

A comparative study of the magnetic properties and phase separation behavior of the rare earth cobaltates, $Ln_{0.5}Sr_{0.5}CoO_3$ ($Ln =$ rare earth)

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Abstract

A comparative study of the magnetic properties of a few members of the $Ln_{0.5}Sr_{0.5}CoO_3$ family with different radii of the A -site cations, $\langle r_A \rangle$, in the range 1.19–1.40 Å has been carried out. The apparent T_c (where the magnetization undergoes an abrupt increase) decreases markedly with $\langle r_A \rangle$ as well as the size-disorder arising from the mismatch in the size of the A -site cations. The value of the magnetization at low temperatures decreases markedly with decrease in $\langle r_A \rangle$ or increase in size-disorder, suggesting that the relative proportion of the ferromagnetic (FM) species decreases relative to that of the paramagnetic (PM) species. Such a variation of the FM/PM ratio with composition and temperature is evidenced from the Mössbauer spectra of $La_{0.5}Sr_{0.5}CoO_3$ as well. The variation of the FM/PM ratio with $\langle r_A \rangle$ and size-disorder, as well as a local-probe study using ^{59}Co Nuclear magnetic resonance spectroscopy suggest that electronic phase separation is an inherent feature of the $Ln_{0.5}Sr_{0.5}CoO_3$ type cobaltates, with the nature of the different magnetic species in the phase-separated system varying with $\langle r_A \rangle$ and size disorder.

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1. Introduction

Lanthanum cobaltates of the general formula $La_{1-x}A_xCoO_3$ ($A =$ divalent alkaline earth) have been known for some time to show compositionally controlled insulator–metal transitions, with a gradual increase in the ferromagnetic (FM) metallic behavior with increase in x , at least up to $x = 0.5$ [1–3]. It was realized a few years ago that $La_{0.5}Sr_{0.5}CoO_3$, which was considered to be a good FM metal, was actually a magnetic cluster-glass with some long-range magnetic ordering wherein frustration arose from inter-cluster interactions at low temperatures [3,4]. The coexistence of FM and glassy behavior in $La_{0.5}Sr_{0.5}CoO_3$ has been examined in detail by magnetic relaxation and other measurements [4], the glassy behavior being indicated by a frequency-dependent maximum in the AC susceptibility data. Glassy ferromagnetism in

$La_{1-x}Sr_xCoO_3$ was investigated in great detail by Wu and Leighton [5], who found that the compositions with $x < 0.18$ consist of mixed phases with the characteristics of both FM and spin-glass behavior. The magnetic behavior of these systems has generally been interpreted in terms of short-range magnetic ordering. Cluster-glass behavior occurs at a high concentration of Sr ($x > 0.3$), where the coalescence of short-range FM clusters is proposed to occur [5]. ^{139}La nuclear magnetic resonance (NMR) studies confirm the coexistence of FM, paramagnetic (PM), and cluster-glass phases in $La_{1-x}Sr_xCoO_3$ [6] and the electronic phase separation in this system has been associated with the formation of isolated nanoscopic FM clusters [6,7]. The insulating side of $La_{1-x}Sr_xCoO_3$ (for small x) generally undergoes phase separation having FM metallic clusters embedded in a non-FM matrix, giving rise to giant magnetoresistance [8]. The glassy behavior in $La_{1-x}Sr_xCoO_3$ is considered to arise from contributions due to a spin-glass-like phase and intercluster interactions [9]. Thus, the cobaltates comprise FM clusters, PM

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matrices and spin-glass-like phases, all contributing to the glassy magnetic behavior. The spin-glass region could act as the interface between the FM regions and the PM matrix.

