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Interaction between the magnetic moments of the 3d and the 4f electrons in manganite, probed by Ga substitution

Langsheng Ling [a,*], Lei Zhang [a], Wei Tong [a], Zhe Qu [a], Li Pi [a,b], Yuheng Zhang [a,b]

[a] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[b] High Magnetic Field Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China

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ABSTRACT

The substitution of Ga for Mn in manganite $Nd_{0.6}Dy_{0.1}Sr_{0.3}MnO_3$ with a ferromagnetic (FM) ground state has been performed to study the influence of the Mn-sublattice magnetic ordering on the magnetic rare-earth sublattice. It is found that the substitution of Mn^{3+} with Ga^{3+} ions results in a sharp decrease of T_C, reflecting the reduction of the double-exchange interactions strength J_{Mn-Mn}. At the same time, a depinning effect of the rare-earth magnetic moment has been observed. This behavior unambiguously proves that the exchange interaction between Mn and rare-earth ions J_{Mn-R} strongly influences the rare-earth magnetic ordering at temperatures below T_C and stabilizes the rare-earth magnetic ground state.

1. Introduction

The manganites of $ABO_{0.3}$ type have attracted great attention from researchers due to fascinating properties, such as colossal magnetoresistance (CMR), charge-ordering (CO), and the applicability [1]. Decades of research have allowed us to completely understand the full range of ordered phases that occur in the $R_{1-x}A_xMnO_3$ perovskites (R=La, Pr, Nd and A=Ca, Sr, Ba) [2]. For samples with $x \leq 0.5$, a complex competition occurs between the ferromagnetic (FM), the paramagnetic (PM), and the antiferromagnetic (AFM) phases. In this regime, the inhomogeneous phase separation (PS) gives rise to the well-known colossal magnetoresistance effect [3–5]. Meanwhile, electron-doped manganites with $x \geq 0.5$ display orbital and charge-ordering with an antiferromagnetic ground state below the charge-ordering (CO) temperature T_{CO} [6,7].

The properties of manganites are not only sensitive to the manganese valency but also strongly affected by chemical factors, such as the average cationic radius $\langle r_A \rangle$ in the A-site [8–10] and the A-site cationic size mismatch [11,12], which is quantified by $\sigma^2 = \sum x_i r_i^2 - \langle r_A \rangle^2$ x_i is the fractional occupancy of A-site ions, and r_i is the corresponding ionic radius) [11]. For instance, when the hole concentration is kept constant in the Mn^{3+}-rich FM compositions, it has been shown that the decrease of $\langle r_A \rangle$ tends to diminish the Mn–O–Mn angle, which consequently reduces the bandwidth (W) and the Curie temperature T_C [9]. In contrast, a small $\langle r_A \rangle$ value is required for the appearance of CMR in the Mn^{4+}-rich manganites [13]. Finally, regardless of the $\langle r_A \rangle$ and the manganese valency, the increase of σ^2 tends to suppress both FM and AFM magnetic interactions and destabilizes the CO [11,12]. These behaviors show the great complexity of the relationships between the chemical factors ($\langle r_A \rangle$, σ^2, carrier nature, and concentration) and the magnetotransport properties of manganites.

The coupling within the rare-earth sublattices is antiferromagnetic and rather weak. In many cases, the rare-earth moments do not exhibit a long-range magnetic order (and if they do, the ordering temperatures are below 10 K) [14]. In manganite, the interaction between the magnetic moment of the rare-earth ions at the A-site and that of the Mn ions at the B-site is complicated. As for the Nd^{3+} ions, researchers found that in the $Nd_{0.7}A_{0.3}MnO_3$ (A=Ca, Sr, Ba, Pb) system, the manganese sublattice is ferromagnetic, and Nd^{3+} aligns parallel to the manganese, contributing an additional $\sim 1\mu_B$ to the total moment. This value is reduced from the free-ion value of $3.3\mu_B$ by the crystal field, which splits the ground state $^4I_{9/2}$ multiplet into five Kramers doublets [15,16]. However, using neutron powder diffraction, Fauth et al. found an antiparallel ordering of Mn and Nd magnetic moments in $Nd_{0.7}Ba_{0.3}MnO_3$ system [17]. Regarding the Gd^{3+} ions, Hemberger et al. have investigated the complex interplay of the 3d and the 4f magnetism in $La_{1-x}Gd_xMnO_3$ single crystals system. They found the magnetic moments of Gd are weakly antiferromagnetically coupled within the sublattice and are antiferromagnetically coupled to the Mn moments [18]. Snyder et al. have found that the rare-earth moments in $Gd_{0.67}Ca_{0.33}MnO_3$ order antiparallel to the manganese, giving rise to ferrimagnetism [19]. It was

* Corresponding author. Tel.: +86 551 5595619; fax: +86 551 5591149.
E-mail addresses: lsling@hmfl.ac.cn (L. Ling), zhangyh@ustc.edu.cn (Y. Zhang).

