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Enhanced magnetoresistance on substitution of Mn in SrRuO₃

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Abstract

We have studied the substitution of a 3d element, namely Mn, at the Ru site of the metallic ferromagnet SrRuO₃. We find that the substitution gives rise to short-range cluster formation which coexists with long-range ferromagnetism. The clusters show a characteristic blocking at a temperature lower than T_c (the ferromagnetic transition temperature). We find that the magnetoresistance of the sample with substitution is higher than that of the parent SrRuO₃ and that the magnetoresistance peaks at the cluster freezing temperature.

1. Introduction

There is renewed interest in understanding the properties of the Ruddlesden–Popper series Sr_{n+1}Ru_nO_{3n+1} owing to the observation of anisotropic superconductivity in Sr₂RuO₄ [1]. The series has been called the *bad metals* since the electrical resistivities of the members exceed the Ioffe–Regal limit for conventional metals at high temperatures [2]. For the end member of the series, SrRuO₃, which is a three-dimensional itinerant ferromagnet, the ferromagnetism is found to arise due to conduction electrons. The ruthenate SrRuO₃ shows strong electron correlations [3] and there is still no consensus as regards the nature of the Ru moment in the system. SrRuO₃ offers the unique possibility of studying itinerant ferromagnetism in the limit $k_F l = O(1)$. The system is characterized by a narrow d band composed of Ru t_{2g} and O 2p orbitals. Until recently it has been understood that the Ru ions carry the magnetic moments, being in the low-spin state ($S = 1$). Polarized neutron scattering experiments revealed the fact that the strong hybridization of the Ru(4d)–O(2p) orbitals results in 10% of the ordered magnetic moment being associated with the oxygen site [4]. The recent observation of spin-glass behaviour in this system [5] has led to the questioning of many important aspects, one of which is the coexistence of short-range spin-glass-like behaviour and long-range ferromagnetic order. In addition to the magnetic properties, the transport properties also show anomalous behaviour. The electrical resistivity of this oxide shows no sign of saturation even up to a temperature of 1500 K and shows an almost linear temperature dependence up to this high temperature [6]. The magnetoresistance is about 12% in this system near the ferromagnetic transition temperature ≈ 160 K (at 6 T) [7]. This is quite large compared

to those of other conventional metallic ferromagnetic systems known so far (showing itinerant ferromagnetism). The magnetization of the system near the ferromagnetic transition shows normal critical behaviour, whereas the transport properties show anomalous behaviour [7]. A lot of work has been done regarding the substitution of other elements at the Sr site. There have been only a few studies on substitution at the Ru site in SrRuO_3 [8]. The substitution of Pb in place of Ru gives rise to a weak ferromagnetic metal and, at higher concentration, a paramagnetic semiconductor [8]. But there has not been any study on the substitution of the 3d transition metal (TM) ion at the Ru site and its effect on the ferromagnetic behaviour and the transport properties. Introduction of 3d TM ions at the Ru sites will hinder the hybridization of the Ru orbitals because of the localized nature of the 3d orbitals. On substitution, the Mn ions will act as localized moments and will tend to form spin clusters along with the Ru ions, thus affecting the magnetic and transport properties of the system. A similar observation has been made recently for Mn-doped CaRuO_3 [9]. It has been reported that the substitution of Mn at the Ru site results in the observation of a Kondo effect in the Mn-substituted system. CaRuO_3 is a non-magnetic metal, while SrRuO_3 is a ferromagnetic metal. Moreover, since SrRuO_3 is a band ferromagnet, a small amount of Mn at the Ru sites in SrRuO_3 may not affect the band ferromagnetism as strongly as it would if that had been an exchange-type ferromagnetism. Also, it is known that the presence of spin clusters gives rise to higher magnetoresistance, which has been studied in the case of doped LaMnO_3 systems [10–12]. It will be interesting to see whether the above statement holds good for metallic systems as well. With the above aim, we have tried to investigate the substitution of Mn in SrRuO_3 .

