



Spin glass-like behaviour in Fe-rich phases of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.1 \leq x \leq 0.4$)

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ABSTRACT

Below their respective ferromagnetic Curie temperatures (T_C), $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.1 \leq x \leq 0.4$) undergo a spin glass-like transition owing to the electronic phase segregation process that creates highly spin disordered regions. At low temperatures, an additional short range magnetic interaction is observed due to large differences in volumes of FeO_6 and MnO_6 octahedra. The magnetoelastic structural change is also reflected in the lattice parameters.

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1. Introduction

$\text{Sr}_2\text{FeMoO}_6$ is perhaps the most important member of double perovskite series of compounds having a general formula, $A_2BB'O_6$ (A represents divalent cations and B and B' are the transition-metal ions). The compound is cubic in the paramagnetic state, but undergoes a magnetoelastic phase transition to tetragonal crystal structure below its ferromagnetic Curie temperature (T_C). In this compound, the spins of $\text{Fe}^{3+}(3d^5)$ and $\text{Mo}^{5+}(4d^1)$ ions are aligned in opposite direction [1]. Although the saturation magnetic moment (M_S) in this configuration is expected to be $4\mu_B$ per formula unit, the experimentally measured moment in bulk material always found to be much smaller ($M_S \sim 2.8\text{--}3.6\mu_B/\text{f.u.}$) [1,2]. The origin of this discrepancy is yet to be unambiguously settled, although various explanations ranging from Fe/Mo anti-site disorder, oxygen deficiency, etc., have been evoked [2–4]. Interestingly, it has been found that substitution of Fe^{3+} by isoelectronic Mn^{2+} ions remarkably changes the properties of $\text{Sr}_2\text{MnMoO}_6$. Although both of Fe^{3+} and Mn^{2+} have identical high spin $3d^5$ configurations, the Mo-ions shed its lone 4d electron resulting an insulating and antiferromagnetic behaviour in $\text{Sr}_2\text{MnMoO}_6$ (Néel temperature, $T_N \sim 10\text{K}$). The crystal structure reduces to monoclinic symmetry, introducing a relative tilting of about 9° between MnO_6 and MoO_6 octahedra [5]. The absence of ferromagnetism in $\text{Sr}_2\text{MnMoO}_6$ can be attributed to the presence of longer $B-O-B'$ bonds, in addition to the absence of any $180^\circ B-O-B'$ bond angle as well as Mo-4d electrons that facilitates ferromagnetic ordering of Fe spins in $\text{Sr}_2\text{FeMoO}_6$ [2].

These contrasting properties of these two compounds make the studies of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ interesting as one can monitor the gradual changes of properties as Mn replaces Fe (or vice versa). A few studies have already been carried out on this system focusing on crystallographic and magnetic properties [6,7]. The T_C found to decrease with increasing Mn content. Surprisingly, both the studies [6,7] claim that the tetragonal structure, which is a signature of magnetoelastic effect, was observed even in the paramagnetic state for $x \geq 0.4$ compounds. So far, no attempts have been made to study the competitions between the ferromagnetic and antiferromagnetic exchange interactions in the microscopic level in these compounds. This assumes significance due to our recent finding of local structural distortions in the Mn-rich phases of the $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.6 \leq x \leq 1.0$) series [8]. In this paper, we present the results of our dc [$M(T, H)$] and ac [$\chi'(f, T)$, $\chi''(f, T)$] magnetic studies on Fe-rich phases of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.1 \leq x \leq 0.4$) [9].

2. Results and discussions

2.1. Synthesis and crystal structure

These compounds have been synthesized using a standard solid-state reaction route [10]. Single phase nature of the compositions has been ascertained by indexing all peaks in the powder X-ray diffraction (XRD) spectra taken at room temperature, considering a tetragonal structure. Full Rietveld analysis of XRD patterns could not be attempted due to low scattering cross section of oxygen atoms present in the system. Lattice parameters obtained from the profile fit analysis are very close to those reported [6,7], except for $\text{Sr}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{MoO}_6$, which turned out to be essentially cubic (Fig. 1). This indicates that the magnetoelastic phase transition, i.e.,

