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Colossal Magnetoresistance in Mn^{2+} Oxypnictides $NdMnAsO_{1-x}F_x$

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Supporting Information

ABSTRACT: Colossal magnetoresistance is a rare phenomenon in which the electronic resistivity of a material can be decreased by orders of magnitude upon application of a magnetic field. Such an effect could be the basis of the next generation of memory devices. Here we report CMR in the antiferromagnetic oxypnictide $NdMnAsO_{1-x}F_x$ as a result of competition between an antiferromagnetic insulating phase and a paramagnetic semiconductor upon application of a magnetic field. Mn^{2+} oxypnictides are relatively unexplored, and tailored synthesis of novel compounds could result in an array of materials for further investigation and optimization.

Transition metal oxides with the perovskite structure have been well studied as a result of the fascinating electronic and magnetic properties which they exhibit. High temperature superconductivity (HTSC) in copper oxides[1] and colossal magnetoresistances (CMR)[2] in manganite perovskites are two particularly important phenomena. CMR has been observed in manganese oxides such as the perovskite $La_{1-x}Sr_xMnO_3$[2,3] and pyrochlore $Tl_2Mn_2O_7$.[4] Magnetoresistance is defined as the change in electrical resistivity, ρ, upon applying a magnetic field, H, so that MR = $(\rho(H) - \rho(0))/\rho(0)$, where $\rho(0)$ and $\rho(H)$ are equal to the resistivity in zero and applied field respectively. Reductions in ρ of up to 99.9% have been observed in thin films of $La_{0.67}Ca_{0.33}MnO_x$ in a 6 T magnetic field. The complete theory of CMR in manganese oxides is not yet established, but the largest magnetoresistance is observed in the vicinity of the paramagnetic to ferromagnetic transition, where a drop in electronic resistivity is also observed. It has been proposed that a dynamic Jahn−Teller effect,[5] the double exchange (DE) mechanism, and spatial electronic phase separation[6] are all essential for the CMR mechanism. CMR has also been reported in other ferromagnetic materials, for example $FeCr_2S_4$[7] and EuO[8] where the magnetotransport properties are very similar to the manganites. The recent discovery of high temperature superconductivity in pnictides such as $LnFeAsO_{1-x}F_x$[9] has led to great interest in these materials. This is the first time that high temperature superconductivity has been observed for a noncuprate material, with a maximum T_c of 55 K being achieved via substitution of oxygen with fluorine[10] or by creating oxygen vacancies.[11] Here we report an investigation of the $NdMnAsO_{1-x}F_x$ analogue which shows antiferromagnetic order of the Mn^{2+} and Nd^{3+} spins below 356 and 23 K respectively. Colossal magnetoresistance is observed at low temperature, and we show that this is a novel mechanism of CMR which is as a result of a second order phase transition in field from an antiferromagnet (AF) to a paramagnet (P). Hence the CMR arises due to competition between an AF insulating phase and a P semiconductor.

Rietveld refinements of 290 and 4 K synchrotron X-ray powder diffraction data were recorded for the material with nominal stoichiometry $NdMnAsO_{0.95}F_{0.05}$ which confirms that the sample is phase pure and crystallizes in the ZrCuSiAs crystal structure previously reported for the parent compound at both temperatures.[12−14] This structure consists of a tetrahedral $[MnAs]^-$ layer sandwiched between slabs of insulating $[NdO/F]^+$ (space group $P4/nmm$; a = 4.048697(3) Å and c = 8.89654(1) Å at 290 K). X-ray diffraction data were also recorded for nominal $NdMnAsO_{1-x}F_x$ (x = 0.050, 0.065, and 0.080) with a Bruker D8 diffractometer. All samples are phase pure, and Rietveld refinement of the data shows that as x increases from 0.05 to 0.08, the a and c cell parameters decrease from 4.0500(1) Å and 8.9040(4) Å to 4.0490(1) Å and 8.8956(4) Å respectively. A similar reduction in cell parameters has been observed for the series $SmFeAsO_{1-x}F_x$[15] and confirms the increase in nominal x.