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suggested that the exchange coupling between the Gd^{3+} and the Mn^{3+}/Mn^{4+} sublattices tends to be antiferromagnetic in an $La_{0.7-x}Gd_xA_{0.3}MnO_3$ (A=Ca, Sr) system [20–22].

These observations revealed that the magnetic moment of the 3d and the 4f electrons can couple antiferromagnetically or ferromagnetically with one another. In this paper, we report the magnetization measurements on the substituted $Nd_{0.6}Dy_{0.1}Sr_{0.3}Mn_{1-x}Ga_xO_{0.3}$ (x=0, 0.02, 0.05, 0.1, 0.2) compounds. Mn^{3+} is substituted by its closest isovalent, but nonmagnetic Ga^{3+} ions to ensure minimal disturbance in the lattice and to effectively vary the double-exchange interaction between Mn ions J_{Mn-Mn} and, consequently, the exchange interaction between Mn and the rare-earth ions J_{Mn-R}. The substitution provides a platform to study the interplay between Mn and the rare-earth ions magnetic moment. We hope to understand the influence of B-site magnetism on the magnetic behavior of rare-earth ions at the A-site. The results show that, while keeping the same crystal structure for all compositions, Ga for Mn substitution leads to a sharp decrease of T_C, reflecting the intended decrease of J_{Mn-Mn}. At the same time, we observe a depinning effect of the rare-earth magnetic moment. This behavior confirms that the exchange fields J_{Mn-R} have a strong influence on the rare-earth magnetic ordering at temperatures below T_C and that they actually stabilize the rare-earth magnetic ground state.

2. Experiment

The polycrystalline $Nd_{0.6}Dy_{0.1}Sr_{0.3}Mn_{1-x}Ga_xO_{0.3}$ (x=0, 0.02, 0.05, 0.1, and 0.2) samples were prepared by a traditional solid-state reaction method [23]. Stoichiometric quantities of high-purity oxide of the rare-earth $Nd_2O_{0.3}$ and $Dy_2O_{0.3}$, $SrCO_{0.3}$, MnO_2, and $Ga_2O_{0.3}$ were thoroughly mixed and ground, then preheated at 1173 K for 24 h. With intermediate grinding, they reacted at 1473 K for 24 h. After the samples were pressed into pellets, a final sintering was carried out at 1573 K for 48 h. The structure and the phase purity of the prepared samples were checked with a powder X-ray diffraction (XRD) method using Cu K_α radiation at room temperature. The XRD pattern proves that the samples are at a single phase with the orthorhombic perovskite structure. Magnetization measurements were performed using a SQUID magnetometer (Quantum Design MPMS). The temperature dependence of the high field magnetization were measured in the VSM mode of a Physical Properties Measurement System (Quantum Design PPMS). The resistivity was measured with a standard four-probe method. The electron spin resonance (ESR) measurements were also carried out on the sample using a Bruker EMX plus 10/12 spectrometer at 9.40 GHz.

3. Results and discussion

Fig. 1 shows the temperature dependence of the magnetization, which was recorded during the warming-up processes with an applied field H=100 Oe under the zero-field-cooled (ZFC) and the field-cooled (FC) conditions. There is a sharp transition from a high-temperature paramagnetic state to a ferromagnetic one. Meanwhile, the Curie temperature is shifted down as the number of Ga^{3+} increases. With further decrease in the temperature, the ZFC and the FC magnetization curves start separating from each other noticeably, and a strong irreversibility (the difference between the FC and the ZFC magnetization) begins to develop. As the temperature decreases, the FC curves increase, but the ZFC curves decrease, resulting in an overall AFM-like behavior. This result implies that regardless of what causes the irreversibility, the anisotropy field, which freezes the spins, is not large.

Because the Mn-sublattice has been diluted, it is straightforward to interpret the changes involving Mn-magnetism. In the present doped system, the substitution of the nonmagnetic Ga^{3+} for the magnetic Mn^{3+} reduces the e_g electron density and consequently attenuates the double-exchange interaction between the Mn^{3+} and the Mn^{4+} ions, causing T_C to decrease. As shown in Fig. 1, T_C decreases dramatically from 230 K to 65 K indicating that the Ga^{3+} doping has a significant effect on the transition temperature. This is direct evidence of the effective reduction of the Mn–Mn interaction strength, J_{Mn-Mn}; thus, we suggest that J_{Mn-R} should be reduced. Most surprisingly, substituting Ga for Mn affects the anomalies in the FC curves below T_C: larger values of x corresponds to stronger increases of magnetization with a decreasing temperature below T_C. We suggest that the magnetization increase should be the development of rare-earth magnetic ordering.

