Magnetic Properties of $Gd_{1-x}Sr_xCoO_{3-\delta}$ (x = 0.67, 0.90 and 0.95)

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Introduction

Lanthanide cobaltates ($Ln_{1-x}Sr_xCoO_{3-\delta}$) (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]. $La_{1-x}Sr_xCoO_{3-\delta}$ 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 (Ln^{3+}/Sr^{2+}, O/vacancy, Co^{3+}/Co^{4+}). Oxygen ionic conductivity changes with the O/vacancy ordering and associated structural relaxation [3]; magnetic behaviour will be affected by the Co^{3+}/Co^{4+} ratio and distribution. We present AC susceptometer results on $Gd_{1-x}Sr_xCoO_{3-\delta}$, where $0.67 \leq x \leq 0.95$.

Sample preparation

Polycrystalline samples of $Gd_{1-x}Sr_xCoO_{3-\delta}$ were prepared from powders of $SrCO_3$ (98+%), $Co(NO_3)_2.6H_2O$ (98%) and Gd_2O_3 (99%). The powders were dissolved in dilute 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. O_2 for 3 days with repeated grinding and pelleting until powder XRD showed the reaction was complete.

Results and discussion

Powder X-ray diffraction (XRD) was used to determine key structural parameters for the materials. A detailed structural study [12] has shown that the materials form a large unit cell based on the perovskite cube but approximately 2×2×4 perovskite cubes in size, spacegroup I4/mmm. However, when x is large (at 0.95), the system is metrically cubic and shows no signs of the supercell even in electron diffraction. Thermogravimetry was used to determine the oxygen stoichiometry of the materials assuming charge neutrality (see table 1). The replacement of Gd^{3+} by Sr^{2+} is balanced by two mechanisms – the formation of Co^{4+} as well as the expected Co^{3+} and the presence of oxygen vacancies in the lattice. Table 1 lists lattice parameters, oxygen content and fraction of Co^{4+}.

The key results to be discussed here are the ac magnetic susceptibility measurements. Figure 1 shows the susceptibilities, real (χ') and imaginary (χ''), for $Gd_{0.33}Sr_{0.67}CoO_{2.82}$ at a range of frequencies.

Table 1: Key parameters for $Gd_{1-x}Sr_xCoO_{3-\delta}$. [a] indicates that this sample was refined using a cubic Pm3m cell, hence no *c/a* ratio is given. Structural values are measured at 295 K using laboratory XRD. [b] Indicates that this sample did not obey the Curie-Weiss law.

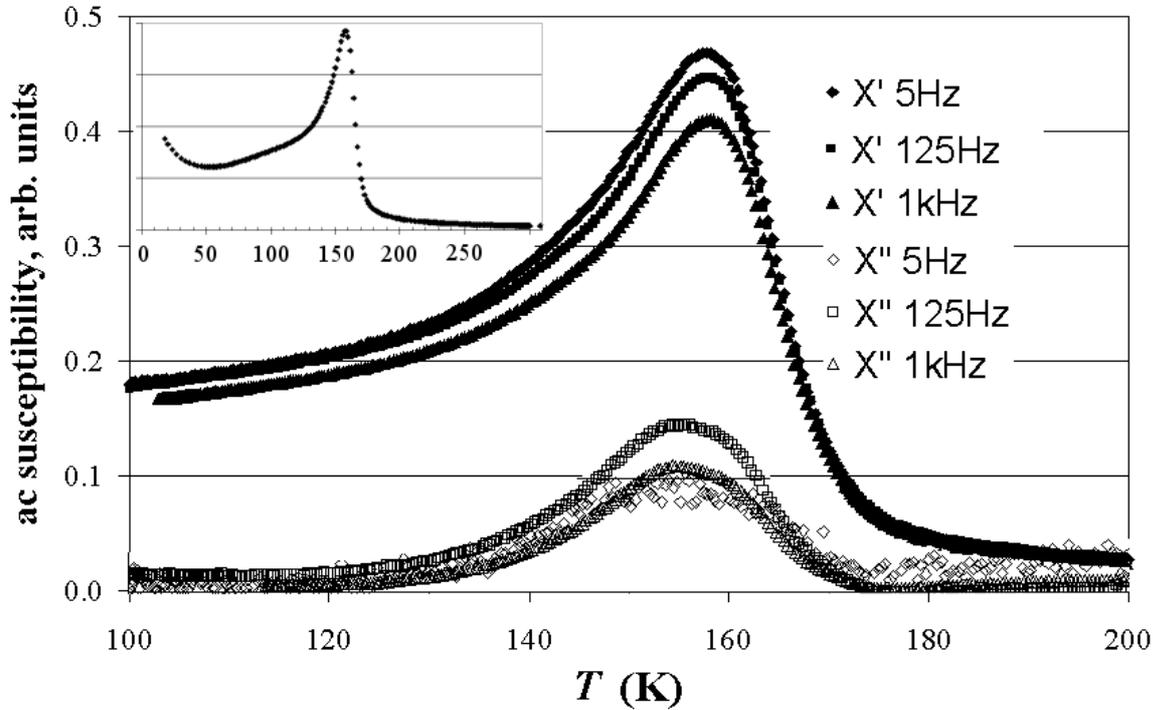| $Gd_{1-x}Sr_xCoO_{3-\delta}$	x = 0.67	x = 0.90	x = 0.95[a]
a (Å)	7.6228(1)	7.6900(3)	3.8498(1)
c (Å)	15.3733(3)	15.4210(8)	
V (Å³)	893.30(3)	911.94(7)	57.059(2)
c/2a	1.0084	1.0027	
Oxygen Content	2.82	2.76	2.78
% Co^{4+}	31	42	52
$T_f(\chi', 125\ Hz)\ (K)$	154(1)	129(1)	127(1)
$T_f(\chi'', 125\ Hz)\ (K)$	158(1)	126(1)	124(1)
Curie-Weiss moment, μ_B	---[b]	3.5(5)	3.5(4)

