Transport and magnetic properties of $Sr_2FeMo_xW_{1-x}O_6$

# Transport and magnetic properties of Sr$_2$FeMo$_x$W$_{1-x}$O$_6$

**Sugata Ray**[1]**, Ashwani Kumar**[1]**, Subham Majumdar**[2]**,**
**E V Sampathkumaran**[2] **and D D Sarma**[1,3]

[1] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560 012, India
[2] Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai-400 005, India

E-mail: sarma@sscu.iisc.ernet.in (D D Sarma)

**Abstract**
We have investigated transport and magnetic properties of a series of double-perovskite alloys in the system Sr$_2$FeMo$_x$W$_{1-x}$O$_6$. These compounds exhibit a metal–insulator transition as a function of doping, $x$. The compounds with $x$ in the range $1.0 \geqslant x \geqslant 0.3$ show metallic behaviour in the resistivity while compounds with $x$ in the range $0.2 \geqslant x \geqslant 0$ are insulating. All compounds with $1.0 \geqslant x \geqslant 0.2$ are ferrimagnetic, while Sr$_2$FeWO$_6$ ($x = 0$) is antiferromagnetic. The magnetization ($M$) is shown to increase slowly with decreasing $x$ in the range $1.0 \geqslant x \geqslant 0.3$ due to an enhanced crystallographic ordering; however, $M$ decreases rapidly with decreasing $x$ thereafter ($x < 0.3$), probably due to composition fluctuations near the critical concentration, $x_c$. Our data suggest primarily Fe$^{3+}$–(Mo, W)$^{5+}$ ordering for $x \geqslant 0.3$, while compositions with smaller $x$ possibly contain both Fe$^{3+}$ and Fe$^{2+}$ species inhomogeneously due to the presence of the W$^{6+}$ state. All samples with $x \geqslant 0.3$ show a significant amount of negative magnetoresistance, as has been observed earlier for Sr$_2$FeMoO$_6$ ($x = 1.0$).

Recently, a double-perovskite oxide system, Sr$_2$FeMoO$_6$, has become an important topic of scientific interest in view of its remarkable magnetoresistive properties [1–3]. Ordered Sr$_2$FeMoO$_6$ has alternating occupancies of Fe$^{3+}$ and Mo$^{5+}$ ions at the B sites of the perovskite ABO$_3$ structure, where A and B represent two cations. This compound is believed to be a ferrimagnet with a very high ferrimagnetic transition temperature ($\sim$450 K) [4]. Each B-site sublattice of Fe$^{3+}$ (3d$^5$) and Mo$^{5+}$ (4d$^1$) is believed to be arranged ferromagnetically, while the two sublattices are coupled to each other antiferromagnetically. It has been suggested [1] that a high degree of ordering between Fe$^{3+}$ and Mo$^{5+}$ in this compound leads to a half-metallic ferromagnetic (HMFM) state, where only minority spins are present at the Fermi level.

[3] Also at: Jawaharlal Nehru Centre for Advanced Research, Bangalore and Condensed Matter Theory Unit, Indian Institute of Science, Bangalore.

