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Intergrain tunneling magnetoresistance in polycrystals of the ordered double perovskite Sr_2FeReO_6

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Intergrain tunneling magnetoresistance (TMR) subsisting up to room temperature has been observed for polycrystalline ceramics of Sr_2FeReO_6, which has ordered double perovskite structure with Curie temperature above 400 K. The first-principles band calculation predicts that Sr_2FeReO_6 shows the half metallic ground state with the ferrimagnetic coupling of Fe and Re spins. The experimental results of electronic and magnetic properties are in accord with this picture. In fact, the magnitude of intergrain TMR with the magnetic field of 7 T at 4.2 and 300 K is as large as 21 and 7%, respectively, reflecting high spin polarization of carriers. [S0163-1829(99)06817-4]

Tunneling-type magnetoresistance (TMR) in perovskite-type transition-metal oxide has recently been investigated extensively.[1–5] Because of high spin polarization inherent to the oxide compounds, carrier motion across the tunneling junction depends sensitively on the relative angle between the magnetic moments on both sides of the ferromagnetic domains which is controlled by a low external field. This has been clearly demonstrated for the trilayer junction composed of the ferromagnetic-metallic layers (mostly manganites) intervened by a nonmagnetic-insulating tunneling barrier layer.[1,2] Furthermore, in polycrystalline manganite samples, field control of the spin dependent scattering of carriers at the grain boundary has also been demonstrated to cause an intergrain TMR-like behavior.[3] Unfortunately, however, in all the manganite systems investigated so far, working temperature was unexpectedly low as compared with their Curie temperatures and hence lower than room temperature.

More recently, Sr_2FeMoO_6 with ordered double perovskite structure has been proposed as another prototype of half metals other than the perovskite manganites. In fact it has been demonstrated that polycrystalline samples of Sr_2FeMoO_6 with the Curie temperature (T_C) of 415 K show a sharp low-field TMR not only at low temperatures but even at room temperature.[6] In this system, the temperature variation of the observed MR magnitude is approximately in accord with that of square of the spin-polarization of the carriers, i.e., $(M/M_s)^2$, M_s being the saturation magnetization, up to room temperature. This means that the spin-dependent scattering at the grain boundary or magnetic domain boundary is a dominant factor for the observed resistance and magnetoresistance. In this paper, we report the finding of an ordered double perovskite, Sr_2FeReO_6, which shows similar TMR characteristics to Sr_2FeMoO_6 despite the difference in the number of $4d/5d$ conduction electrons.

In the ordered double perovskites $A_2B'B''O_6$ (A being alkaline-earth or rare-earth ion), transition metals B' and B'' occupy the transition metal sites (perovskite B sites) alternatively as depicted in the inset of Fig. 1. According to literature[7] there are many combinations in $A_2B'B''O_6$ which show the ferromagnetic or ferrimagnetic states. The motivation of the present study is to explore other prospective half metallic compounds as a TMR material in a broad family of the ordered double perovskite.[7] In the light of high T_C, Sr_2FeReO_6,[8,9,10,11] whose T_C was reported to be 401 K, was chosen in this study and the TMR effect in polycrystalline samples has been explored as a hallmark of high-T_C half metal.