2. Experimental details

The polycrystalline samples with Mn = 10%, 20% and the parent compound were prepared by the solid-state reaction technique (increasing the Mn concentration requires high-pressure techniques; hence we had to stop at 20% substitution). SrCO_3 , RuO_2 and MnO_2 in the stoichiometric ratio were mixed well and the hard pressed pellets were fired at 1200 °C for 24 hours. The pellets were reground, pelletized and fired again at 1250 °C for an additional 24 hours. The samples were characterized by means of XRD using a Cu $K\alpha$ source. The XRD patterns of the samples are shown in figure 1. The sample with $x = 0.1$ showed no peak broadening or extra phases whereas the $x = 0.2$ sample showed slight peak broadening. Substitution of a higher Mn content requires high-pressure synthesis and, due to the slight distortion of the $x = 0.2$ compound, we will not be including this in our discussion. The structure of SrMnO_3 is hexagonal under normal preparation conditions and high-temperature synthesis is required for the preparation of the cubic phase [13]. The samples were orthorhombic and the lattice parameters decreased with increasing Mn content. The shrinking of the lattice is due to the ionic radius of Mn^{4+} (0.54 Å) being smaller than that of Ru^{4+} (0.62 Å) [14]. The lattice parameters calculated from the x-ray spectra using CELREF are tabulated in table 1. The dc magnetization [15] and ac susceptibility [16] measurements

Table 1. Lattice parameters of the substituted SrRuO_3 calculated using CELREF from the x-ray spectra.

Sample	a (Å)	b (Å)	c (Å)
SrRuO_3	5.5544	5.5108	7.8365
$\text{SrRu}_{0.9}\text{Mn}_{0.1}\text{O}_3$	5.5534	5.4801	7.8359
$\text{SrRu}_{0.8}\text{Mn}_{0.2}\text{O}_3$	5.5526	5.4273	7.8337

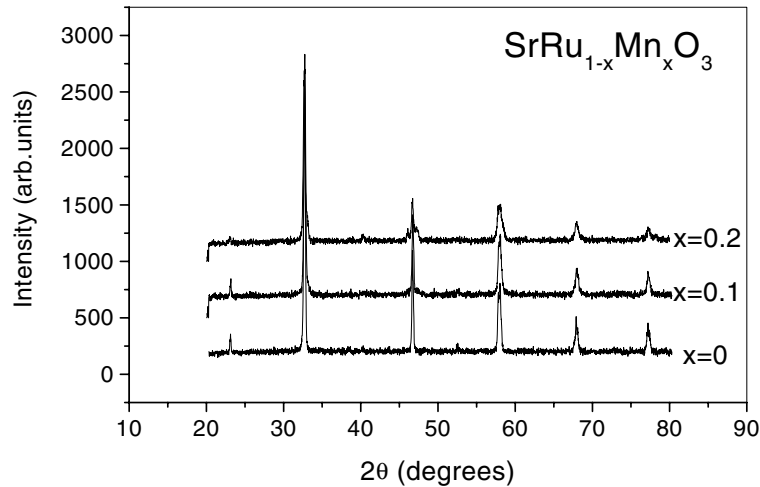


Figure 1. XRD patterns of the samples of SrRu_{1-x}Mn_xO₃. The peak broadening for the $x = 0.2$ sample is quite evident.

were carried out in home-made cryostats over the temperature ranges $20 \text{ K} < T < 180 \text{ K}$ and $80 \text{ K} < T < 180 \text{ K}$ respectively. The magnetotransport measurements were carried out in a nitrogen cryostat from 77 K to near room temperature.

3. Results

3.1. Magnetic characterization

The results of the dc zero-field-cooled magnetization measurements are given in figure 2. Each of the samples shows a ferromagnetic transition at $T = 160 \text{ K}$ but there is a distinct feature developing at low temperatures below T_c . (The position of the second peak is marked

