Grain-boundary room-temperature low-field magnetoresistance in Sr_2FeMoO_6 films

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Thin films of (001)-oriented Sr_2FeMoO_6 have been epitaxially deposited or $LaAlO_3$ and $SrTiO_3$ (001) substrates by pulsed laser deposition. The deposition conditions were optimized. Single-phase Sr_2FeMoO_6 was obtained in 100 mTorr 99.999% Ar gas at 825 °C. Transport and magnetic data showed a metallic temperature dependence and a saturation magnetization M_s at 10 K of $3.2\mu_B$/f.u. However, the Curie temperature $T_C \approx 380$ K was reduced from 415 K found for tetragonal polycrystalline best ceramics, which lowers M_s at 300 K in the thin films to $1.5\mu_B$/f.u. compared to $2.2\mu_B$/f.u. in the ceramics. A low remanence was attributed to the presence of antiphase boundaries. A Wheatstone bridge arrangement straddling a bicrystal boundary was used to verify that spin-dependent electron transfer through a grain boundary and not an antiphase boundary is responsible for the low-field magnetoresistance found in polycrystalline samples below T_C.
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Extensive interest has been focused on the extrinsic magnetoresistance (MR) below T_C found in polycrystalline $La_{1-x}A_xMnO_3$ (A=alkaline earth) on sweeping an applied field through the coercivity H_c. This half-metallic ferromagnetic system also exhibits an intrinsic colossal magnetoresistance (CMR) above T_C. Measurements of the low-field MR below T_C have been made on polycrystalline ceramics,[1] polycrystalline thin films,[2,3] epitaxial thin films grown on bicrystal substrates,[4] and on step-edge thin films.[5] In these materials, a significant MR at liquid-helium temperatures decreases with increasing temperature and vanishes before T_C is reached. These studies have shown that spin-dependent electron transfer across grain boundaries between grains with different orientations of their spontaneous magnetization M_s is responsible for the observed MR.[6] However, in these materials, the transfer is not direct from the bulk of one grain to that of the other; the mobile electron is captured in a grain-boundary state before tunneling to the adjacent grain, which reduces the MR.[7] Low-field MR has also been observed for tunneling between $La_{1-x}A_xMnO_3$ films across a $SrTiO_3$ interlayer,[8,9] but the operating temperature remains below 77 K, even for a $T_C=370$ K in $La_{0.67}Sr_{0.33}MnO_3$. A room-temperature low-field MR in the ordered double perovskite Sr_2FeMoO_6 has been reported recently.[10–13] Complete ordering of Fe and Mo on the M sites of this metallic AMO_3 perovskite is predicted to give a half-metallic ferromagnetism with localized majority-spin electrons on the Fe atoms ferromagnetically aligned by itinerant minority-spin electrons shared by both Fe and Mo atoms in the equilibrium reaction Fe(III)+Mo(V)=Fe(II)+Mo(VI). Whether the reaction is biased more strongly to the left or the right, the spin-only saturation magnetization for such a model would be $M_s(0)\approx 4\mu_B$/f.u. But the inability to obtain an $M_s(5\,\mathrm{K})=4\mu_B$/f.u. and an unusual B–H hysteresis loop with a low remanence, B_r, and coercivity, H_c, suggest that there may be an antiferromagnetic spin-density wave superimposed on the ferromagnetic component.[14] Moreover, such a hysteresis loop suggests that intragranular magnetoresistance may compete with spin-dependent electron transfer across a grain boundary in this material. Further characterization of the bulk material has been frustrated by an inability to prepare single crystals. We have therefore grown single-crystal films epitaxially on single-crystal substrates and bicrystal substrate to obtain further information on this compound and on spin transfer across a grain boundary.

