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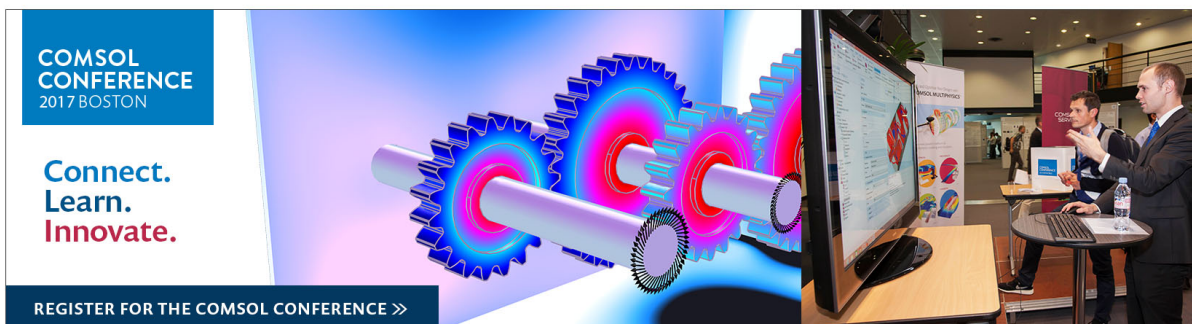
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Coexistence of intrinsic and extrinsic magnetoresistance in the double-perovskite $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$ system

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In a recent study, it was shown that by partially substituting Mo with W in the double-perovskite $\text{Sr}_2\text{FeMoO}_{6-w}$ system, the magnetoresistivity can be enhanced. [K.-I. Kobayashi, T. Okuda, Y. Tomioka, T. Kimura, and Y. Tokura, *J. Magn. Magn. Mater.* **218**, 17 (2000).] In order to explain the increase in the magnetoresistivity a series of W-substituted $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$ samples with $0 \leq x \leq 1$ was synthesized. Upon increasing the W content, the samples began to exhibit coexistence of paramagnetism and ferrimagnetism at 300 K. Signatures of antiferromagnetic ordering appeared around $T_N \approx 50$ K for $x \geq 0.6$. In samples with $0.7 \leq x \leq 0.8$ a broad peak was observed in the magnetoresistance data at temperatures corresponding to the Néel temperature. The peak was found to have its origin in the colossal magnetoresistance effect. The W-substituted samples were partially ferrimagnetic and therefore also exhibited the tunneling-type magnetoresistance, which is characteristic of pure $\text{Sr}_2\text{FeMoO}_{6-w}$. The coexistence of the two types of magnetoresistance effect is responsible for the enhancement of the overall magnetoresistance value. A slight enhancement in the magnetoresistance values around 300 K for the strongly W-substituted samples was found to be related to a second colossal magnetoresistance peak related to the para- to ferrimagnetic transition at T_c . © 2001 American Institute of Physics. [DOI: 10.1063/1.1366357]

Recently tunneling magnetoresistivity (TMR) was confirmed at room temperature in powder samples of the double-perovskite $\text{Sr}_2\text{FeMoO}_{6-w}$ system.¹ The origin of the TMR effect has been claimed to be in the half-metallic nature of the phase. Band calculations indicate localized spin-up Fe d electrons, while the antiferromagnetically coupled spin-down d electron of Mo is itinerant. The Mo d electrons give rise to a spin-polarized current. By applying a magnetic field to a specimen the scattering of the spin-polarized charge carriers at magnetic domain walls is strongly suppressed, which results in reduced resistivity.¹ The absence of strong MR effects in single crystals of $\text{Sr}_2\text{FeMoO}_{6-w}$ supports this notion.² By partially replacing Mo with W a substantial enhancement in MR has been observed.³ The authors explain the enhancement as a development of an insulating wall between the ferrimagnetic half-metallic grains. The thickness of the wall is believed to strongly influence the scattering of the spin-polarized charge carriers.

The $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$ perovskite system was characterized already more than 30 years ago.^{4,5} In particular the drastic decrease in electric conductivity upon W substitution had been reported earlier. It was shown that for the $\text{Sr}_2\text{FeWO}_{6-w}$ phase all W atoms adopted the W^{6+} state, and consequently Fe entered the Fe^{2+} state.⁶ This would lead to a complete localization of the valence electrons, explaining the decrease in conductivity. In the earlier works on the $\text{Sr}_2\text{FeMoO}_{6-w}$ phase a Fe^{3+} high-spin state was assigned to Fe. However, our recent ⁵⁷Fe Mössbauer study revealed that

the itinerant d electron of the formally pentavalent Mo influences the valence state of Fe, resulting in the +2.5 fluctuating mixed-valence state.⁷ A neutron diffraction study also revealed decreased spin values at both the Fe and Mo sites,⁸ which supports the notion of a mixing valence. Additional support for the mixed-valence picture was found in a recent magnetization study.⁹ In this letter we report the results from a systematic study on the influence of tungsten substitution on the magnetic and magnetoresistance properties.

