

# Magnetic Properties of $\text{Dy}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ( $x = 0.67$ to $0.95$ )

D.J. Goossens<sup>a</sup>, K.F. Wilson<sup>b,c</sup> and M. James<sup>d</sup>

<sup>a</sup> *Research School of Chemistry, Australian National University, Canberra, Australia.*

<sup>b</sup> *Department of Physics, Australian National University, Canberra, Australia.*

<sup>c</sup> *School of Physics, University of New South Wales, Sydney, Australia.*

<sup>d</sup> *Bragg Institute, Australian Nuclear Science & Technology Organisation, Sydney, Australia.*

AC magnetic susceptibility of  $\text{Dy}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  has been measured from 17 to 320 K for a range of samples,  $x = 0.67$  to  $0.95$ . For  $x = 0.95$  the system enters a spin glass state at approximately 131K on cooling, as shown by a large cusp in the imaginary susceptibility. For smaller  $x$ , the system enters a magnetically ordered state at approximately 280K. This state shows evidence for a spin state transition in the Co ions at 90K, but no evidence of glassiness.

At room temperature the system is tetragonal,  $I4/mmm$ , becoming closer to cubic as  $x$  increases; at  $x = 0.95$  the system is metrically cubic. As  $x$  increases the fraction of  $\text{Co}^{4+}$  also increases, as shown by TGA. At  $x = 0.95$  over 50% of the Co sites are  $4+$ , and the mixture of exchange interactions is thought to give rise to the spin glass state. At smaller  $x$  the system appears weakly ferromagnetic, probably due to local ferromagnetic clusters and the Dy moments remain paramagnetic over the instrumental range. Keywords: perovskite magnetism, ac susceptibility.

## 1. Introduction

Lanthanide cobaltates ( $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ) (Ln = lanthanide ion) with perovskite-derived structures are of potential use in solid oxide fuel cells [1-4] and oxygen separation [5-6]. The materials show magnetic glassiness [7-8] and ferromagnetism [9].  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  has been widely studied [10, for example]. Interest has recently increased in phases with the smaller lanthanide ions such as Ho, Y and Dy [11]. This work adds to a systematic exploration of the structure and magnetic properties of this family of materials.

The physical properties of these materials depend on composition ( $\text{Ln}^{3+}/\text{Sr}^{2+}$ , O/vacancy,  $\text{Co}^{3+}/\text{Co}^{4+}$ ). Oxygen ionic conductivity changes with the O/vacancy ordering and associated structural relaxation [3]; magnetic behaviour changes with the  $\text{Co}^{3+}/\text{Co}^{4+}$  ratio and distribution. We present AC susceptometer results on  $\text{Dy}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ , where  $0.67 \leq x \leq 0.9$ .

## 2. Sample preparation

Polycrystalline samples of  $\text{Dy}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  were prepared from powders of  $\text{SrCO}_3$  (98+%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98%) and  $\text{Dy}_2\text{O}_3$  (99%). The powders were dissolved in dilute  $\text{HNO}_3$  and a mixture of metal oxides was formed via decomposition of a citric acid-ethylene glycol sol-gel. The ash was pelleted and sintered at 1100 °C under 1 atm.  $\text{O}_2$  for 3 days with repeated grinding and pelleting until powder x-ray diffraction (XRD) showed the reaction was complete.

## 3. Results

### 3.1 XRD Analysis

XRD measurements used a Scintag Inc. XGEN 4000 x-ray diffractometer at room temperature using  $\text{Cu K}\alpha$  radiation and a flat-plate sample holder. Data were collected over

$5^\circ \leq 2\theta \leq 105^\circ$ , in  $0.025^\circ$ , 10 s per step. This allowed verification of the structure and purity. All samples studied were pure phase samples which formed a tetragonal superlattice approximately  $2 \times 2 \times 4$  times the fundamental cubic perovskite cell. Table 1 shows the evolution of the tetragonal ratio,  $c/2a$  with  $x$ . At  $x = 0.95$  the data could be refined on a simple perovskite cube, indicating that the system was metrically cubic.

### 3.2 TGA Analysis

To find  $\delta$  thermogravimetry of *ca.* 70mg samples of  $\text{Dy}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  was carried out using a SETARAM TAG24. Samples were reduced to  $\text{Dy}_2\text{O}_3$ , SrO and Co metal under 3.5% hydrogen in nitrogen over a temperature range of 25-900 °C. Table 1 shows  $\delta$  and the percentage of  $\text{Co}^{4+}$ .  $\delta$  is almost independent of  $x$ , so as  $\text{Sr}^{2+}$  replaces  $\text{Dy}^{3+}$  charge is balanced by increasing the  $\text{Co}^{4+}$  content.