This compound exhibits a large negative magnetoresistance (MR) at 5 K as well as at 300 K; it is believed to be driven by the complete spin polarization at the Fermi energy ($E_F$) in the HMFM state. It has also been reported [2] that a disorder between the $Fe^{3+}$ and $Mo^{5+}$ occupancies destroys the HMFM state and as a consequence the colossal magnetoresistance also decreases. $Sr_2FeWO_6$ is another compound which belongs to the same double-perovskite oxide family, but shows very different electrical transport and magnetic behaviours. $Sr_2FeWO_6$ is insulating throughout the temperature range with an antiferromagnetic ordering below 37 K [5, 6]. $Sr_2FeWO_6$, in contrast to $Sr_2FeMoO_6$, contains $W^{6+}$ ($5d^0$) and $Fe^{2+}$ ($3d^6$) species [5, 6]. In view of the $5d^0$ electronic configuration of $W^{6+}$, the $Fe^{2+}$ ions are believed to couple antiferromagnetically with each other via Fe–O–W–O–Fe-type super-exchange interaction. Since $Sr_2FeMoO_6$ and $Sr_2FeWO_6$ have contrasting transport properties, it is expected that an alloy system of these compounds, $Sr_2FeMo_xW_{1-x}O_6$ would show a metal–insulator transition as a function of $x$. Different groups have reported [5, 7] MIT in this series of compounds as a function of doping. In the earlier report [5], the critical concentration, $x_c$, was reported to be between 0.4 and 0.5; however, a more recent study [7] reports $x_c \approx 0.25$. The present work is partly motivated by this large discrepancy in the reported $x_c$-values. Moreover, two distinctly different models have been proposed in order to explain this MIT. In one scenario [5], Fe is believed to be in the 3+ state up to $x_c$, starting from $x = 1$, with one itinerant electron from each of the Mo and W sites. For $x < x_c$, Fe transforms into the 2+ state converting Mo and W into 6+ states and giving rise to the insulating behaviour. Thus, a valence transition is the driving force for the MIT in this scenario. In the more recent work [7], it has been proposed that Mo always remains in the 5+ state, while W is in the 6+ state throughout the composition range, implying that there is no valence transition of Mo or W ions at the critical concentration. However, every $W^{6+}$ doping in place of $Mo^{5+}$ will require the transformation of one $Fe^{3+}$ to $Fe^{2+}$ for charge neutrality. Thus, the system is viewed as an inhomogeneous distribution of metallic $Sr_2FeMoO_6$ and insulating $Sr_2FeWO_6$ parts, the MIT at the critical composition being driven by the percolation threshold of the system. The system remains in the macroscopically metallic, ferrimagnetic state of $Sr_2FeMoO_6$ with a distribution of small clusters of insulating and antiferromagnetic $Sr_2FeWO_6$ in the large-$x$ region. With higher doping of W, the insulating $Sr_2FeWO_6$ clusters grow in size, eventually engulfing the metallic $Sr_2FeMoO_6$ clusters for $x < 0.3$, giving rise to the observed MIT. In view of these diverse suggestions for the origin of MIT, we have synthesized a series of $Sr_2FeMo_xW_{1-x}O_6$ compounds. We have carried out resistivity, magnetization and magnetoresistance measurements on these samples in order to obtain an understanding of the electrical and magnetic properties, thereby throwing light on the nature of the MIT present in the system as a function of $x$. We show that the samples with $x \geqslant 0.3$ are ferrimagnetic metals, while with $x \leqslant 0.2$, they are insulating. Thus we find $x_c \sim 0.25$ in agreement with the results of [7], but in contrast to $0.5 > x_c > 0.4$ reported in [5]. In order to explain all known properties of this solid solution, we show that it is necessary to incorporate ideas both from the valence transition scenario and from that of the existence of inhomogeneous phases and percolating networks.

$Sr_2FeMoO_6$ ($x = 1.0$) has been prepared using the solid-state route reported in [1, 4]. The starting materials, $SrCO_3$, $MoO_3$ and $Fe_2O_3$, were mixed thoroughly and calcined at 900 °C in air for three hours and then reduced in a flow of 10% $H_2$ in Ar at 1200 °C for two hours. The x-ray diffraction data establish the presence of a single phase with a high degree of ordering at the Fe and Mo cation sites [2]. The other members of the series, $Sr_2FeMo_xW_{1-x}O_6$ with $x = 0.8, 0.6, 0.3, 0.2$ and 0, were prepared by the following reaction:

$$12SrCO_3 + 3Fe_2O_3 + x(5MoO_3 + Mo) + (1-x)(5WO_3 + W)$$
$$= 6Sr_2FeMo_xW_{1-x}O_6 + 12CO_2.$$
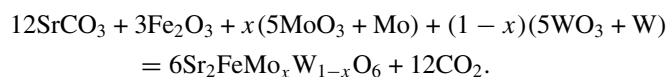
These compounds were prepared by the melt-quenching method under an Ar atmosphere. This method has been described in detail previously [2]. After the synthesis, all of these compounds were annealed at 1300 °C for six hours in an Ar atmosphere in order to achieve a homogeneous phase which has been confirmed by the energy-dispersive analysis of x-rays (EDAX) for different grains of the samples. X-ray diffraction data for all samples show that pure and highly ordered phases are obtained by this method.