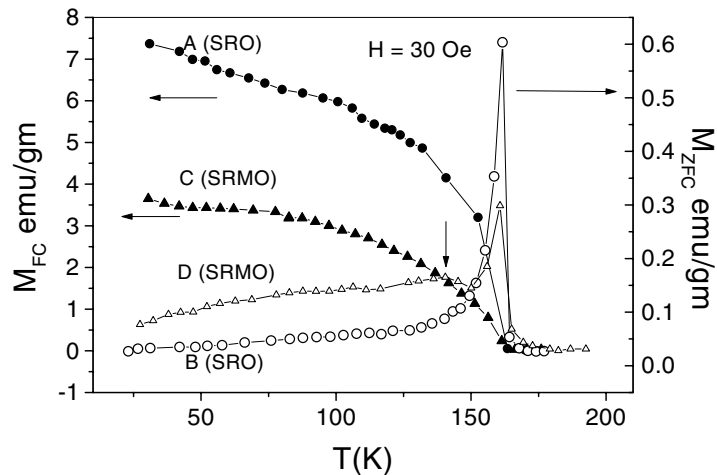


Figure 2. Magnetizations of SrRuO₃ (SRO) and SrRu_{0.9}Mn_{0.1}O₃ (SRMO) samples. A (C) and B (D) show the zero-field-cooled and the field-cooled data for SRO (SRMO).

in the figure by the arrow.) It is important to note that the long-range ferromagnetism is maintained even after the substitution of Mn in the system. Figure 3 shows the ac susceptibility measurements of the parent compound SrRuO_3 . The inset shows χ' , which has a very negligible temperature shift as a function of frequency. χ'' shows a very systematic shift towards lower temperature as the frequency increases. This is in the opposite sense compared to that for spin-glass systems and is possible in a ferromagnetic material if there are FM clusters due to chemical or lattice disorder effects. We will discuss the implication of this observation in the next section. Figure 4 shows the ac susceptibility measurements for the $x = 0.1$ sample for three different frequencies. Although the shift in χ' is not very evident, χ'' shown in the inset of figure 4 shows a clear shift in the temperature as the frequency changes. It is worth pointing out that the shift in the peak is towards a higher temperature as the driving frequency increases and is clearly different from that seen for the parent compound. This shift in the peak around 140 K, although small, indicates that there is short-range magnetic cluster freezing. To establish clearly that there is indeed cluster freezing, we show in figure 5 the coercivity as a function of temperature obtained by means of hysteresis measurements on the $x = 0.1$ sample. The sudden increase of H_c below a temperature of 138 K is clear evidence that there is cluster freezing taking place at that temperature. This is a very good confirmation of our hypothesis that there are essentially two types of magnetic interaction present in the system on substitution of Mn: both long-range ferromagnetism and short-range magnetic cluster formation.

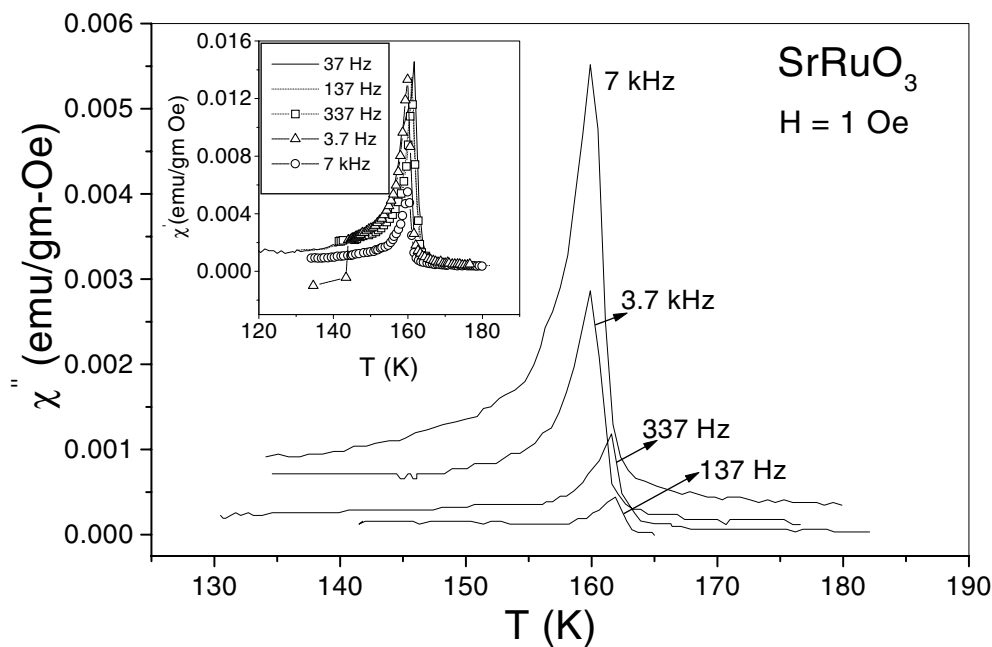


Figure 3. The ac susceptibility of the parent compound. χ'' shows a characteristic shift in the peak towards lower temperature as the frequency increases. This indicates that there is no short-range order in the parent compound. See the text for details.

