Strong 4f electron interaction and magnetic ordering modification in Nd$_{1-x}$Er$_x$MnO$_3$ (0 ≤ x ≤ 0.5)

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Strong 4f electron interaction and magnetic ordering modification in Nd$_{1-x}$Er$_x$MnO$_3$ (0 ≤ x ≤ 0.5)

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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, ferroelectric polarization can be observed because of an inverse Dzyaloshinsky-Moriya (DM) interaction. When La$^{3+}$ is replaced by much smaller atoms, such as Er$^{3+}$, the orthorhombic structure will be disturbed, and the hexagonal structure becomes stable, so that ErMnO$_3$ has a frustrated triangular spin arrangement on the Mn$^{3+}$ sublattice.

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$^{3+}$-Y$_2$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$^{3+}$. Gadolinium ions 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 14 T 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

![FIG. 1. (Color online) XRD patterns for Nd$_{1-x}$Er$_x$MnO$_3$ samples (a); x dependence of lattice parameters (b); theoretical tolerance factors and spontaneous stress (c); and Mn-O bond distances, Mn-O-Mn bond angles inter-plane and in-plane, and Nd/Er-Mn distances (d).](image-url)
static Jahn-Teller orbital ordering. Theoretical tolerance factors were calculated in form of $t = (R_n + R_o)/\sqrt{2}$ ($R_{Mn}^{3+} + R_{O}^{2-}$), as shown in Figure 1(c), where ionic radius $R_A = (1 - x)^*R_{Nd}^{3+} + x^*R_{Er}^{3+}$ 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 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$^{3+}$, which has been well studied. 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$_3$.10

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 Ne`el 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(c) 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 for $x = 0$, 0.1, and 0.5 under different cooling fields. For $x = 0$, a clear peak can be identified at 79 K at 1 T (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 ~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

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FIG. 2. (Color online) Field cooling temperature dependence of magnetic moment: (a) $x = 0$, 20, and –20 Oe (cooling field); (b) $x = 0$, 100, and –100 Oe; (c) $x = 0$, 0.1, 0.2, and 0.33; (d) $x = 0.33$, 100 Oe, and $x = 0.5$, 100 Oe.

FIG. 3. (Color online) Magnetic hysteresis loops for $x = 0$–0.5 measured at 30 K and 5 K, and for $x = 0$ at 20 K, 35 K, and 55 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$^{3+}$.

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$^2$M. B. Salamon and M. Jaime, Rev. Mod. Phys. 73, 583 (2001).


$^{10}$See supplementary material at http://dx.doi.org/10.1063/1.3659897 for M-T curves and spin state.