

Cation size disorder as the crucial determinant of the unusual magnetic and electronic properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 415

(<http://iopscience.iop.org/0953-8984/16/3/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 07:51

Please note that [terms and conditions apply](#).

# Cation size disorder as the crucial determinant of the unusual magnetic and electronic properties of $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$

Asish K Kundu and C N R Rao<sup>1</sup>

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur PO, Bangalore-560064, India

E-mail: cnrrao@jnrcasr.ac.in

Received 4 November 2003

Published 9 January 2004

Online at [stacks.iop.org/JPhysCM/16/415](http://stacks.iop.org/JPhysCM/16/415) (DOI: 10.1088/0953-8984/16/3/018)

## Abstract

An investigation of three series of cobaltates of the formulae  $\text{Gd}_{0.5-x}\text{Ln}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{Ln} = \text{Nd}$  or  $\text{La}$ ) and  $\text{La}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  demonstrates the effects of the average radius of the A-site cations,  $\langle r_A \rangle$ , on the magnetic and electrical properties. Thus, the anomalous magnetic properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ , such as the transitions in the range 220–290 K, disappear, even with a small substitution of Nd or La in place of Gd, and a gradual evolution of ferromagnetism occurs at low temperatures (130–190 K).  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_3$ , on the other hand, shows increasing ferromagnetic properties with increase in  $x$  although the  $\langle r_A \rangle$  decreases, suggesting the role of size disorder. Studies of cobaltates of the type  $\text{Ln}_{0.5-x}\text{Ln}'_x\text{A}_{0.5-y}\text{A}'_y\text{CoO}_{3-\delta}$  with fixed  $\langle r_A \rangle$  values of 1.317 and 1.289 Å (the latter corresponding to  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ ), reveal that on decreasing the size disorder, the materials become ferromagnetic with relative high  $T_c$  values. These cobaltates also exhibit size disorder controlled metal–insulator transitions, the compositions with high disorder being insulators. The properties of  $\text{Dy}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  are consistent with the presence of size disorder in this material.

## 1. Introduction

Rare earth cobaltates of the type  $\text{Ln}_{0.5}\text{A}_{0.5}\text{CoO}_3$  ( $\text{Ln} = \text{rare earth}$ ,  $\text{A} = \text{alkaline earth}$ ), especially those with  $\text{A} = \text{Sr}$ , are, by and large, ferromagnetic with some of them exhibiting metallic behaviour [1–5]. These properties arise because of the presence of  $\text{Co}^{3+}\text{–O–Co}^{4+}$  states in these cobaltates. The ferromagnetic  $T_c$  increases with the increase in the size of the A-site cations. When  $\text{A} = \text{Ba}$ , ferromagnetism occurs when  $\text{Ln} = \text{La}$  ( $T_c = 190$  K) and

<sup>1</sup> Author to whom any correspondence should be addressed.

Nd ( $T_c = 130$  K), but when Ln = Gd, the material shows unusual magnetic and electrical properties. Thus,  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ , which is charge-ordered at room temperature, shows an increase in magnetization around 280 K, without ever reaching a high value of the magnetic moment [6–9]. Furthermore,  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  is an insulator, unlike  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  which is metallic. The average radius of the A-site cations,  $\langle r_A \rangle$ , as well as the size disorder arising from the cation size mismatch, as measured by the variance  $\sigma^2$ , are known to play important roles in determining the properties of rare earth manganates and cobaltates [9, 10]. Here, the variance  $\sigma^2$  is defined as  $\sigma^2 = \sum x_i r_i^2 - \langle r_A \rangle^2$ , where  $x_i$  is the fractional occupancy of A-site ions,  $r_i$  is the corresponding ionic radii and  $\langle r_A \rangle$  is the weighted average radius calculated from  $r_i$  values [10]. It appeared that the large value of  $\sigma^2$  in the  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  ( $0.033 \text{ \AA}^2$ ) compared to that of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  ( $0.016 \text{ \AA}^2$ ) could be responsible for the absence of ferromagnetism and metallicity in the former.

In order to understand the unusual properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ , we have carefully investigated cobaltates of the type  $\text{Gd}_{0.5-x}\text{Ln}_x\text{Ba}_{0.5}\text{CoO}_3$  (Ln = La, Nd) and  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_3$ , wherein the  $\langle r_A \rangle$  varies progressively with increase in  $x$ . The latter system is of interest because  $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  with a smaller  $\langle r_A \rangle$  shows a ferromagnetic transition ( $T_c \sim 140$  K), unlike  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ . In addition, we have studied several cobaltate compositions where  $\langle r_A \rangle$  was kept constant, but the magnitude of the size disorder,  $\sigma^2$ , was varied. For this purpose, cobaltate compositions  $\text{Ln}_{0.5-x}\text{Ln}'_x\text{A}_{0.5-y}\text{A}'_y\text{CoO}_{3-\delta}$ , with fixed  $\langle r_A \rangle$  values of 1.317 and 1.289 Å corresponding to  $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  and  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ , respectively, have been investigated. In all these studies, we have determined the oxygen stoichiometry of the samples by redox titrations and ensured that none of the observed trends in the properties arose from the differences in the oxygen content. The present study establishes that the unusual properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  arise mainly due to the disorder caused by the size mismatch between the Gd and Ba ions, a conclusion also supported by a comparison of the properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  with  $\text{Dy}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ .

