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LETTER TO THE EDITOR

Origin of the cluster-glass-like magnetic properties of the ferromagnetic system $La_{0.5}Sr_{0.5}CoO_3$

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Abstract. The magnetic behaviour of $La_{0.5}Sr_{0.5}CoO_3$ at low magnetic fields has been studied by ac susceptibility, and field cooled (FC) and zero field cooled (ZFC) magnetization measurements. The cluster-glass-like magnetic behaviour of the compound is found to originate from its magnetocrystalline anisotropy as similar properties are observed for ferromagnetic systems also. The cluster glass freezing temperature and its magnetic field dependence, the irreversibility between the FC and ZFC magnetization curves, the shape of the low-field susceptibility curves, etc are related to the magnitude and temperature variation of the coercivity (H_c) which is a measure of the anisotropy, and the ratio H_A/H_c where H_A is the applied magnetic field.

The substituted perovskite system $La_{1-x}Sr_xCoO_3$ has been studied extensively during the last five decades to understand the interesting magnetic and electrical transport properties that they exhibit [1–9]. The parent compound, $LaCoO_3$, is a nonmagnetic semiconductor, and on substitution of Sr^{2+} for La^{3+}, the paramagnetic Curie temperature increases from negative to positive for $x > 0.1$, indicating the onset of strong ferromagnetic exchange interactions and the system shows metallic behaviour for $x > 0.2$ [1]. For $x = 0.5$ ($T_c \approx 250$ K), each Co^{3+} in the lattice is surrounded by six Co^{4+} neighbours, which gives maximum Co^{3+}–Co^{4+} ferromagnetic interactions. The effective paramagnetic moment obtained from the slope of the $\chi^{-1}(T)$ curves for various values of x are comparable to the calculated spin-only moments assuming a uniform distribution of these cobalt ions in the lattice with Co^{3+} and Co^{4+} ions in the high-spin ($t_{2g}^4e_g^2$) and low-spin (t_{2g}^5) states, respectively [1, 3]. The saturation moment in the ferromagnetic state is, however, lower than the expected values. Saito *et al*, from XPS studies, have recently concluded that the intermediate-spin state is realized in the ferromagnetic phase [9].

From a detailed study of the magnetic properties of $La_{1-x}Sr_xCoO_3$ ($0 \leqslant x \leqslant 0.5$) Itoh *et al* [4] have shown that no true ferromagnetic long-range ordering takes place as reported earlier [1] and there exists a spin glass region for $0 \leqslant x \leqslant 0.18$ and a cluster glass region for $0.18 \leqslant x \leqslant 0.5$. For the cluster glass compositions ($x > 0.18$), the M_{ZFC} curves show a broad maximum and the M_{FC} curves show a monotonic increase below the magnetic transition whereas a cusp in the M_{ZFC} curve is obtained in the spin glass region. The conclusion that $x > 0.18$ belongs to the cluster glass region is based on the findings that (i) a large difference between M_{FC} and M_{ZFC} is observed, (ii) there is no magnetic saturation at low temperatures and at very high magnetic fields and (iii) M_{ZFC}

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shows long-time relaxation effects not observed in ferromagnetic systems, which are also the characteristics of a spin glass system.

The ferromagnetic perovskite oxide $SrRuO_3$ has a single type of magnetic ion, Ru^{4+}, so the probability for the formation of ferromagnetic clusters is negligible (in the La–Sr–Co–O system, because of the possibility for partial ordering of Co^{3+} and Co^{4+} ions, clusters may be formed), also shows the irreversible magnetic behaviour when measured at low magnetic field strengths [10]. Ac magnetic susceptibility measurement on $SrRuO_3$ shows a sharp peak close to the Curie temperature (cusp at 160 K and $T_c = 161$ K) and the M_{FC} and the M_{ZFC} curves show large differences below T_c. Similar behaviour has also been reported recently for other oxide magnetic systems, which order ferromagnetically, as evidenced from neutron diffraction studies [11–14]. The divergence of the M_{FC} and the M_{ZFC} curves of these systems below a certain temperature is ascribed to their spin-glass-like behaviour. This implies that some of the characteristic features of a cluster glass or a spin glass system are also the characteristics of a ferromagnetic system. We have investigated the magnetic behaviour of $La_{0.5}Sr_{0.5}CoO_3$ which is reported as a cluster glass system, at different magnetic field strengths under field cooled and zero field cooled conditions. A comparison of the results with those of $SrRuO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ which are ferromagnetic systems, indicates that $La_{0.5}Sr_{0.5}CoO_3$ is also a ferromagnetic system. The cluster-glass-like features of the compound originate from its magnetocrystalline anisotropy.