In the rare earth cobaltates of the general formula $Ln_{1-x}A_xCoO_3$ (Ln = rare earth other than La), analogous to the lanthanum derivatives previously discussed, the magnetic and electronic properties are affected by the relative size or radius of the A -site cations $\langle r_A \rangle$, as well as the disorder arising from the mismatch between the A -site cations [1,10–12]. The disorder is generally expressed in terms of the parameter σ^2 , which is defined as the variance of the A -cation radius distribution [13]. Size-disorder is indeed known to favour electronic phase separation in rare earth manganates. The rare earth cobaltates provide an interesting system to examine the effects of both $\langle r_A \rangle$ and σ^2 . Some of the members of the $Ln_{0.5}Sr_{0.5}CoO_3$ family such as those with $Ln = Pr$ and Nd appear to exhibit apparent FM transitions accompanied by glassy behavior [12,14]. A double magnetic transition in $Pr_{0.5}Sr_{0.5}CoO_3$ has been reported [15], but the nature of the transition is difficult to understand. $Nd_{1-x}Sr_xCoO_3$ compositions ($0.0 < x < 0.6$) seem to show a magnetic behavior similar to that of $La_{1-x}Sr_xCoO_3$, including electronic phase separation [16]. Thus, ^{59}Co NMR studies indicate the existence of phase separation in $Nd_{1-x}Sr_xCoO_3$ ($0.0 < x < 0.5$) [17].

In view of the interesting magnetic and electrical properties of the $Ln_{0.5}Sr_{0.5}CoO_3$ family of cobaltates, we have carried out a comparative study of a few members of $Ln_{0.5}Sr_{0.5}CoO_3$ associated with different $\langle r_A \rangle$ values in the range 1.196–1.400 Å. Since we could not prepare $Dy_{0.5}Sr_{0.5}CoO_3$ with $\langle r_A \rangle$ of 1.196 Å in pure form, we have examined a cobaltate with the composition $Dy_{0.34}Nd_{0.16}Sr_{0.40}Ca_{0.10}CoO_3$ with a comparable $\langle r_A \rangle$. We considered it important to compare the magnetic and related properties of these materials, not only as a function of the A -site cation radius, but also of the size disorder, σ^2 , arising from the size mismatch between A -site cations. In doing so, we have investigated the properties of well-characterized materials, with special attention to glassy behavior and electronic phase separation. For this purpose, we have re-examined the magnetic properties as well as the literature data based on the use of local probes such as Mössbauer spectroscopy and NMR spectroscopy [18,19]. In the case of $Dy_{0.34}Nd_{0.16}Sr_{0.40}Ca_{0.1}CoO_3$ with the lowest $\langle r_A \rangle$, we have carried out a ^{59}Co

NMR spectroscopic study to examine the nature of phase separation.

2. Experimental procedure

Polycrystalline samples of $Ln_{0.5}Sr_{0.5}CoO_3$ were prepared by the conventional solid-state reaction method. Stoichiometric mixtures of the starting oxide materials, Ln_2O_3 , $SrCO_3$, $CaCO_3$ and Co_3O_4 , were weighed in the desired proportions and milled with propanol. After drying, they were calcined in air at 1223 K and after few intermediate grindings, the powders sintered at 1373 K for 24 h in air. The samples were then reground and the monophasic polycrystalline powders were hydrostatically pressed in small pellets and sintered at 1473 K for 48–60 h in air. The pellets were consequently annealed in an oxygen atmosphere from 673 to 1173 K, and the oxygen contents were determined by iodometric titrations. The oxygen content was in the range 2.97 ± 0.03 . The lattice parameters and space groups were determined using Proszki and are presented in Table 1 along with the values of the A -site cation radius and σ^2 .

The phase purity of the cobaltates was established by recording the X-ray diffraction patterns in the 2θ range of 10 – 90° with a Seiferts 3000 TT diffractometer and STOE/STADI-P using $CuK\alpha$ radiation. The sample compositions were qualitatively confirmed using energy dispersive X-ray analysis (EDX) with a LEICA S440I scanning electron microscope fitted with a Si–Li detector. A Quantum Design physical properties measurement system (PPMS) was used to investigate the magnetic properties of the samples. The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization was measured in different applied magnetic fields. The dynamics of the magnetic response was studied by AC susceptibility measurements at different frequencies. In the measurements of the temperature dependence of the ZFC magnetization, the samples were cooled from 300 to 10 K in zero-field, the field applied at 10 K and the magnetization recorded on re-heating the sample.

