Competition between the crystal field and the exchange field in Er3+ doped NdMnO3

Fang Hong
University of Wollongong, fh640@uowmail.edu.au

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

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

S X. Dou
University of Wollongong, shi@uow.edu.au

http://ro.uow.edu.au/engpapers/5072

Publication Details
Competition between the crystal field and the exchange field in Er3+ doped NdMnO3

Fang Hong, Zhenxiang Cheng, Xiaolin Wang, and Shixue Dou

Citation: Appl. Phys. Lett. 101, 121913 (2012); doi: 10.1063/1.4754613
View online: http://dx.doi.org/10.1063/1.4754613
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v101/i12
Published by the American Institute of Physics.

Related Articles
Ferromagnetic resonance analysis of internal effective field of classified grains by switching field for granular perpendicular recording media
Quantitative interpretation of the very fast electronic relaxation of most Ln3+ ions in dissolved complexes
Magnetism and superconductivity in the Heusler alloy Pd2YbPb
Control of the exchange coupling in granular CoPt/Co recording media
J. Appl. Phys. 109, 07B752 (2011)
First principles study on the local magnetic anisotropy near surfaces of Dy2Fe14B and Nd2Fe14B magnets
J. Appl. Phys. 109, 07A702 (2011)

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT
The pervoskite LaMnO$_3$ is a classic manganite, a good study subject and the object of great physical interest, in which the Jahn-Teller distortion and the orbital ordering play a critical role in determining the antiferromagnetic interaction. It shows typical A-type antiferromagnetism (AFM) at 140 K because of the orbital ordering. When divalent ions are doped into the La$^{3+}$ sites, such as La$_{1-x}$Ca$_x$MnO$_3$, the manganese ions will be in the forms of both Mn$^{3+}$ and Mn$^{5+}$, allowing the magnetoresistance effect to occur. On the other hand, when the La$^{3+}$ site is totally replaced by other rare earth ions, unique physical properties can be observed. A-type AFM still exists in SmMnO$_3$, in which Sm$^{3+}$ has a smaller ionic radius than that of La$^{3+}$, but it is a canted A-type AFM with a weak ferromagnetic (FM) component. The complex magnetic phase diagram and multiferroic properties have been well studied in DyMnO$_3$ and TbMnO$_3$. When La$^{3+}$ is replaced by much smaller atoms, such as Er$^{3+}$, extremely strong distortion will be introduced, which favours the hexagonal structure, so that ErMnO$_3$ has a frustrated triangular spin arrangement on the Mn$^{3+}$ sublattice. It seems that the magnetic rare earth ions do not affect the antiferromagnetic interaction of the Mn$^{3+}$ sublattice too much beyond the distortion effect. On the contrary, the low temperature behaviour of magnetic rare earth ions is strongly dependent on the exchange field. Therefore, the low temperature behaviour of magnetic rare earth ions is strongly dependent on the exchange field. At the same time, the exchange field and the crystal field may compete or cooperate with each other. To elucidate this complex behaviour, we studied the specific heat in the Nd$_{1-x}$Er$_x$MnO$_3$ system. Considering that the Er$^{3+}$ ion size is a little smaller than that of Nd$^{3+}$, the crystal field could be modified slightly by Er$^{3+}$ doping. In addition, our previous work shows that the interaction between Nd$^{3+}$ and Mn$^{3+}$ is significantly disturbed by Er$^{3+}$ doping, and the doped atomic Mn$^{3+}$ antiferromagnetic ordering is also consequently modified, which indicates variation in the exchange field. In this case, this is an ideal system to study the relationship between the crystal field and the exchange field. The specific heat study in this system will help to understand the low temperature behaviour of magnetic rare earth ions in other similar systems.

Polycrystalline samples of Nd$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.1, 0.2, 0.33, 0.5$) were made by the traditional solid state reaction method with Nd$_2$O$_3$ (99.9%), Er$_2$O$_3$ (99.9%), and MnCO$_3$ (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, 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 specific heat was measured using the thermal relaxation technique with a 14 T physical properties measurement system (PPMS).