## 2. Experimental procedure

Polycrystalline samples of  $\text{Ln}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  (Ln = La, Nd, Gd, or Dy),  $\text{Gd}_{0.5-x}\text{Ln}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  (Ln = La, Nd),  $\text{La}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  and  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_{3-\delta}$  were prepared by the conventional ceramic method. Stoichiometric mixtures of the respective rare earth oxides, alkaline earth carbonates and  $\text{Co}_3\text{O}_4$  were weighed in desired proportions and milled for a few hours with propanol. After the mixed powders were dried, they were calcined in air at 900 °C followed by heating at 1000 and 1100 °C for 12 h each in air. The powders thus obtained were pelletized and the pellets sintered at 1200 °C for 12 h in air. To improve the oxygen stoichiometry the samples were annealed in an oxygen atmosphere at a lower temperature (<800 °C). The oxygen stoichiometry was determined by iodometric titrations. The error in the determination of oxygen content was  $\pm 0.02$ . The oxygen stoichiometry in the cobaltates studied by us was generally around  $2.94 \pm 0.06$ .

The phase purity of the samples was established by recording the x-ray diffraction patterns in the  $2\theta$  range of 10–80° with a Seiferts 3000 TT diffractometer, employing Cu K $\alpha$  radiation. The unit cell parameters of  $\text{Gd}_{0.5-x}\text{Ln}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  (Ln = La, Nd) are listed in table 1 along with the weighted average radius  $\langle r_A \rangle$ , and the  $\sigma^2$  values. The  $\langle r_A \rangle$  values were calculated using the Shannon radii for 12-coordination in the case of rhombohedral cobaltates, and for 9-coordination in the case of the orthorhombic ones. The uncertainties in the unit cell parameters are  $\pm 0.004$  Å. In tables 2 and 3, we give the structural parameters of  $\text{La}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  and  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_{3-\delta}$ , respectively, along with

**Table 1.** The structure and properties of Gd<sub>0.5-x</sub>Ln<sub>x</sub>Ba<sub>0.5</sub>CoO<sub>3-δ</sub>.

Composition <i>x</i>	$\langle r_A \rangle$ (Å)	$\sigma^2$ (Å <sup>2</sup> )	Space group	Lattice parameters (Å)			<i>V</i> (Å <sup>3</sup> )
				<i>a</i>	<i>b</i>	<i>c</i>	
0.0	1.289	0.033	<i>Pmmm</i>	11.708	11.633	7.533	1026
Ln = Nd							
0.1	1.294	0.031	<i>Pmmm</i>	11.729	11.660	7.535	1030
0.2	1.300	0.029	<i>Pmmm</i>	11.752	11.668	7.548	1035
0.3	1.305	0.028	<i>Pmmm</i>	11.699	11.656	7.583	1034
0.4	1.311	0.026	<i>Pmmm</i>	11.759	11.686	7.586	1042
0.5	1.317	0.024	<i>Pmmm</i>	11.717	11.684	7.602	1041
Ln = La							
0.1	1.299	0.030	<i>Pmmm</i>	11.673	11.687	7.575	1033
0.25	1.316	0.025	<i>Pmmm</i>	11.712	11.684	7.630	1044
0.3	1.321	0.024	<i>Pmmm</i>	11.717	11.683	7.640	1046
0.4	1.459	0.028	<i>R<math>\bar{3}C</math></i>	5.481	—	—	164
0.5	1.485	0.016	<i>R<math>\bar{3}C</math></i>	5.486	—	—	165

**Table 2.** The structure and properties of La<sub>0.5-x</sub>Nd<sub>x</sub>Ba<sub>0.5</sub>CoO<sub>3-δ</sub>.

Composition <i>x</i>	$\langle r_A \rangle$ (Å)	$\sigma^2$ (Å <sup>2</sup> )	Space group	Lattice parameters (Å)			<i>T<sub>c</sub></i> (K)
				<i>a</i>	<i>b</i>	<i>c</i>	
0.0	1.485	0.016	<i>R<math>\bar{3}C</math></i>	5.486	—	—	190
0.1	1.476	0.019	<i>R<math>\bar{3}C</math></i>	5.482	—	—	180
0.2	1.332	0.019	<i>Pmmm</i>	11.688	11.651	7.692	177
0.3	1.327	0.021	<i>Pmmm</i>	11.711	1.676	7.622	164
0.4	1.322	0.022	<i>Pmmm</i>	11.704	11.691	7.623	150
0.5	1.317	0.024	<i>Pmmm</i>	11.717	11.684	7.602	130

**Table 3.** The structure and properties of Gd<sub>0.5</sub>Ba<sub>0.5-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub>.

Composition <i>x</i>	$\langle r_A \rangle$ (Å)	$\sigma^2$ (Å <sup>2</sup> )	Space group	Lattice parameters (Å)			<i>T<sub>c</sub></i> (K)
				<i>a</i>	<i>b</i>	<i>c</i>	
0.0	1.289	0.033	<i>Pmmm</i>	11.708	11.633	7.533	—
0.1	1.273	0.030	<i>Pmmm</i>	11.653	11.608	7.522	—
0.2	1.257	0.026	<i>Pmmm</i>	11.587	11.571	7.524	—
0.3	1.241	0.021	<i>Pmmm</i>	11.582	11.555	7.499	133
0.4	1.225	0.016	<i>Pnma</i>	5.389	7.599	5.380	145
0.5	1.209	0.010	<i>Pnma</i>	5.371	7.558	5.371	150

the ferromagnetic  $T_c$  values. Magnetization ( $M$ ) measurements were made with a vibrating sample magnetometer (Lakeshore 7300) in an applied magnetic field of 500 Oe. Electrical resistivity ( $\rho$ ) measurements were carried out from room temperature to 20 K by the four-probe method.