^{59}Co NMR experiments were performed in a Bruker MSL100 pulse spectrometer with a 7.04 T superconducting magnet. Temperature variation studies were made in an Oxford cryostat with ITC503 temperature controller in the range 75–300 K. A home built NMR probe with a silver rf coil was used to avoid spurious signals. The spectrum at

Table 1
Structural data of $Ln_{0.5}Sr_{0.5}CoO_3^{(a)}$

$A =$	$\langle r_A \rangle$ (Å)	σ^2 (Å) ²	Space group	a	b	c	α, β, γ
La	1.400	0.0020	$R-3c$	5.423			59.8
Gd	1.209	0.0100	$Pnma$	5.380	7.60	5.37	90
$Dy_{0.34}Nd_{0.16}Sr_{0.40}Ca_{0.10}$	1.1963	0.0100	$Pnma$	5.368	7.565	5.365	90
$Dy_{0.21}Nd_{0.44}Sr_{0.23}Ca_{0.27}$	1.1963	0.007	$Pnma$	5.377	7.556	5.421	90
$Dy_{0.06}Nd_{0.44}Sr_{0.23}Ca_{0.27}$	1.1966	0.004	$Pnma$	5.371	7.548	5.375	90

9-Coordination was used for Gd and Dy and 12-coordination for La and Nd. The uncertainty in the lattice parameters is less than ± 0.001 Å.

any temperature being very broad we use frequency sweep technique by exciting at suitable frequency step and recording the amplitude of the Fourier transformed spin echo signal at each step. The optimum pulse condition was set by taking $\pi/2$ pulse length as 5–7 μs and pulse separation τ as 40 μs . This ensured that the spin echo intensities would not depend on the relaxation effects. To have a reasonable signal/noise ratio we had to take about 96 000 accusations at each point.

3. Results and discussion

Magnetic properties of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ are fairly well understood. Although it shows a sharp transition in magnetization around 240 K (T_c), it exhibits a significant divergence between the FC and ZFC magnetization data (Fig. 1a) and shows a frequency-dependent AC susceptibility maximum around 165 K, suggesting a glassy nature [4]. More importantly, glassy ferromagnetism is accompanied by phase separation wherein FM clusters exist within a PM matrix. Evidence for the occurrence of phase separation in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ has also been provided by these studies [6]. We find evidence for phase separation in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ from the ^{57}Co Mössbauer spectroscopic data available in the literature [19]. The Mössbauer spectra show the presence of a PM signal in addition to the six-finger pattern due to the FM-type species over a range of compositions and a wide range of temperatures. We present the results derived from the Mössbauer study in Fig. 2, where we have plotted the variation of the ferromagnetic to paramagnetic (FM/PM) ratio with the composition. The FM/PM ratio increases with x . However, the PM feature continues to exist also for the $x = 0.5$

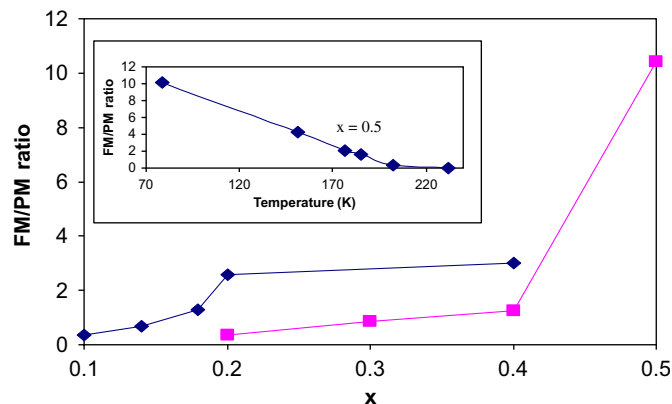


Fig. 2. Variation of the ratio of the ferromagnetic (FM) to paramagnetic (PM) species with composition in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$: squares, Mössbauer data at 78 K from Bhide et al. [19]; diamonds, NMR data at 1.9 K from Kuhns et al. [18]. The inset shows the temperature variation of the FM/PM ratio of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ taken from the Mössbauer data.

composition, even at low temperatures. The inset of Fig. 2 shows the temperature variation of the FM/PM ratio, showing an increasing trend with decreasing temperature, as one would expect. While the FM/PM ratio increases with a decrease in temperature, the PM phase continues to exist well below T_c (~ 220 K). Clearly, this observation is a direct evidence for phase separation in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. Along with the ^{57}Co Mössbauer results, we have given the results from a recent NMR study [18] for compositions up to $x = 0.4$ in Fig. 2, for purpose of comparison. The Mössbauer data were recorded at 78 K, while the NMR data were collected at 1.9 K. In the NMR study, the FM component was determined in zero field, while the non-FM component was determined in an applied field of 9.97 T. We can see from Fig. 2 that the data from the two different local probes are comparable.