Specific heat measurements were conducted from 2 K to certain temperatures above the magnetic transition temperature. The temperature dependence of $C_p/T$ for samples with $x \leq 0.5$ is presented in Figure 1. The peak at higher temperature is assigned to the AFM ordering of Mn$^{3+}$. To calculate the magnetic contribution to the antiferromagnetic transition, a third order polynomial background is subtracted from the experimental data to exclude the contribution from phonons and electrons. A fitting example is presented in Figure 2(a) for the sample with $x = 0$, and the residual magnetic contributions of all samples are shown in Figure 2(b). It is obvious that the specific heat peaks shift to lower temperature when $x$ increases, which is the result of an enhanced Jahn-Teller effect. The magnetic entropy of magnetic ordering is shown in Figure 2(c), calculated in the form of

$C_0/T$ for samples with $x = 0, 0.1, 0.2, 0.33, 0.5$ were made by the traditional solid state reaction method with Nd$_2$O$_3$ (99.9%), Er$_2$O$_3$ (99.9%), and MnCO$_3$ (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, 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 specific heat was measured using the thermal relaxation technique with a 14 T physical properties measurement system (PPMS).

Specific heat measurements were conducted from 2 K to certain temperatures above the magnetic transition temperature. The temperature dependence of $C_p/T$ for samples with $x \leq 0.5$ is presented in Figure 1. The peak at higher temperature is assigned to the AFM ordering of Mn$^{3+}$. To calculate the magnetic contribution to the antiferromagnetic transition, a third order polynomial background is subtracted from the experimental data to exclude the contribution from phonons and electrons. A fitting example is presented in Figure 2(a) for the sample with $x = 0$, and the residual magnetic contributions of all samples are shown in Figure 2(b). It is obvious that the specific heat peaks shift to lower temperature when $x$ increases, which is the result of an enhanced Jahn-Teller effect. The magnetic entropy of magnetic ordering is shown in Figure 2(c), calculated in the form of

$C_0/T$ for samples with $x = 0, 0.1, 0.2, 0.33, 0.5$ were made by the traditional solid state reaction method with Nd$_2$O$_3$ (99.9%), Er$_2$O$_3$ (99.9%), and MnCO$_3$ (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, 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 specific heat was measured using the thermal relaxation technique with a 14 T physical properties measurement system (PPMS).

Specific heat measurements were conducted from 2 K to certain temperatures above the magnetic transition temperature. The temperature dependence of $C_p/T$ for samples with $x \leq 0.5$ is presented in Figure 1. The peak at higher temperature is assigned to the AFM ordering of Mn$^{3+}$. To calculate the magnetic contribution to the antiferromagnetic transition, a third order polynomial background is subtracted from the experimental data to exclude the contribution from phonons and electrons. A fitting example is presented in Figure 2(a) for the sample with $x = 0$, and the residual magnetic contributions of all samples are shown in Figure 2(b). It is obvious that the specific heat peaks shift to lower temperature when $x$ increases, which is the result of an enhanced Jahn-Teller effect. The magnetic entropy of magnetic ordering is shown in Figure 2(c), calculated in the form of

$C_0/T$ for samples with $x = 0, 0.1, 0.2, 0.33, 0.5$ were made by the traditional solid state reaction method with Nd$_2$O$_3$ (99.9%), Er$_2$O$_3$ (99.9%), and MnCO$_3$ (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, 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 specific heat was measured using the thermal relaxation technique with a 14 T physical properties measurement system (PPMS).