Two series of cobaltates of the general formula Ln<sub>0.5-x</sub>Ln'<sub>x</sub>A<sub>0.5-y</sub>A'<sub>y</sub>CoO<sub>3-δ</sub> with fixed  $\langle r_A \rangle$  values of 1.317 and 1.289 Å were prepared to study the effect of the A-site cation size mismatch on the properties by the ceramic procedure. The structural parameters of these cobaltates are given in table 4, along with the ferromagnetic  $T_c$  values.

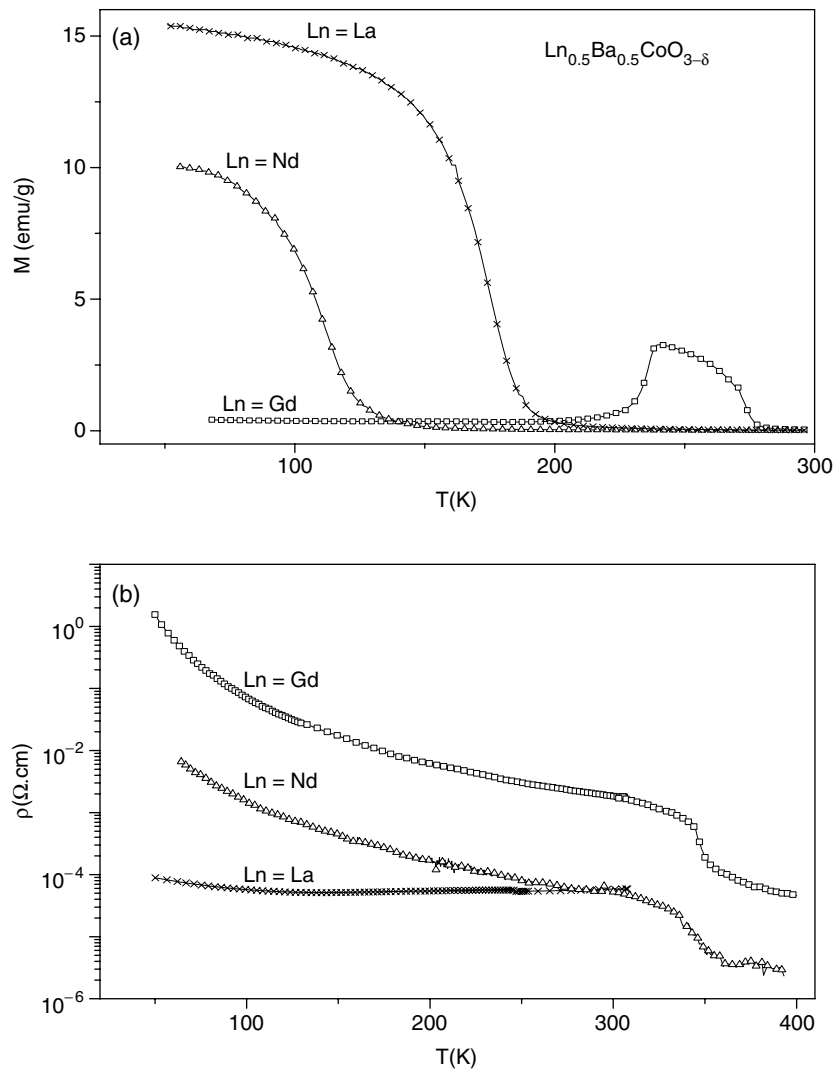
**Table 4.** The structure and properties of  $\text{Ln}_{0.5-x}\text{Ln}'_x\text{A}_{0.5-y}\text{A}'_y\text{CoO}_{3-\delta}$  with fixed  $\langle r_A \rangle$  values.

Composition	$\sigma^2$ ( $\text{\AA}^2$ )	Space group	Lattice parameters ( $\text{\AA}$ )			$T_c$ (K)
			$a$	$b$	$c$	
$\langle r_A \rangle = 1.317 \text{ \AA}$						
$\text{La}_{0.22}\text{Pr}_{0.28}\text{Ba}_{0.4}\text{Sr}_{0.1}\text{CoO}_3$	0.0170	<i>Pnma</i>	5.470	7.726	5.471	190
$\text{Pr}_{0.5}\text{Ba}_{0.45}\text{Sr}_{0.05}\text{CoO}_3$	0.0200	<i>Pmmm</i>	11.688	11.666	7.639	166
$\text{Nd}_{0.1}\text{Pr}_{0.4}\text{Ba}_{0.46}\text{Sr}_{0.04}\text{CoO}_3$	0.0207	<i>Pmmm</i>	11.682	11.650	7.634	160
$\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$	0.0235	<i>Pmmm</i>	11.717	11.684	7.602	130
$\text{Pr}_{0.39}\text{Gd}_{0.11}\text{Ba}_{0.5}\text{CoO}_3$	0.0239	<i>Pmmm</i>	11.715	11.674	7.609	—
$\langle r_A \rangle = 1.289 \text{ \AA}$						
$\text{La}_{0.29}\text{Gd}_{0.21}\text{Ba}_{0.3}\text{Sr}_{0.2}\text{CoO}_3$	0.0184	<i>Pnma</i>	5.447	7.685	5.425	220
$\text{Gd}_{0.17}\text{Pr}_{0.33}\text{Ba}_{0.35}\text{Sr}_{0.15}\text{CoO}_3$	0.0211	<i>Pmmm</i>	11.633	11.591	7.600	155
$\text{Gd}_{0.22}\text{Nd}_{0.28}\text{Ba}_{0.4}\text{Sr}_{0.1}\text{CoO}_3$	0.0248	<i>Pmmm</i>	11.658	11.639	7.569	128
$\text{Gd}_{0.1}\text{Sm}_{0.4}\text{Ba}_{0.42}\text{Sr}_{0.08}\text{CoO}_3$	0.0276	<i>Pmmm</i>	11.658	11.638	7.551	—
$\text{Gd}_{0.35}\text{Nd}_{0.15}\text{Ba}_{0.45}\text{Sr}_{0.05}\text{CoO}_3$	0.0287	<i>Pmmm</i>	11.728	11.651	7.542	—
$\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$	0.0329	<i>Pmmm</i>	11.708	11.633	7.533	—