To argue the anticipated half metallic feature, we first show the electronic structure of ordered double perovskite Sr_2FeReO_6, which was calculated by the full potential augmented plane-wave (FLAPW) method based on the generalized gradient approximation (GGA).[12] The calculation was carried out by postulating the cubic structure with $a = 7.89$ Å (Ref. 9) and the position of bridging oxygen at the center between the Fe and Re sites. The cutoff energy for the basis function is 12 Ry and the number of sampling k points in the irreducible Brillouin zone is 32. The density of states obtained by this calculation is shown in Fig. 1. At the Fermi level (E_F), there exists density of states only in the down-spin band and no state in the up-spin band. Namely, there is an energy gap (~1 eV) between the occupied Fe e_g band and the unoccupied Re t_{2g} band in the up-spin state. This half metallic nature gives rise to 100% spin polarized charge carriers in the ground state. The occupied up-spin band near below E_F mainly consists of Fe $3d$ electrons forming the localized spins on the Fe sites. On the contrary, the down-spin band around E_F is mainly occupied by hybridized Re $5d$ t_{2g} and Fe $3d$ t_{2g} states. The predicted electronic feature for Sr_2FeReO_6 quite resembles that for Sr_2FeMoO_6, implying the presence of half metallic ground state as a generic feature for a broad class of the ordered double perovskites. As compared with the case of Sr_2FeMoO_6 (Fig. 1 of Ref. 6), where partial density of states (DOS) of Mo(t_{2g}) in the down-spin band is comparable with that of Fe(t_{2g}) at the

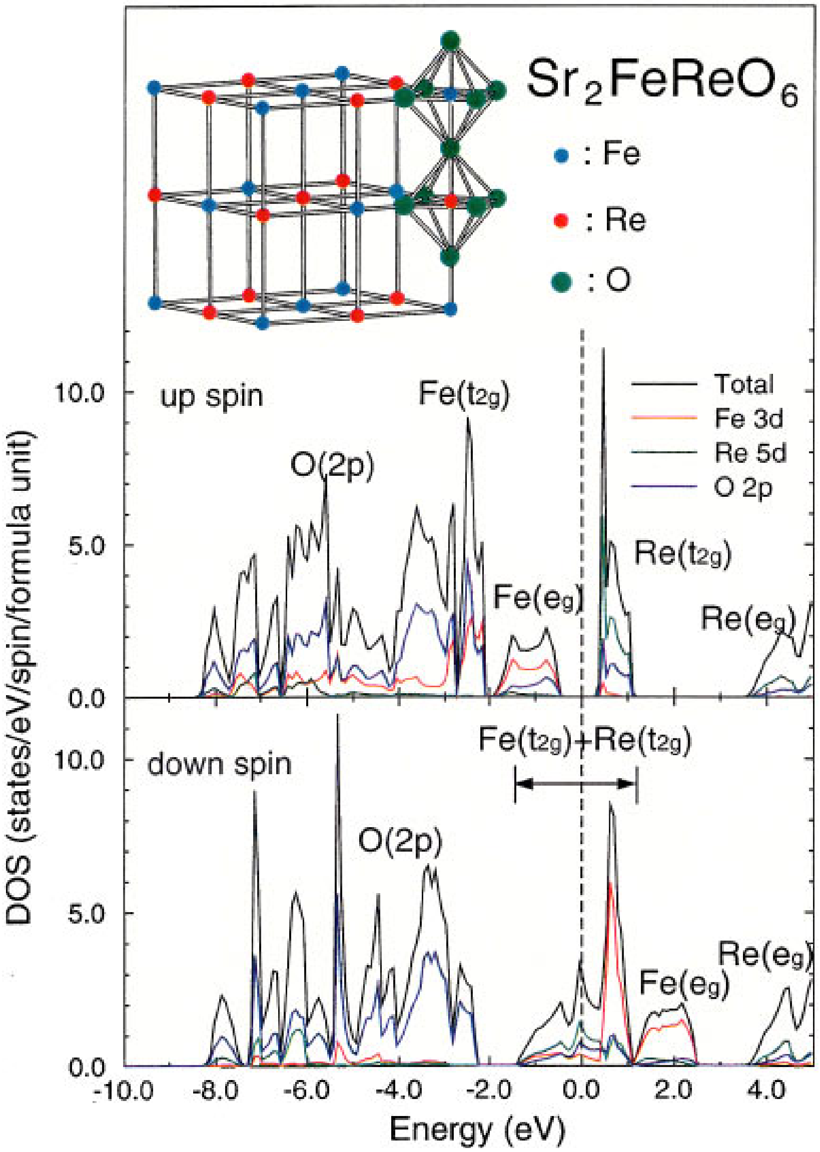

FIG. 1. (Color) The density of states of Sr_2FeReO_6. The inset shows the schematic structure of ordered double perovskite, $A_2B'B''O_6$, where the different transition metal atoms, B' and B'', occupy the perovskite B site alternatively along the [111] direction, respectively forming $B'O_6$ and $B''O_6$ octahedra. The electronic structure was calculated by the full potential augmented plane-wave (FLAPW) method based on the generalized gradient approximation (GGA) (Ref. 8) (see text).