The preparation and chemical characterization of the $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$ samples followed the procedure reported in Ref. 10. The phase purity, crystal symmetry, and lattice parameters of the samples were checked by x-ray diffraction (XRD: MAC Science M18XHF²²; Cu $K\alpha$ radiation). Energy-dispersive x-ray analysis (TEM-EDX Kevex Sigma) was used to confirm the distribution of elements in the samples. Oxygen contents were checked by Coulometric titrations. Resistivity measurements under an applied field of -7 – 7 T, in a direction perpendicular to the current flow, were carried out in the temperature range of 5–300 K (Quantum Design: PPMS). The samples were measured in both a field-scanning mode (constant temperature) and a temperature-scanning mode (constant external field). A standard four-probe technique was used. For these measurements the samples were pelletized under a pressure of 10 MPa. The pellets were shaped into parallelepipeds with a cross section of 2–5 mm². Gold electrode pads were vacuum-deposited directly on the sample surface. The spacing between the electrodes was controlled with a 0.05 mm Au wire. Ag leads were attached to the Au pads using Ag paste. The magnetization measurements in the temperature range of 5–300 K were done using a dc superconducting quantum interference device magnetometer (Quantum Design: MPMS-5S), in an external field of 5000 Oe.

In Fig. 1 XRD patterns for the samples are presented. Up

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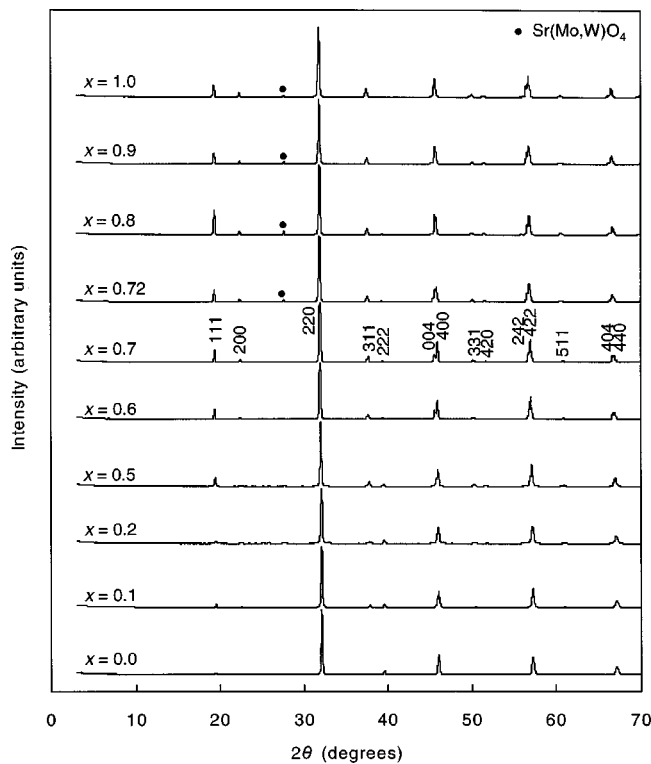


FIG. 1. X-ray diffraction patterns of the $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$ samples. No impurities are seen up to $x=0.70$. A tetragonal indexing was readily performed for all peaks in the pattern of the $\text{Sr}_2\text{Fe}(\text{Mo}_{0.30}\text{W}_{0.70})\text{O}_6$ sample.

to $x=0.70$ no impurity phases were observed even in high-resolution scans, indicating a complete solid-solubility of Mo and W and conservation of the double-perovskite structure. For higher x values traces of $\text{Sr}(\text{Mo},\text{W})\text{O}_4$ were seen. The structure of the lightly substituted samples was best described by the cubic space group $Fm\bar{3}m$. For higher W contents the tetragonal space group $I4/mmm$ gave a better agreement with the XRD data. The transition from the cubic to the tetragonal space group occurred gradually in the region $0.6 \leq x \leq 0.8$. Using TEM-EDX the distribution of the local compositions in single grains of $\sim 1.6 \mu\text{m}$ were measured at 3–4 spots $\sim 0.3 \mu\text{m}$ apart (excluding the area near grain boundaries) in several samples. The result obtained for two grains of $\text{Sr}_2\text{Fe}(\text{Mo}_{0.30}\text{W}_{0.70})\text{O}_6$ was in at %: 48(3)% Sr, 30(20)% Fe, 6(1)% Mo, and 17(2)% W, the theoretical values being: 50%, 25%, 7.5%, and 17.5%, confirming the solid solubility of Mo and W on a submicron scale. The oxygen content, i.e., the $6-w$ value, of the samples ranged from 5.97(3) to 6.03(3) atoms per formula unit for the $x=0.0$ and 1.0 samples, respectively, as determined by coulometric titrations. Although a slight increasing trend was observed the difference is yet of the same order as the statistical error.