Two magnetic transitions are evidenced from the magnetic susceptibility data below ∼23 K. This is similar to the parent compound NdMnAsO where the first transition corresponds to antiferromagnetic ordering of Nd^{3+} moments and the second transition to saturation of the ordered Nd^{3+} moments.[14] There is no divergence of zero field cooled (ZFC) and field cooled (FC) susceptibility at either of these transitions. There is no evidence of a ferromagnetic component upon increasing the magnetic field, $\mu_0 H$, from 0 to 7 T at 4 K, but there is a subtle change in slope at 3.5 T.

Powder neutron diffraction data evidence antiferromagnetic order of the Mn^{2+} moments below 356 (2) K, where the Mn^{2+} moments align parallel to c with the same magnetic structure as previously reported for NdMnAsO.[12−14] There is no appreciable change in T_N (Mn) with 5% F doping; this transition is not observed in the magnetic susceptibility data. Below 23 K (T_N (Nd)), antiferromagnetic order of the Nd^{3+} moments is detected with spins aligned parallel to the basal plane. At the same time a spin reorientation of the Mn^{2+} moments into the ab plane is observed as previously reported for NdMnAsO[13,14] so that at 20 K, T_{SR}, the Mn^{2+} moments are fully aligned parallel to the basal plane. There is no evidence of

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magnetic phase separation upon cooling as previously observed in CMR manganites.[16]

Upon substitution of O^{2-} with F^-, electrons are doped into the system, and it is assumed that the conduction carriers are confined to the covalent $[MnAs]^-$ layer as opposed to the insulating $[LaO/F]^+$ slab. The electronic properties are observed to change remarkably with 5% F^- substitution, and CMR is surprisingly observed at low temperature. Figure 1a shows the temperature variation of the 7 T magnetoresistance of $NdMnAsO_{1-x}F_x$ for x = 0.050, 0.065, and 0.080. For all samples −MR is observed below ∼75 K and its magnitude increases exponentially as the temperature is reduced. Below T_{SR} the magnitude of the magnetoresistance rises sharply and increases further as the temperature is lowered. CMR is not observed in the parent compound,[12−14] which suggests that the charge carriers are the electrons generated by the substitution of F^- for O^{2-}. Figure 1b shows the field variation of the −MR for $NdMnAsO_{0.95}F_{0.05}$ at several different fixed temperatures. Below T_{SR} the −MR can be fit to the equation $-MR = A + BH + CH^2$ (A, B, and C are constants) between 0.5 and 3.5 T but deviates from this equation at higher fields. Above T_{SR}, the data can be fit to the same equation. The −MR is reversible with field and reaches a value of −95% at 3 K in a 9 T field which is comparable to perovskite and pyrochlore manganites.[2−4] This is surprising given the very different electronic and magnetic properties of $NdMnAsO_{0.95}F_{0.05}$ compared to other CMR materials[2,4,7,8] and suggests a novel CMR mechanism. The MR observed here cannot be attributed to spin polarized tunnelling across domain or phase boundaries, where typically an appreciable low field (<1 T) MR is detected.[17,18] Furthermore, there is no correlation between the field variation of the magnetization and the MR.