Fermi level, the partial DOS of Re(t_{2g}) in Sr_2FeReO_6 is 3–4 times larger than that of Fe(t_{2g}) at the Fermi level. This may reflect the change in nominal number of $4d/5d$ conduction electrons ($Re^{5+}=5d^2$ vs $Mo^{5+}=4d^1$).

Sr_2FeReO_6 was prepared by the solid-state reaction. The mixture of raw materials, SrO, Fe_2O_3, Re_2O_7, and metallic Re powder were weighed to a prescribed molar ratio and pelletized in a glove box in pure Ar atmosphere, and calcination was carried out at 900 °C for 3 h in evacuated silica capsules. Pellets were finely pulverized and pelletized again and sintered at 1200 °C for 2 h in evacuated capsules (sample 1). Sintered pellets were then annealed at 1150 °C for 2 h in a stream of pure Ar gas (sample 2). X-ray diffraction powder pattern shows that sample 1 includes only a small amount of unidentified hetero-phase(s) which almost vanishes after annealing. Rietveld analysis indicated that the degree of ordering of Fe and Re on the B site was attained as large as around 95%. Chemical composition of Sr, Fe, and Re of these samples, before and after annealing in Ar flow, was confirmed to be stoichiometric (Sr:Fe:Re = 2:1:1) by ICP (induction coupled plasma) analysis within the error of 1%. This denies the probability of precipitation of a high Fe/Re ratio phase by volatilization of Re. Resistivity and magnetic properties were measured with dc four-probe method and a superconducting quantum interference device magnetometer, respectively.

Resistivity of samples 1 and 2 show different temperature dependence as displayed in Figs. 2(a) and 2(c). At zero magnetic field, resistivity of sample 1 (without annealing) exhibits nearly T-linear decrease with decreasing temperature down to 60 K and has a nearly saturated value around $3\times10^{-3}\ \Omega$ cm at temperatures below 20 K. The observed metallic feature in the ferromagnetic state [see also Fig. 2(b)] is in accord with the half metallic nature predicted in Fig. 1. Application of magnetic field slightly decreases the resistivity only in a lower temperature region but does not signifi-

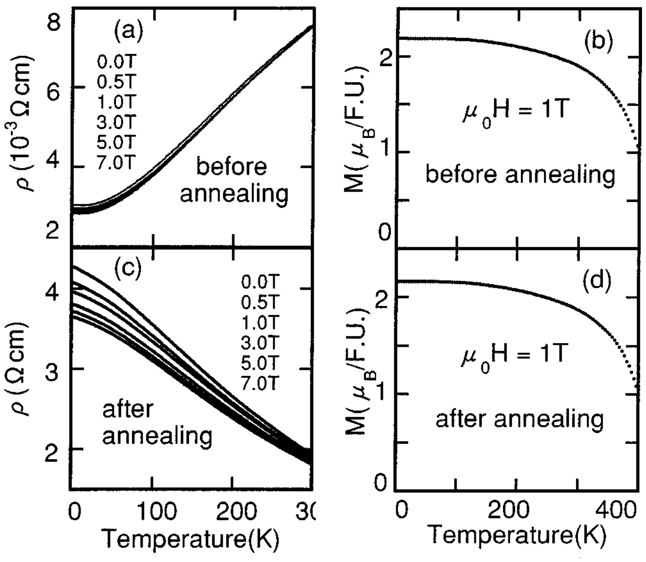

FIG. 2. (a) and (c) The temperature dependence of resistivity of polycrystalline samples of Sr_2FeReO_6 at zero field and under a magnetic field of 0.5, 1, 3, 5, and 7 T; sample 1 (before annealing) and 2 (after annealing, see text), respectively. (b) and (d) The temperature dependence of magnetization measured at 1 T for samples 1 and 2, respectively.