### 3. Results and discussion

Before we discuss the results of our investigations of the cobaltate compositions of type  $\text{Gd}_{0.5-x}\text{Ln}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) and  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_{3-\delta}$ , it would be in order to briefly examine the properties of the parent compound  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  based on the literature [6–9] and our own measurements. In figure 1(a), we compare the magnetization data of  $\text{Ln}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  with  $\text{Ln} = \text{La}, \text{Nd}$  and  $\text{Gd}$  to show how  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  is uniquely different from  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.95}$  and  $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.94}$ . The last two cobaltates show ferromagnetic (FM) transitions around 190 and 130 K, respectively, with saturation magnetic moments of 0.67 (1.43) and 0.45 (0.57)  $\mu_B$  at a field of 500 Oe (5 kOe in parentheses).  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  shows an increase in magnetization starting around 280 K, reaching a maximum value around 240 K, with an associated magnetic moment of only 0.15  $\mu_B$  at 500 Oe (0.21  $\mu_B$  at 5 kOe). The magnetization drops sharply around 230 K to an antiferromagnetic state, and the AFM transition is destroyed by magnetic fields. The increase in magnetization in  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  at 280 K is clearly not due to an FM transition. An FM transition should have occurred at temperatures lower than 130 K, considering that  $\text{Gd}^{3+}$  is much smaller than  $\text{Nd}^{3+}$ . The observed magnetic properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  could arise from electronic phase separation arising from the large cation size disorder [11–13]. The electrical properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  are also different from those of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.95}$ , as can be seen from figure 1(b). Thus,  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.95}$  shows a nearly temperature-independent resistivity from 300 to 20 K.  $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.94}$  and  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$ , on the other hand, show transitions around 360 K due to charge-ordering. The resistivity of the Gd derivative is much higher than that of the Nd derivative, although both are insulators.

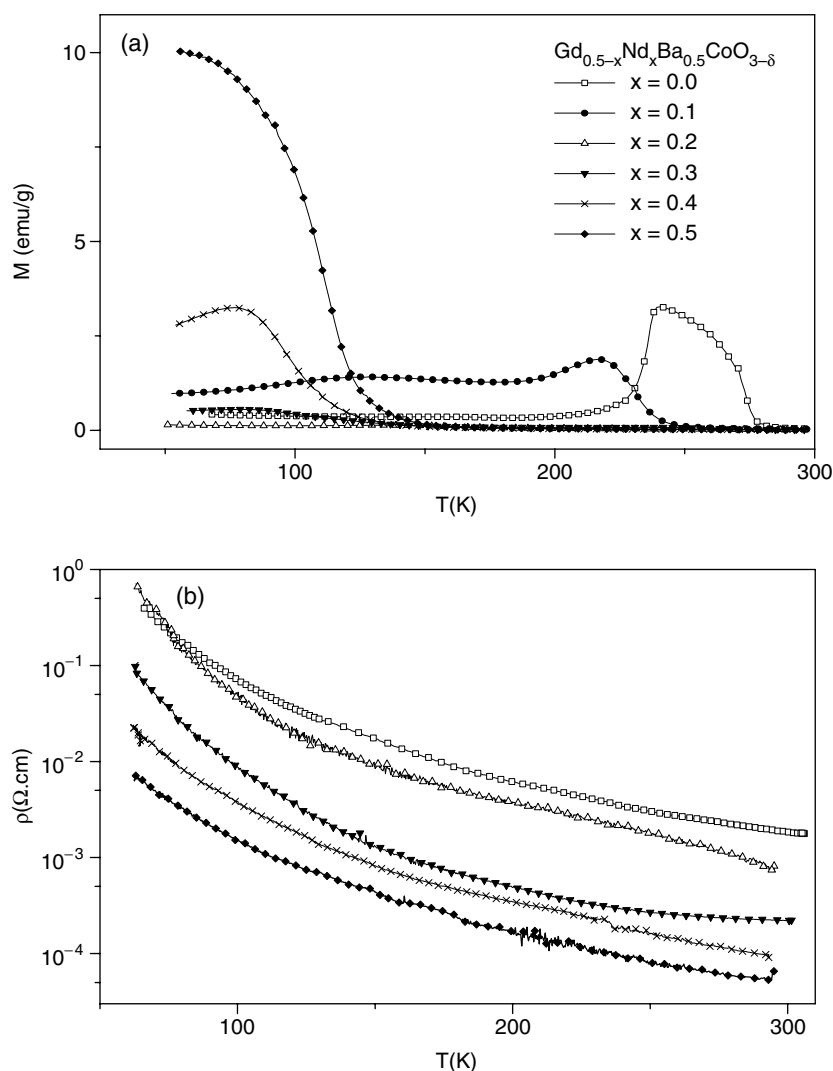
In order to study the effects of cation size, we have examined the magnetic and electrical properties of several series of cobaltates. We show the magnetization and resistivity data of  $\text{Gd}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  in figure 2. With increase in  $x$ , we observe the evolution of ferromagnetism. What is interesting is that the 280 K magnetic transition of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  disappears even when  $x \geq 0.1$ . When  $\text{Ln} = \text{Nd}$ , we observe a complex behaviour for  $x = 0.1$ , with a magnetic transition around 220 K. We observe no obvious magnetic transitions in the 200–280 K region for  $0.1 < x < 0.4$ . The  $x = 0.3$  composition shows a small increase in