A single-phase polycrystalline $La_{0.5}Sr_{0.5}CoO_3$ sample was synthesized by the ceramic method. The field cooled (FC) and the zero field cooled (ZFC) magnetization measurements were made on a EG&G PAR vibrating sample magnetometer (VSM) model 4500 (80–300 K). Hysteresis loops were recorded (H = 15 kOe) after cooling the sample through the transition temperature in zero applied magnetic field. Ac susceptibility measurements were made by the mutual inductance method using a closed-cycle helium cryostat (15–300 K).

Figure 1 shows the M_{FC} and the M_{ZFC} curves of $La_{0.5}Sr_{0.5}CoO_3$, measured at four

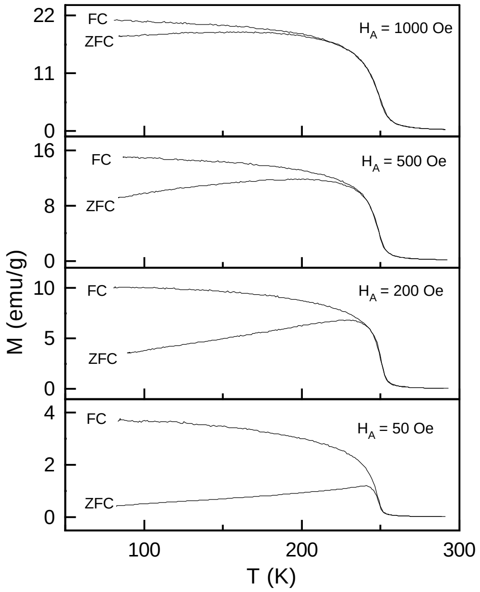

Figure 1. Field cooled (FC) and zero field cooled (ZFC) magnetization curves of $La_{0.5}Sr_{0.5}CoO_3$ measured at different magnetic fields (H_A) as indicated.

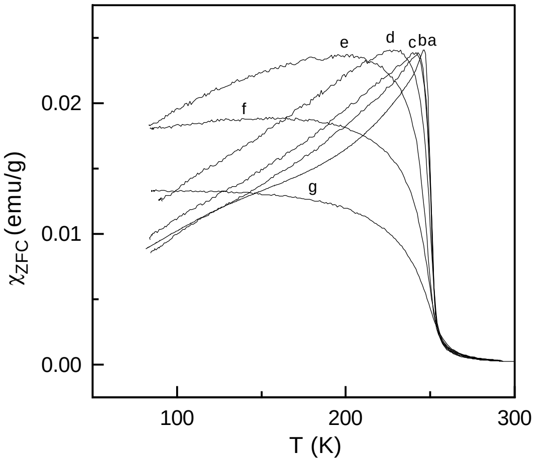

Figure 2. Temperature variation of the ac susceptibility of $La_{0.5}Sr_{0.5}CoO_3$ measured at $H_A = 10$ Oe (curve a) and its zero field cooled (ZFC) susceptibilities (curves b–g) measured at different magnetic fields; (b) $H_A = 50$ Oe, (c) $H_A = 100$ Oe, (d) $H_A = 200$ Oe, (e) $H_A = 500$ Oe, (f) $H_A = 1000$ Oe and (g) $H_A = 2000$ Oe.

Table 1. Cusp temperature, T_f, and the temperature below which M_{FC} and M_{ZFC} show irreversible behaviour, T_{irr}, of $La_{0.5}Sr_{0.5}CoO_3$, measured at different applied magnetic field strengths.

H_A (Oe)	10 (ac)	50	100	200	500	1000	2000
T_f (K)	246	243	241	228	200	155	—
T_{irr} (K)	—	248	247	244	236	225	169

different magnetic fields (H_A). All the curves show a magnetic transition at $T_c = 249$ K, the magnetic transition becomes broad as H_A is increased from 50 Oe to 1000 Oe. The M_{ZFC} curve recorded at 50 Oe shows a maximum (cusp) at $T_f = 243$ K and below T_f the magnetization decreases continuously as the temperature is decreased. Both the M_{FC} and the M_{ZFC} curves meet at 248 K. As H_A is increased, the cusp in the M_{ZFC} curve becomes broad and the cusp is shifted to lower temperatures. The rounding off of the cusp in the M_{ZFC} curve, as well as shifting of the maximum to lower temperatures as the applied field strength is increased, can be clearly seen in figure 2 which shows the χ_{ZFC} curves measured at various field strengths. For comparison, the ac susceptibility curve measured at 10 Oe and 27 Hz is also shown. The ac susceptibility curve shows a peak at $T_f = 246$ K. The temperature at which maximum susceptibility is observed (T_f) and the temperature below which irreversible behaviour is observed (T_{irr}) are given in table 1 for each applied field.

