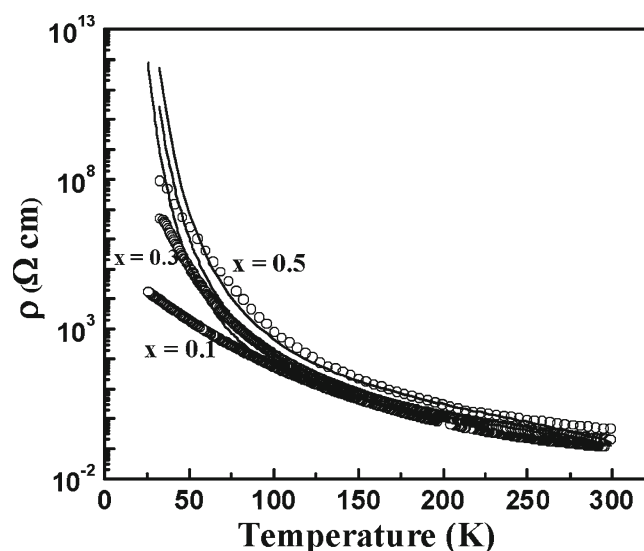


Figure 4. Variation of resistivity with temperature for samples with $x = 0.1, 0.3$ and 0.5 . Lines show theoretically fit plots.

Figure 3 shows magnetic relaxation measurements for the sample with $x = 0.1$ after applying and removing a field of 500 Oe at 5 K. The slope of the curve is negative and decreases with time. It indicates the randomization of the spins due to competing AFM and FM interactions and gets trapped in the AFM potential well due to favourable energy state at fixed temperature scale (thermal energy is constant). This result is also consistent with M–T plots for the sample with $x = 0.1$. Similar trend has been observed in the NSMO compound (López *et al* 2001). This kind of relaxation behaviour can be attributed to the coexistence of FM and AFM interactions between magnetic ions, which produced distribution of energy barriers (López *et al* 2001).

The temperature dependence of resistivity behaviour for samples with $x = 0.1, 0.3$ and 0.5 is shown in figure 4. The resistivity values increase as the concentration of cobalt ion increases due to suppression of DE that leads to ferromagnetism. The population of Co (IS) changes to LS state at low temperatures, which creates an additional distortion in the lattice due to the smaller ionic size of the low, spin Co^{3+} ion. As a result, buckling of CoO_6 octahedra increases, which in turn affect the charge transfer integral along with the Co–O–Co bonds (Asthana *et al* 2005). This effect is probably the reason for monotonous increase in the resistivity behaviour of the Co containing samples. A slight variation in the slope, especially at lower temperature, has been observed among these samples which supports the possibility of electronic phase separation. However, magnetic phase separation is dominating in these samples due to the presence of highly anisotropic Co-ion. The resistivity data has been understood using the correlated small polaron-hopping model discussed in detail elsewhere (Asthana *et al* 2006). The spin–spin scattering increases as the concentration of Co increases due to buckling of CoO_6 octahedra. The activation energy for polaron hopping varies from 550 K (for $x = 0.1$) to 750 K (for $x = 0.5$) with small polaron stabilization energy constant (300 K). The number of charge carriers decreases with increasing Co content as a result of which resistivity values increase. The Co substitution suppresses the DE interactions, hence, a higher activation energy is required for hopping of the e_g electrons.

4. Conclusions

All the samples of the series, $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($0.1, 0.3$ and 0.5), crystallized in orthorhombic structure. The magnetothermal irreversibility in $M(T)$ data increases with Co content due to combined effect of the gradual population of HS (or IS) state to LS state with decreasing temperature and magnetic anisotropy. The large coercivity and thermal irreversibility are attributed to the anisotropic nature arising due to Co(IS) state, which is a JT ion and Nd^{3+} ion with large orbital moments. The CO-phase disappears with increasing Co-content which suggests the simultaneous presence of magnetic phases which are sensitive to the

magnetic field. The non-saturating M–H behaviour data support the electronic phase separation as well as spin transitions in the system. The variation of magnetic phases due to the presence of possible variable spin states needs to be further studied through the more sophisticated instrumentation like photomagnetic studies.

Acknowledgement

The author is thankful to Prof. Joonghoe Dho and Dr Cedric Desplanches for the discussion as well as suggestions.

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