**Figure 1.** Temperature variation of (a) the magnetization,  $M$ , ( $H = 500$  Oe) and (b) the electrical resistivity,  $\rho$ , of  $\text{Ln}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{Ln} = \text{La}$ ,  $\text{Nd}$  or  $\text{Gd}$ ).

magnetization around 125 K, and the increase becomes more marked when  $x = 0.4$ . When  $\text{Ln} = \text{La}$ , there is no magnetic transition in the 200–280 K region for  $0.1 < x < 0.25$ . A distinct FM transition occurs at  $x = 0.5$  in the case of  $\text{Nd}$ , and at  $x = 0.4$  in the case of  $\text{La}$ . It is interesting that the FM characteristics start emerging at low temperatures ( $< 150$  K) in these cobaltate compositions around an  $\langle r_A \rangle$  value of  $1.30 \text{ \AA}$ . Clearly, with increasing  $x$ , the size of ferromagnetic clusters increases, eliminating the phase separation at small  $x$ , caused by size disorder. It is noteworthy that in  $\text{Pr}_{1-x}\text{A}_x\text{CoO}_3$  ( $0 \leq x \leq 0.5$ ,  $\text{A} = \text{Sr}, \text{Ba}$ ) spin or cluster glass behaviour has been found at low temperatures [14]. Spin glass behaviour is found in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $x < 0.1$ ), but with increasing  $x$  ferromagnetism manifests itself [15].

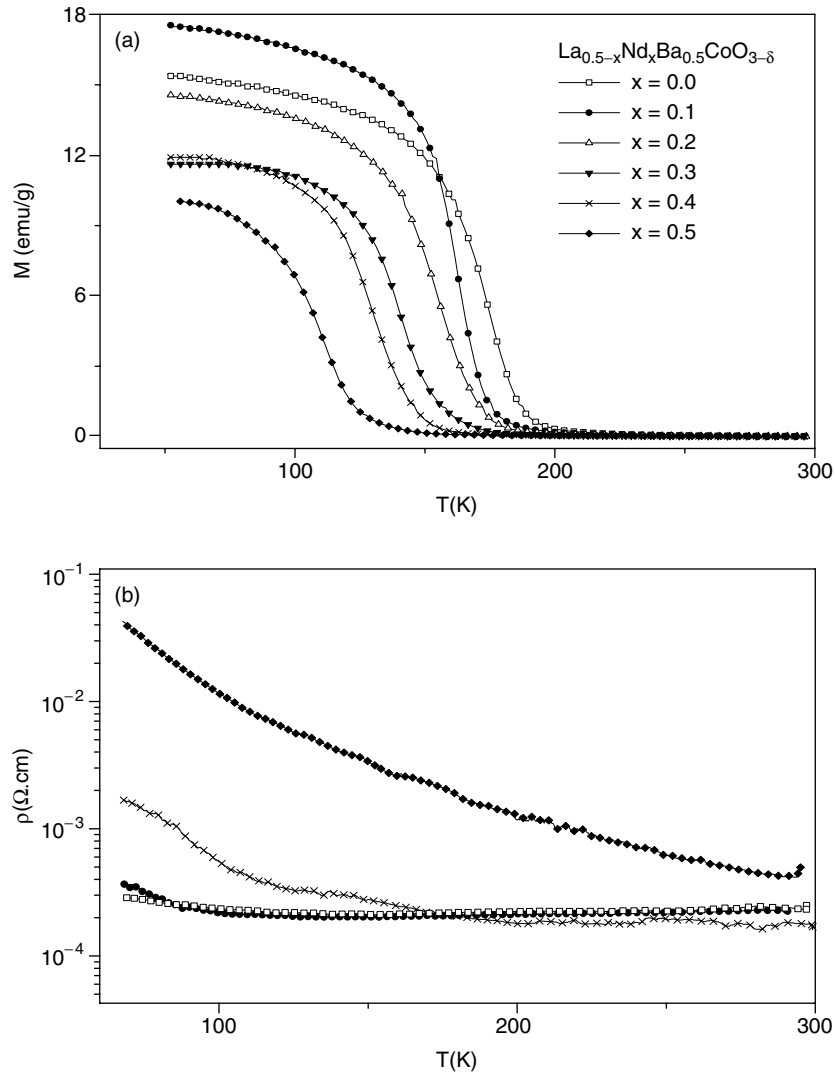
The resistivity data of the  $\text{Gd}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  compositions show insulating behaviour, but the resistivity decreases significantly with increasing  $x$ , the  $x = 0.5$  composition exhibiting the lowest resistivity (figure 2(b)). When  $\text{Ln} = \text{La}$ , the resistivity decreases with



**Figure 2.** Temperature variation of (a) the magnetization and (b) the electrical resistivity of  $\text{Gd}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ .

increasing  $x$ , becoming temperature independent for  $x = 0.5$ . All the other compositions are insulating. Considering that with increase in  $x$ , there is significant increase in  $\langle r_A \rangle$  in the two  $\text{Gd}_{0.5-x}\text{Ln}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) series of cobaltates, the changes observed can essentially be attributed to the effects of cation size. Our measurements on the  $\text{La}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_3$  system confirm this observation. In figure 3, we show the magnetization and resistivity data of this system. There is a decrease in  $T_c$  with increase in  $x$  in this series as expected, with an accompanying increase in the resistivity. Although the changes in the properties in this series of cobaltates is essentially due to cation size effects, it should be noted that there is also a small increase in  $\sigma^2$  with increasing  $x$  in this system.

