An AC Susceptibility Study of Strontium Cobaltates, $Ln_{1-x}Sr_xCoO_{3-\delta}$ where Ln = Y, Ho and Dy.

K.F. Wilson[a], D.J. Goossens[b], J.M. Cochrane[a] and M. James[b]

[a] *School of Physics, University of New South Wales, Sydney, 2052.*
[b] *The Bragg Institute, Lucas Heights, 2234, Australia.*

We discuss the AC susceptibility of members of the $Ln_{1-x}Sr_xCoO_{3-\delta}$ family of materials where $0.66 \leq x \leq 0.9$ and Ln = Y, Dy and Ho. The materials exhibit ferro- or ferrimagnetic ordering below room temperature. Despite the disorder introduced by mixed Co valence states, no glassiness is apparent in the imaginary part of the AC susceptibility or in the frequency dependence of the transition temperature. In addition, in the Dy and Ho materials it is found that the rare earth moments do not couple to the Co magnetic lattice.

1. Introduction

Rare earth cobaltates $(Ln_{1-x}Sr_xCoO_{3-\delta})$ (Ln = lanthanide ion) with perovskite derived structures are of interest for applications in solid oxide fuel cells [1-4] and as membranes for oxygen separation [5-6]. The materials show a range of magnetic behaviour including glassiness [7-8] and ferromagnetism [9]. $La_{1-x}Sr_xCoO_{3-\delta}$ has been extensively studied [10 for example]. Recently interest has increased in perovskite–related phases with smaller lanthanide ions [11]. This work is part of a systematic study of the structure and magnetic properties of this large family of compounds.

The physical properties of these materials are strongly dependent upon composition $(Ln^{3+}/Sr^{2+}, O/vacancy, Co^{3+}/Co^{4+})$. Oxygen ionic conductivity, for example, is known to be affected by O/vacancy ordering and associated structural relaxation [3]; magnetic behaviour will be affected by the related Co^{3+}/Co^{4+} ratio and distribution. We present AC susceptometer results on a range of $Ln_{1-x}Sr_xCoO_{3-\delta}$, where $0.66 \leq x \leq 0.9$ and $Ln^{3+} = Y^{3+}$, Ho^{3+} and Dy^{3+}.

2. Sample preparation

Polycrystalline samples of $Ln_{1-x}Sr_xCoO_{3-\delta}$ were prepared from powders of $SrCO_3$ (98+%), $Co(NO_3)_2.6H_2O$ (98%) and Y_2O_3 (99.99%), Dy_2O_3 (99.9%) or $Ho(NO_3)_3.5H2O$ (99.9%). The powders were dissolved in dilute nitric acid and a mixture of the metal oxides was formed via the decomposition of a citric acid-ethylene glycol sol-gel. The residues were pelleted and sintered at 1100 °C under flowing oxygen for up to 3 days with intermediate re-grinding and re-pelleting until no further reaction was evident by powder X-ray diffraction.

3. Results

3.1 XRD Analysis

Powder X-ray diffraction (XRD) measurements used a Scintag Inc. XGEN 4000 X-ray diffractometer at room temperature using Cu K_α radiation and a flat-plate sample holder. Data for structural refinement were collected over $5°\leq 2\theta \leq 105°$, in 0.025° steps, with integration times of 10 s. This allowed verification of the structure and purity. All samples studied were pure phase samples which formed a tetragonal superlattice phase with dimensions approximately 2×2×4 times the fundamental cubic perovskite lattice parameter.

3.2 TGA Analysis

Thermogravimetry of *ca.* 70mg samples of $Ln_{1-x}Sr_xCoO_{3-\delta}$ were carried out using a SETARAM TAG24 Simultaneous TGA and DTA. Samples were reduced under 3.5% hydrogen in nitrogen over a temperature range of 25 - 900 °C at a heating rate of 5 °C/minute. TGA showed $\delta = 0.23 \pm .02$ ($x = 0.67$) and $\delta = 0.35 \pm .02$ ($x = 0.9$) and was largely independent of Ln but dependent on x. From this, we find that 80% of the Co sites are Co^{3+} for both $x = 0.67$ and $x = 0.9$; there is a large population of Co^{4+} ions in the system.