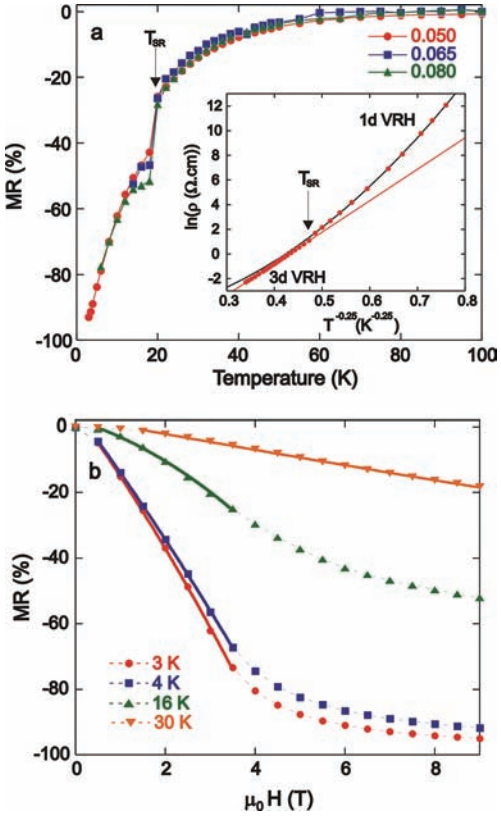

Figure 1. (a) The variation of the 7 T magnetoresistance with temperature for $NdMnAsO_{1-x}F_x$ with nominal x = 0.050, 0.065, and 0.080. The inset shows a crossover from three-dimensional variable range hopping to one-dimensional variable range hopping below T_{SR} for x = 0.05; T_{ES} = 922 K and $T_0 = 4 \times 10^5$ K in the low and high temperature regions respectively. (b) The field dependence of the magnetoresistance at selected temperatures between 3 and 30 K. The solid lines show fits to the equation $-MR = A + BH + CH^2$.

Figure 2a shows a portion of the 4 K neutron diffraction pattern where upon applying a magnetic field it is apparent that the intensity of the [100] magnetic peak decreases. There is no change in intensity of any of the other magnetic or nuclear peaks, and hence there is no evidence of an increasing ferromagnetic component with field. Consequently there is no canting or reorientation of the spins with field, which is in agreement with the variable field magnetic susceptibility data. There is also no change in lattice parameters upon increasing the magnetic field (a = 4.0571(2) and 4.0570(1) Å and c = 8.8971(6) and 8.8973(5) Å at 0 and 5 T respectively). The field variation of the magnetic structure was determined by Rietveld refinement of the neutron diffraction data, so that the decreased intensity of the [100] magnetic peak can be modeled by a reduction in both the antiferromagnetically ordered Nd^{3+} and Mn^{2+} moments with increasing field. The Nd^{3+} and Mn^{2+} moments are reduced from 2.09 (3) μ_B to 1.36 (3) μ_B and from 3.83 (2) μ_B to 3.56 (2) μ_B respectively upon increasing $\mu_0 H$ from 0 to 5 T. Upon returning the field to 0 T, the Mn^{2+} and

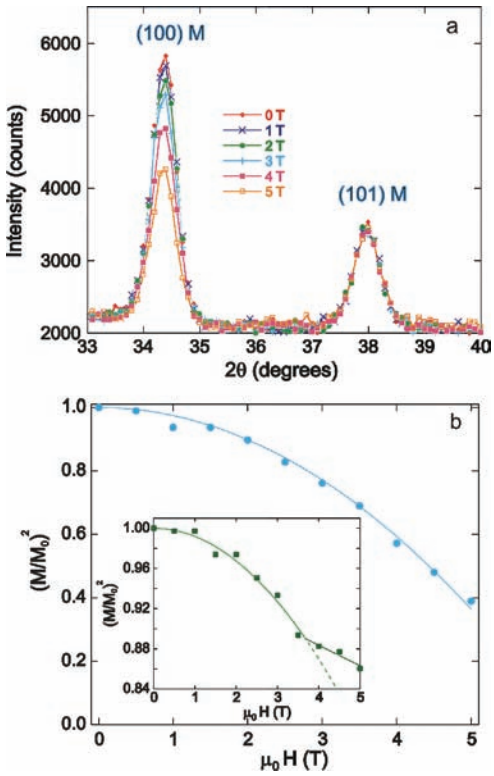

Figure 2. (a) A portion of the 4 K neutron diffraction pattern showing a reduction in intensity of the (100) magnetic diffraction peak with increasing magnetic field ($\mu_0 H$) from 0 to 5 T. (b) Variation of the normalized Nd^{3+} moment with $\mu_0 H$; the data are fit to the equation $M^2 = M_0^2[1 - (H/H_m)^2]$. The inset shows the variation of the normalized Mn^{2+} moment with $\mu_0 H$; the data are fit to the equation $M^2 = M_0^2[1 - (H/H_m)^2]$ between 0 and 3.5 T, and a clear inflection point is observed at 3.5 T.