Sr_2FeMoO_6 films were deposited by pulsed laser deposition with a KrF (wavelength 248 nm) eximer laser. Stoichiometric Sr:Fe:Mo=2:1:1 targets were prepared by the same procedures used to make single-phase polycrystalline ceramic Sr_2FeMoO_6.[11] The films were deposited on polished (001) planes of single-crystal $LaAlO_3$ and $SrTiO_3$, which have room-temperature lattice parameters 4% and 1% larger, respectively, than cubic Sr_2FeMoO_6. The laserbeam energy was estimated to be 2 to 3 J/cm^3. Both the deposition temperature and the atmosphere proved critical for the deposition of epitaxial films. In oxygen atmosphere ($P_{O_2}=10^{-2}$ Torr) and even in a low-purity argon atmosphere, the obtained thin film is a yellow insulator. The thin film grown in high vacuum (8×10^{-6} Torr) shows good conductivity and dark-blue color; however, magnetization and x-ray diffraction measurements show that the main phase of the film is $SrMoO_3$. Both reducing and strongly oxidizing atmospheres result in phase separation. Carefully tuning the deposition atmosphere is necessary to stabilize the Sr_2FeMoO_6 phase.

The best Sr_2FeMoO_6 films were deposited in 100 mTorr 99.999% Ar at 825 °C substrate temperature. A film thickness of 1000 Å was obtained with 10 000 pulses and a distance of 5 cm between the substrate and the target. The films had the same dark color as the ceramic target. EDX analysis gave a film composition Sr:Fe:Mo:≈2:1:1. X-ray-diffraction patterns, Fig. 1, showed the films to have a (001) orientation with a perpendicular lattice parameter $c=7.99$ Å on $LaAlO_3$ and 7.91 Å on $SrTiO_3$. In comparison with the lattice param-

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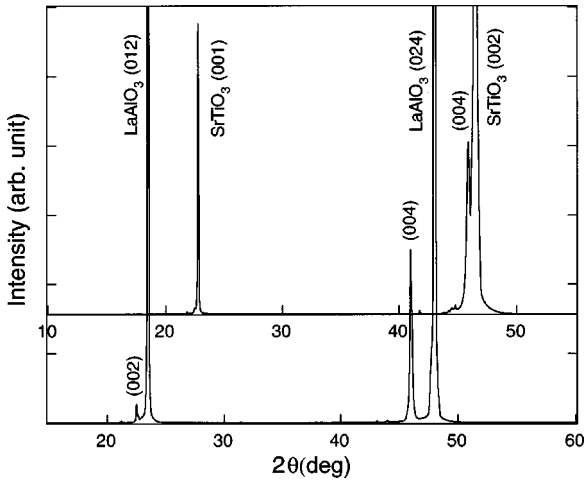

FIG. 1. X-ray diffraction of Sr_2FeMoO_6 thin films deposited on $SrTiO_3$ (upper) and $LaAlO_3$ (bottom) (001) single-crystal substrates.

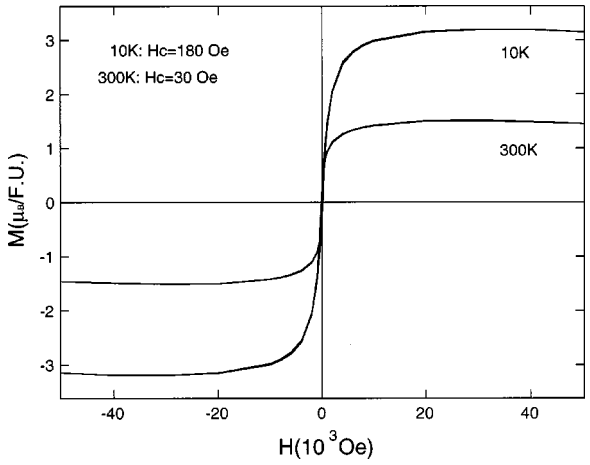

FIG. 3. The B–H loop of a Sr_2FeMoO_6 film measured with a dc magnetometer from −5 to 5 T at 10 and 300 K; H was in the plane of the film. Saturation moment is $3.2\mu_B$/f.u. and $1.5\mu_B$/f.u. at 10 and 300 K. Coercivity is 180 and 21 Oe at 10 and 300 K.

eter $c=7.89$ Å in the ceramic sample, the large c parameter in the films appears to be caused by the misfits in the a-b plane between the film and substrate. The transport and magnetic measurements showed no dependence on the substrate.