The electrical resistivities ($\rho$) of all of the samples are shown in figure 1 on a logarithmic scale as functions of temperature ($T$). Evidently, $\rho$ versus $T$ plots clearly demarcate two regimes. The first group with $x \geqslant 0.3$ have low resistivities and exhibit metallic behaviour, while the compositions with $x \leqslant 0.2$ are insulating. Thus, these results clearly establish a metal–insulator transition as a function of the composition with $0.3 > x_c > 0.2$. This value of the critical composition is in agreement with that reported in [7]; however, the critical composition $0.5 > x_c > 0.4$ reported in [5] is significantly different from the present finding. This is most probably due to the grain boundary effects which appear to influence the transport properties of these sintered samples substantially. For example, the resistivity values of the composition with $x = 0.6$ are higher compared to those of $x > 0.3$ compositions, though the values for all of the metallic compositions are the same within one order of magnitude. This is
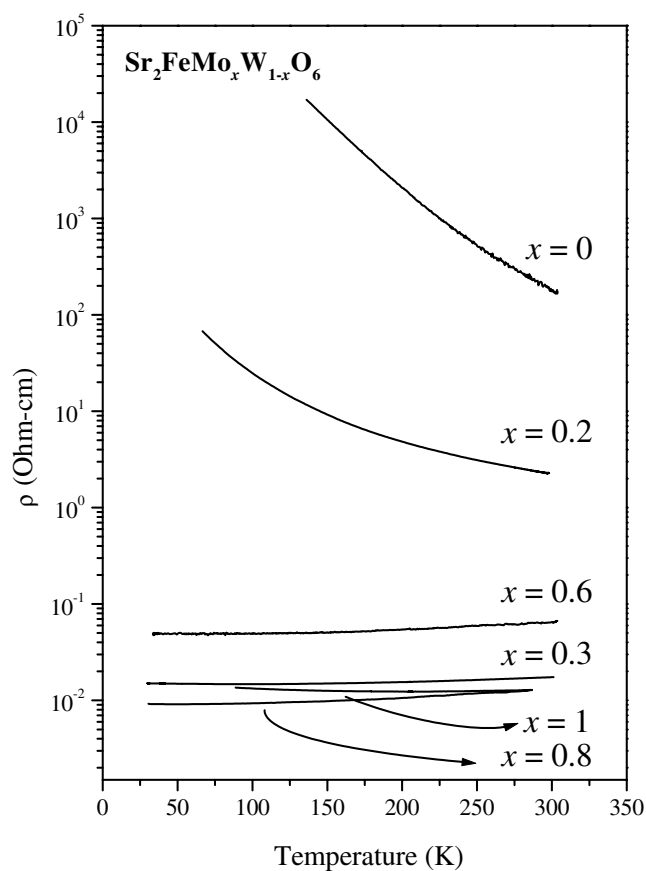


**Figure 1.** The electrical resistivity of $Sr_2FeMo_xW_{1-x}O_6$ as a function of temperature, plotted on a logarithmic scale.

most likely to be due to a higher contribution from the grain boundaries in the $x = 0.6$ sample. It is also to be noted that the resistivities of these metallic samples (see figure 1) are rather large (10–100 m$\Omega$ cm; the values are reported to be within 1–100 m$\Omega$ cm in [5,7]), once again indicating a significant contribution from grain boundaries in these sintered polycrystalline samples. We have also observed a time-dependent change in the resistivity of the metallic samples. Though the magnitude of the resistivity does not change significantly with time, the temperature coefficient of resistivity tends to change sign over a period of time, indicating a slow oxidation of grain surfaces and introduction of an insulating grain boundary layer. This possibly explains why in the earlier study the critical composition was thought to be between 0.4 and 0.5 on the basis of the temperature coefficient of resistivity of these compounds [5]. The resistivity data presented here were collected from freshly prepared samples within a day of the synthesis.

In order to understand the origin of the insulating behaviour of samples with $x \leqslant 0.2$, we have analysed $\rho(T)$ in some detail. We found that a single activated dependence of $\rho$ on $T$ cannot account for the entire range of resistivity data of $Sr_2FeWO_6$. This is often the case for insulating oxide samples [8], as the low-temperature transport tends to be dominated by a very low density of localized states introduced by impurities and non-stoichiometry within the band-gap region of the stoichiometric compound, while the high-temperature behaviour is contributed by the thermally activated charge carriers across the band gap. In view of these two contributions to the conductivity, we model the conductivity dependence on temperature, $\sigma(T)$, as

$$\sigma(T) = \sigma_{01} \exp[-E_g/2k_BT] + \sigma_{02} \exp[-(T_0/T)^{1/4}].$$

The first term in the above expression represents the activated behaviour, while the second one accounts for variable-range hopping (VRH) within the localized low density of states in the midgap region. We show the best fit to the conductivity in terms of the above expression for $\sigma(T)$ as a solid line through the experimental data points (open circles in figure 2). Evidently, we obtain a good fit in this procedure for the entire range of data with an activation energy of about 0.3 eV. In the same figure, we have also shown the contribution of the activated term to the total conductivity by the long-dashed line, and the contribution of the variable-range hopping by the short-dashed line. Evidently, the activated behaviour dominates over the VRH contribution throughout the temperature range except for at the lowest temperatures, indicating only a small influence from states introduced by defects.