3.2. Transport and magnetotransport

It will be interesting to see the effect of the Mn substitution on the transport (resistivity and magnetoresistance) of the system. Since the substitution of Mn in the parent compound is

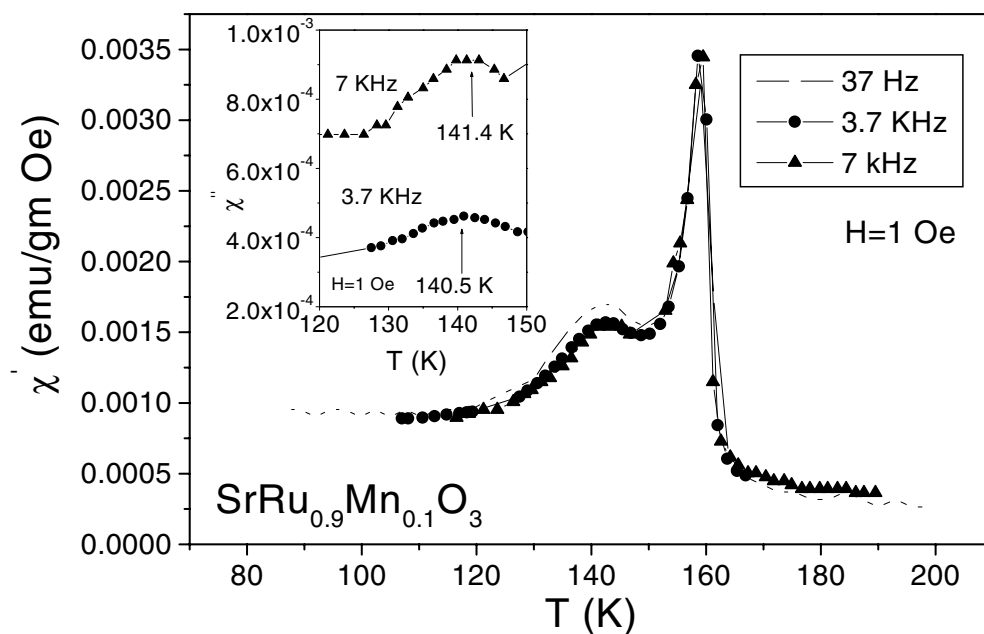


Figure 4. The ac susceptibility of the Mn-substituted sample showing the peak at T_G . The inset shows χ'' , showing a shift in the peak temperature as a function of frequency, indicating the presence of clusters.

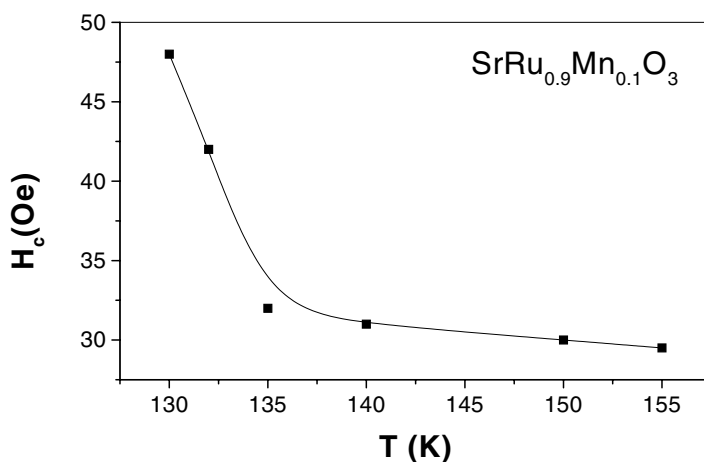


Figure 5. Variation of the coercive field H_c as a function of temperature for $x = 0.1$ showing the onset of cluster freezing at $T \approx 138$ K.