3.3 Susceptibility

Magnetic measurements were made using a Lakeshore 7000 series AC susceptometer with a closed cycle helium refrigerator (17 K $< T <$ 324 K). Measurements were made in drift mode with a heater switched on manually when the sample reached room temperature. Maximum RMS magnetic field was 20 Oe and AC frequency could be varied from 5 Hz to 10 kHz, although limited magnetic fields could be applied at 10 kHz.

Samples with $x = 0.67$ and 0.9 and Ln = Ho, Dy and Y were measured ($H_{AC} = 6.25$ Oe, $H_{DC} = 0$ Oe, $f = 125$ Hz) to establish transition temperatures. For $x = 0.67$ the imaginary susceptibility, χ'', was in all cases within error of zero, so glassiness is not present. The real part, χ', showed a cusp at close to room temperature in all samples (see Table 1). The Ho and Dy samples showed a Curie-Weiss $1/T$ susceptibility contribution from the rare earths.

Fig. 1a shows the cusp in χ' for the $Y_{0.33}Sr_{0.67}CoO_{3-\delta}$ sample. Ho is shown in Fig. 1b along with a Curie-Weiss fit which yielded a Ho moment of 10.3 ± 0.4 μ_B, close to the rare-earth free ion moment of 10.6 μ_B. The Curie-Weiss component was subtracted out to leave a curve similar to the signal observed in the $Y_{0.33}Sr_{0.67}CoO_{3-\delta}$ sample, showing that as expected the rare earth moments do not couple to the Co lattice. This is shown, inset, in Fig. 1b.

Table 1: Magnetic ordering temperatures.

Sample	T_c (K)
$Y_{0.33}Sr_{0.67}CoO_{3-\delta}$	292(1)
$Ho_{0.33}Sr_{0.67}CoO_{3-\delta}$	285(2)
$Dy_{0.33}Sr_{0.67}CoO_{3-\delta}$	267(4)
$Y_{0.1}Sr_{0.9}CoO_{3-\delta}$	318(1)
$Ho_{0.1}Sr_{0.9}CoO_{3-\delta}$	> 322
$Dy_{0.1}Sr_{0.9}CoO_{3-\delta}$	293(1)

Repeating these experiments at $f = 2.5$ kHz, showed no change in the position of the cusp in χ'. This, coupled with χ'' remaining at zero at all temperatures, shows that the system is not glassy, despite the difference in field cooled/zero field cooled susceptibility observed in DC magnetometry. [12]. A possible explanation is given in [8], where magnetocrystalline anisotropy is invoked.
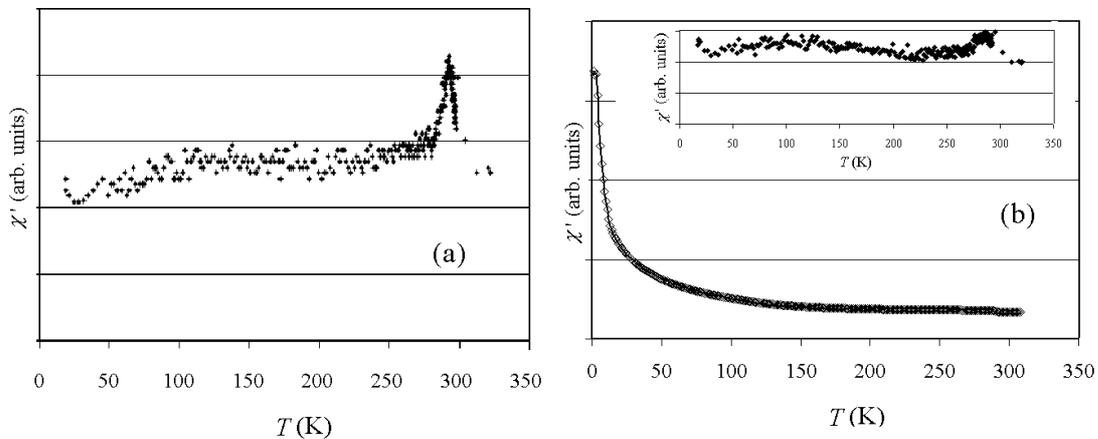