The conductivity of $Sr_2FeMo_{0.2}W_{0.8}O_6$ deviates very pronouncedly from the activated behaviour as illustrated by the $\ln(\sigma)$ versus $1000/T$ plot, shown in the inset of figure 3. Interestingly, the conductivity over the entire range of temperatures is very well described by a single variable-range-hopping term, as illustrated by the linear dependence of $\ln(\sigma)$ on $T^{-1/4}$, shown in the main frame of the figure. This suggests that Mo doping in $Sr_2FeWO_6$ introduces a significant density of states at the Fermi energy, $E_F$, thereby leading to a complete dominance of the variable-range-hopping contribution. This change of transport behaviour is consistent with the notion that Mo is in the $Mo^{5+}$ $4d^1$ state, with the 4d density of states spanning the Fermi energy, while W in the parent compound, $Sr_2FeWO_6$, is in the $5d^0$ state with no states being contributed from the W 5d states at $E_F$. It is to be noted that this conclusion is also in agreement with the Mössbauer results [5]; Mössbauer data clearly show that Fe exists in both 2+ and 3+ states for $x = 0.3$, while it is only in the 2+ state for $x = 0$. The conversion of $Fe^{2+}$ in $Sr_2FeWO_6$ to $Fe^{3+}$ on Mo doping in this concentration regime must be due to the doping of $Mo^{5+}$ in place of $W^{6+}$ species.

Magnetization ($M–H$) curves at different temperatures (300, 77 and 5 K) for the five compositions ($x = 1.0$, 0.8, 0.6, 0.3 and 0.2) are shown in figure 4. The magnetic field
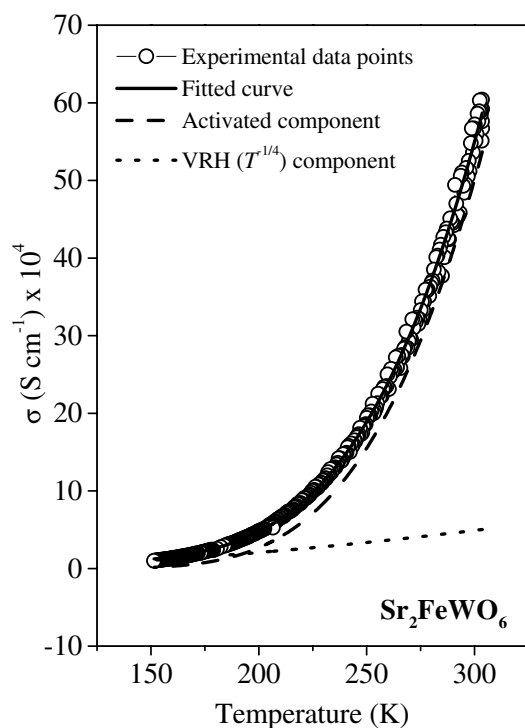
**Figure 2.** The electrical conductivity (open circles) of $Sr_2FeWO_6$ as a function of temperature. The solid line shows the best fit using the relation described in the text. The contributions from the activated component (long-dashed line) and the VRH component (short-dashed line) are also shown.

required for saturation is very low, typically 0.7 T, for compounds with $1.0 \geqslant x \geqslant 0.3$; very narrow hysteresis loops for this range of compositions suggest that these materials are soft ferrimagnets even at 300 K. For the $x = 0.2$ sample, however, the saturation of magnetization could not be achieved even with a field of 6 T; also the hysteresis loop is comparatively broad in this case. We show the observed high-field magnetization at 5 K as a function of the composition, $x$, in figure 5(a). From this figure, we find that the saturation magnetization ($M_s$) for the $x = 1.0$ sample is 3.14 $\mu_B$ per formula unit (f.u.) at 5 K, in good agreement with the previously reported value [1]. It is interesting to note that the saturation magnetization has an overall increasing trend starting form $x = 1$ and reaches a maximum (4.0 $\mu_B$/f.u.) for the $x = 0.3$ sample. The magnetization data on $Sr_2FeMo_{0.6}W_{0.4}O_6$ deviate slightly from the increasing trend. We believe this to be possibly due to an increased amount of grain boundary phase in this compound. This is consistent with the enhanced resistivity of the sample (see figure 1). This increasing trend of magnetization is also in agreement with a previous report [7]. Beyond $x = 0.3$, we find a sharp drop in the magnetization of the $x = 0.2$ sample, with $M_s = 2.62$ $\mu_B$/f.u. at 6 T. These results in conjunction with the transport data in figure 1 and Mössbauer results [5] provide an understanding of the MIT in this complex system. We argue that the continuous increase of the $M_s$-value with decreasing Mo doping down to $x = 0.3$ is a direct consequence of increasing $Fe^{3+}$ and $(W, Mo)^{5+}$ ordering with increasing W concentration. The extent of the ordering in these compounds can be easily estimated from the order-related diffraction peak [2] at $2\theta = 19.6°$, normalized by the highest-intensity diffraction peak appearing at $2\theta = 32.1°$. We show the normalized intensity of the diffraction