In order to understand the role of size disorder due to cation size mismatch, we have investigated two series of cobaltates with fixed  $\langle r_A \rangle$  values of 1.317 and 1.289 Å, corresponding to those of  $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  and  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ . We show the results of the magnetization

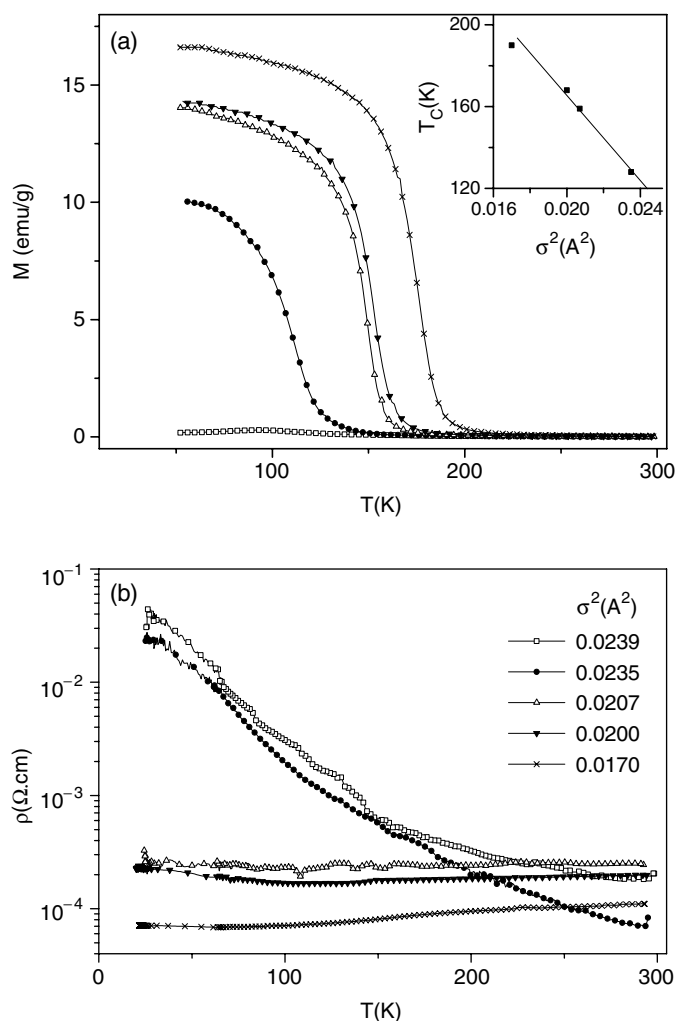


**Figure 3.** Temperature variation of (a) the magnetization and (b) the electrical resistivity of  $\text{La}_{0.5-x}\text{Nd}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ .

measurements in figures 4(a) and 5(a), respectively. The data in figure 4(a) for a fixed  $\langle r_A \rangle$  of  $1.317 \text{ \AA}$ , show that the  $T_c$  decreases as  $\sigma^2$  increases, eventually destroying ferromagnetism at a high value of  $\sigma^2$  ( $\approx 0.024 \text{ \AA}^2$ ). The linear relation between  $T_c$  and  $\sigma^2$  gives a slope of  $10830 \pm 300 \text{ K \AA}^{-2}$  with an intercept,  $T_c^0$ , of  $385 \pm 2 \text{ K}$ . Here,  $T_c^0$  represents the  $T_c$  value of the disorder-free cobaltate in this series.

The data in figure 5(a), corresponding to a fixed  $\langle r_A \rangle$  of  $1.289 \text{ \AA}$ , are interesting. With decrease in  $\sigma^2$ , the magnetic behaviour of this system changes markedly. Thus, when  $\sigma^2 = 0.028 \text{ \AA}^2$ , we do not see the magnetic anomaly of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  at  $280 \text{ K}$ . When  $\sigma^2 = 0.021 \text{ \AA}^2$ , we observe a ferromagnetic transition with a  $T_c$  of  $\sim 160 \text{ K}$ . When  $\sigma^2$  is  $0.0184 \text{ \AA}^2$ , the  $T_c$  reaches  $220 \text{ K}$ , a value higher than that of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ . These data clearly demonstrate that the absence of ferromagnetism in  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ , as well as its