Table 1: Various parameters versus  $x$ . {1} indicates this ratio was fixed by refining in a cubic spacegroup.  $T_{cusp}$  is  $T$  for the cusp in  $\chi'$  indicating onset of magnetic LRO, except for  $x = 0.95$ , where it is the glass temperature.

$x$	$c/2a$	$\delta$	% $\text{Co}^{4+}$	$T_{cusp}$ (K)
0.67	1.0080(2)	0.22(2)	23(1)	267(4)
0.75	1.0040(2)	0.25(2)	25(1)	
0.80	1.0033(2)	0.29(2)	21(1)	
0.90	1.0020(3)	0.21(3)	48(1)	293(1)
0.95	{1}	0.22(4)	52(2)	131(1)

### 3.3 Susceptibility

Magnetic measurements were made using a Lakeshore 7000 series AC susceptometer with a closed cycle helium refrigerator ( $17 \text{ K} < T < 324 \text{ K}$ ). Fig. 1 shows the real part of the AC susceptibility,  $\chi'$ , against  $T$  for  $x = 0.67$  and  $0.9$  ( $H_{AC} = 6.25 \text{ Oe}$ ,  $H_{DC} = 0 \text{ Oe}$ ,  $f = 125 \text{ Hz}$ ).

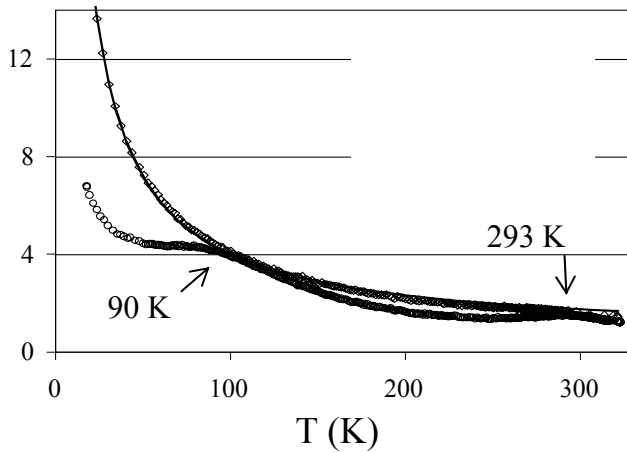


Fig. 1:  $\chi'$  for  $x = 0.67$  and  $x = 0.9$ . Fit is Curie-Weiss fit to  $x = 0.67$ :  $\chi = A/(T-\Theta)$

There are cusps at 267 K ( $x = 0.67$ ) and 293 K ( $x = 0.9$ ). The cusp for  $x = 0.67$  is not apparent on this scale. The hump in the  $x = 0.9$  data at 90K is evidence of a spin state transition in the Co, possibly from low spin  $\text{Co}^{3+}$  ( $S = 0$ ) to intermediate ( $S = 1$ ) or high spin ( $S = 2$ ) [13]. These features can be seen in the  $x = 0.67$  sample if the Curie-Weiss paramagnetism is subtracted out. The cusps at  $\sim 280\text{K}$  are the transitions from paramagnetism to a magnetically ordered state. Neutron scattering results from  $\text{Y}_{0.33}\text{Sr}_{0.67}\text{CoO}_{3-\delta}$  [14] show this state is predominantly

antiferromagnetic. The susceptibility shows a small ferromagnetic component which is likely due to ferromagnetic clusters (due to compositional variations) which are unaligned in the zero field neutron experiments but easily partially aligned by an applied magnetic field (used during a bulk measurement) [15]. The  $x = 0.95$  sample shows a cusp at 131K (Fig. 2) and also shows a peak in the imaginary part of the susceptibility ( $\chi''$ ) at  $129 \pm 1 \text{ K}$ , indicating glassiness. From Table 1, at this composition the  $\text{Co}^{4+}$  fraction is over 50%, causing a mixture of ferromagnetic and antiferromagnetic interactions, resulting in frustration and thus glassiness [16].

The large paramagnetic signal in the samples with smaller  $x$  is due to the Dy ions,

which have a large paramagnetic moment. A Curie-Weiss fit suggests  $10.8 \pm 0.3 \mu_B$  per Dy and  $\Theta = -3 \pm 3$  K at  $x = 0.67$ .  $10.8 \mu_B$  agrees well with an expected  $10.6 \mu_B$ . The paramagnetic contribution falls with Dy content (Fig. 1). There is no evidence ( $x = 0.67, 0.9$ ) that the Dy and Co moments couple at the measured temperatures, with  $\Theta$  for the Dy atoms being within error of 0 K.