acting like a localized spin, it will produce the same effect as a magnetic impurity in the system. Hence we would expect the resistivity of the doped system to be greater than that of the parent compound. This is precisely what is observed. The resistivities of the samples are shown in figure 6. The change of slope in the resistivity at the critical temperature of the parent sample is clearly seen and, as the Mn concentration increases, the change of slope in the resistivity seems to become less important. The magnetoresistances of the samples are shown

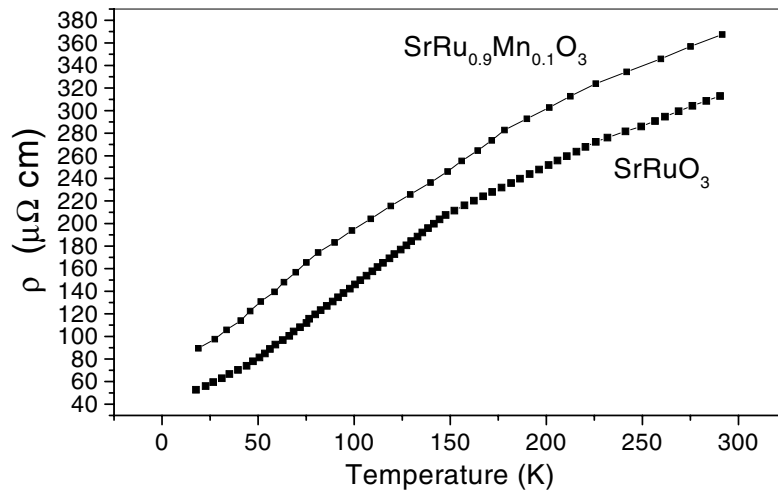


Figure 6. Resistivities of the parent and the $x = 0.1$ sample.

in figure 7. The important observation is that of the increase in the MR for the doped sample as compared to the parent sample. The inset of figure 7 shows the variation of the MR as a function of T , for the doped sample at a field of 7 kG. It is clear that the MR shows an increase around $T = 140$ K which is near T_G for the doped sample. The MR of the parent compound is negative and shows a maximum at the ferromagnetic transition temperature $T_c = 160$ K [7]. The MR is about 2% at a field of 1 T (10 kG) for SrRuO_3 . The MR of the doped sample peaks at a temperature closer to T_G than T_c and its value is higher than that for the parent SrRuO_3 . It is about 4% at 7 kG at $T \approx 140$ K.

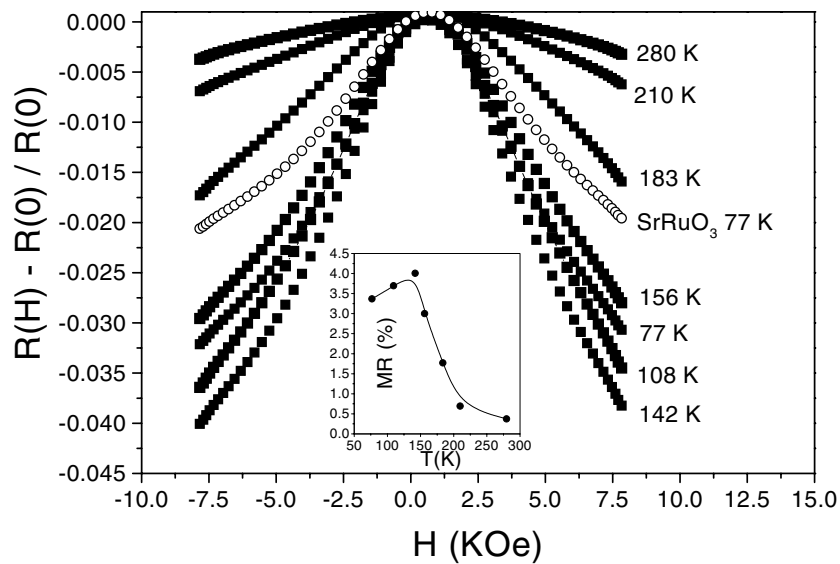


Figure 7. Magnetoresistances at different temperatures as functions of field for the Mn-substituted sample (closed symbols) along with the MR for the parent system (open symbols) at 77 K. The inset shows the MR as a function of temperature for the SRMO system.