Figure 1: ac susceptibility of $Gd_{0.33}Sr_{0.67}CoO_{2.82}$ at a range of frequencies, normalised for measurement frequency. χ'' has been scaled up by a factor of 10 for visibility. Inset shows greater temperature range for 125 Hz measurement to show the increase at low temperatures due to Gd paramagnetism.

The fact that χ'' is non-zero is important (figure 1), as other materials ($Ho_{1-x}Sr_xCoO_{3-\delta}$, for example [13]) show very different susceptibilities at $x = 0.67$. For Ln = Ho, Dy and Y a small peak at close to room temperature is observed, while a large peak in χ' such as that shown in figure 1 at ~154 K and a non-zero χ'' only occurs when $x \sim 0.95$ (and the Co^{4+} fraction $\sim 50\%$). $Gd_{1-x}Sr_xCoO_{3-\delta}$ shows non-zero χ'', evidence of magnetic glassiness, at all three compositions. T_f, the spin freezing temperature, is higher for $x = 0.67$ as the greater

fraction of rare earth causes a reduction in lattice parameters and a resulting increase in Co orbital overlap. The trace tails up at low T, suggesting that the Gd moments are disordered and beginning to show a paramagnetic signature at very low temperatures and hence can be ignored at temperatures close to T_f (figure 1, inset).
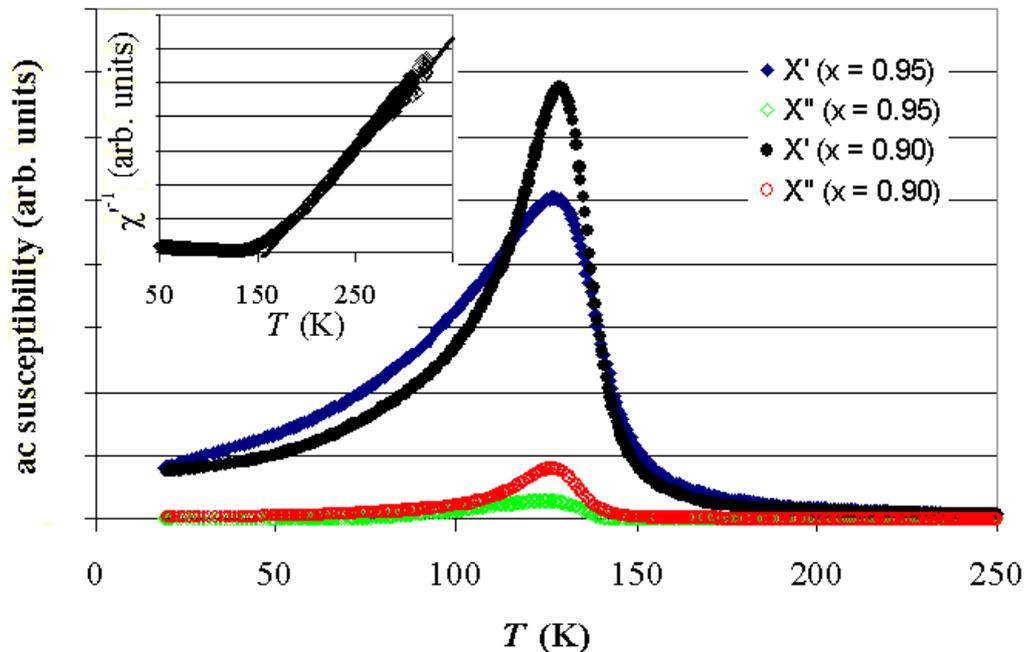

