Strong 4f electron interaction and magnetic ordering modification in Nd1-xErxMnO3 (0 less than or equal to x less than or equal to 0.5)

Fang Hong
fh640@uowmail.edu.au

Zhenxiang Cheng
University of Wollongong, cheng@uow.edu.au

Xiaolin Wang
University of Wollongong, xiaolin@uow.edu.au

Follow this and additional works at: https://ro.uow.edu.au/engpapers

Part of the Engineering Commons
https://ro.uow.edu.au/engpapers/3158

Recommended Citation
Hong, Fang; Cheng, Zhenxiang; and Wang, Xiaolin: Strong 4f electron interaction and magnetic ordering modification in Nd1-xErxMnO3 (0 less than or equal to x less than or equal to 0.5) 2011, 192503-1-192503-3.
https://ro.uow.edu.au/engpapers/3158

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
Strong 4f electron interaction and magnetic ordering modification in Nd$_{1-x}$Er$_x$MnO$_3$ (0 ≤ x ≤ 0.5)

Fang Hong, Zhenxiang Cheng,a) and Xiaolin Wang

Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2519, Australia

(Received 20 August 2011; accepted 19 October 2011; published online 7 November 2011)

Structural and magnetic properties have been studied in perovskite Nd$_{1-x}$Er$_x$MnO$_3$ (0 ≤ x ≤ 0.5). Er$^{3+}$ doping enhances the Jahn-Teller distortion, strongly affects the Nd$^{3+}$-Mn$^{3+}$ interaction, destroys the intermediate state below the antiferromagnetic transition temperature in NdMnO$_3$, and breaks the antiparallel arrangement between Nd$^{3+}$ and Mn$^{3+}$ spin ordering. The decreasing ferromagnetic component in magnetic hysteresis loops at 30 K indicates that the canted angles vary with x. These results offer strong evidence for the interaction between rare earth ions and transition metal ions and competition among rare earth ions as well. © 2011 American Institute of Physics.

[doi:10.1063/1.3659897]

The manganites have aroused great interest during the past several years because of the magnetoresistance effect. During these years, more attention has been paid to some manganites due to their unique multiferroic properties. Abundant magnetic phase transitions are observed in these manganites. LaMnO$_3$ shows typical A-type antiferromagnetism (AFM) at 140 K because of the orbital ordering arising from the distorted perovskite structure. A-type AFM still exist in SmMnO$_3$, in which Sm$^{3+}$ has a smaller ionic radius than La$^{3+}$, but it is canted A-type AFM with a weak ferromagnetic (FM) component. The magnetic properties become much more complicated in orthorhombic DyMnO$_3$, which experiences a sinusoidal incommensurate AFM transition at 39 K and a spiral spin ordering below 18 K, after which experiences a sinusoidal incommensurate AFM transition at 39 K and a spiral spin ordering below 18 K, after which experiences a sinusoidal incommensurate AFM transition at 39 K and a spiral spin ordering below 18 K, after which experiences a sinusoidal incommensurate AFM transition at 39 K and a spiral spin ordering below 18 K, after which experiences a sinusoidal incommensurate AFM transition at 39 K and a spiral spin ordering below 18 K.

To well understand the mechanisms behind the different magnetic properties in these manganites, it is necessary to illustrate the interaction between the rare earth ions and Mn$^{3+}$. In the Er$_{1-x}$Y$_x$MnO$_3$ system, the strong geometrical frustration effect in YMnO$_3$ becomes weaker and weaker as the Er$^{3+}$ content increases, but the ordered moments are very stable without strong doping dependence, which suggests that there is strong coupling between Er$^{3+}$ and Mn$^{3+}$. Ga$^{3+}$ with 4f electrons has been introduced to replace La$^{3+}$ in LaMnO$_3$, and spin canting of Mn$^{3+}$ can polarize the 4f spins in Ga$^{3+}$. In the Eu$_{1-x}$Y$_x$MnO$_3$ system, the rare earth ions are both non-magnetic, and ferroelectric polarization is observed below the AFM transition temperature in samples with x ≥ 0.3, presumably due to the emergence of spiral spin ordering only on the Mn$^{3+}$ sub-lattice.

Up to now, there has been no report on the interaction between magnetic rare earth ions and their competition with Mn$^{3+}$. In this work, we study the structural and magnetic properties in the Nd$_{1-x}$Er$_x$MnO$_3$ system. Both Nd$^{3+}$ and Er$^{3+}$ are magnetic rare earth ions with 4f electrons but with quite different moments. Our results show that Er$^{3+}$ doping destroys the intermediate state and antiparallel coupling between Nd$^{3+}$ and Mn$^{3+}$ ordering in NdMnO$_3$ and probably induces the rotation of canted angles of Mn$^{3+}$ ordering.