In Fig. 2 results from the magnetization measurements are presented. The $x \geq 0.9$ samples are antiferromagnetic with Néel temperatures of ~ 30 K. A broad antiferromagnetic transition is also visible in the $x=0.6, 0.7,$ and 0.8 samples at $T_N \approx 50$ K. In these samples ferrimagnetism and antiferromagnetism are thus simultaneously present, as reported in Ref. 3. The antiferromagnetic ordering is believed to be concentrated to areas where the Fe atoms are surrounded by zero-spin W^{6+} neighbors, while the ferrimagnetic order arises from the antiferromagnetic coupling between adjacent

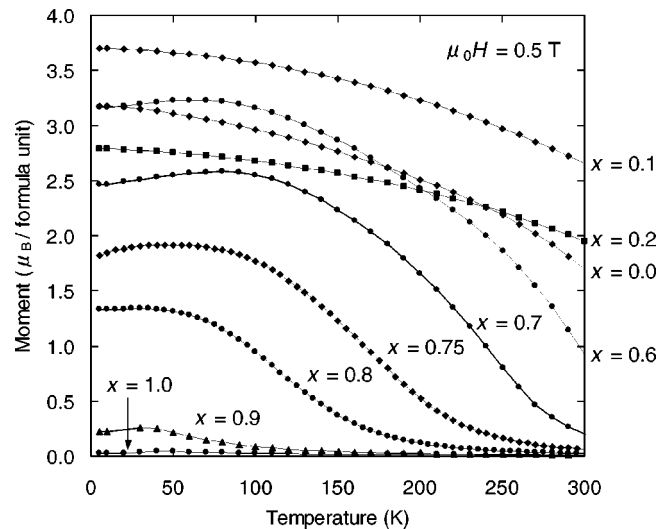


FIG. 2. Magnetic moment vs temperature for $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$.

Mo and Fe spins.³ There seems to be a systematic difference between the T_N values for the pure $\text{Sr}_2\text{FeWO}_{6-w}$ and the $0.6 \leq x \leq 0.8$ samples. The difference is probably related to distribution of Mo and W in the lattice. Also in the $x=0.5$ sample evidence for the coexistence of the two magnetic orderings was revealed from the ^{77}Fe Mössbauer spectrum recorded at 77 K.¹¹ As the Néel temperature is lower than 77 K, the portion of iron that orders antiferromagnetically appeared as a paramagnetic component in the spectrum. A well-developed magnetic sextet was observed for the portion which was ferrimagnetically ordered.

A qualitative picture of the magnetoresistance properties was obtained from temperature scans of the resistance. In Fig. 3 the magnetoresistance as a function of temperature, obtained using fields of 0 and 7 T, is presented. The magnetoresistance value is here defined by

$$\text{MR}(T, H) = \frac{\rho(T, 0) - \rho(T, H)}{\rho(T, H)} \cdot 100\%, \quad (1)$$

where H denotes the external field. For $x \leq 0.2$ the magnitude of the MR value increases smoothly upon decreasing temperature. This is a typical behavior for the tunneling-type

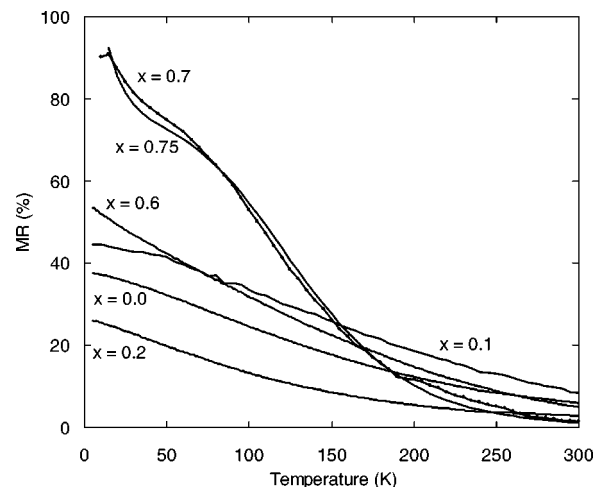


FIG. 3. Magnetoresistance vs temperature for the $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$ samples. The resistivity data were recorded in external fields of 0 and 7 T.