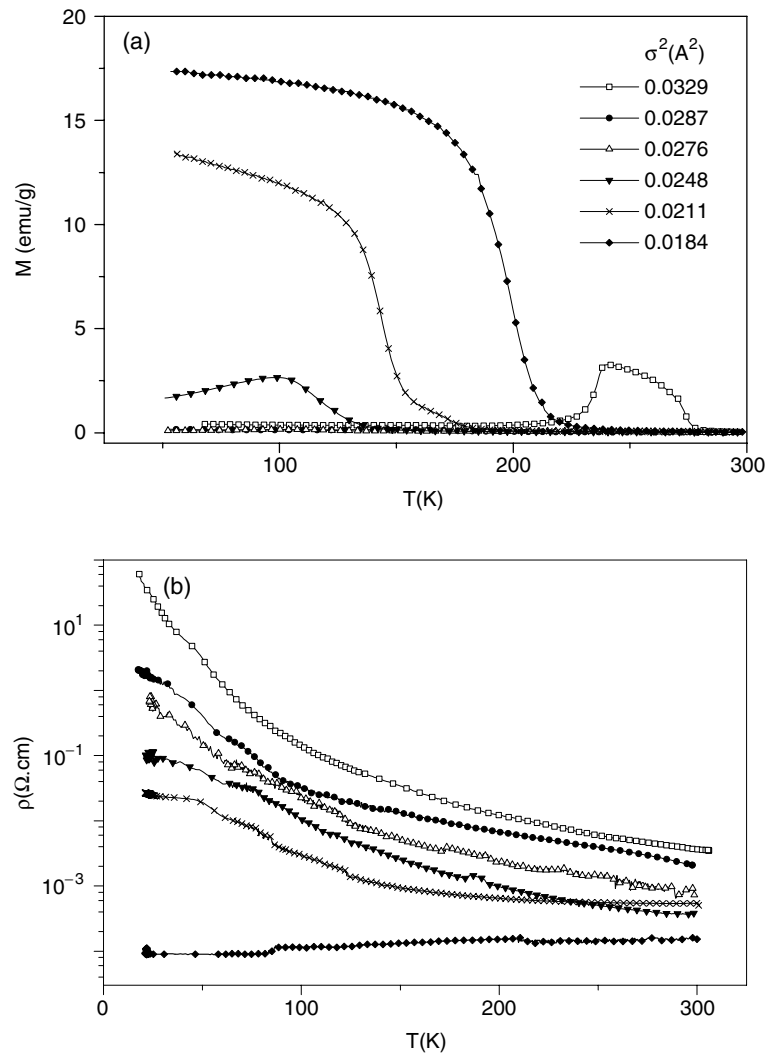




**Figure 4.** Temperature variation of (a) the magnetization and (b) the electrical resistivity of  $\text{Ln}_{0.5-x}\text{Ln}'_x\text{A}_{0.5-y}\text{A}'_y\text{CoO}_{3-\delta}$  with a fixed  $\langle r_A \rangle$  value of 1.317  $\text{\AA}$ .

unusual magnetic properties, such as the magnetic anomaly at 280 K, are almost entirely due to the disorder arising from the cation size mismatch. Such size disorder can give rise to electronic phase separation as in rare earth manganates [11–13]. Thus, in the series of compounds  $\text{La}_{0.7-x}\text{Ln}_x\text{Ca}_{0.3}\text{MnO}_3$  ( $\text{Ln} = \text{Pr, Nd, Gd, Y}$ ) the size disorder increases with the decreasing size of the Ln ion and increasing  $x$ . Accordingly, phase separation occurs at lower  $x$  with decreasing size. The situation is similar to  $\text{Gd}_{0.5-x}\text{Ln}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{Ln} = \text{Nd or La}$ ) compounds.

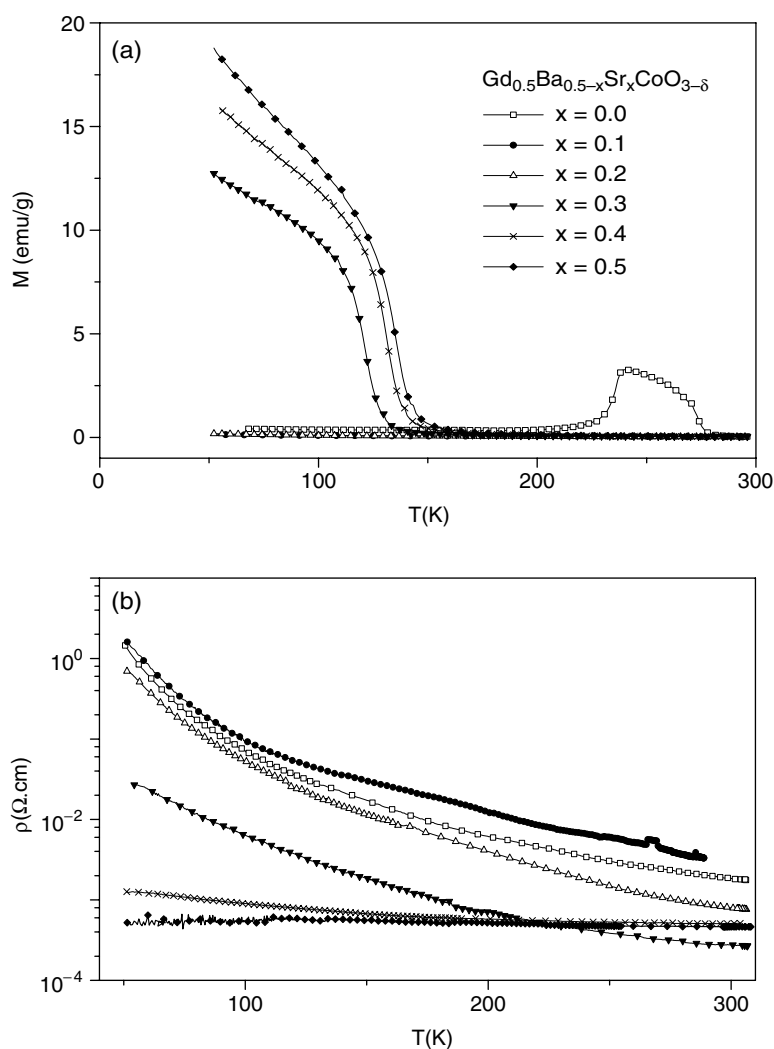
The electrical resistivity behaviour of the two series of cobaltates with fixed  $\langle r_A \rangle$  values corroborate the results from the magnetic measurements. In figures 4(b) and 5(b), we show the resistivity data for the two series to demonstrate how the resistivity increases with increase in  $\sigma^2$ . Interestingly, we observe disorder-induced insulator–metal transitions in both series of cobaltates, the cobaltate compositions with  $\sigma^2 < 0.02 \text{\AA}^2$  showing metallic behaviour. Such disorder-induced insulator–metal transitions are indeed novel.



