Perovskite Phases

International Edition: DOI: 10.1002/anie.201506540
German Edition: DOI: 10.1002/ange.201506540

Large Magnetization and Frustration Switching of Magnetoresistance in the Double-Perovskite Ferrimagnet Mn_2FeReO_6

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***Abstract:** Ferrimagnetic $A_2BB'O_6$ double perovskites, such as Sr_2FeMoO_6, are important spin-polarized conductors. Introducing transition metals at the A-sites offers new possibilities to increase magnetization and tune magnetoresistance. Herein we report a ferrimagnetic double perovskite, Mn_2FeReO_6, synthesized at high pressure which has a high Curie temperature of 520 K and magnetizations of up to 5.0 μ_B which greatly exceed those for other double perovskite ferrimagnets. A novel switching transition is discovered at 75 K where magnetoresistance changes from conventional negative tunneling behavior to large positive values, up to 265 % at 7 T and 20 K. Neutron diffraction shows that the switch is driven by magnetic frustration from antiferromagnetic Mn^{2+} spin ordering which cants Fe^{3+} and Re^{5+} spins and reduces spin-polarization. Ferrimagnetic double perovskites based on A-site Mn^{2+} thus offer new opportunities to enhance magnetization and control magnetoresistance in spintronic materials.*

Around 650 $A_2BB'O_6$ double perovskite oxides with an alternating (rocksalt) order of B and B′ cations are known.[1] An important subgroup are ferrimagnetic, spin-polarized conductors which combine large-spin 3d transition-metal B cations and small-spin 4d or 5d B′ ions,[2] for example Fe^{3+} (spin $S=5/2$) and Mo^{5+} ($S=1/2$) in Sr_2FeMoO_6.[3] Strong antiferromagnetic coupling between B and B′ spins leads to ferrimagnetism with a Curie temperature of $T_C=410$ K, and half-metallicity with a high degree of spin polarization P results. The predicted magnetization per double-perovskite formula unit is $M=4\ \mu_B$ and the highest reported value for non-magnetic A-cations is $M=4.1\ \mu_B$ for $Sr_2Fe(Mo_{0.6}W_{0.4})O_6$.[4] Ferrimagnetic double perovskites show large, low-field tunneling magnetoresistance (TMR) effects which have been exploited in spintronic devices, such as magnetic tunnel junctions.[5,6] Magnetoresistance ($MR=[R(H)-R(0)]/R(0)$ for resistances R measured in magnetic field H and at $H=0$) is given by $MR=-P^2M^2/(1+P^2M^2)$ in a simple TMR model,[2] so new materials with large values of P and M are desirable.

Ferrimagnetic double perovskites synthesized at ambient pressure have relatively large non-magnetic A^{2+} (A = Ca, Sr, Ba) cations. However, high pressure can be used to introduce smaller, magnetic, transition-metal cations at perovskite A-sites, and $Ca_{0.5}Cu_{1.5}FeReO_6$ (the 134 type quadruple perovskite $CaCu_3Fe_2Re_2O_{12}$ where 75 % of the A-sites contain $S=1/2$ Cu^{2+} ions with 1:3 cation order) was recently reported to have an enhanced $M=4.35\ \mu_B$ and a high $T_C=560$ K, although with modest $MR=-4$ % at 5 T and 10 K.[7] High pressure stabilizes $S=5/2$ Mn^{2+} ions at the A sites of a few perovskites, such as $MnVO_3$[8] and the double perovskite Mn_2FeSbO_6,[9] both of which have low-temperature incommensurate antiferromagnetic spin orders, and the 134 types ζ-Mn_2O_3[10] and $MnCu_3V_4O_{12}$.[11] We have explored possible Mn^{2+}-based ferrimagnetic double perovskites and we report herein the new material Mn_2FeReO_6 which shows large M and a novel MR switching transition.