Figure 3 shows the M_{FC} and the M_{ZFC} behaviour of $SrRuO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ which are ferromagnetic systems. For $SrRuO_3$, the M_{ZFC} curve ($H_A = 100$ Oe) shows a sharp peak at $T_f = 160$ K ($T_c = 161$ K), whereas for $La_{0.7}Ca_{0.3}MnO_3$ the M_{ZFC} curve ($H_A = 40$ Oe) shows a broad maximum ($T_f = 230$ K, $T_c = 245$ K) and M_{ZFC} decreases with temperature showing only a small variation and little deviation from the M_{FC} curve. A comparison of the extent of irreversibility shows that $SrRuO_3$ shows maximum irreversibility followed by $La_{0.5}Sr_{0.5}CoO_3$ and the least for $La_{0.7}Ca_{0.3}MnO_3$ (M_{FC}/M_{ZFC} at 82 K measured at the lowest field strengths for the three systems is 27.5, 8.3 and 1.8, respectively).

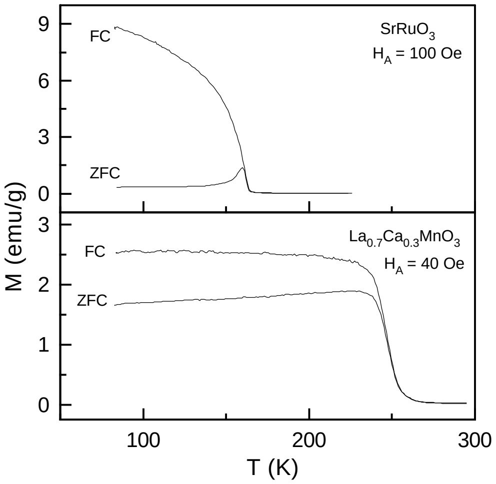

Figure 3. Field cooled (FC) and zero field cooled (ZFC) magnetization curves of SrRuO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$.

A comparison of the FC and ZFC magnetic behaviour of the three different oxide systems shows that they differ only in the nature and shape of their magnetization curves. Irreversible behaviour and a maximum (cusp) in the M_{ZFC} curve are common for all the three oxides (both SrRuO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ also show field dependence of the T_f and broadening of the cusp [15]). For many of the magnetic systems reported in the literature (including ferrimagnetic, antiferromagnetic and high-T_c oxide superconductors) which show the spin-glass-like features such as a cusp in the ac susceptibility curve, irreversibility between the FC and ZFC curves etc, large value of coercivity is observed below their spin glass freezing temperatures [14, 16–19]. The coercivity is related to the magnetocrystalline anisotropy according to the relation, $H_c(T) = 2K_1/M_s$ (K_1 and M_s are the anisotropy constant and saturation magnetization, respectively) [20].

Temperature variation of the H_c of La$_{0.5}$Sr$_{0.5}$CoO$_3$, SrRuO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ is compared in figure 4. A comparison of the nature of the temperature variation of the M_{ZFC} curves (see figure 1 and figure 3) with that of the corresponding H_c curves shows some striking similarities. The shape of the ZFC curve (or ac susceptibility curve) depends on the magnitude and the temperature variation of H_c. For La$_{0.5}$Sr$_{0.5}$CoO$_3$, H_c varies from 50 Oe to 350 Oe as the temperature is decreased below the T_c (1.64 Oe K^{-1}) whereas for La$_{0.7}$Ca$_{0.3}$MnO$_3$ the variation is from 15 Oe to 35 Oe (0.11 Oe K^{-1}). A similar but inverse difference is observed in their ZFC susceptibility behaviour also. Below T_f, the χ_{ZFC} of La$_{0.5}$Sr$_{0.5}$CoO$_3$ decreases much faster than that of La$_{0.7}$Ca$_{0.3}$MnO$_3$, as the temperature is decreased. For SrRuO$_3$ a sharp increase in H_c is observed below its T_c within a temperature range of 30 K (66.5 Oe K^{-1}) and correspondingly a sharp decrease in χ_{ac} and χ_{ZFC} is observed below T_c within the same temperature region. The low field χ_{ac} and χ_{ZFC} curves of the three compounds along with the corresponding $H_c^{-1}(T)$ curves are compared in figure 5. It can be seen that the χ_{ZFC} curve below the T_f varies inversely with coercivity and the shape of the χ_{ZFC} or χ_{ac} curves at low measuring fields is determined by the shape of the H_c^{-1}(T) curve.