Figure 1a: Real part of AC susceptibility for $Y_{0.33}Sr_{0.67}CoO_{3-\delta}$ with $H_{DC} = 0$ Oe, $H_{AC} = 6.28$ Oe and $f = 125$ Hz. Figure 1b: Same for $Ho_{0.33}Sr_{0.67}CoO_{3-\delta}$. Solid line is Curie-Weiss fit. Inset gives χ' of $Ho_{0.33}Sr_{0.67}CoO_{3-\delta}$ with $1/T$ component removed.

Equivalent results for the $x = 0.9$ samples are shown in figure 2. These again show a high temperature peak (Table 1), with the Curie-Weiss component scaled down with the reduced Ln concentration (figure 2b). No feature was apparent in χ''. A low temperature cusp is seen in both plots which was not as apparent, although present, in figure 1. The mechanism for this is under investigation, but a spin state transition in the Co^{3+} is a possibility [13].
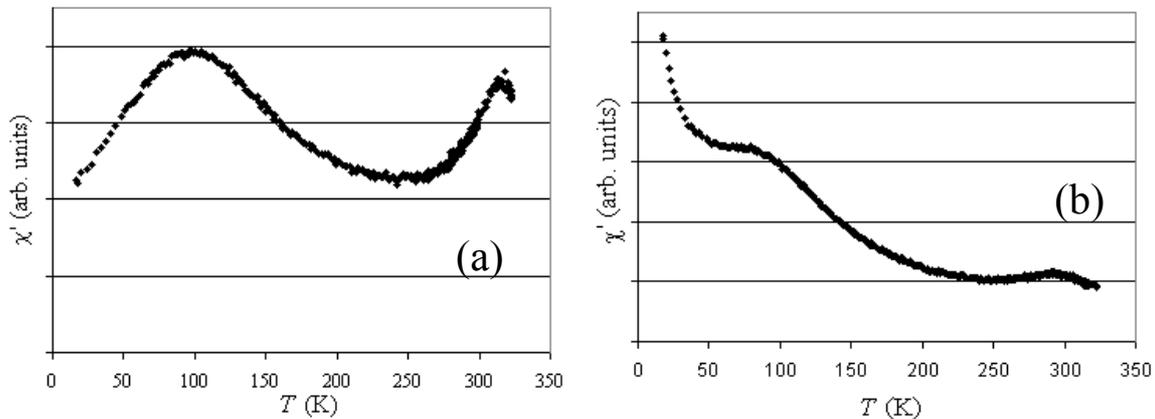

Figure 2a: Real part of AC susceptibility for $Y_{0.1}Sr_{0.9}CoO_{3-\delta}$ with $H_{DC} = 0$ Oe, $H_{AC} = 6.28$ Oe and $f = 125$ Hz. Figure 2b: Same for $Ho_{0.1}Sr_{0.9}CoO_{3-\delta}$. Note large hump at about 100 K, visible in both plots.

4.   Conclusions

We have explored the magnetic behaviour of some cobaltates, $Ln_{1-x}Sr_xCoO_{3-\delta}$, and shown them to be ferro- or ferrimagnetic. The FC/ZFC hysteresis observed using DC susceptibility does not indicate glassiness despite the presumed existence of magnetic disorder due to the mixed cobalt valency. When Ln = Dy or Ho, the rare earth moment does not couple with the Co lattice which is not surprising for these $4f$ electron atoms.

Acknowledgments

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