Polycrystalline samples of Nd$_{1-x}$Er$_x$MnO$_3$ (x = 0, 0.1, 0.2, 0.33, 0.5, and 1.0) were made by the traditional solid state reaction method. Stoichiometric amounts of raw oxide powder were weighed and then mixed in an agate mortar, which was followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950 °C for 10 h and sintered at 1450 °C for 48 h. The crystal structures of the samples were examined by x-ray diffraction at room temperature (XRD, model: GBC MMA), using Cu Kα radiation at λ = 1.54056 Å. The Rietveld refinement calculations were conducted via FULLPROF software to obtain the lattice parameters and bond information. The magnetic measurements were carried out using a 14T physical properties measurement system (PPMS). The XRD patterns of the samples are presented in Figure 1(a). When the doping rate x is no more than 0.5, samples always exhibit the orthorhombic structure. The x dependence on the lattice parameters is given in Figure 1(b). The relation $b > a > c/\sqrt{2}$ can be found for each sample and suggests a...
static Jahn-Teller orbital ordering. Theoretical tolerance factors were calculated in form of $t = (R_{A} + R_{O})/\sqrt{2} (R_{Mn} + R_{O})$, as shown in Figure 1(c), where ionic radius $R_{A} = (1 - x)R_{Nd}^{3+} + xR_{Er}^{3+}$ and $R_{O}^{2-}$ is the radius of the oxygen ion. On increasing $x$, the structure diverges further from the ideal structure. This is confirmed by the increasing spontaneous stress calculated in form of $2(b-a)/(b+a)$, as shown in Figure 1(c). The $x$ dependence of the Mn-O bond distances, the Mn-O-Mn bond angles, inter-plane/in-plane, and the Nd/Er-Mn distances are shown in Figure 1(d). When the doping rate $x$ is 0.1, significant changes in the Mn-O bond distances, the Mn-O-Mn bond angles, inter-plane/in-plane, and the Nd/Er-Mn distances are observed. The Mn-O bond distance and Mn-O-Mn bond angle in the sample with $x = 0.5$ also show relatively big changes compared with the other samples ($x = 0$, 0.2, and 0.33), in which the bond distances and bond angles remain very close. On increasing $x$ from 0 to 0.33, the Nd/Er-Mn distances decrease monotonically.

As shown in Figure 2, the field cooling (FC) temperature dependence of the magnetic moment was measured in various fields. Figure 2(a) shows the M-T curves of NdMnO$_3$ in 20 Oe and $-20$ Oe, while Figure 2(b) shows the M-T curves in 100 Oe and $-100$ Oe. In these figures, we can always observe a transition at 79 K. In addition, another transition can also be observed around 15 K, where negative/positive moments change to positive/negative moments. The transition at high temperature showing the weak FM (WFM) property is assigned to the canted A-type AFM transition of Mn$^{3+}$. The low temperature transition is assigned to FM ordering of Nd$^{3+}$. Considering the sign change in the moment at low temperature, we can claim that the magnetic vector of Nd$^{3+}$ ordering is opposite to the magnetic vector of Mn$^{3+}$ ordering, meaning that Nd$^{3+}$ couples with Mn$^{3+}$ antiferromagnetically. Similar spin arrangements between rare earth ions and transition metal ions are also found in SmMnO$_3$ (Ref. 14) and GdMnO$_3$. The FC temperature dependence of the magnetic moment was examined for the other four samples, as shown in Figures 2(c) and 2(d). For $x < 0.5$, the magnetic moments suddenly increase at certain temperatures, which become lower and lower with increasing $x$, suggesting a shift in the magnetic phase transition temperature. This increase is due to the FM component in the canted A-type AFM ordering of Mn$^{3+}$. The downshift in the Néel temperature ($T_N$) is due to enhanced Jahn-Teller distortion. For $x = 0.5$, such a sudden increase in moment cannot be observed, which is probably due to the disappearance of the FM component. The FM-like behaviour for $x < 0.5$ is confirmed by the magnetic hysteresis loops measured at temperatures below $T_N$, as shown in Figures 3(a)–3(d). The M-H loop of the sample with $x = 0.5$ measured at 30 K in Figure 3(e) shows typical paramagnetic/AFM behaviour, confirming the disappearance of the FM component. In contrast to NdMnO$_3$, the moment shows no sign change in the M-T curves in the low temperature range for the other four samples, in spite of reduced Nd/Er-Mn distances. This indicates that the orderings in NdMnO$_3$ are severely disturbed by Er$^{3+}$ doping.