The shape of the peak (cusp) in the ZFC curves (measured at the lowest fields) is also found to depend on the magnitude of H_c. For SrRuO$_3$, the value of H_c at 160 K (T_c =

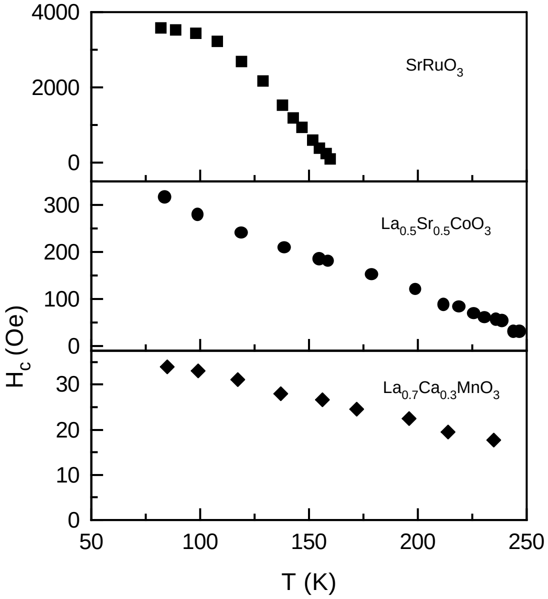

Figure 4. Temperature variation of the coercivity (H_c) of $SrRuO_3$, $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ below their Curie temperatures.

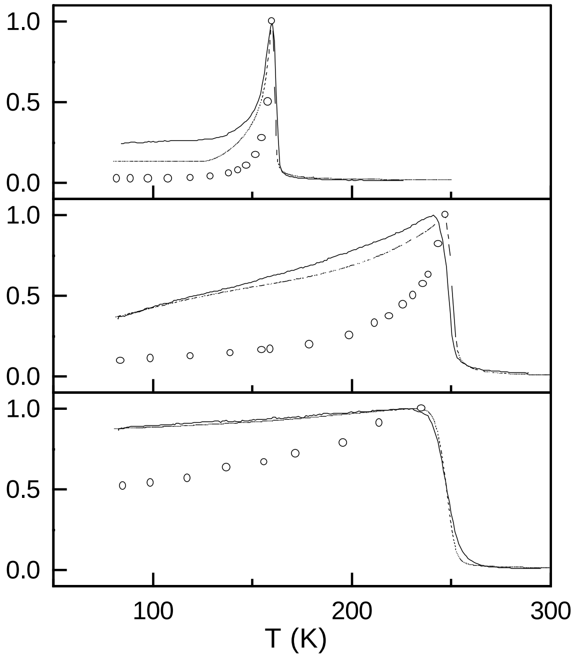

Figure 5. Normalized $\chi_{ac}(T)$ (broken line), $\chi_{ZFC}(T)$ (solid line) and $H_c^{-1}(T)$ (circles) curves of $SrRuO_3$, $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.7}Ca_{0.3}MnO_3$. χ_{ac} is measured at $H_A = 10$ Oe and the χ_{ZFC} curves measured at $H_A = 100$ Oe for $SrRuO_3$, $H_A = 50$ Oe for $La_{0.5}Sr_{0.5}CoO_3$ and $H_A = 40$ Oe for $La_{0.7}Ca_{0.3}MnO_3$ are shown for comparison.

161 K) is greater than 100 Oe, which is greater than the applied field (H_A = 100 Oe), for $La_{0.5}Sr_{0.5}CoO_3$ the value of H_c at 246 K (T_c = 249 K) is comparable to H_A (H_c ~40 Oe, H_A = 50 Oe) and for $La_{0.7}Ca_{0.3}MnO_3$, H_c at 242 K (T_c = 245 K) is much lower than H_A (H_c = 15 Oe at 242 K, H_A = 40 Oe). Further, it can be seen that the M_{ZFC} behaviour of $La_{0.5}Sr_{0.5}CoO_3$ (figure 1) at H_A = 500 Oe ($H_A > H_c$) is similar to that of $La_{0.7}Ca_{0.3}MnO_3$ measured at 40 Oe, both the curves showing a broad maximum and then linearly decreasing with decreasing temperature. This implies that if the ZFC magnetization is recorded at a field strength much less than the coercivity immediately below T_c, a sharp peak may be obtained as observed for $SrRuO_3$. For $La_{0.7}Ca_{0.3}MnO_3$, even the ac susceptibility recorded at 10 Oe does not show any sharp peak due to the comparable values of H_c and H_A.