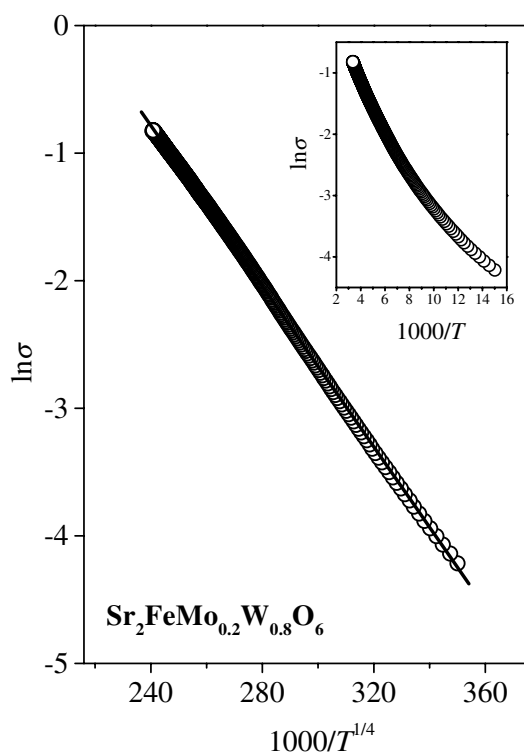**Figure 3.** The $\ln\sigma$ versus $1000/T^{1/4}$ plot for $Sr_2FeMo_{0.2}W_{0.8}O_6$. The inset shows the $\ln\sigma$ versus $1000/T$ dependence.

peak at $2\theta = 19.6°$ in figure 5(b) as a function of the composition. This plot clearly shows that the ordering increases systematically with increasing W concentration. Here we need to distinguish between two regimes, namely $x \geqslant 0.3$ and $x < 0.3$. For $x \geqslant 0.3$, $M_s$ increases with the increase in the ordering, i.e. with decreasing $x$. It has been shown recently from extensive band-structure calculations that the magnetic moment of these samples decreases with increasing disorder between the Fe and Mo sites. The fully ordered sample is expected to have a magnetic moment of 4 $\mu_B$/f.u. arising from the ferrimagnetic coupling between the $Fe^{3+}$ $3d^5$ and $Mo^{5+}$ $4d^1$ states, also supported by the band-structure results [9]. Thus, the reduction of the magnetic moment of as-prepared $Sr_2FeMoO_6$ from the theoretically expected value (4 $\mu_B$/f.u.) to 3.1 $\mu_B$ is due to the presence of finite disorder in the sample; Rietveld analysis of the x-ray diffraction pattern suggests a $\sim$90% ordering in this sample [2]. With increasing ordering as a consequence of increasing W content, the system eventually attains the full moment of 4 $\mu_B$/f.u. at $x = 0.3$ (see figures 5(a) and 5(b)). This is clear evidence for the existence of both Mo and W in the 5+ state down to $x = 0.3$ starting from $x = 1$ in the present case. This is also supported by previous Mössbauer data [5] showing the existence of only $Fe^{3+}$ and a complete absence of $Fe^{2+}$ for $1.0 \geqslant x \geqslant 0.5$. Though the early Mössbauer data did point to the presence of $Fe^{2+}$ at $x = 0.3$ indicating a valence transition, we believe that these are due to chemical inhomogeneities in samples prepared by different routes; we comment on this at a later stage. However, our results clearly suggest a chemically homogeneous system containing $Fe^{3+}$ and $(Mo, W)^{5+}$ in the range $1.0 \geqslant x \geqslant 0.3$, in contrast to a model containing a percolating path of $Sr_2FeMo^{5+}O_6$ clusters in a matrix of $Sr_2FeW^{6+}O_6$ antiferromagnetic insulating phase
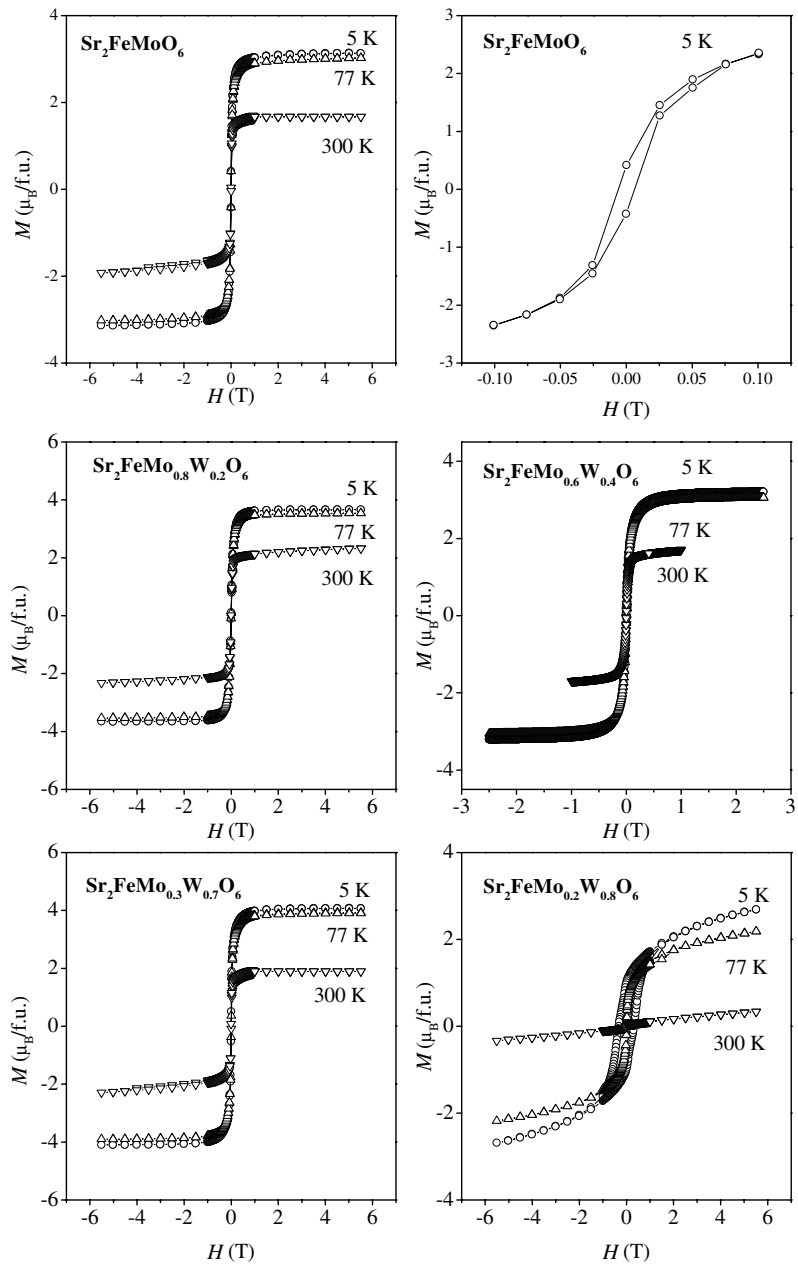
**Figure 4.** Magnetization ($M-H$) curves of $Sr_2FeMo_xW_{1-x}O_6$ at different temperatures (5, 77 and 300 K). The upper right panel shows the magnetization of the $x = 1.0$ sample in the low-field region.