The unique M-H loop of NdMnO$_3$ at 30 K is probably attributable to variation in the intermediate state at high fields. To confirm the existence of this intermediate state and study its origin, another M-H loop was collected at 20 K, which also shows abnormal behaviour. However, this state disappears at 35 K, as proved by the M-H loop at that temperature. Meanwhile, the temperature dependence of the magnetic moment was measured at different magnetic fields (supplementary information, Figure S1). To extract the detailed information from M-T curves, Figure 4 presents the temperature dependence of dM/dT, which is consistent with the results from M-H loops measured at temperatures below $T_N$, as shown in Figure 4(a), and it shifts to 88.1 K at 5 T (shown in Figure 4(b)), which corresponds to the AFM transition. Meanwhile, an intermediate state transition is observed at $\sim 33.5$ K at 1 T with a sharp increase in dM/dT, which is consistent with the results from M-H loops at 30 K and 35 K. The intermediate state transition can also be found at 5 T in Figure 4(b). Hence, both the M-H loop at 20 K and dM/dT for NdMnO$_3$ further confirm the existence of an intermediate state at 30 K. The intermediate state should be ascribed to the coexistence state of short range Nd$^{3+}$ ordering and long range Mn$^{3+}$ ordering. We propose the spin configuration shown with the M-H loop at 20 K in...
Figure 3(b), which also applies to the M-H loop at 30 K. At high magnetic field, the FM vectors of the Mn$^{3+}$ spins have the same spin direction as the Nd$^{3+}$ spins. When the field sweeps from $+/−7000$ Oe to $−+/+7000$ Oe, the spin direction of Mn$^{3+}$ does not change, but the Nd$^{3+}$ spins gradually flip. On further increasing the field, the Mn$^{3+}$ spins flip, and their FM vectors show the same direction as Nd$^{3+}$ again. The negative remnant moment sweeping from A to B (positive from C to D) in the M-H loop at 20 K is due to the bigger total moment of Nd$^{3+}$ compared to Mn$^{3+}$. To determine the actual spin configuration, further study is needed based on neutron diffraction. However, this intermediate state is not observed in the other samples, as confirmed by Figures 4(c) and 4(d). The disappearance of the intermediate state further confirms that Er$^{3+}$ doping severely affects the interactions among Mn$^{3+}$ and Nd$^{3+}$ ions.

The magnetic hysteresis loops at 30 K also reflect the subtle magnetic evolution. The coercive field and remanent moment increase when the Er$^{3+}$ doping rate x is 0.1, as compared with the behaviour of NdMnO$_3$, and then decrease gradually with increasing x. No obvious coercive field is observed in the sample with x = 0.5. The coercive field and remanent moment should be determined by the magnitude of the FM component, which is dominated by the canted angle of Mn$^{3+}$ spin ordering in the ab-plane. Curie-Weiss law fitting shows that the spin states of Mn$^{3+}$ in all samples are high spin state (supplementary information, Figure S2 and Table I). Hence, according to the changes discussed above, the proposed magnetic ordering of Mn$^{3+}$ with no applied magnetic field is presented in Figure 5, which shows the variation in the canted angle of Mn$^{3+}$ spins in the ab-plane. The canted angle increases as x changes from 0 to 0.1, as can be seen in Figures 5(a) and 5(b), corresponding to the increasing remanent moment. Then, the angle decreases continuously with increasing x, as illustrated in Figures 5(c) and 5(d), which corresponds to the decreasing remanent moment. In the sample with x = 0.5, the spins are arranged in collinear AFM, as illustrated in Figure 5(e), corresponding to the typical A-type AFM hysteresis loop shown in Fig. 3(e).

Low temperature magnetic hysteresis loops at 5 K are also presented in Figure 3(f). Clear FM behaviour can be observed in samples with x < 0.5. When x = 0.5, the sample presents typical paramagnetic/AFM properties, indicating that Nd$^{3+}$ ordering is absent above 5 K, and the FM component of Mn$^{3+}$ ordering disappears, which is in accordance with the analysis of the M-T curve and M-H loop at 30 K.

In conclusion, perovskite Nd$_{1-x}$Er$_x$MnO$_3$ compounds with magnetic rare earth ions have been studied based on structural and magnetic properties. Stronger distortion is induced after Er$^{3+}$ doping, which is responsible for the decreasing $T_N$. The intermediate state and the antiparallel arrangement between Nd$^{3+}$ FM ordering and Mn$^{3+}$ WFM ordering in NdMnO$_3$ are destroyed by Er$^{3+}$ doping. Meanwhile, the canted angles of Mn$^{3+}$ ordering vectors probably rotate and disappear with varying x. These results show that there are strong interactions between Nd$^{3+}$/Er$^{3+}$ and Mn$^{3+}$, and competition between Nd$^{3+}$ and Er$^{3+}$.

Zhenxiang Cheng thanks the Australian Research Council for support through a Future Fellowship (FT 0990287). The authors also thank Dr. Tania Silver for her kind help in revision of the manuscript.

1^2 M. B. Salamon and M. Jaime, Rev. Mod. Phys. 73, 583 (2001).
1^15 See supplementary material at http://dx.doi.org/10.1063/1.3659897 for M-T curves and spin state.