For $SrRuO_3$, studies on single crystals have already shown that the compound possess very high magnetocrystalline anisotropy [21, 22]. The high value of the anisotropy is then responsible for the low magnetization values observed for $SrRuO_3$ [21] and $La_{0.5}Sr_{0.5}CoO_3$. For polycrystalline $SrRuO_3$, $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.7}Ca_{0.3}MnO_3$, the saturation moments obtained at $0.5T_c$ (measured at 1.5 T) are 0.75, 1.51 and 3.45 μ_B, respectively. The corresponding expected values are 2 (low spin Ru^{4+}, t_{2g}^4), 2.5 ($0.5Co^{3+}$ and $0.5Co^{4+}$) and 3.7 ($0.7Mn^{3+}$ and $0.3Mn^{4+}$) μ_B, respectively. The ratio of the observed to calculated saturation moments for the three compounds are 0.37, 0.6 and 0.93, respectively, which shows that $SrRuO_3$ is highly anisotropic and $La_{0.7}Ca_{0.3}MnO_3$ is the least anisotropic. A similar trend is observed in the extent of irreversibility and the drop in the susceptibility below T_f, which indicates that magnetocrystalline anisotropy is responsible for the spin-glass-like properties of these ferromagnetic compounds.

For the $La_{1-x}Sr_xCoO_3$ system the coercivity increases as the strontium concentration is decreased [5]. The Curie temperature is also decreased on decreasing Sr concentration [1, 4]. Therefore, if the ZFC measurements are made at a fixed field strength on compounds with differing Sr concentrations (for example, Itoh *et al* [4] made the ZFC measurements at 20 Oe for all the compositions), it may be expected that the low Sr containing compositions, with their high value of coercivity at low temperatures, would give rise to well defined cusps in their ZFC magnetization curves. In other words, if the H_c below the T_c of a particular Sr-rich composition is less than or comparable to the applied field, a broad maximum will be observed in the ZFC curve whereas at the same measuring field strength, the low Sr containing compositions, because of their higher coercivity below T_c, would show a cusp immediately below the magnetic transition temperatures. The difference between T_{irr} and T_f would depend on the H_A/H_c ratio and the compositional homogeneity of the sample. The first factor may be understood from the present results. It has been shown that the T_c of the compositionally inhomogeneous samples of low Sr containing compositions are higher than that expected when processed at low temperatures, due to the presence of ferromagnetic Sr-rich compositions as impurities and these samples show a wide difference between the T_{irr} and T_f values [23]. This is because irreversibility between the FC and the ZFC curves is observed just below the Curie temperature of the Sr-rich ferromagnetic phase present as an impurity. Thus, if high-T_c ferromagnetic compositions are present in the samples as an impurity (which implies opening up of a hysteresis loop and lower coercivity value immediately below the T_c of the composition with the highest T_c in the series) the cusp or maximum in the ZFC curve will be observed at a lower temperature than T_{irr}. The magnetic transition will be very broad due to contributions from the magnetization curves of different compositions with varying Curie temperatures. Itoh *et al* [4] have observed a broad maximum and a cusp in the ZFC susceptibility curves of the compositions with $x > 0.18$ and $x < 0.18$, respectively and a large difference between T_{irr} and T_f for the La-rich compositions ($x < 0.18$). This may be due to the presence of Sr-rich compositions in these samples because for Asai *et al* [24] when measured on single-crystal samples of $La_{0.88}Sr_{0.12}CoO_3$, T_f and T_{irr} are found to be close together whereas for Itoh *et al* [4], the difference between M_{FC} and M_{ZFC} persists up to 200 K for the polycrystalline sample of the same composition and for all the other compositions below $x < 0.18$.

The present results indicate that the magnetocrystalline anisotropy is the main factor in determining the shape of the M_{ZFC} curve and therefore the divergence of FC and ZFC magnetization curves below a certain temperature is associated with the opening up of a hysteresis loop and the finite value of the coercivity below the transition temperature. The cusp temperature, T_f, and its departure from the Curie temperature, T_c, is defined by the magnitude of the applied magnetic field in relation to the anisotropy field at a certain temperature. As both $SrRuO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ are established as ferromagnetic systems which show irreversible M_{FC} and M_{ZFC} behaviour, it may be concluded that $La_{0.5}Sr_{0.5}CoO_3$ which is reported as a cluster glass system is actually a ferromagnetic system.

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