The film resistivity, Fig. 2, shows a metallic temperature dependence. The conductivity of the single-crystal film is about two orders of magnitude higher than that of a polycrystalline ceramic having a weakly semiconductive temperature dependence; see the inset of Fig. 2. These results indicate a strong electron scattering occurs at the grain boundaries of the polycrystalline ceramic.

The magnetic characteristics of the films were studied with a DC SQUID magnetometer (Quantum Design) with the applied field parallel to the film. The films showed little B–H hysteresis at both 10 and 300 K, Fig. 3; the small coercivity H_c of the films decreased from 180 Oe at 10 K to only 21 Oe at 300 K, which is close to the H_c values found[11] for single-phase cubic ceramics. The saturation moments at 5 T were $3.2\mu_B$/f.u. at 10 K and $1.5\mu_B$/f.u. at 300 K, where Kobayashi *et al.*[10] reported, for a tetragonal ceramic sample with a Curie temperature $T_C \approx 415$ K, values of $3.0\mu_B$/f.u. and $2.2\mu_B$/f.u. The films had a $T_C \approx 380$ K, as obtained from the $M(T)$ curve of Fig. 4 taken in an $H=500$ Oe from 10 to 700 K.

A 1000 Å film of Sr_2FeMoO_6 was then deposited epitaxially on a (001) surface of a bicrystal having two (001) crystals misaligned by 24°. To detect the grain-boundary resistance, a Wheatstone bridge was patterned lithographically, as described in detail in Ref. 14. A MR contributed by the artificial grain boundary was detected from 20 to 300 K, as shown in Fig. 5. This experiment verifies that the low-field MR is due to spin-dependent electron transfer across the grain boundary.

Although x-ray diffraction showed that the Sr_2FeMoO_6 thin films had good crystallinity, the B–H hysteresis loop of the film had the unusual characteristics of those for the ceramic samples: a low saturation magnetization, a remarkably low remanence, and a small coercivity. We suggest that this behavior is due to the formation of antiphase boundaries at the interface of perfectly ordered regions having a different phase of the Fe, Mo ordering, as illustrated in Fig. 6.[11]

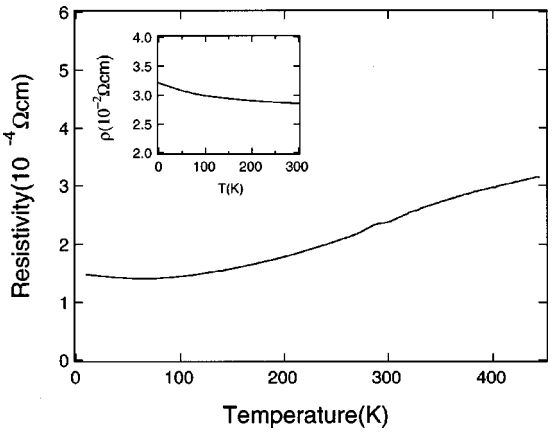

FIG. 2. Curve of resistivity versus temperature of a Sr_2FeMoO_6 epitaxial thin film deposited on $LaAlO_3$ substrate. The inset is the $\rho(T)$ curve of a polycrystalline ceramic (Ref. 10).

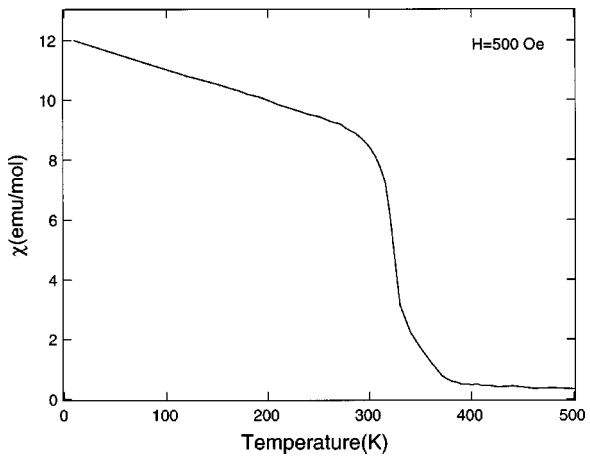

FIG. 4. Susceptibility of a Sr_2FeMoO_6 film from 10 to 500 K obtained with a 500 Oe magnetic field. Magnetic transition temperature is about 380 K.