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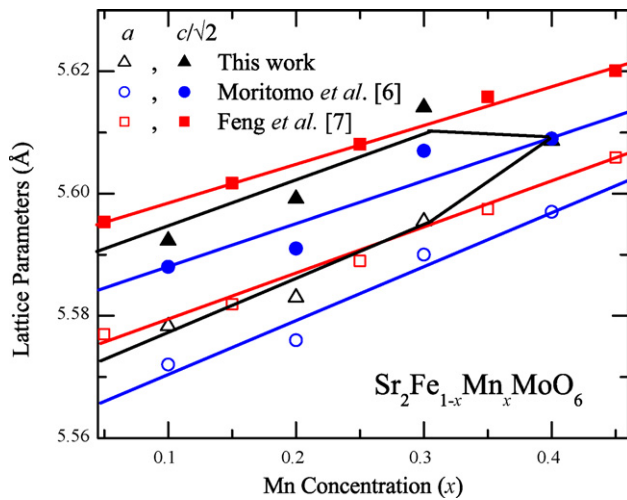


Fig. 1. Lattice parameters, a and $c/\sqrt{2}$ for $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.05 \leq x \leq 0.45$). The solid lines are guides to eye.

paramagnetic cubic to ferromagnetic tetragonal, takes place below room temperature for this composition that we have synthesized, and can be further corroborated from the magnetic measurements, as discussed in Section 2.2.

2.2. Dc magnetic susceptibility

The dc magnetic susceptibility results reveal that all the compounds order ferromagnetically (Fig. 2) and the T_C , defined as the inflexion point of the magnetic susceptibility, decreases with increasing Mn content. Fig. 3 presents the Curie temperatures estimated from ac magnetic susceptibility data (Section 2.3), and are found to be slightly higher ($\sim 20\text{K}$) than those obtained from dc magnetic susceptibility data. Although the T_C s thus estimated are slightly smaller than those reported in the literature [6,7], the onsets of ferromagnetic transition (T_C (onset)) are found to be much higher. The differences between T_C (onset) and T_C is a measure of the broadness of magnetic transition in a material. Since the T_C (onset) is close to our experimental limit (350 K) for $x = 0.3$ composition, true paramagnetic region remain out of reach for most of the compounds studied here, except for $\text{Sr}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{MoO}_6$. The high values of T_C (as well as T_C (onset)) for compositions having $x \leq 0.3$ is consistent with the observed tetragonal structure obtained at

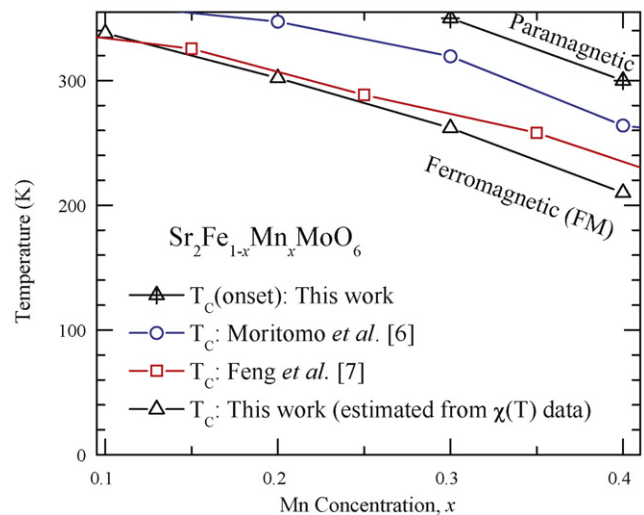


Fig. 3. Magnetic phase diagram for $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.1 \leq x \leq 0.4$).

room temperature (Fig. 1). Since both the T_C (onset) as well as T_C of $\text{Sr}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{MoO}_6$ are lower than room temperature where the material is paramagnetic (Fig. 3), the crystal structure at room temperature remains cubic. Our result thus clearly demonstrates that the tetragonal deviation in these compounds only takes place due to the magnetoelastic effect associated with paramagnetic to ferromagnetic transition.

