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Large room-temperature intergrain magnetoresistance in double perovskite $SrFe_{1-x}(Mo\,or\,Re)_xO_3$

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We report significant intergrain magnetoresistance (IMR) in polycrystalline double perovskites of $SrFe_{1-x}(Mo\,or\,Re)_xO_3$ at *room temperature*. Systematics of the temperature dependence of IMR indicates that the observed large room-temperature IMR in $SrFe_{1/2}Mo_{1/2}O_3$ originates from the *ferrimagnetic* nature of insulating grain boundaries as well as the half-metallicity of this perovskite. Our results indicate that a new avenue for spin-polarized tunneling junctions is to utilize insulating interface layers with ferromagnetic or ferrimagnetic coupling. © *1999 American Institute of Physics.* [S0003-6951(99)00412-X]

The half-metallic ferromagnets have attracted much interest as a source of fully spin-polarized charge carriers for tunneling junctions.[1,2] One of recent interests in half-metals has focused on the large intergrain magnetoresistance (IMR) in granular materials whose transport properties are dominated by spin-polarized tunneling through insulating grain boundaries (GB).[3–8] This negative IMR—a phenomenon at temperatures (T) below the Curie temperature (T_C)—results from the enhanced intergrain tunneling by reducing the relative angle of the magnetizations in adjacent grains by applying magnetic field. This type of tunneling MR is technologically important. However, the fast T decay of IMR and the small magnitude ($<1\%$) at room temperature (RT) even for materials with $T_C>$RT present applicational limitations. The half-metallic ferromagnets studied so far include perovskite manganites, CrO_2 and phyrochlore $Tl_2Mn_2O_7$.[3–10] We have investigated the IMR effect in various other ferromagnetic, metallic oxides with T_C much higher than RT. Herein, we report significant low-field IMR in the double perovskites of $SrFe_{1-x}(Mo\,or\,Re)_xO_3$ at RT as well as low T.

We, first, consider the electronic and magnetic properties of $SrFe_{1-x}(Mo\,or\,Re)_xO_3$. $SrFe_{1/2}Mo_{1/2}O_3$, forming in the double perovskite structure with the NaCl-type Fe/Mo ionic ordering, shows a metallic behavior and a large saturation moment with T_C of 410–450 K.[11,12] The extended orbital of $4d^1$ (Mo^{5+}) probably accounts for the metallicity, and the $S=5/2$ spin of Fe^{3+} ($3d^5$) is expected to be mostly localized. It is reasonable to assume that the itinerant $4d^1$ ($S=1/2$) spin is antiferromagnetically coupled with the localized, half-filled $3d^5$ spins avoiding the Hund's rule energy, which is a kind of the double exchange mechanism.[13] This consideration is consistent with the observed ferrimagnetic (FIM) ordering.[11] This double exchange process implies the high degree of spin polarization of the conduction electrons.

Similar electronic and magnetic properties are expected in $SrFe_{2/3}Re_{1/3}O_3$ with $3d^5(Fe^{3+})$ and $5d^1(Re^{6+})$, where the NaCl-type ionic ordering of Fe^{3+} and Re^{6+} occurs.[14] There can be an antiferromagnetic (AM) coupling between itinerant $5d^1$ ($S=1/2$) spins and localized, half-filled $3d^5$ ($S=5/2$) spins through the double exchange mechanism. Indeed, this system is metallic and FIM with T_C of 475 K.[14] On the other hand, there exist a large number of adjacent Fe ions in $SrFe_{2/3}Re_{1/3}O_3$ because of the Fe ions in Re site (1/6 Fe ions per formula unit for the complete ionic ordering). The superexchange coupling between neighboring Fe ions is expected to be AM, consistent with the observed, relatively small saturation moment.[14] Note that the properties of $SrFe_{1/2}Re_{1/2}O_3$ with $Fe^{3+}(3d^5)$ and $Re^{5+}(5d^2)$ is significantly different from those of $SrFe_{2/3}Re_{1/3}O_3$. $SrFe_{1/2}Re_{1/2}O_3$ ($T_C\approx 415$ K) is a FIM insulator with a large saturation moment.[14]