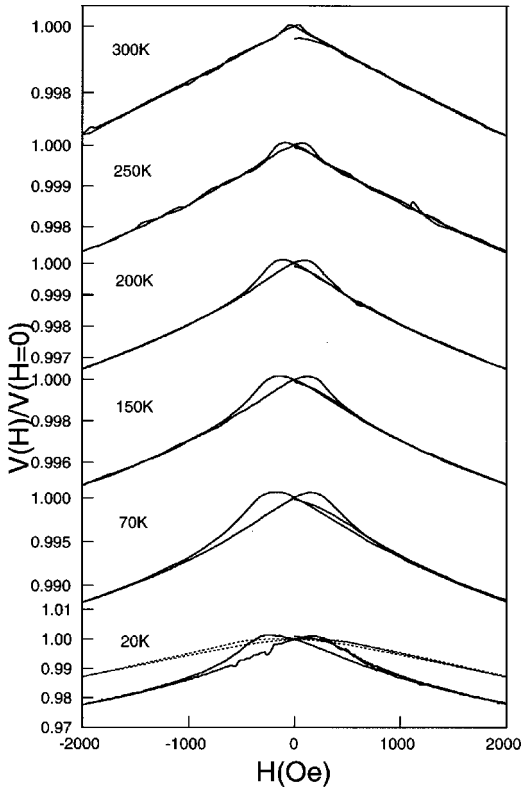

FIG. 5. Magnetoresistance of the Wheatstone bridge measured from −2000 to 2000 Oe at different temperatures. The applied magnetic field was parallel to the current flow at the grain boundary. The dotted line shows the magnetoresistance measured by one of the arms not crossing the grain boundary. (V is the output of Wheatstone bridge.)

Strong antiferromagnetic Fe–O–Fe interactions and weak Mo–O–Mo interactions across a phase boundary would orient the two regions antiparallel in the zero field, but they would be oriented parallel in a relatively low field with a 360° domain wall parallel to the boundary. The small MR observed in the single-crystal films is probably due to tunneling across antiphase boundaries; tunneling across domain walls does not give a large MR.

In summary, we have succeeded in preparing Sr_2FeMoO_6 single-crystal films with an (001) orientation by pulsed laser deposition on the (001) surface of $LaAlO_3$ and $SrTiO_3$ single-crystal substrates. A higher $M_s(10\,\mathrm{K}) = 3.2\mu_B$/f.u. indicates a greater degree of order of the Fe and Mo atoms and/or fewer antiphase boundaries in the films than in the ceramic cubic phase, and the Curie temperature remains close to that of the cubic phase, despite the higher magnetization. A Wheatstone bridge pattern straddling a bicrystal boundary was used to confirm that the low-field MR

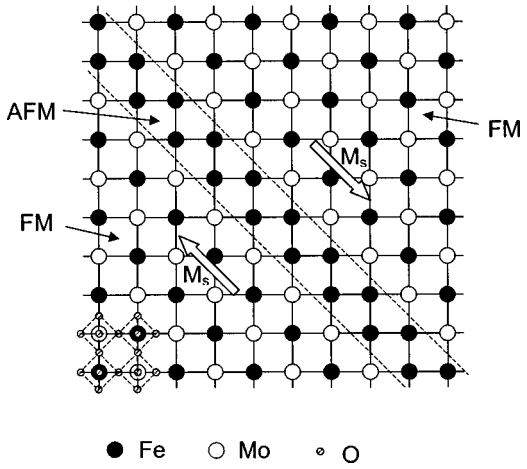

FIG. 6. Diagram of an antiphase boundary. FM indicates ordered Sr_2FeMoO_6 ferromagnetic domains. AFM indicates antiferromagnetic coupling across the antiphase boundary. M_s represents magnetizations in the zero applied field.

observed below T_C in polycrystalline Sr_2FeMoO_6 is primarily due to spin-dependent transfer across grain boundaries and not to an intragranular effect.

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