The isothermal magnetization measured at 5 K shows decrease in the saturation magnetization (M_S) with increasing Mn concentrations (Fig. 4). While the higher limit of M_S can be determined from the limit $M_{1/H \rightarrow 0}$, the lower limit of M_S have been determined from high field magnetization data that follows the relation:

$$M(H) = M_S(0) + M_{lin}(H) \quad (1)$$

where $M_{lin} \propto H$ represents the contributions in magnetisation arising out of the magnetic spins that are not participating in the ferromagnetic ordering. Both the higher and lower limits of M_S 's thus estimated are found to be much smaller than the theoretical value of $4\mu_B$ (Fig. 4: inset (a)). Interestingly, both the remnant magnetisation (M_r) and the coercive field (H_C) are found to increase with increasing Mn concentration, although M_S gets reduced (Fig. 4: inset (b)). This unusual result indicates increasing formation of

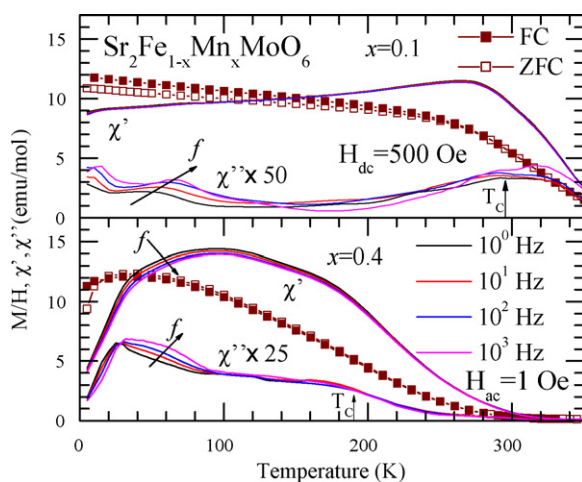


Fig. 2. Dc $[M(T)/H]$ and ac $[\chi'(f,T), \chi''(f,T)]$ magnetic susceptibility for the $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($x = 0.1$ and 0.4) system.

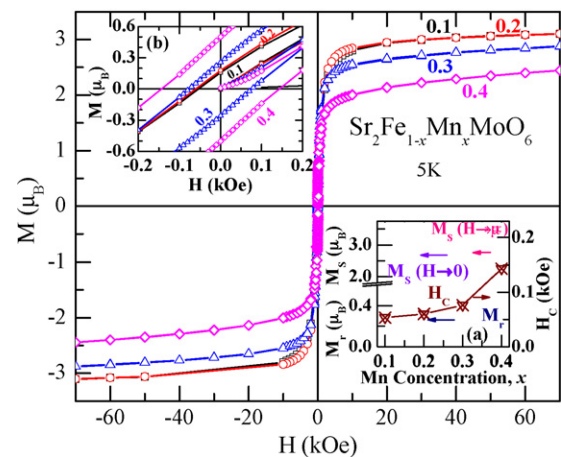


Fig. 4. Field dependence of magnetisation for $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.1 \leq x \leq 0.4$). Inset (a): saturation magnetisation estimated at $H \rightarrow 0$ and $H \rightarrow \infty$, as well as remnant magnetisation (M_r) and coercive field (H_C). Inset (b): field dependence of magnetisation at low field region.

spin glass states in the materials with increasing Mn concentration. The idea of a gradual transformation from a less magnetically anisotropic soft ferromagnet ($\text{Sr}_2\text{FeMoO}_6$) towards a more magnetically anisotropic hard magnet can be ruled out as the other end member of the series, $\text{Sr}_2\text{MnMoO}_6$, is an antiferromagnet only [5]. We would like to point out here that the occurrence of such spin glass-like phenomenon has not been mentioned in the studies of $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.1 \leq x \leq 0.4$) compounds reported earlier [6,7].

A closer look at the dc magnetic susceptibility measured under zero field cooled (ZFC) and field cooled (FC) condition exhibits irreversible behaviour (Fig. 2). The occurrence of such irreversibility (i.e., bifurcation between the $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$) starting from even just below T_C has been reported earlier in cluster/reentrant spin glass phases [11]. The presence of any inhomogeneous magnetic disorder is believed to be manifested in such behaviour. Since $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ contains both the ferromagnetic ($3d^5(\text{Fe})-4d^1(\text{Mo})$) as well as antiferromagnetic ($3d^5(\text{Mn})-4d^0(\text{Mo})$) exchange interactions (existing even in the paramagnetic state), the possibility of not satisfying both types of exchange interactions simultaneously at a given site is quite finite. This results in a magnetic exchange frustration, and such system is known as spin glass (SG) system. However, since spin glass system exhibits random yet cooperative, non-collinear freezing of spins, true bulk spin glass state cannot take place in a magnetically ordered solid [12,13], as is the case here.