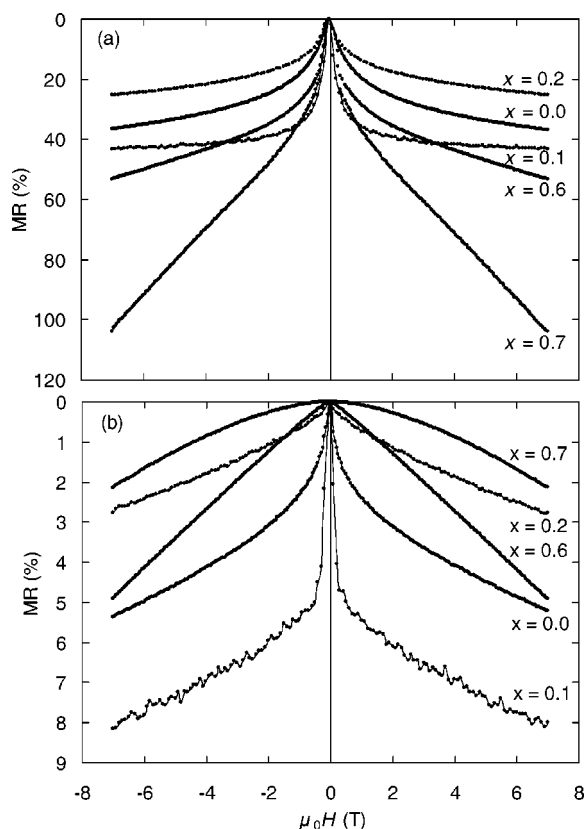


FIG. 4. Magnetoresistance vs applied external field for the $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_{6-w}$ samples at (a) 5 and (b) 300 K.

magnetoresistance, i.e., the TMR value strongly reflects the overall sample magnetization. The large MR value obtained for the $x=0.1$ sample is probably due to the slightly improved sample quality, as evidenced by a corresponding maximum in the sample magnetization curves of Fig. 2. It has been suggested that a small amount of W substituting for Mo reduces the disorder between the Fe and Mo sites,³ known to be present in most nonsubstituted $\text{Sr}_2\text{FeMoO}_{6-w}$ samples.¹ Upon further increasing the W content, the magnitude of the MR value goes through a broad peak at around 50 K (samples $x=0.7$ and 0.75). The position of this broad local maximum corresponds well to the Néel temperatures of the samples, indicating that the paramagnetic to antiferromagnetic transition gives rise to this CMR-type effect, which is superimposed on the TMR background, Fig. 3. When temperature is decreased further the TMR portion increases further. Close to $T=30$ K the MR value deviates again strongly from the TMR background and a rather sharp CMR peak is obtained. This second peak is believed to be related to the paramagnetic to antiferromagnetic transition in small islands of pure $\text{Sr}_2\text{FeWO}_{6-w}$ phase. Judging from the magnetization data given in Fig. 2 the transition to the AF state covers a broad temperature range, which explains the occurrence of two separate CMR peaks. At 5 K both the TMR background and the lower tail of the CMR peak produce the high MR values reported, e.g., in Ref. 3. In Fig. 4 the magnetoresistance recorded at various temperatures, as a function of the applied field, is presented. For low W contents the magnetoresistance values clearly saturate already in moderate fields, whereas an almost linear MR versus field dependence is observed when the W content increases. In fact, this is an

additional indication of the presence of two different MR mechanisms. For the nonsubstituted $\text{Sr}_2\text{FeMoO}_{6-w}$ phase, exhibiting pure TMR, a fast saturation of the MR values in rather low fields is obtained, as the materials are soft and the saturation magnetization is low, i.e., full grain/domain alignment is obtained for moderate fields. The CMR contribution, on the other hand, is an intrinsic effect, which may increase strongly throughout the range of the applied field. This is particularly the case at 300 K, where the heavily substituted samples exhibit almost no tunneling-type MR effect, but still a rather clear CMR behavior. For instance $\text{Sr}_2\text{Fe}(\text{Mo}_{0.3}\text{W}_{0.7})\text{O}_{6-w}$, which is paramagnetic at and below 300 K and thus has a zero TMR contribution, still exhibits a small MR effect, Fig. 4.

The presence of CMR around 300 K seems to be related to the paramagnetic to ferrimagnetic transition, the T_c of which is close to 300 K for the $x=0.6$ and 0.7 samples. Also in samples with isovalent Ba-for-Sr substitution, the magnetoresistance versus temperature data indicated the presence of both TMR and CMR.¹² In this case the Ba substitution brings the Curie temperature down to ~ 300 K, with the result that a CMR peak associated with the para- to ferrimagnetic transition at T_c in the $\text{Ba}_2\text{FeMoO}_{6-w}$ phase becomes clearly visible. The contribution from the TMR effect extrapolates to zero at around T_C as expected.

With an eye on potential applications, using appropriate chemical substitutions it may be possible to enhance the MR value significantly, by retaining a strong TMR effect and superimposing a CMR peak in the region, where one wishes to achieve the highest resistivity versus field sensitivity.

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