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Nd^{3+} moments refine to 3.86 (2) and 2.10 (3) μ_B respectively so that the reduction in magnetic moments with field is reversible. The Mn^{2+} and Nd^{3+} moments in the parent compound NdMnAsO are 3.72(1) and 1.94(1) μ_B respectively[17] so that there is a small increase in both moments with F^- doping.

Above 80 K the electronic behavior of $NdMnAsO_{0.95}F_{0.05}$ is dominated by thermally activated charge carriers across a band gap so that $\rho = \rho_0 \exp(E_g/2kT)$ (E_g = 23 meV). The temperature variation of the resistivity can be modeled by three-dimensional variable range hopping (VRH) of the carriers below 75 K[19] (phonon assisted tunnelling of electrons between localized states so that the resistivity, ρ, is defined as $\rho = \rho_0 \exp(T_0/T)^{0.25}$). The inset to Figure 1a evidences a subtle electronic transition at T_{SR} as the resistivity data can no longer be fit well to the three-dimensional VRH equation below 20 K. This can be modeled as a crossover from three- to one-dimensional Efros Shklovskii VRH;[20] an excellent fit is obtained to this model down to the lowest temperature measured. This suggests that reorientation of Mn^{2+} spins into the basal plane at 20 K results in enhanced Coulomb correlations between localized electrons so that a soft Coulomb gap pinned at the Fermi level opens up and Efros Shklovskii (ES) VRH is observed (Figure 1a), i.e. that the spin orientation has a strong influence on the hopping mechanism so that when the spins align in the basal plane, the electron correlations are enhanced and the transport is diminished.

Upon application of a magnetic field both the Mn^{2+} and Nd^{3+} ordered moments reduce (Figure 2) in magnitude, the electron correlations diminish, and an increase in electronic transport is observed so that a large increase in magnitude of the negative magnetoresistance is observed at T_{SR} (Figure 1a). Figure 2b shows that the reduction of the ordered Nd^{3+} moment with field at 4 K can be well fit by the standard expression $M^2 = M_0^2[1 - (H/H_m)^\gamma]$[21] ($M_0$ is the moment in zero field, H_m is the critical field for the magnetic order, and $\gamma = 2$), which describes the magnetic field dependence of the magnetic moment for a second order phase transition to the paramagnetic phase and is derived from Ginzburg–Landau theory. Fits to this equation result in H_m = 6.3(5) T so that antiferromagnetic order of the Nd^{3+} spins is expected to vanish at this field. A slightly different variation of the ordered Mn^{2+} moment is observed (Figure 2b (inset)) so that the data for $\mu_0 H$ = 0–3.5 T can be fit to the same equation with H_m =11.1(2) T. However at 3.5 T there is a clear inflection point. This subtle change at 3.5 T is also seen in the 4 K field evolution of the magnetization and the variable field magnetoresistance data (Figure 1b). Below T_{SR}, it is also not possible to fit the field variation of the MR or the Mn^{2+} moment by a single function over the field range measured.

Figure 3 shows that there is in fact a correlation between the field variation of the ordered Mn^{2+} moment and the observed magnetoresistance across the field range measured (0–5 T) at 4 K. The MR is related to the Mn^{2+} moment so that $-MR = (\Delta M/C)^{1/2}$; $\Delta M = M(0) - M(H)$, where $M(H)$ is the Mn^{2+} moment in field, $M(0)$ is the Mn^{2+} moment when $\mu_0 H$ = 0 T, and C is a constant (0.4 μ_B at 4 K) which equates to the moment reduction that would theoretically result in a −MR of 100%. The same relation is not detected with the field reduction of the Nd^{3+} moment. This clearly shows that it is the field suppression of the basal plane Mn^{2+} moment which is the origin of the CMR observed in $NdMnAsO_{1-x}F_x$ below T_{SR} so that the electron correlations are weaker in the paramagnetic phase, resulting in dramatically increased electron transport. It