2.3. Ac magnetic susceptibility

To understand the dynamics of any possible spin glass-like behaviour, ac susceptibility measurements ($\chi'(f,T)$, $\chi''(f,T)$; $f \cong 1, 10, 100$ and 1000 Hz) have been performed (Fig. 2). The basic features of the real component of the ac susceptibility, $\chi'(T)$, closely resemble that of zero field cooled dc magnetic susceptibility of the corresponding samples. However, the imaginary component, $\chi''(T)$, exhibit the following notable features: (i) A peak found at T_C and is associated with paramagnetic to ferromagnetic transition. (ii) At low temperatures, another peak having a very weak temperature dependence, has also been observed. Similar peak has been noticed earlier in the Mn-rich phases too and argued to be associated with short range magnetic order due to mismatch in volume distribution of FeO_6 ($\sim 9.5 \text{ \AA}^3$) and MnO_6 ($\sim 13.4 \text{ \AA}^3$) in $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ [8]. Below this peak temperature, the structural effect dominates over thermal energy. The discernible drop in magnetic susceptibility ($\chi'(T)$) around the same temperature also support this concept of presence of short range order. (iii) The third feature is the existence of another peak at the intermediate temperature which is highly frequency dependent. Similar frequency dependent peak is often seen in the RSG/CG systems described earlier [12,13]. As the Mn concentration increases, the low temperature peak caused by local structural distortion as mentioned above shifts towards higher temperature and appear to overlap with this frequency dependent peak. As a result, identification of the exact peak temperature of this feature is not possible, particularly for samples with higher Mn concentrations ($x \geq 0.3$) (Fig. 2). Although a minor frequency dependence is discernible in $\chi'(T)$ around the same temperature, no major drop in $\chi'(T)$ is associated around that temperature. Such behaviour is characteristic of disordered ferromagnetic system with competing ferromagnetic and antifer-

romagnetic interactions. In such systems, one may find that a few magnetic clusters, each acting as “super” moments, are formed in the system due to inhomogeneous doping and is responsible for this glassy nature. Among the double perovskite compounds, similar cluster-glass or spin glass-like behaviour has been reported earlier in $\text{Sr}_2\text{Fe}_{1-x}\text{Co}_x\text{MoO}_6$ and was interpreted by invoking an electronic phase segregation scenario where substitution of Fe by Co creates metallic ferromagnetic and insulating antiferromagnetic clusters throughout the samples, that in turn yield highly spin disordered regions responsible for spin glass-like behaviour [14]. This spin glass/cluster glass-like behaviour is not a bulk phenomena, but confined to these spin disordered regions only. It may be noted here that $\text{Sr}_2\text{Fe}_{1-x}\text{Co}_x\text{MoO}_6$ may be considered to be similar to $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ in the sense that $\text{Sr}_2\text{CoMoO}_6$ is an antiferromagnet [15] as is the case in $\text{Sr}_2\text{MnMoO}_6$ [5]. Although $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ may have a stronger magnetic anisotropy due to the monoclinic nature of $\text{Sr}_2\text{MnMoO}_6$ (in contrast to the tetragonal crystal structure of $\text{Sr}_2\text{CoMoO}_6$), the nature of the ac magnetic susceptibilities are very similar for both $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ and $\text{Sr}_2\text{Fe}_{1-x}\text{Co}_x\text{MoO}_6$, thus discarding magnetic anisotropy as origin of the observed spin glass-like behaviour in the present system. Studies of non-linear field effect, i.e. measurements of ac magnetic susceptibility under different ac field as well as under different dc biased field, along with the transmission electron microscopic studies to determine the existence of electronic phase segregation are necessary for the proper understanding of the origin of spin glass-like behaviour observed here.

3. Conclusions

In conclusion, we have studied the magnetic properties of inhomogeneous ferromagnetic system $\text{Sr}_2\text{Fe}_{1-x}\text{Mn}_x\text{MoO}_6$ ($0.1 \leq x \leq 0.4$) which exhibit spin glass-like behaviour due to the possible presence of highly spin disordered regions that are created as a result of the electronic phase segregation process.

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