Polycrystalline $SrFe_{1/2}Mo_{1/2}O_3$ and $SrFe_{2/3}Re_{1/3}O_3$ were, first, prepared by standard solid state reaction in inert gas atmosphere. The stoichiometric materials of $SrCO_3$, Fe_2O_3, MoO_3, and ReO_3 were mixed, and then sintered at 1050 °C for 24 h under Ar atmosphere. Thereafter, the specimens were sintered at 800 °C for 1 h under ~25 kbar pressure by using a piston-cylinder-type high pressure apparatus. This high pressure sintering ensures complete chemical reactions and also induces better intergranular connection, important for transport measurements. X-ray diffraction patterns of all the samples were taken with a Rigaku x-ray geigerflex diffractometer using Cu $K\alpha$ radiation. Magnetization (M) was measured by using a superconducting quantum interference device (SQUID) magnetometer, and resistivity (ρ) was measured using the four probe technique.

Figure 1 shows the x-ray results on two specimens. In $SrFe_{2/3}Re_{1/3}O_3$, a small amount of the $FeRe_2$ second phase exists with the major phase of the ordered perovskite $SrFe_{2/3}Re_{1/3}O_3$, whereas $SrFe_{1/2}Mo_{1/2}O_3$ shows a clean single phase pattern. The patterns correspond to a cubic ($Fm3m$)

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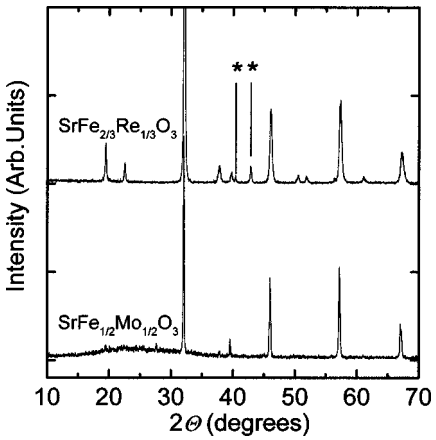

FIG. 1. X-ray diffraction patterns of $SrFe_{1-x}M_xO_3$ (M=Mo, Re). Upper and lower patterns correspond to $SrFe_{2/3}Re_{1/3}O_3$ and $SrFe_{1/2}Mo_{1/2}O_3$, respectively. The second phase ($FeRe_2$) peaks are noted by*.

symmetry ($a=7.87$ Å) with a slight tetragonal distortion, consistent with ionic ordering.[15]

The results of ρ and M measurements as a function of field at RT are shown in Fig. 2. $SrFe_{1/2}Mo_{1/2}O_3$ exhibits the large negative MR of 6% in 15 kOe. This large IMR effect at RT is remarkable in comparison with that of other half-metallic ferromagnets such as perovskite manganites, $Tl_2Mr_2O_7$ and CrO_2 (<1%).[5–8] The characteristic feature of IMR is a rapid drop in low fields, followed by a slow decrease in higher fields. This crossover field is associated with the onset field of magnetization saturation in the hysteresis loops shown in the bottom panel of Fig. 2. The saturation value at RT ($1.3\,\mu_B$) is significantly smaller than the full magnetization moment of $3.6\,\mu_B$ at low T. This value of $3.6\,\mu_B$ is rather close to the expected one, $4\,\mu_B$, for the FIM coupling between $Fe^{3+}(3d^5;S=5/2)$ and $Mo^{5+}(4d^1;S=1/2)$.

$SrFe_{2/3}Re_{1/3}O_3$ shows a smaller IMR effect (1.5% at 15 kOe) and a hard FM behavior with a small saturation value