Figure 2: ac susceptibility of $Gd_{0.1}Sr_{0.9}CoO_{2.76}$ and $Gd_{0.05}Sr_{0.95}CoO_{2.78}$ at 125 Hz, normalised for sample mass. Inset shows fit of the Curie-Weiss law to the $x = 0.95$ data.

Figure 2 shows a Curie-Weiss fit to the susceptibility above the freezing temperature, T_f, for $x = 0.95$ (inset). This fit gives an effective moment of 3.5 ± 0.5 μ_B, compared with a moment of $5.1 \pm 0.2\mu_B$ per Co ion for $Ho_{0.05}Sr_{0.95}CoO_{3-\delta}$ [13]. The moment in the Ho sample is close to that expected from a mix of high spin Co^{3+} and high spin Co^{4+}. The smaller moment in $Gd_{0.05}Sr_{0.95}CoO_{2.78}$ raises the possibility that some of the spins are not in the high-spin state; given that each of the two Co oxidation states has three spin states, the fraction in each state cannot be calculated. At $x = 0.67$, the susceptibility above T_f does not obey the Curie-Weiss law, but requires a positive additive constant to fit, suggesting that at this composition the system is not paramagnetic above T_f but that some fraction of the moments are ordered. Similar materials with $x = 0.67$ and Ln = Ho, Dy or Y, show a weak phase transition in the Co lattice at around room temperature to an antiferromagnetic state containing ferromagnetic clusters, and show glassiness without this order at $x = 0.95$ [13,14]. It is likely that $Gd_{0.33}Sr_{0.67}CoO_{2.82}$ is behaving in an intermediate fashion in which some of the moments, due to local variations in composition, are ordering at room temperature, but with a signal too weak to be observed beneath the strong signal due to the paramagnetic moments that unfreeze on heating through T_f. Subtraction of the paramagnetic signal reveals a trace which increases as T falls through T_f, then flattens out. The signal is evidence for ferromagnetism. A peak at around 300 K is possible, but cannot be considered reliable.

For rare earth cobaltates for which the lanthanide ion better matches the Sr^{2+} ion in size, the archetypal example being lanthanum, glassiness extends over a considerable region of the composition range. Much work has centred on $La_{0.5}Sr_{0.5}CoO_3$, for example [7-9]. The behaviour of these Gd compounds can be viewed as points on the continuum from the

smaller, heavier lanthanides which show a reduced solid solution range and a narrow spinglass region at small rare earth fractions through to the lighter, larger lanthanides which show a full solid solution range and broad regions of glassiness at intermediate rare earth fractions. The larger ionic sizes of La^{3+} and similar ions allows a more random distribution of rare earth on the Sr sites due to the reduction in strain, as evidenced by the lack of superstructure in structural studies [15]. This creates greater frustration within the sample as the interfacial area in between ferro- and antiferromagnetic regions increases as magnetic cluster sizes fall. Hence with a more structurally random system, giving more smaller magnetic clusters and no long-range magnetic order, the glassiness sets in over a wider range of compositions.

Conclusions

We have examined the magnetic properties of $Gd_{1-x}Sr_xCoO_{3-\delta}$ from 17 to 320 K for a range of samples, x = 0.67, 0.90 and 0.95. The materials are found to show peaks in the real and imaginary parts of the ac susceptibility and the positions of these peaks show frequency dependence, indicative of spinglass behaviour. At x = 0.67, for temperatures between T_f (~154 K) and 320 K, the curve cannot be fitted by a Curie-Weiss law, suggesting that the material is ordered to some extent. Based on the behaviour of related materials, we suggest a state with an antiferromagnetic matrix containing ferromagnetic clusters. Structural studies have shown the Gd cobaltates to be structurally intermediate between cobaltates containing smaller lanthanides and those containing larger lanthanides. This appears to result in magnetic behaviour which is also intermediate

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