It is of interest to examine the glassy phases and phase separation occurring in the other rare earth cobaltate compositions of the type $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. In the case of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, the magnetization data show the occurrence of two transitions around 220 and 100 K as described by Mahendiran and Schiffer [15]. The magnetic behavior of this cobaltate has been discussed sufficiently in the literature and we shall, therefore, comment on one or two specific features. This cobaltate exhibits a slight frequency-dependent hump at 200 K and besides well-defined transitions at 220 and 100 K in the AC susceptibility data. The frequency-dependent hump at 200 K is similar to the 165 K transition in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ described by Nam et al. [4], possibly arising from the presence of relatively large magnetic clusters responsible for a cluster-glass behavior. The 100 K transition is probably due to the presence of much smaller clusters. It thus appears that there are different types of magnetic species in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, as also evidenced by the temperature-induced changes in the magnetic domain structure [20]. In these cobaltates, just as in the analogous manganates, large

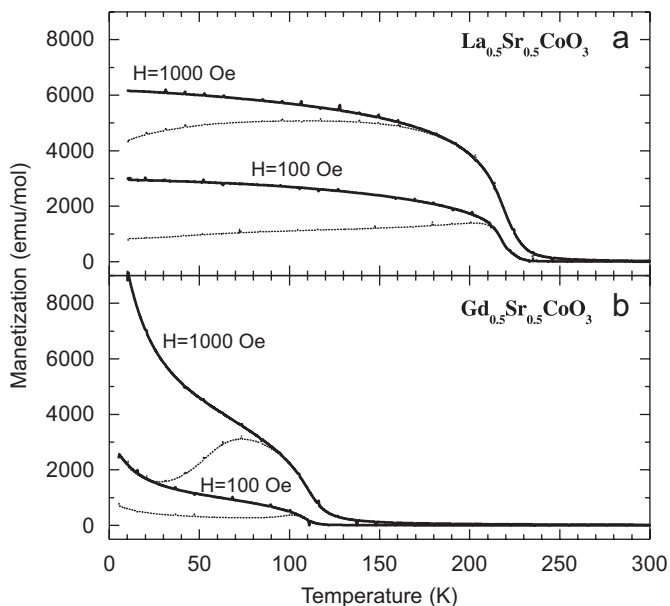


Fig. 1. DC Magnetization versus temperature plots for $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, (a) $\text{Ln} = \text{La}$, (b) $\text{Ln} = \text{Gd}$. Full and dotted curves denote FC and ZFC data, respectively. The increase in magnetization at low temperatures in (b) is due to the Gd contribution.

FM clusters will be metallic while the very small ones will be para- or anti-FM and insulating. In the case of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$, there is some evidence for electronic phase separation from magnetic properties as well as NMR spectroscopy [16,17]. Preliminary ^{57}Co Mössbauer data show the coexistence of a PM signal along with a six-finger pattern due to FM species just as in the case of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.

The temperature-dependent DC magnetization data of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ under FC and ZFC conditions are shown in Fig. 1(b). The magnetization data found by us are comparable to those of Luo et al. [21]. We note divergence in the ZFC and FC behavior as in magnetically disordered systems. What is particularly noteworthy is that the magnetization value in $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, specially at temperatures below the relatively sharp transition around 110 K (T_c) is much smaller than in the La analogue (see Fig. 1(b)). We observe the effect of decreasing $\langle r_A \rangle$ on the magnitude of magnetization distinctly in the case of $\text{Dy}_{0.34}\text{Nd}_{0.16}\text{Sr}_{0.40}\text{Ca}_{0.10}\text{CoO}_3$, with a $\langle r_A \rangle$ of 1.196 Å,

compared to $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ with an $\langle r_A \rangle$ of 1.209 Å (see Fig. 3(a)). Since the carrier concentration or the $\text{Co}^{3+}/\text{Co}^{4+}$ ratio remains constant in these cobaltates, a possible explanation for such a decrease in magnetization is that the proportion of the PM species relative to that of the FM species increases with the decrease in the size of the rare earth ion. It is entirely understandable that the proportion of the relatively large clusters responsible for ferromagnetism decreases with the decrease in $\langle r_A \rangle$. Such a behavior is found in rare earth manganates of the type $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ as well [22]. The occurrence of increased antiFM interactions with the decrease in $\langle r_A \rangle$ is not likely to be a main cause for the decrease in the magnetization because the cobalt ions would not be in the high-spin state at low temperatures. We shall be discussing this aspect later in the paper.