Specific heat measurements were conducted from 2 K to certain temperatures above the magnetic transition temperature. The temperature dependence of $C_p/T$ for samples with $x \leq 0.5$ is presented in Figure 1. The peak at higher temperature is assigned to the AFM ordering of Mn$^{3+}$. To calculate the magnetic contribution to the antiferromagnetic transition, a third order polynomial background is subtracted from the experimental data to exclude the contribution from phonons and electrons. A fitting example is presented in Figure 2(a) for the sample with $x = 0$, and the residual magnetic contributions of all samples are shown in Figure 2(b). It is obvious that the specific heat peaks shift to lower temperature when $x$ increases, which is the result of an enhanced Jahn-Teller effect. The magnetic entropy of magnetic ordering is shown in Figure 2(c), calculated in the form of
there is also a magnetic contribution from Mn$^{3+}$ ordering. To clarify the contribution from the Schottky anomaly and magnetic ordering, specific heat fitting was carried out. Generally, the total specific heat is made up of four distinct contributions: lattice, electron, hyperfine, and magnetic ordering, which can be described as below:

$$C = C_{lat} + C_{elec} + C_{hyp} + C_{mag}.$$  \hspace{1cm} (2)

The lattice contribution can be written as $C_{lat} = \beta_1 T^3 + \beta_2 T^5$. In most cases, the contribution of $\beta_2 T^5$ is not considered, as it is too small. For a typical antiferromagnetic insulating material, the conductive electron contribution, $C_{elec} = \gamma T$, can be ignored.$^{12}$ Likewise, the hyperfine contribution, $C_{hyp} = z/T^2$, is very small above 2 K and can also be ignored.$^{19}$ LaMnO$_3$ is known as a typical A-type antiferromagnet, and the spin wave excitations could lead to an extra contribution to specific heat and give a $T^2$ term.$^{21}$ The contribution can also be understood to originate from the ferromagnetic and antiferromagnetic spin fluctuations.$^{22}$ According to the report of Woodfield et al., an A-type antiferromagnetic spin wave excitation will contribute to specific heat in the form of $C_{mag} = 0.058 k_B T^5 / D p D z$, where $D p D z$ is the spin wave stiffness coefficient.$^{21}$ In our study, this $T^2$ term contribution should be considered because Nd$_{1-x}$Er$_x$MnO$_3$ is also an A-type antiferromagnetic system. Therefore, the specific heat can be written in a simple way

$$C = C_{lat} + C_{mag}. \hspace{1cm} (3)$$

Considering the Schottky anomaly at low temperature, the final specific heat should be in the form of

$$C = C_{lat} + C_{mag} + C_{Sch}. \hspace{1cm} (4)$$

The Schottky anomaly comes from the ground state splitting of the rare earth ions Nd$^{3+}$ and/or Er$^{3+}$, and the corresponding specific heat contribution follows the expression:

$$C_{Sch} = R' (E/k_B T)^2 \exp(E/k_B T)/[1 + \exp(E/k_B T)]^2, \hspace{1cm} (5)$$

where $R$ is the ideal gas constant, $E$ is the splitting energy of ground state doublets, and $k_B$ is the Boltzmann constant.

Figure 3 presents the fitting results of representative samples with $x = 0$ and 0.2. The fitting results of other three samples are given in the supplementary material.$^{23}$ The fitting curves well match the experimental data, which is indicative of good fitting quality. It is found that the lattice and spin wave dominate the contributions to the specific heat at relatively higher temperatures. However, the Schottky anomaly plays a more important role at low temperature, especially below 15 K. The Nd$^{3+}$ ground state splitting of the sample with $x = 0$ is found to be 27.8 $k_B$, which is close to the Nd$^{3+}$ ground state splitting energy of 27.15 $k_B$ in powder NdCrO$_3$.\hspace{1cm} (25) However, this splitting is bigger than that found in single crystal NdMnO$_3$, in which the splitting is about 20 $k_B$.$^{13,25}$ The difference is probably due to the size effect, which has also been observed in Yb$_2$Ti$_2$O$_7$ (Ref. 26) and Gd$^{3+}$ doped SrCl$_2$,\hspace{1cm} (27) and can affect the crystal field. The splitting of the Nd$^{3+}$ ground state doublets decreases to