**Figure 5.** Temperature variation of (a) the magnetization and (b) the electrical resistivity of  $\text{Ln}_{0.5-x}\text{Ln}'_x\text{A}_{0.5-y}\text{A}'_y\text{CoO}_{3-\delta}$  with a fixed  $\langle r_A \rangle$  value of  $1.289 \text{ \AA}$ .

Further support for the observation that cation size disorder crucially determines the properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$  is provided by our study of the  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_{3-\delta}$  series of cobaltates. Here, the  $x = 0.5$  composition, corresponding to  $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ , has a smaller  $\langle r_A \rangle$  than  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$ , and yet it shows ferromagnetic features (figure 6(a)). The 280 K magnetic anomaly of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  disappears even when  $x = 0.1$  and the apparent  $T_c$  increases with increase in  $x$  in the series. This behaviour is clearly due to size disorder, since  $\sigma^2$  decreases with increase in  $x$ . Accordingly, this system exhibits an insulator–metal transition with increase in  $x$  or decrease in  $\sigma^2$  (see figure 6(b)). It appears that a  $\sigma^2$  value larger than  $0.02 \text{ \AA}^2$  generally destroys ferromagnetism in the cobaltates and changes the metal into an insulator.

That the electrical and magnetic properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  are controlled by cation size disorder is supported by our preliminary studies of  $\text{Dy}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.91}$ , with a  $\sigma^2$  value



**Figure 6.** Temperature variation of (a) the magnetization,  $M$ , and (b) the electrical resistivity,  $\rho$ , of the cobaltates  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_{3-\delta}$ .

of  $0.037 \text{ \AA}^2$ .  $\text{Dy}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.91}$  shows a sharp increase in magnetization around 290 K and an antiferromagnetic type transition at 255 K. The general features of the Dy compound are thus similar to those of the Gd compound, except for the higher transition temperatures. The larger size disorder and associated phase separation in  $\text{Dy}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.91}$  could cause such differences.

#### 4. Conclusions

The present investigation shows that the ferromagnetic metallic state, generally found in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.95}$  and other analogous cobaltates of the type  $\text{Ln}_{0.5}\text{A}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{Ln}$  = rare-earth,  $\text{A}$  = alkaline earth), does not manifest itself in  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$ , mainly because of the disorder arising from the size mismatch between the Gd and the Ba ions.

Accordingly, if the size disorder is reduced, keeping the average size of the A-site cations the same, the material becomes ferromagnetic, reaching a  $T_c$  of 220 K. It appears that reducing the size disorder diminishes the electronic phase separation in this system. The crucial role of size disorder is also evidenced in the properties of  $\text{Gd}_{0.5}\text{Ba}_{0.5-x}\text{Sr}_x\text{CoO}_{3-\delta}$ , where with increasing  $x$ , the material becomes ferromagnetic, although the  $\langle r_A \rangle$  decreases.  $\text{Dy}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.91}$ , with an even greater size disorder than  $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.9}$ , shows similar properties, but the transition temperatures are higher, possibly due to the greater phase separation due to the increased size disorder.

### Acknowledgment

The authors thank BRNS (DAE), India, for support of this research.

### References

- [1] Jonker G H and van Santen J H 1953 *Physica* **19** 120
- [2] Goodenough J B and Raccach P M 1967 *Phys. Rev.* **155** 932
- [3] Bhide V G, Rajoria D S, Rao C N R, Rao G R and Jadhao V G 1975 *Phys. Rev. B* **12** 2832
- [4] Rao C N R, Prakash O, Bahadur D, Ganguly P and Nagabhushana S 1977 *J. Solid State Chem.* **22** 353
- [5] Senaris-Rodriguez M A and Goodenough J B 1995 *J. Solid State Chem.* **118** 323
- [6] Troyanchuk I O, Kasper N V, Khalyavin D D, Szymczak H, Szymczak R and Baran M 1998 *Phys. Rev. Lett.* **80** 3380
- [7] Troyanchuk I O, Kasper N V, Khalyavin D D, Szymczak H, Szymczak R and Baran M 1998 *Phys. Rev. B* **58** 2418
- [8] Moritomo Y, Takeo M, Liu X J, Akimoto T and Nakamura A 1998 *Phys. Rev. B* **58** R13334
- [9] Vanitha P V, Arulraj A, Santosh P N and Rao C N R 2000 *Chem. Mater.* **12** 1666
- [10] Rodriguez-Martinez L M and Attfield J P 1996 *Phys. Rev. B* **80** R15622
- [11] Dagotto E, Hotta T and Moreo A 2001 *Phys. Rep.* **344** 1  
Dagotto E, Burgoyne J and Moreo A 2003 *Solid State Commun.* **126** 9
- [12] Rao C N R and Vanitha P V 2002 *Curr. Opin. Solid State Mater. Sci.* **6** 97
- [13] Sudheendra L and Rao C N R 2003 *J. Phys.: Condens. Matter* **15** 3029
- [14] Yoshii K, Tsutsui S and Nakamura A 2001 *J. Magn. Magn. Mater.* **226–230** 829
- [15] Yoshii K, Abe H and Nakamura A 2001 *Mater. Res. Bull.* **36** 1447