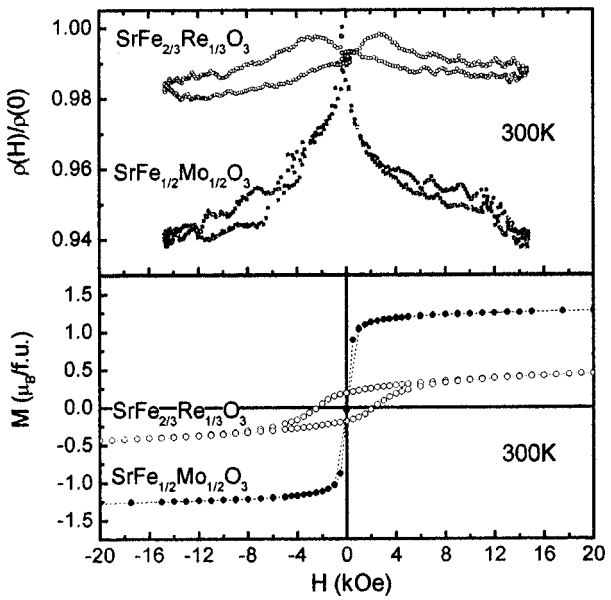

FIG. 2. Top panel: the magnetic field dependence of the normalized resistivity $SrFe_{1/2}Mo_{1/2}O_3$ and $SrFe_{2/3}Re_{1/3}O_3$. Bottom panel: the magnetic hysteresis loops for $SrFe_{1/2}Mo_{1/2}O_3$ and $SrFe_{2/3}Re_{1/3}O_3$ at 300 K.

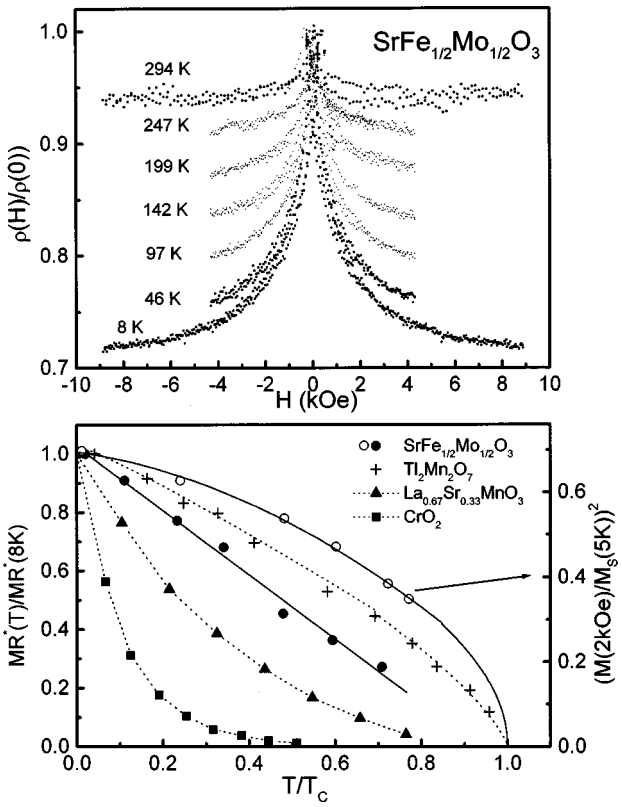

FIG. 3. Top panel: the magnetic field dependence of the normalized resistivity of $SrFe_{1/2}Mo_{1/2}O_3$ at various temperatures. Bottom panel: the normalized MR* of $SrFe_{1/2}Mo_{1/2}O_3$, defined as $MR^*=[\rho(0)-\rho(2kOe)]/\rho(0)$, plotted as a function of the reduced temperature (T/T_C) with those of $Tl_2Mn_2O_3$, CrO_2 and $La_{0.87}Sr_{0.33}MnO_3$ (taken from Ref. 5–7).

($0.9\,\mu_B$). ρ of $SrFe_{2/3}Re_{1/3}O_3$ becomes maximum at the coercive field where $M=0$, and the crossover field for IMR is consistent with the magnetization saturation field. The hard FM behavior probably originates from the large magnetic anisotropy due to the crystallographic anisotropy of Fe environment in this Fe-rich compound.[14] The electronic and magnetic disorder due to the Fe ions in Re site may also be responsible for the somewhat smaller IMR effect and the large ρ ($\sim 3\ \Omega$ cm at RT; $\rho \approx 0.01\,\Omega$ cm at RT in $SrFe_{1/2}Mo_{1/2}O$). Another reason for the smaller IMR in $SrFe_{2/3}Re_{1/3}O_3$ can be the low degree of spin polarization because the wide band of $5d^1(Re^{6+})$ may not be completely split below T_C.

In order to gain further insights into the origin of large IMR at RT, we have investigated the T dependence of IMR in $SrFe_{1/2}Mo_{1/2}O_3$. Top panel of Fig. 3 shows that the magnitude of the rapid ρ drop in low fields increases with decreasing T (IMR=27% at 8 K in 9 kOe).