4. Discussion

The first aspect to discuss is whether the parent compound shows spin-glass behaviour with long-range ferromagnetism as reported recently. It is clear from figure 3, which shows the ac response of the parent compound, that SrRuO₃ does not show any sign of spin-glass order as suggested by Reich *et al* [5]. In a true spin-glass type of ordering we would expect a shift of the transition temperature towards a higher temperature as the driving frequency increases. The shift in χ'' to lower temperature as a function of frequency is an indication that there are FM clusters with a size distribution. In our sample, these clusters are due to the polycrystalline nature of the sample and are not a result of any chemical inhomogeneity, since the XRD indicates a single-phase sample. This observation is very strong evidence that there is no short-range ordering due to magnetic frustration in the sample which could give rise to a spin-glass type of behaviour.

We will now discuss the effect of the substitution of Mn in the system. We will assume a nominal composition of the compounds and hence the Mn substituted in the system is in the 4+ state. The substituted Mn ions form a localized impurity and the Ru(4d)–Mn(3d), being nearest neighbours, form local clusters which are magnetic. The origin of short-range clusters is the competing ferromagnetic/antiferromagnetic interaction between the substituted Mn and the Ru ions and these clusters start freezing at a temperature T_G , below the ferromagnetic transition temperature. It is well known that the blocking/freezing process in a cluster-glass type of system is commensurate with a drop in the magnetization. This generally manifests itself as a broad maximum in the temperature dependence of the magnetization, since various clusters are blocked out at different temperatures. This phenomenon of cluster freezing is evident in our system from the magnetization which shows a characteristic peak and a drop in the magnetization below the freezing temperature T_G . This is also confirmed by the ac susceptibility which shows a slight shift in T_G as a function of frequency. A quantitative measure of the frequency shift is obtained by calculating $(\Delta T_G/T_G)$ per decade of frequency as given by $\Delta T_G/[T_G \Delta(\log \omega)]$. This quantity is found to be of the order of 0.007 for the Mn-substituted sample as calculated from the shift in χ' as a function of frequency. This value agrees very well with those for other metallic spin-glass systems such as CuMn which have values of 0.004–0.006 [17].

The interesting aspect of the substitution of the Mn in place of Ru appears in the magnetoresistance which shows an increased value compared to that of the parent compound. The increase in the magnitude of the magnetoresistance on substitution of Mn can be explained as a combination of two effects. With the application of the external magnetic field the spin clusters are aligned, thus giving rise to a decrease in the scattering and hence a negative magnetoresistance. This is in addition to the facts that the system also exhibits ferromagnetism and the spin-dependent scattering decreases as the magnetic field is applied, giving rise to a negative magnetoresistance. Hence the higher value of the MR in the Mn-substituted system is caused by a combination of these two effects. The higher values of the magnetoresistance in systems with spin clusters have been observed earlier. In a study of the substitution of transition metal elements in place of Mn in the colossally magnetoresistive oxide system $RE_{1-x}A_xMn_{1-y}T_yO_3$, the higher magnetoresistance is observed for samples with spin clusters, but the samples are either semiconducting or insulating [10–12]. This is in contrast to the case for our system, where we have observed higher magnetoresistances in samples with spin clusters but whose conductivity is quite high. It is also important to note that the MR is highest at the cluster freezing temperature and this gives us an indication that the coexistence of FM as well as short-range clusters can in fact provide good conditions for observing higher magnetoresistance values.

5. Conclusions

To conclude, we have seen that the introduction of Mn at the Ru site induces cluster formation. This cluster formation does not seem to affect the metallic nature of the SrRuO₃ drastically, although the metallicity decreases with increase in the Mn content. The magnetoresistance shows a higher value due to the orientation of the spin clusters and hence a decrease in the scattering due to these clusters together with the magnetic field also decreasing the spin-dependent scattering in ferromagnetic systems. This study throws open an important question regarding the coexistence of short-range clusters and long-range ferromagnetism, and the implication of obtaining a higher magnetoresistance in a metallic system.

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