$\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ shows a nearly frequency-independent peak representing the presence of one type of magnetic species [20]. The AC susceptibility behavior of $\text{Dy}_{0.34}\text{Nd}_{0.16}\text{Sr}_{0.40}\text{Ca}_{0.10}\text{CoO}_3$ shown in Fig. 3(b) is similar to that of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, with a single peak around 110 K. Such a behavior has been noted earlier in the $\text{Ln}_{1-x}\text{Ca}_x\text{CoO}_3$ system [11,14]. The AC susceptibility data in Fig. 3(b), however, indicates some frequency dependence, probably due to disorder effects.

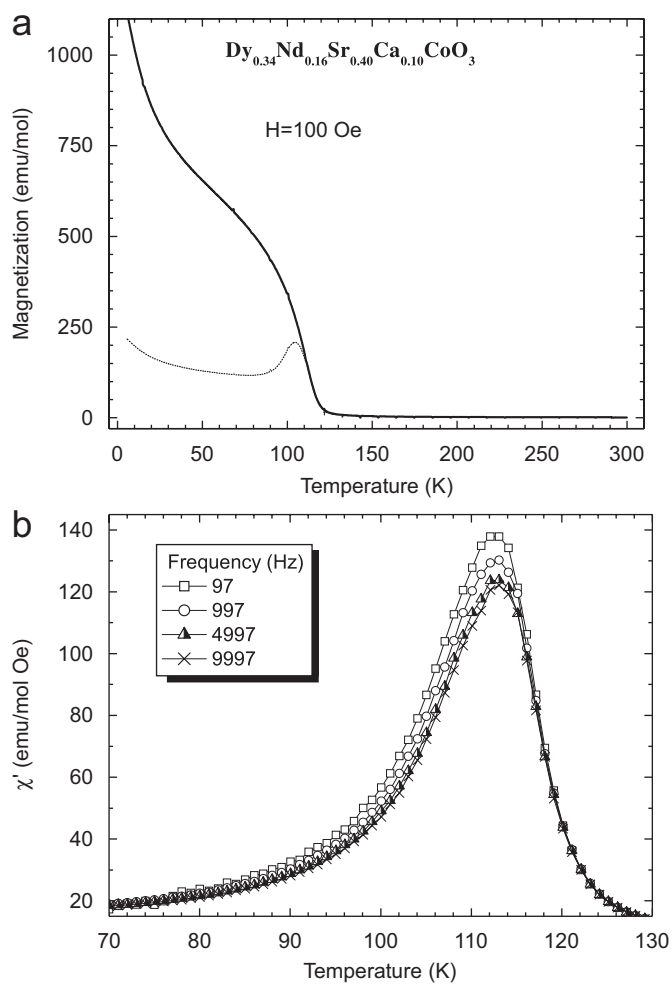


Fig. 3. (a) DC Magnetization and (b) AC susceptibility data for $\text{Dy}_{0.34}\text{Nd}_{0.16}\text{Sr}_{0.40}\text{Ca}_{0.10}\text{CoO}_3$. In (a) FC (full curve), ZFC (broken curve). Increase in magnetization at low-temperatures is due to the rare earth contribution.