throughout the composition range [7]. In our results, we not only observe an *increase* of $M_s$, but also recover the full moment, proving the system to be homogeneous in the ferrimagnetic state. This is further evidenced by the fact that the conductivities of all of the samples in the range $1.0 \geqslant x \geqslant 0.3$ are similar.
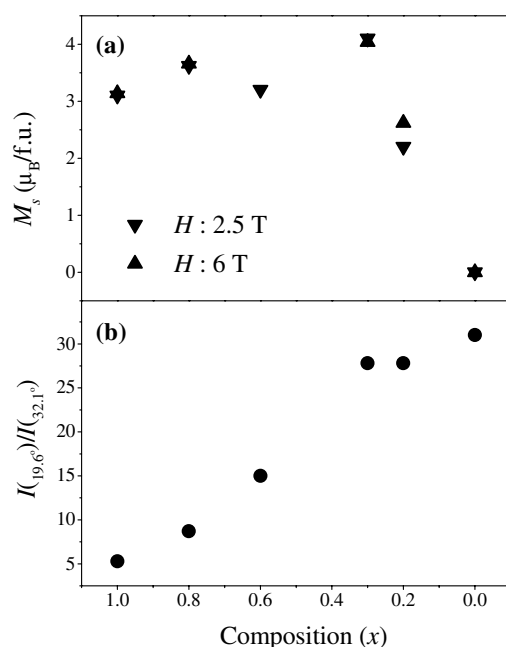
**Figure 5.** (a) The saturation magnetizations ($M_s$) as a function of composition ($x$) at two different fields, 2.5 T (downward-pointing triangles) and 6 T (upward-pointing triangles). (b) The variation in intensity of the order-related diffraction peak at $2\theta = 19.6°$, normalized with the most intense peak at $2\theta = 32.1°$, as a function of composition ($x$).