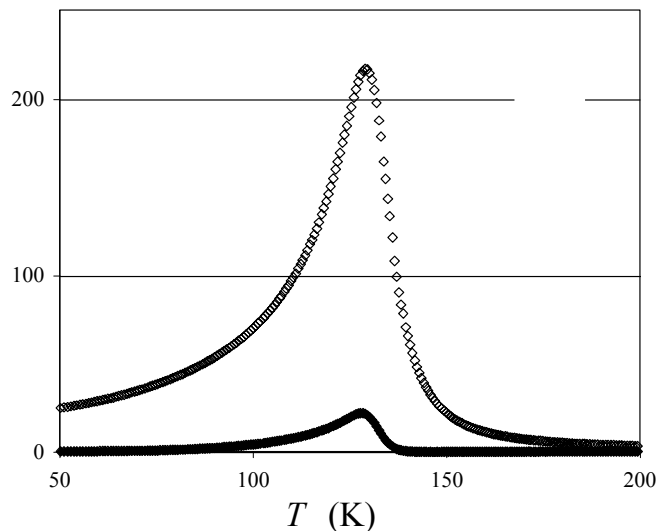


Fig. 2:  $\chi'$  and  $\chi''$  for  $x = 0.95$ . Note cusp in  $\chi''$  as well as  $\chi'$ . Same scale as Fig.1: note large response.

#### 4. Conclusions

$\text{Dy}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  undergoes a magnetic phase transition at  $\sim 280\text{K}$  for  $x < 0.95$  and the rare earth moment does not couple with the Co lattice over the temperature range measured. At  $x = 0.95$  the system enters a glassy phase below 130K due to the mixed population of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$ . Both  $\chi'$  and  $\chi''$  show large cusps at the spin glass transition, while the lack of evidence of Dy paramagnetism and the very large response opens the question of whether the Dy moments are coupling to the Co lattice at this composition.

#### Acknowledgments

We thank Mr. D. Cassidy (ANSTO) for TGA and AINSE for funding. KFW thanks Dr J. Cochrane (UNSW) for technical support.

#### References

- [1] S. J. Skinner, *International Journal of Inorganic Materials*, **3**, 113 (2001).
- [2] H. Y. Tu, Y. Takeda, N. Imanishi and O. Yamamoto, *Solid State Ionics*, **100**, 283 (1997).
- [3] R. H. E. van Doorn and A. J. Burggraaf, *Solid State Ionics*, **128**, 65 (2000).
- [4] S. B. Adler, *Solid State Ionics*, **111**, 111 (1998).
- [5] A. V. Kovalevsky, V. V. Kharton, V. N. Tikhonovich, E. N. Naumovich, A. A. Tonoyan, O. P. Reut and L. S. Boginsky, *Materials Science and Engineering*, **B52**, 105 (1998).
- [6] V. V. Kharton, A. A. Yaremchenko, A. V. Kovalevsky, A. P. Viskup, E. N. Naumovich, and P. F. Kerko, *J. Membrane Sci.*, **163**, 307 (1999).
- [7] S. Mukherjee, R. Ranganathan, P. S. Anilkumar and P. A. Joy, *Phys. Rev. B.*, **54**, 9267 (1996).
- [8] P. S. Anil Kumar, P. A. Joy and S. K. Date, *J. Phys.: Condens. Matter*, **10**, L487 (1998).
- [9] K. Asai, O. Yokokura, N. Nishimori, H. Chou, J. M. Tranquada, G. Shirane, S. Higuchi, Y. Okajima and K. Kohn, *Phys. Rev. B.*, **50**, 3025 (1994).
- [10] G. H. Jonker and J. H. Van Santen, *Physica*, **19**, 120 (1953).
- [11] S. K. Jeong, M. G. Kim, K. H. Kim, and C. H. Yo, *Bull. Korean Chem. Soc.*, **17**, 794 (1996)
- [12] M. James, D. J. Goossens, X. L. Wang, and M. Ionescu, 'Magnetic properties of  $\text{Y}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ', AIP Condensed Matter Meeting 2003.
- [13] M. Itoh and J. Hashimoto, *Physica C*, **341-348**, 2141 (2000).
- [14] D. J. Goossens, K. F. Wilson, M. James, X. L. Wang, *to be published*.
- [15] J. Wu and C. Leighton, *Phys. Rev. B* **67**, 174408 (2003)
- [16] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüninger and T. Lorenz, *Phys. Rev. B* **66**, 020402(R) (2002)