cantly in a higher temperature region. Thus the ρ-T curve directly reflects the metallic character of the Sr_2FeReO_6 grains, and the grain boundaries of Sr_2FeReO_6 without annealing do not effectively scatter the carriers in a spin dependent manner. The existence of a small amount of hetero phase(s) present in sample 1, that is only discernible difference from sample 2, seems to play no essential role.

On the contrary, resistivity of sample 2 (after annealing) is apparently larger than the sample 1 by three orders of magnitude, but only moderately increases with decreasing temperature in the order of 10^0 Ω cm. In the case of sample 2, application of magnetic field distinctly decreases the resistivity over the whole temperature region below 300 K. The magnitude of MR in this sample decreases with increasing temperature not steeply but only gradually just like the case of Sr_2FeMoO_6.[6] Note, however, that the temperature dependence of magnetization at 1 T is almost the same for both Sr_2FeReO_6 samples as shown in Figs. 2(b) and (d). Moreover, the magnetization curve (M-H) is also almost identical for the both samples at 4.2 or 300 K. The observed saturation magnetization of $2.7\mu_B$/f.u. at 4.2 K is comparable with the ideal value of $3\mu_B$/f.u. in the case of a perfect 1:1 ordering of Fe and Re on the B sites. These indicate that the annealing procedure affects only the nature of the grain boundary of polycrystalline Sr_2FeReO_6 and causes negligible effect on the grain bulk. Thus the grain bulk of the ceramics should be metallic but the nature of conduction pass, i.e., through grain boundary, is very sensitive to the annealing in inert gas. The resistance of the annealed sample is dominated by the carrier scattering at the grain boundaries which has been widely observed for polycrystalline ceramics samples. Incidentally, the slight MR observed in sample 1 (before annealing) at 4.2 K may also be ascribed to the same mechanism which is effective only at a relatively small portion of grain boundaries.

In the case of Sr_2FeMoO_6, ρ value has been reported in the order of 10^{-2} Ω cm, and ranges from 0.005–0.5 Ω cm depending on the sintering or annealing conditions.[6] In the case of Sr_2FeReO_6, however, intermediate state has not been observed between those exhibited in Figs. 2(a) and (c). This suggests that the character of the grain boundaries as a spin dependent scatterer appears quite different in Sr_2FeReO_6 and Sr_2FeMoO_6, although their detailed nature and origin are not known at all.

We show the isothermal MR for sample 2 (after annealing) at 4.2 and 300 K in Fig. 3. We define the magnitude of MR as

$$MR(T,H)=[\rho(T,H_{\mathrm{peak}})-\rho(T,H)]/\rho(T,H). \qquad (1)$$

Here, H_{peak} is the magnetic field where ρ takes a maximal value. Then, $MR(4.2\,\mathrm{K}, 7\,\mathrm{T})$ and $MR(300\,\mathrm{K}, 7\,\mathrm{T})$ are as large as 21 and 7%, respectively. It should be noticed that a sharp low-field MR is observed in good coincidence with the steep magnetization process shown in the lower panels of each figure in Fig. 3. In the isothermal MR curve at 4.2 K, H_{peak} coincides with the coercive field. Such a close correlation between the MR and the magnetic-domain rotation as