In the regime of $x < 0.3$, we find a sudden decrease in the $M_s$-value. This observation in conjunction with the Mössbauer data [5] exhibiting the existence of both $Fe^{2+}$ and $Fe^{3+}$ for $0.3 > x \geqslant 0$, suggests that there is a valence transition across the critical composition, $x_c$. It would appear that W transforms into the 6+ state for $x < x_c$, while Mo continues to be in the 5+ state. Thus, charge neutrality requires the formation of $Fe^{2+}$ and $Fe^{3+}$ states. In this inhomogeneous phase, $Sr_2FeWO_6$-like regions with the $W^{6+}$ $5d^0$ configuration, being antiferromagnetic, do not contribute significantly to the saturation magnetization and, consequently, $M_s$ decreases rapidly. On the other hand, the $Sr_2FeMoO_6$-like phase with the $Mo^{5+}$ $4d^1$ configuration continues to be in the ferrimagnetic state, thereby still retaining a large magnetization for $x = 0.2$. This scenario for the $x < 0.3$ regime is consistent with the one reported by Kobayashi *et al* [7], though the authors have proposed this model for the full range of compositions. But still this model alone cannot explain all the experimental results and the samples cannot be thought of as a simple mixture of $Sr_2FeMoO_6$ and $Sr_2FeWO_6$ even in this range of compositions. Otherwise, we would expect only 20% of the full magnetization value, i.e. $M_s = 0.8 \, \mu_B$/f.u., for the $Sr_2FeMo_{0.2}W_{0.8}O_6$ sample, whereas the experimentally observed value is 2.6 $\mu_B$/f.u. One possible reason of such a high $M_s$ for the $x = 0.2$ sample is that $Sr_2FeMoO_6$-like clusters tend to polarize the neighbouring $Sr_2FeWO_6$ regions magnetically, enhancing the magnetization. The alternative scenario is that the composition fluctuation is not as extreme as to form separated $Sr_2FeMoO_6$-like and $Sr_2FeWO_6$-like regions. For example, $Sr_2FeMo_{0.2}W_{0.8}O_6$ can also be thought of as a combination of equal amounts (50%) of ferrimagnetic $Sr_2FeMo_{0.3}W_{0.7}O_6$ and antiferromagnetic $Sr_2FeMo_{0.1}W_{0.9}O_6$. In this case, it is easy to see that the sample will appear to have half of the $M_s$ (i.e. 2.0 $\mu_B$/f.u.) corresponding to $Sr_2FeMo_{0.3}W_{0.7}O_6$—which is in better agreement with the experimentally observed value.

Obviously, more work is required to establish the microscopic composition fluctuation in this system for the large-$x$ regime.

Sr$_2$FeMoO$_6$ shows a significant, sharp drop in resistance on application of a magnetic field even at room temperature [1, 2]. In order to complete the study, we have also measured the magnetoresistance for all of the compositions at room temperature; the negative magnetoresistances that we have obtained for $x = 0.2, 0.3, 0.6, 0.8$ and $1.0$ at 5 T are 1%, 0.7%, 8%, 3% and 9%, respectively. We have performed magnetoresistance measurements in more detail for $x = 0.3, 0.6$ and $1.0$ samples, shown in figure 6. The magnetoresistance effect was found to be the largest for the $x = 1$ compound. The magnetoresistance value

$$[\rho(H, T) - \rho(0, T)]/\rho(0, T)$$

for Sr$_2$FeMoO$_6$ was as much as 37% at 4.2 K. For $x = 0.6$ and $0.3$, the corresponding values are 30% and 8%, respectively, at 4.2 K with an applied field of 5.5 T. These values correspond to 60%, 44% and 9% of the MR if the percentage of the MR is obtained by normalizing with $\rho(H, T)$ instead of $\rho(0, T)$. All three compounds exhibit a sharp drop in resistance at a very
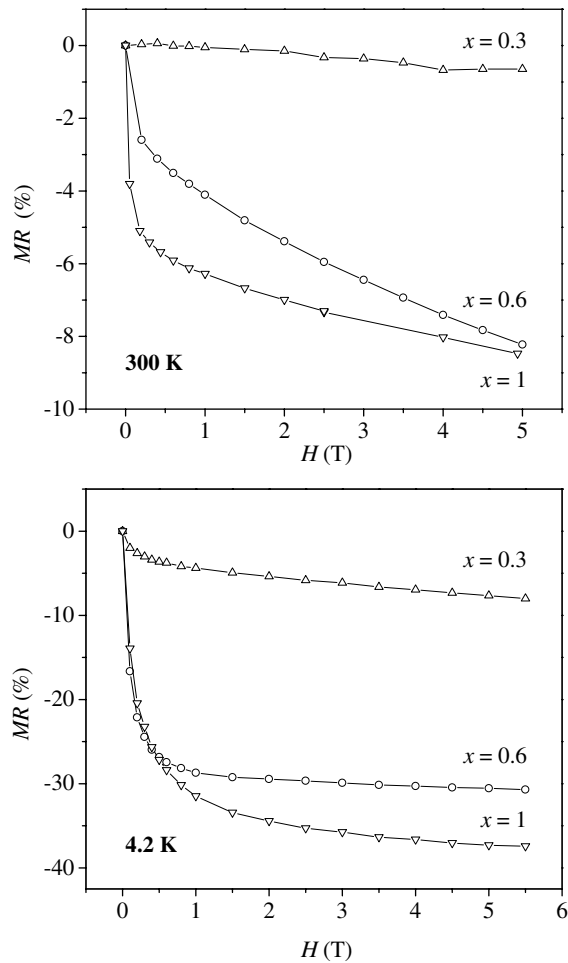