Mn_2FeReO_6 was synthesized at high pressure (11 GPa) and temperature (1400 °C). Experimental details are in Supporting Information. Powder X-ray- and neutron-diffraction fits (Figure 1) show that this new material has a mono-

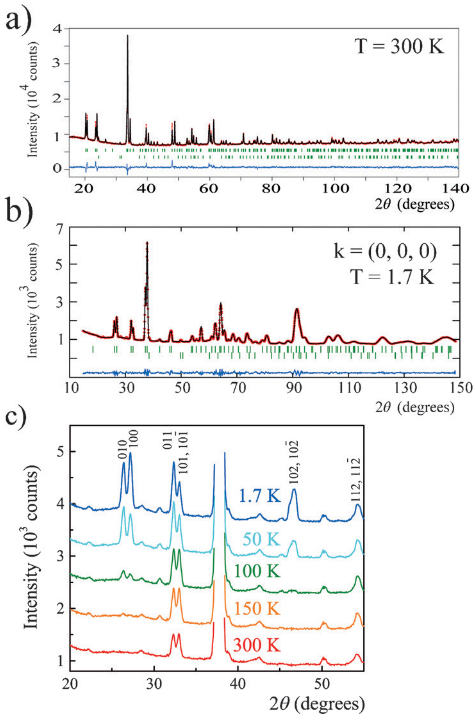

Figure 1. a) Fit to the room-temperature X-ray profile of Mn_2FeReO_6, lower reflection markers are for 1.5 wt% of ReO_2 impurity. b) Fit of crystal and magnetic structure models to 1.7 K neutron data. c) Low-angle neutron-diffraction profiles with magnetic diffraction peaks indexed. Appearance of peaks below 150 K evidences onset of antiferromagnetic Mn spin order, and changes between 100 and 50 K mark the 75 K reorientation transition driven by magnetic frustration.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201506540. Open data for this article are at http://dx.doi.org/10.7488/ds/288.

clinically distorted double-perovskite structure similar to that of Ca_2FeReO_6.[2] Mn, Fe, and Re are highly ordered over the three $A_2BB'O_6$ cation sites, with only Mn at A sites and a very small antisite disorder (which is important for obtaining a high P) of 1.4% for Fe/Re at B/B′ sites. This material is the first double-perovskite with magnetic transition-metal cations at all positions; $S = 5/2$ Mn^{2+} at the A-sites, and $S = 5/2$ Fe^{3+} and $S = 1$ Re^{5+} at B and B′ sites.

Magnetization measurements in Figure 2 reveal that Mn_2FeReO_6 has a high $T_C = 520$ K, comparable with 530 K for Ca_2FeReO_6 and 560 K for $Ca_{0.5}Cu_{1.5}FeReO_6$.[2,7] The observed magnetizations for Mn_2FeReO_6 exceed those for other ferrimagnetic double perovskites at high and low field strengths. $M = 3.5$ μ_B at 300 K and 7 T exceeds room-temperature values for all other double-perovskite ferrimagnets, and the maximum $M = 5.0$ μ_B at 75 K is a record in this materials class. Magnetic fields of 30 T were used to obtain saturated M up to 3.3 μ_B for other A_2FeReO_6 (A = Ca, Sr, $Sr_{0.5}Ba_{0.5}$) double perovskites,[12] but Mn_2FeReO_6 could offer spectacular magnetizations up to a theoretical $M = 13$ μ_B if $S = 5/2$ Mn^{2+} spins are aligned with the $S = 5/2$ Fe^{3+} spins, antiparallel to $S = 1$ Re^{5+}, at similar high fields. Although high-field M is enhanced by alignment of fluctuating Mn^{2+} spin components, it is notable that remnant values (at zero field during cycling as shown in the inset to Figure 2b) of $M_r = 2.8$ μ_B at 75 K and 1.1 μ_B at 300 K also exceed those of other double-perovskite ferrimagnets, which typically have $M_r < 2$ μ_B at 5 K and $\ll 1$ μ_B at 300 K.[2]