A striking systematics can be found in the comparison of the experimental results of the T dependence of IMR in various half-metallic ferromagnets as shown in the bottom panel of Fig. 3. The low-field MR of $SrFe_{1/2}Mo_{1/2}O_3$, defined as $MR^*=[\rho(0)-\rho(2kOe)]/\rho(0)$, is plotted as a function of the reduced temperature (T/T_C) with those of $Tl_2Mn_2O_3$, CrO_2 and $La_{0.87}Sr_{0.33}MnO_3$.[5–7] The MR* of CrO_2 ($T_C=395$ K) decays rapidly, while $Tl_2Mn_2O_7$ ($T_C=120$ K) shows the slowest MR* decrease with T. The MR* of $SrFe_{1/2}Mo_{1/2}O_3$ ($T_C=410-450$ K) reveals the slow T decay similar to that of $Tl_2Mn_2O_7$, and the MR* of perovskite

$La_{0.67}Sr_{0.33}MnO_3$ ($T_C = 365$ K) decays fast with increasing T, similar to that of CrO_2. Obviously, there is no correlation between T_C and the T dependence of MR*. However, it appears that the T dependence of IMR critically depends on the magnetic property of grain boundary (GB). At the GB in $SrFe_{1/2}Mo_{1/2}O_3$ where the FIM coupling due to the double exchange mechanism is absent because of lack of electron itinerancy, the superexchange coupling between localized Fe^{3+} and Mo^{5+} spins is also expected to be FIM. In other words, the magnetic coupling at GB is still FIM even though the GB can be insulating. This situation is similar to that of $Tl_2Mn_2O_7$.[6,16] $Tl_2Mn_2O_7$ is a FM metal below T_C, probably due to the double exchange coupling, and the insulating GB of $Tl_2Mn_2O_7$ is also expected to be FM because the superexchange coupling between Mn^{4+} ions is FM due to the relatively small bond angle ($\sim 135°$) of Mn^{4+}–O–Mn^{4+}. These situations are clearly in contrast with the perovskite manganites and CrO_2 cases where insulating GB is expected to be AF, different from the bulk ferromagnetism.[4,5,7,8] In fact, the AF nature of GB should be more clear in CrO_2 than in perovskite manganites because of the Cr_2O_3 (an AF insulator)—like GB of CrO_2 samples.[7,8] Therefore, we can conclude that IMR decrease slowly with increasing T when the magnetic coupling at insulating GB is similar to that of metallic bulk.

In the primal model of electron tunneling across an intergranular insulating barrier, MR is given by $\Delta\rho/\rho = -(JP/4kT)[M^2(H,T) - M^2(0,T)]$ where J, P, and M correspond to the exchange coupling constant, polarization of the tunneling electron, and magnetization, respectively.[5,17] This model does not take account of the magnetic properties of the insulating barrier. The electronic transport through interfacial spins can be governed by the double exchange-type hopping from a grain to a GB, followed by another hopping from the GB to a neighboring grain.[18] When the grain spins are aligned in applied field, the conduction in this second-order tunneling model is given by $\sigma \propto \langle 1 + 2S_bS\cos\theta + S_b^2S^2\cos^2\theta\rangle$ where θ is the angle between the spins of the GB (S_b) and the grain (S). Even in this model, low-field MR* basically follows the T dependence of M^2 where M is the magnetization close to grain surface. The fast T decay of MR* in perovskite $La_{0.67}Sr_{0.33}MnO_3$—where the magnetic coupling at GB is expected to be different from the bulk magnetic coupling—has been attributed to the fast T decay of surface magnetization, decreasing faster than bulk magnetization.[19] On the other hand, when the magnetic coupling at GB is similar to the bulk FM (or FIM) coupling, we expect that the surface magnetization reduction with T is similar to that of bulk magnetization. This observation is clearly consistent with the slow T reduction of MR* for $SrFe_{1/2}Mo_{1/2}O_3$ and $Tl_2Mn_2O_7$, which in fact follows roughly the square of bulk magnetization.

In summary, we have investigated the IMR effects in polycrystalline specimens of ordered perovskite $SrFe_{1/2}Mo_{1/2}O_3$[18,20] and $SrFe_{2/3}Re_{1/3}O_3$. We found large IMR at RT in $SrFe_{1/2}Mo_{1/2}O_3$ where the magnetic coupling at insulating GB is expected to be similar to the FIM coupling within metallic grains. These results, combined with previous reports, indicate that the field effect of electron tunneling in FM metal-insulator-FM metal junctions can be greatly enhanced when the insulating layer is FM or FIM.

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