**Figure 6.** Percentage magnetoresistance for $x = 0.3, 0.6$ and $1$ in $Sr_2FeMo_xW_{1-x}O_6$ at 300 K (upper panel) and 4.2 K (lower panel).

low applied field ($\sim 0.5$ T). This part of the magnetoresistance is believed to be dominated by an intergrain spin-dependent carrier scattering process, for which the half-metallic ferromagnetic state plays a crucial role by providing highly polarized states at $E_F$. The spin polarization is expected to increase with more Fe and (W, Mo) cation ordering and we have already pointed out from our magnetization measurements that this ordering increases significantly with decreasing Mo concentration down to $x = 0.3$. Thus, it would be expected that the magnetoresistance should increase with decreasing Mo content. In contrast, our experimental results show an opposite trend. We believe that this is possibly due to grain boundary effects (e.g. changing grain boundary thickness or the chemical composition at the grain boundaries from sample to sample) present in the polycrystalline samples over which we do not have much control. This may also be responsible for the non-monotic values of MR obtained by us at room temperature as a function of the composition.

The results reported here clearly show that the physical properties of $Sr_2FeMo_xW_{1-x}O_6$ change from those of ferrimagnetic metal to those of antiferromagnetic insulator with increasing doping of W by Mo. The critical composition, $x_c$, is found to be between 0.2 and 0.3. The resistivity and magnetization results separate the compositions into two regimes, namely $x \geqslant 0.3$ and $x < 0.3$. The compounds with $x \geqslant 0.3$ show ferrimagnetic, metallic behaviour with relatively large $M_s$-values, proving the presence of $Fe^{3+}$ ($3d^5$) and (W, Mo)$^{5+}$ ($nd^1$) states throughout, while there is possibly a valence transition to $Fe^{2+}$ states for $x < 0.3$ compounds. This valence transition plays a key role in the metal–insulator transition as a function of $x$ for this series of compounds. The valence transition of Fe from the 3+ to the 2+ state for $x < 0.3$ can lead to the formation of small ferrimagnetic, metallic clusters of $Sr_2FeMo_{x'}W_{1-x'}O_6$ ($x' \geqslant 0.3$) in the antiferromagnetic, insulating matrix of $Sr_2FeMo_{x''}W_{1-x''}O_6$ ($x'' \leqslant 0.2$), due to fluctuations in the chemical composition. All compounds in the range $1.0 \geqslant x \geqslant 0.2$ exhibit negative magnetoresistance even at room temperature, with significantly more pronounced negative magnetoresistances at lower temperatures.

## References

[1] Kobayashi K-I, Kimura T, Sawada H, Terakura K and Tokura Y 1998 *Nature* **395** 677
[2] Sarma D D, Sampathkumaran E V, Ray S, Nagarajan R, Majumdar S, Kumar A, Nalini G and Guru Row T N 2000 *Solid State Commun.* **114** 465
[3] Sarma D D, Mahadevan P, Saha-Dasgupta T, Ray S and Kumar A 2000 *Phys. Rev. Lett.* **85** 2549
[4] Nakagawa T 1968 *J. Phys. Soc. Japan* **24** 806
[5] Nakagawa T, Yoshikawa K and Nomura S 1969 *J. Phys. Soc. Japan* **27** 880
[6] Kawanaka H, Hase I, Toyama S and Nishihara Y 2000 *Physica* B **281+282** 518
[7] Kobayashi K-I, Okuda T, Tomioka Y, Kimura T and Tokura Y 2000 *J. Magn. Magn. Mater.* **218** 17
[8] Maiti K, Vasanthacharya N Y and Sarma D D 1997 *J. Phys.: Condens. Matter* **9** 7507
[9] Saha-Dasgupta T 2000 unpublished