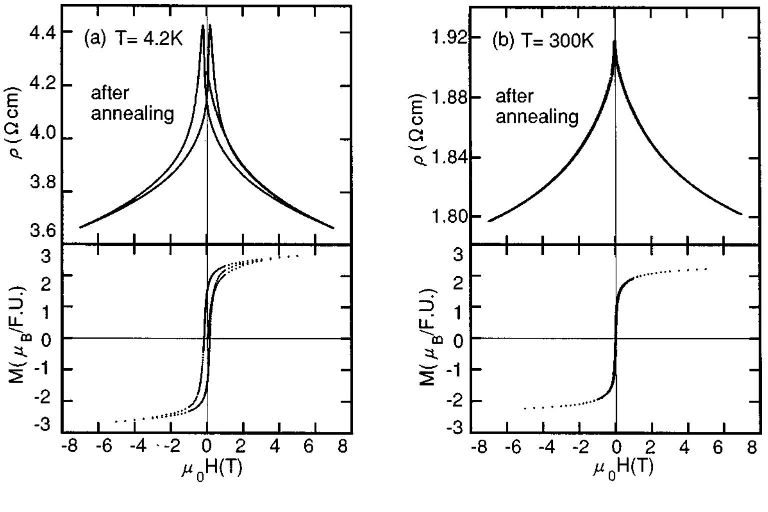

FIG. 3. Isothermal magnetoresistance $\rho(H)$ (upper panels) and magnetization M curves (lower panels) for polycrystalline ceramics (sample 2, see text and the caption of Fig. 2) of Sr_2FeReO_6 at 4.2 K (a) and 300 K (b).

well as the gradually decreasing magnitude of MR with temperature ensures that the observed MR is due to the field suppression of the spin dependent scattering, namely field enhancement of carrier tunneling, at the grain or domain boundaries.

In conclusion, we have shown that the ordered double perovskite Sr_2FeReO_6 is a half metal by the first-principles electronic structure calculation. In accord with the band-theory prediction, the compound (properly processed) shows the ferromagnetic metallic ground state with the saturation magnetization of $2.7\mu_B$/f.u. [comparable with the ideal value of $3\mu_B$/f.u. arising from the antiferromagnetic coupling between Fe^{3+} ($S=\frac{5}{2}$) and Re^{5+} ($S=\frac{2}{2}$)]. Annealing in Ar atmosphere changes only the character of the grain boundary of Sr_2FeReO_6 but not that of grain bulk. As a result, in succession to Sr_2FeMoO_6, the annealed sample of Sr_2FeReO_6 was demonstrated to show the spin dependent tunneling-type giant magnetoresistance which subsists up to room temperature. The ordered double perovskite compounds, including Sr_2FeMoO_6 and Sr_2FeReO_6, can thus be a new class of prospective magnetoelectronic materials possibly with half metallic characteristics working at room temperature.

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[1] J. Z. Sun, W. J. Gallagher, P. R. Dumcombe, L. Krusin-Elbaum, R. A. Altman, A. Gupta, Yu Lu, G. Q. Gong, and Gang Xiao, Appl. Phys. Lett. **69**, 3266 (1996).

[2] Yu Lu, X. W. Li, G. Q. Gong, Gang Xiao, A. Gupta, P. Lecoeur, J. Z. Sun, Y. Y. Wang, and V. P. Dravid, Phys. Rev. B **54**, R8357 (1996).

[3] H. Y. Hwang, S.-W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).

[4] H. Y. Hwang and S.-W. Cheong, Nature (London) **389**, 942 (1997).

[5] H. Y. Hwang and S.-W. Cheong, Science **278**, 1607 (1997).

[6] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, Nature (London) **395**, 677 (1998).

[7] F. S. Galasso, *Structure, Properties and Preparation of Perovskite-type Compounds* (Pergamon, London, 1969).

[8] J. Longo and R. Ward, J. Am. Chem. Soc. **83**, 2816 (1961).

[9] A. W. Sleight, J. Longo, and R. Ward, Inorg. Chem. **1**, 245 (1962).

[10] M. Abe, T. Nakagawa, and S. Nomura, J. Phys. Soc. Jpn. **35**, 1360 (1973).

[11] A. W. Sleight and J. F. Weiher, J. Phys. Chem. Solids **33**, 679 (1972).

[12] J. P. Pedrew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).