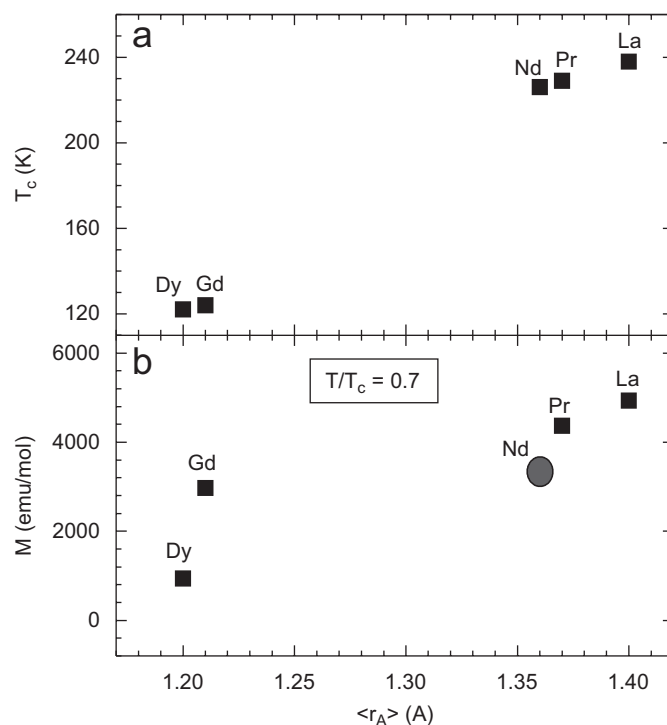


Fig. 4. Variation of (a) T_c and (b) FC magnetization at 1000 Oe with $\langle r_A \rangle$ at 120 K in $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and $\text{Dy}_{0.34}\text{Nd}_{0.16}\text{Sr}_{0.40}\text{Ca}_{0.10}\text{CoO}_3$ (Dy in the figure). The $\langle r_A \rangle$ values for La and Nd are for 12-coordination as given by the rhombohedral or monoclinic structure, while those for Gd and others are for 9-coordination in the orthorhombic structure. The magnetization data for the Nd system was estimated from the data collected at a field of 500 Oe. In (b), the values of M are at the same T/T_c value ($= 0.7$).

In the $Ln_{0.5}Sr_{0.5}CoO_3$ series, the T_c or the apparent T_c (where the magnetization shows an abrupt increase) decreases with $\langle r_A \rangle$, as can be seen in Fig. 4(a). Such a decrease in T_c with decrease in $\langle r_A \rangle$ corresponds to a well-established behavior [11,22,23]. Since the value of the magnetization below T_c is related to the proportion of the FM clusters, we have plotted the variation of magnetization with $\langle r_A \rangle$ at a fixed T/T_c of 0.7 in $Ln_{0.5}Sr_{0.5}CoO_3$ in Fig. 4(b). In this figure, we have also included the data on $Dy_{0.34}Nd_{0.16}Sr_{0.40}Ca_{0.10}CoO_3$ and $Nd_{0.5}Sr_{0.5}CoO_3$ [24]. From this figure, we see that the magnetization value decreases with $\langle r_A \rangle$, indicating an increase in the proportion of the PM species relative to that of the FM species. The reason that the magnetization value does not increase markedly at T_c in some of the cobaltates as in a good ferromagnet (or even as in $La_{0.5}Sr_{0.5}CoO_3$) is because of the presence of a minor proportion of the large FM clusters. The recent data on $Y_{0.5}Sr_{0.5}CoO_3$ [25] are consistent with the trends in Fig. 4.

It is known from the recent literature that the electronic and magnetic properties of rare earth manganates and cobaltates, are sensitive not only to the average size of the A -site cation, but also to the size-disorder arising from the A -site cation size mismatch [13,22,26,27]. We have examined whether size disorder plays a role in the $Ln_{0.5}Sr_{0.5}CoO_3$ system as well. For this purpose, we have fixed the $\langle r_A \rangle$ equal to that of $Dy_{0.5}Sr_{0.5}CoO_3$ (1.196 Å) and prepared compositions with different values of σ^2 . We show the magnetization data of these compounds in Fig. 5. We have plotted the T_c values against σ^2 in the inset of Fig. 5. The T_c increases with a decrease in σ^2 and the T_c value corresponding to the disorder-free case ($\sigma^2 = 0.0$) is 217 ± 2 K. The linear relation between T_c and σ^2 gives a slope of 9667 ± 192 K Å⁻², which is comparable to that reported in the literature [24]. Thus, increasing size disorder

or σ^2 favors electronic phase separation, giving rise to magnetic clusters of different size ranges (a feature found in rare earth manganates as well), while decreasing σ^2 increases the FM/PM ratio.