![Figure 1. Temperature dependence of $C_p/T$ for Nd$_{1-x}$Er$_x$MnO$_3$ for $x = 0$, 0.1, 0.2, 0.33, and 0.5.](121913-2Hongetal.Appl.Phys.Lett.101.121913(2012).)
23.25 \, k_B \, \text{when } x = 0.2, \text{ and to } 26.1 \, k_B \, \text{when } x = 0.5. \text{ The doping rate dependence of the Nd}^{3+} \, \text{ground state splitting energy, } E_1, \text{ is plotted in Figure 4(a), where it shows nonlinear behaviour. It is clear that the splitting energies are reduced after doping. We tentatively use a parabolic profile to fit the splitting energy curve, except for the data point of the sample with } x = 0.1 \text{ in Figure 4(a), and get an empirical formula}

\begin{align*}
E_1 &= 28 - 44.4x + 79.8x^2.
\end{align*}

After doping with Er^{3+}, the static Jahn-Teller distortion becomes stronger, which could induce enhancement of the crystal field, except in the case of \( x = 0.1 \). Meanwhile, the interaction between the Nd^{3+} \text{ and the Mn}^{3+} \text{ ions is significantly reduced, and the exchange field is consequently reduced. Accordingly, the Nd}^{3+} \, \text{ground state splitting energy decreases. This is primarily due to the reduced exchange field, which still plays a dominating role, rather than the enhanced crystal field. As the Er}^{3+} \, \text{doping rate } x \text{ increases to } 0.5, \text{ the enhanced crystal field exceeds the exchange field and induces a higher Nd}^{3+} \, \text{ground state splitting energy. Therefore, the competition between the exchange field and the crystal field determines the nonlinear doping rate dependence of the Nd}^{3+} \, \text{ground state splitting energy. For the sample with } x = 0.1, \text{ however, the enhanced ferromagnetic component of the Mn}^{3+} \text{ sublattice, corresponding to an enhanced exchange field, fails to induce stronger Nd}^{3+} \, \text{ground state doublet splitting. This anomalous splitting possibly stems from the significant lattice change compared with } x = 0.2 \text{ and } 0.33, \text{ which further confirms the competition between the crystal field and the exchange field.}

As for Er^{3+}, \text{ the ground state doublet splitting energies shown as } E_2 \text{ in Figure 4(b) are all quite close, around } 10 \, k_B. \text{ A tentative linear relation can be found}

\begin{align*}
E_2 &= 8.5 + 4.5x.
\end{align*}

Considering the competition between the exchange field and the crystal field found at the Nd^{3+} sites and assuming that a very similar crystal field applies to the Er^{3+} sites, this linear behaviour is then mainly dominated by a possible linear change in the crystal field rather than the exchange field. In this case, the interaction between Er^{3+} \text{ and Mn}^{3+} \text{ should be much weaker compared with that between Nd}^{3+} \text{ and Mn}^{3+}.\)
component induced by the Dzyaloshinsky-Moriya interaction. This anomaly is also the consequent result of the anomaly found in the magnetic entropy at $x = 0.1$ as shown in Figure 2(c).

In summary, the specific heat of the Er$^{3+}$ doped rare earth manganate NdMnO$_3$ has been systematically studied. There are two clear bumps in the temperature dependence of the specific heat: One is associated with the antiferromagnetic transition of the Mn$^{3+}$ sublattice, and the other is due to the Schottky anomaly because of the Nd$^{3+}$/Er$^{3+}$ ground state doublet splitting. The Nd$^{3+}$ ground state splitting energies show a nonlinear dependence on the doping rate. Both the molecular exchange field and the variations in the crystal field are responsible for the ground state doublet splitting, and their competition effect decides the nonlinear behaviour of the doping rate dependent Nd$^{3+}$ ground state splitting. The Er$^{3+}$ ground state splitting energy is linearly dependent on the doping rate, which is due to the dominance of the crystal field over the exchange field. The spin wave stiffness coefficient can be well fitted by a linear profile with a negative slope, except for the case of $x = 0.1$. These results provide a quasi-quantitative analysis to determine the relationship between the crystal field and the exchange field, and its effect on magnetic rare earth ions.

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.

23. See supplementary material at http://dx.doi.org/10.1063/1.4754613 for other fitting results.