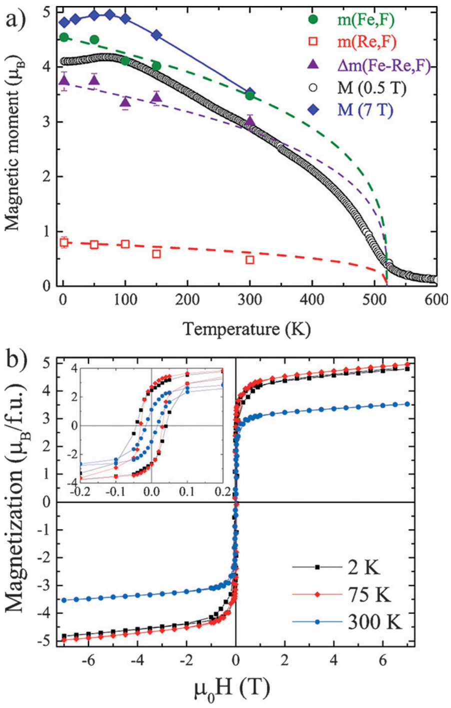

Figure 2. a) Temperature dependence of magnetization M per Mn_2FeReO_6 unit. Measurements at 0.5 T were collected during warming, and 7 T points are from hysteresis data such as in (b). Antiparallel Fe and Re moments m from neutron analysis and their net difference are also shown with Brillouin function fits (dashed lines). b) Magnetization-field hysteresis loops. The low-field inset shows a small magnetic anisotropy with a coercive field of 43 mT at 2 K.

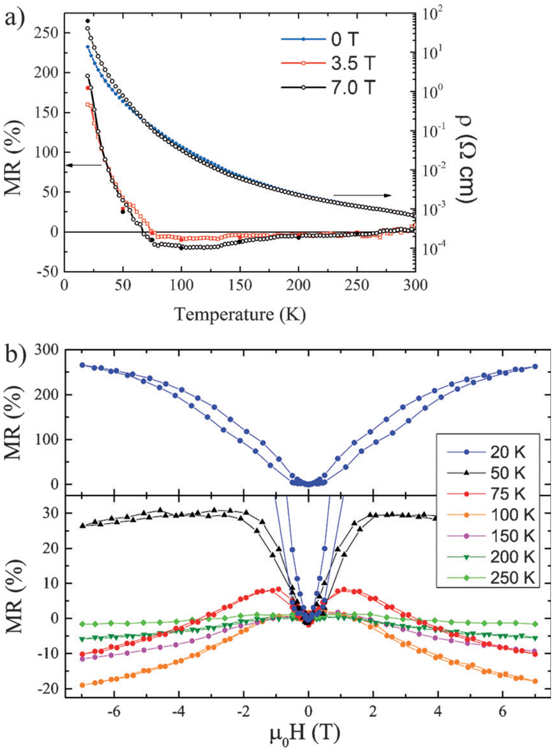

Figure 3. a) Temperature dependence of zero-field and 7 T resistivities for Mn_2FeReO_6, and of magnetoresistance MR at fields of 3.5 and 7 T, showing the switching transition at 75 K. Open MR points are from R–T measurements at constant H, and closed points are from MR–H data in (b). b) Variations of MR for magnetic field cycled between +7 and −7 T, with the large positive response at 20 K shown in the upper panel.

Resistivity measurements in Figure 3a reveal bulk semiconducting behavior for a ceramic pellet of Mn_2FeReO_6. This behavior is consistent with the change from metallicity to semiconductivity as A^{2+} cation size decreases from Ba to Ca in ceramic A_2FeReO_6 samples,[2] as Mn is even smaller than Ca. Ca_2FeReO_6 undergoes a metal to insulator (semiconductor) transition at 140 K driven by orbital ordering of the $5d^2$ Re^{5+} states.[13] Our neutron refinements reveal elongated ReO_6 octahedra consistent with Jahn–Teller distortion at 2–300 K (see Supporting Information), so it is likely that Mn_2FeReO_6 has an orbitally ordered insulating ground state, with any insulator to metal transition occurring only above 300 K. The Mn_2FeReO_6 pellet shows negative high-field MR which increases on cooling to $MR = -19\%$ at 7 T and 100 K, but MR takes large positive values below a sharp discontinuity at 75 K. This crossover is unprecedented in ferrimagnetic double perovskites where negative MR is consistently observed. MR–H data in Figure 3b show that the positive contribution emerges at low fields and high temperatures, increases near the transition ($MR = 8\%$ at 1 T at 75 K), and is dominant at low temperatures with $MR = 265\%$ at 7 T and 20 K. Hence, Mn_2FeReO_6 does not show large low-field magnetoresistances at room temperature