It would be in order to comment on the spin states of cobalt in $Ln_{0.5}Sr_{0.5}CoO_3$, since they would be relevant to the study of these materials with a local probe such as ⁵⁹Co NMR spectroscopy. At room temperature as well as near T_c , these compounds seem to have cobalt ions in the intermediate spin (IS) state ($t_{2g}^5e_g^1$ and $t_{2g}^4e_g^1$) rather than the high-spin (HS) state ($t_{2g}^4e_g^2$ and $t_{2g}^3e_g^2$) [28]. They may, however, form low-spin (LS) states ($t_{2g}^6e_g^0$ and $t_{2g}^5e_g^0$) at low temperatures. ⁵⁹Co NMR studies would be able to identify the presence of low-spin Co ions in different environments. The low-spin ion concentration is sensitive to $\langle r_A \rangle$ and would be favored by low $\langle r_A \rangle$ [28].

We have been able to carry out a ⁵⁹Co NMR study of $Dy_{0.34}Nd_{0.16}Sr_{0.40}Ca_{0.10}CoO_3$ since with a low $\langle r_A \rangle$ it has the highest proportion of low-spin Co^{3+} . There is one publication on ⁵⁹Co NMR study of $DyCoO_3$ [29]. Low field (4–12 MHz) continuous wave ⁵⁹Co NMR measurements gave $K_{iso} = 1.89\%$ with respect to $K_3Co(CN)_6$ with negligible quadrupolar interaction. On the other hand, depending on the Sr concentration, $Nd_{0.5}Sr_{0.5}CoO_3$ showed $K_{iso} = 1.7$ – 1.8% and quadrupolar interaction of 0.6–0.7 MHz [17,18,29]. In a system containing magnetic ions, the most general Hamiltonian for a nucleus having spin $I = 7/2$ in the presence of a magnetic field H_0 is written as

$$H = H_0 + H_{chem} + H_M + H_Q,$$

where H_0 is the Zeeman term, H_{chem} represents the temperature independent chemical shift interaction including the contribution from orbital paramagnetism in metal, which is analogous to the van Vleck PM susceptibility, H_M is due to magnetic hyperfine interaction, and H_Q is the electric quadrupole interaction. We shall neglect H_Q term, since the parent Dy cobaltite show no quadrupolar interaction. Thus the line shape for this system is mainly governed by magnetic interaction arising due to Dy/Nd moment and the distribution of the PM HS/IS cobalt ions surrounding the LS cobalt ions. The resonance frequency ν of a given transition is $\nu = \nu_R[1 + K_{iso} + K_{ax}(3\cos^2\theta - 1) + K_{an}\sin^2\theta\cos^2\varphi]$ where the symbols have their usual meanings.

Typical NMR spectra of $Dy_{0.34}Nd_{0.16}Sr_{0.40}Ca_{0.10}CoO_3$ are shown in Fig. 6. Clearly, two types of line shapes are present in the entire temperature range as seen from the fitted curves. In the range $200 < T < 300$ K, a more or less symmetric spectrum with linewidth (2β) $> K_{ax}$ is obtained, consistent with the large magnetic moment of Dy ion. The relevant NMR parameters are $K_{iso} = 2.45\%$, $K_{ax} = 0.1\%$ and $\beta = 75$ kHz, respectively. In addition to the original line, another broad and asymmetric spectrum appears around 200 K. Below 200 K each spectrum was, therefore, fitted to two components. These features are observable in the range $80 < T < 200$ K

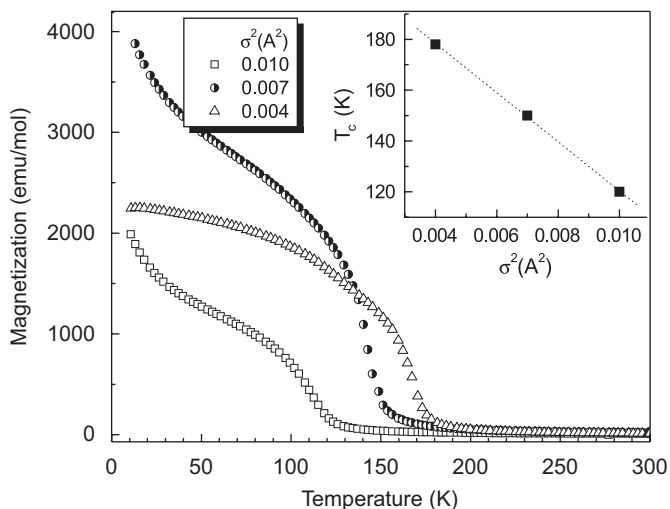


Fig. 5. Temperature variation of magnetization of the last three compounds in Table 1 with a fixed $\langle r_A \rangle$ of 1.196 Å and variable σ^2 . The data were collected under FC conditions at 1000 Oe. Inset shows variation of T_c with σ^2 .