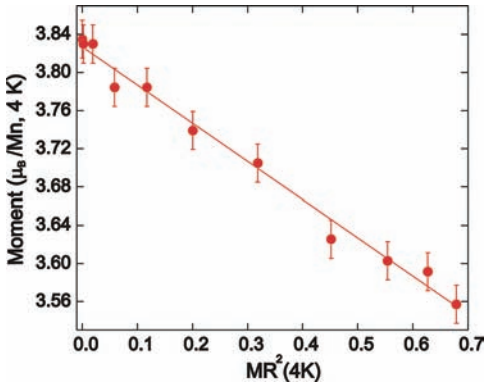

Figure 3. The results show an empirical correlation between the observed −MR and the field reduced Mn^{2+} moment recorded at 4 K with H = 0 − 5 T (every 0.5 T) for $NdMnAsO_{0.95}F_{0.05}$.

is remarkable that only a 7% reduction of the Mn^{2+} moment results in an 86% reduction in the electronic resistivity. It is highly likely that there is electronic phase separation into insulating and semiconducting regions upon application of a magnetic field. Presumably the MR observed above T_{SR} has the same origin, but the difference in electronic transport of AF and paramagnetic phases is greater below T_{SR}; i.e., the difference in the electronic transport of the antiferromagnetic and paramagnetic phases is less significant when the Nd^{3+} moments are unordered and the Mn^{2+} spins are aligned parallel to c. A further variable field neutron diffraction study above T_{SR} is necessary to confirm this. Large negative magnetoresistances have previously been reported for the antiferromagnetic Zintl compound $Eu_{14}MnBi_{11}$ as a result of increased ferromagnetic fluctuations with field;[22] at all temperatures below T_N there is a linear correlation between the −MR and the raw moment (which increases with field). The same correlation is not observed for $NdMnAsO_{1-x}F_x$ in which there is no evidence of ferromagnetic fluctuations at any temperature.

The origin of the second order phase transition, which results in the reduction of both the Mn^{2+} and Nd^{3+} moments with increasing magnetic field at 4 K, is as yet unknown. In most antiferromagnetic materials, the exchange coupling is stronger than other internal interactions so that strong magnetic fields are required to destroy the antiferromagnetic order and align the sublattice magnetizations with the field (spin flip transition into the field-aligned paramagnetic state). The application of the smaller magnetic fields applied here should result in only a slight distortion from the antiparallel alignment. Uniaxial antiferromagnets such as $NiCl_2.6H_2O$[23] are well documented to display spin-flop transitions or spin rotations with field, but there is no evidence of such transitions from the variable field susceptibility and neutron diffraction data. The Mn^{2+} spins order antiferromagnetically below 356 K in $NdMnAsO_{0.95}F_{0.05}$ which suggests that there is strong antiferromagnetic exchange coupling between Mn^{2+} moments so that the second order phase transition to a paramagnetic phase with field is unexpected and suggests the presence of an antiferromagnetic instability.

It is possible that the competing single-ion anisotropy which results in the low temperature spin reorientation transition[13,14] is also the origin of the field induced paramagnetism. An alternative explanation is that there is a hidden order parameter; indeed the decrease of magnetic intensity of the Mn^{2+} moment with field at 4 K does not follow a simple power

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law, but shows a clear inflection point at 3.5 T (Figure 2b (inset)). Such behavior has previously been observed in the heavy fermion material URu_2Si_2 as a result of a linear coupling between a hidden order parameter and the antiferromagnetic moment,[21] and it appears that a similar complex underlying physics is also present in $NdMnAsO_{1-x}F_x$.

In conclusion we have shown a novel mechanism of CMR in the oxypnictide material $NdMnAsO_{1-x}F_x$ which further highlights the exotic properties of transition metal pnictides. CMR in manganites arises when a magnetic field enhances ferromagnetic alignment of spins at the paramagnetic−ferromagnetic (disorder−order) boundary. Here we show that CMR is also possible in Mn^{2+} pnictides at the antiferromagnetic−paramagnetic (order−disorder) transition in field. These results demonstrate that it is possible to observe CMR solely as a result of competition between different phases in field which have divergent electronic properties.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data including magnetization data, neutron, and X-ray synchrotron diffraction figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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