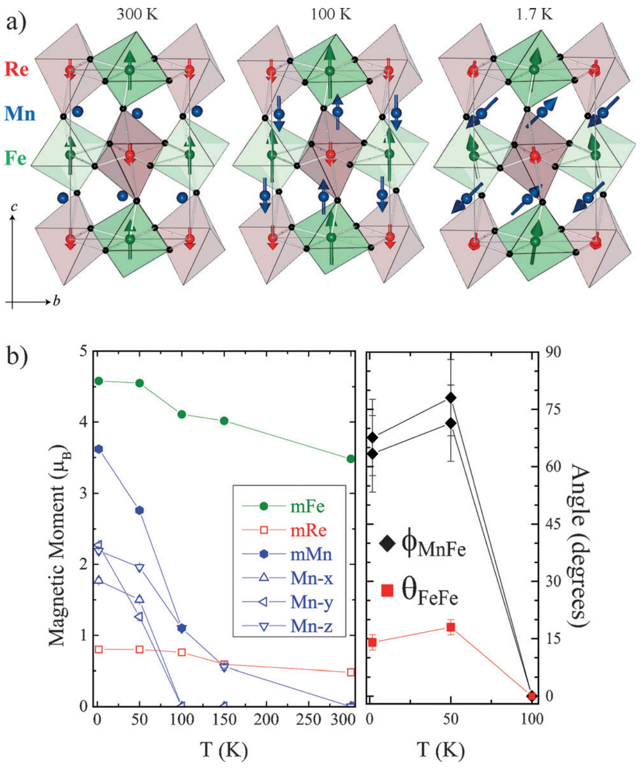

Figure 4. a) Magnetic orders in Mn_2FeReO_6 at representative temperatures, spins shown by arrows. b) Temperature variations of the total ordered Fe, Re, and Mn moments and of the Mn *x*, *y*, and *z* components. Variations of canting angles φ_{MnFe} (where the angle between Mn and Fe spins that are antiparallel at 100 K is 180°–φ_{MnFe}) and the Fe–Fe spin canting angle θ_{FeFe} are also shown.

despite a large *M*, as the positive *MR* contribution largely cancels the negative TMR effect.

Three spin-ordering regimes (Figure 4a) have been discovered in Mn_2FeReO_6 from analysis of magnetic neutron diffraction (Figure 1), as described in Supporting Information. The antiparallel order of the Fe^{3+} and Re^{5+} moments at 300 K is like those in other ferrimagnetic double perovskites, and there is no measurable moment at the Mn sites. However, at 150 and 100 K additional magnetic reflections reveal a partial antiferromagnetic order of the Mn spins, collinear with the Fe and Re moments. This result shows that Mn-O-Mn interactions are antiferromagnetic. Changes in the magnetic peaks between 100 and 50 K reveal that the *MR* switch is associated with a magnetic reorientation transition at $T_M = 75$ K, below which Mn_2FeReO_6 has non-collinear magnetic order with spin components in *x*, *y*, and *z* directions (Figure 4). This reflects competition between Mn-O-Mn, Fe-O-Re, and Mn-O-Fe/Re exchange interactions that introduces magnetic frustration. Neighboring Mn and Fe spins that are antiparallel above T_M become canted by approximately 70°, showing that symmetric Heisenberg exchange is largely frustrated and weaker antisymmetric (Dzyaloshinskii–Moriya) interactions favoring perpendicular orientation are influential below T_M. Mn moments are antiferromagnetically aligned but the Fe order is no longer purely ferromagnetic, with spins in successive *ab*-plane layers canted by $\theta_{FeFe} \approx 15°$ (Figure 4). The rise in antiferromagnetic Mn order below $T_M = 75$ K reduces the fluctuating Mn^{2+} spin components and the field-induced magnetization, as seen in Figure 2a.