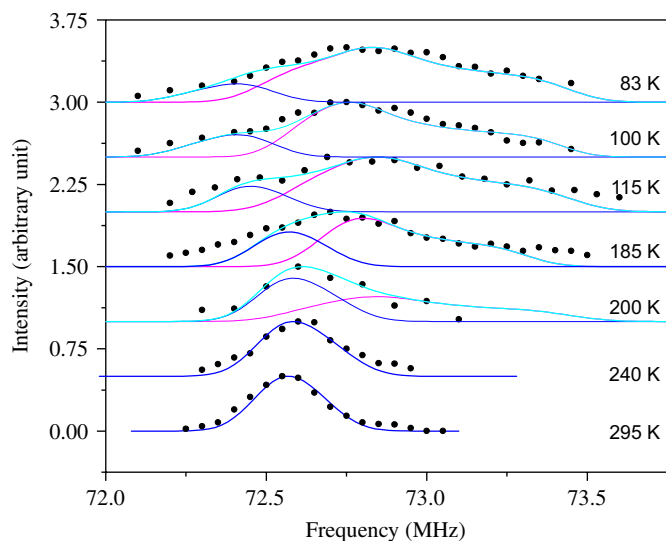


Fig. 6. Cobalt NMR spectra of $\text{Dy}_{0.34}\text{Nd}_{0.16}\text{Sr}_{0.4}\text{Ca}_{0.10}\text{CoO}_3$.

and seem to be composed of two NMR lines arising from different cobalt environments. The original component decreases in intensity, whereas the broad component grows in intensity as the temperature is lowered. This feature continues down to 115 K, and there is no change thereafter in the relative variation of the intensity of the two components, implying a stable environment. The smaller component has the same K_{iso} down to 115 K as mentioned earlier. Below 115 K, there is a small decrease in K_{iso} , indicating the presence of a small portion of the hole-poor region. The broad component has a large K_{iso} , varying from 2.8% to 3% as the temperature is lowered; K_{ax} also varies from 0.3% to 0.37%, the large shift indicating the presence of a magnetic environment. The possibility of the long-range order can be eliminated as we obtain NMR lines even below 80 K. It is more likely to be a signature of the presence of magnetic clusters around the LS cobalt ions. Based on the NMR data, we conclude that it is a coexistence of hole-poor LS region along with hole-rich magnetic clusters at low temperatures without any long-range magnetic order. The clusters occur even at 200 K implying thereby the occurrence of phase separation over a wide temperature range.

4. Conclusions

Evidence for electronic phase separation in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ is provided by Mössbauer spectroscopy besides magnetization and NMR studies. In the $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (Ln = rare earth) series, the value of the “apparent” ferromagnetic (FM) T_c , where the magnetization shows an abrupt increase, decreases with the decrease in the average radius of the A -site cations, $\langle r_A \rangle$. This is accompanied by a marked decrease in the value of the magnetization at low temperatures ($T < T_c$), indicating a decrease in the proportion of the FM species or the ratio of

the FM to the PM phases. This behavior is a manifestation of the phase separation. At small $\langle r_A \rangle$ or high size disorder, σ^2 , the FM/PM ratio becomes negligibly small even at low temperatures. The FM/PM ratio increases on decreasing σ^2 even when $\langle r_A \rangle$ is small. Our ^{59}Co NMR study of a cobaltate with small $\langle r_A \rangle$ provides evidence for the occurrence of phase separation. It appears that phase separation is common in the $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ type cobaltates, but the nature of the species present varies with $\langle r_A \rangle$ and σ^2 . High $\langle r_A \rangle$ and low σ^2 favor large magnetic clusters present along with PM and glassy phases. Small $\langle r_A \rangle$ and large σ^2 , on the other hand, favor relatively small PM clusters occurring in different environments.

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