We have also synthesized the double-perovskite (CaMn)-$FeReO_6$ (results are in Supporting Information) which demonstrates that dilution of Mn^{2+} with non-magnetic Ca^{2+} ions suppresses the Mn^{2+} spin-ordering transition and the *MR* switch. *MR* is negative to low temperatures with $MR = -32\,\%$ at 7 T and 20 K comparable to values of double perovskites, such as Sr_2FeMoO_6 which has −30 % at 7 T and 4 K.[2]

Antiferromagnetic Mn^{2+} spin order would be completely frustrated with respect to ferrimagnetic Fe–Re order in a cubic double perovskite, but the monoclinic symmetry of Mn_2FeReO_6 breaks the equivalence of couplings of Fe or Re to spin-up and spin-down Mn^{2+} neighbors. Hence the antiferromagnetically ordered Mn spin components observed at 100 and 150 K couple to the Fe and Re spin order and enhance ferrimagnetism, as evidenced by high M_r and spin polarization. The enhancement is evidenced by a slight change of magnetization slope (Figure 2a) and increase in high-field *MR* (Figure 3a) below around 200 K. The broadness of these features suggests that Mn spin order may be induced by local interactions with ferrimagnetic Fe and Re moments, rather than through a spontaneous transition within the Mn spin sublattice. This is consistent with the collinear order of a small ordered Mn^{2+} moment, (e.g. 1.1 μ_B at 100 K) in this regime.

The magnetic transition at $T_M = 75$ K marks the onset of spontaneous Mn^{2+} spin order and frustration leads to a non-collinear magnetic structure with canting of Fe^{3+} spins. In double-exchange models of ferrimagnetic $A_2FeB'O_6$ double perovskites,[14] the probability of electron hopping between cations depends on the alignment of their core spins as $\cos(\theta_{FeFe}/2)$,[15,16] so the experimentally observed canting of $\theta_{FeFe} \approx 15°$ only corresponds to a 1 % decrease in electron hopping. However, the sharp switch in *MR* at T_M shows that the effects of antiferromagnetism are amplified by magnetic fields, probably through increased Fe spin canting, and neutron measurements in applied fields will be needed to verify this. The positive *MR* is intrinsic to the bulk material, in contrast to the negative TMR which is an interfacial effect. Thermal changes between positive and negative MR regimes are only known in a few materials, such as the spinel $Zn_{0.95}Cu_{0.05}Cr_2Se_4$, through change of conduction mechanism at a 25 K ferromagnetic transition,[17] and at 50 K in GdSi from effects of Gd 4f-spin transitions on magnetopolarons,[18] but the mechanism in Mn_2FeReO_6 is very different and arises from coexistence of ferrimagnetic conducting FeRe and antiferromagnetic Mn spin networks in the same phase.

In conclusion, this study shows that novel ferrimagnetic double perovskites with magnetic transition metals at all cation sites can be synthesized at high pressure.[19] A very high degree of Mn/Fe/Re order over the three $A_2BB'O_6$ cation sites is observed in Mn_2FeReO_6. The large $S = 5/2$ spin of Mn^{2+} significantly enhances magnetization—Mn_2FeReO_6 has the highest reported remnant and high field values for a double perovskite despite antiferromagnetic interactions between Mn spins. This Mn antiferromagnetism introduces an intrinsic positive MR effect that tends to cancel out the negative low-field TMR at ambient temperatures, and becomes dominant below a $T_M = 75$ K spin reorientation transition where magnetic frustration leads to spin canting. Further exotic magnetoresistance or other spintronic phenomena may be generated from couplings between spin, lattice, and charge degrees of freedom in other Mn-based double perovskites. Although high pressures are required for the bulk synthesis of these materials, epitaxial stabilization may enable thin films to be deposited for device applications, as demonstrated for the multiferroic double perovskite Bi_2MnNiO_6.[20]

Acknowledgements

We acknowledge EPSRC and STFC for support and the provision of beam time at ILL. We thank C. Ritter (ILL) for assistance with neutron-diffraction experiments.

Keywords: ferrimagnetic double perovskites · high-pressure chemistry · magnetic properties · magnetoresistance · perovskite phases

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12074–12077
Angew. Chem. **2015**, *127*, 12242–12245

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Received: July 15, 2015