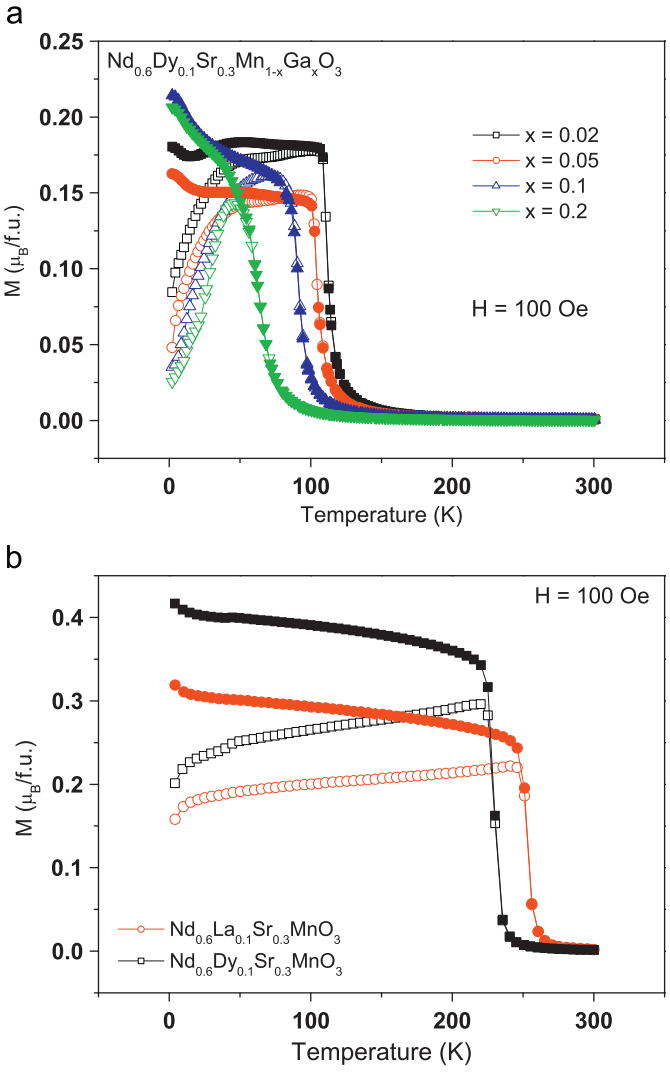

Fig. 1. Temperature dependence of the magnetization (ZFC empty symbol; FC solid symbol) for $Nd_{0.6}Dy_{0.1}Sr_{0.3}Mn_{1-x}Ga_xO_{0.3}$ (x=0.02, 0.05, 0.1, and 0.2) (a); $Nd_{0.6}La_{0.1}Sr_{0.3}MnO_3$ and $Nd_{0.6}Dy_{0.1}Sr_{0.3}MnO_3$ (b).

For the sake of comparison, the magnetization of $Nd_{0.6}La_{0.1}Sr_{0.3}MnO_3$ is also shown in Fig. 1. With the substitution of Dy^{3+} for La^{3+} ions, T_C decreases from 256 K to 230 K, while the magnetization increases by roughly $0.1\mu_B$, as estimated from the FC curve. The introduction of Dy^{3+} ions brings two effects: the smaller radius of the Dy^{3+} ions, which results in the decrease of $\langle r_A \rangle$, and the large local magnetic moment of the Dy^{3+} ions. Therefore, the decrease of $\langle r_A \rangle$ weakens the double-exchange interaction between the Mn ions and causes the decrease of T_C. Meanwhile, the local magnetic moments of the Dy^{3+} ions orient

parallel to the Mn-sublattice, increasing the total magnetic moment.

The micro-magnetism of the sample has been investigated through the ESR spectra, which is shown in Fig. 2. At the temperature above T_C, only the paramagnetic signals with $g \approx 2$ can be detected. When the temperature is lower than T_C, the resonance lines deviate from the standard shape for a paramagnetic signal, and the FM signals with $g > 2$ begin to manifest themselves at the lower resonance field. Finally, at the low temperature range, only small FM signals can be detected, and the resonance field decreases with decreasing temperature, which indicates that the PM phase transfers into the strong FM phase. The

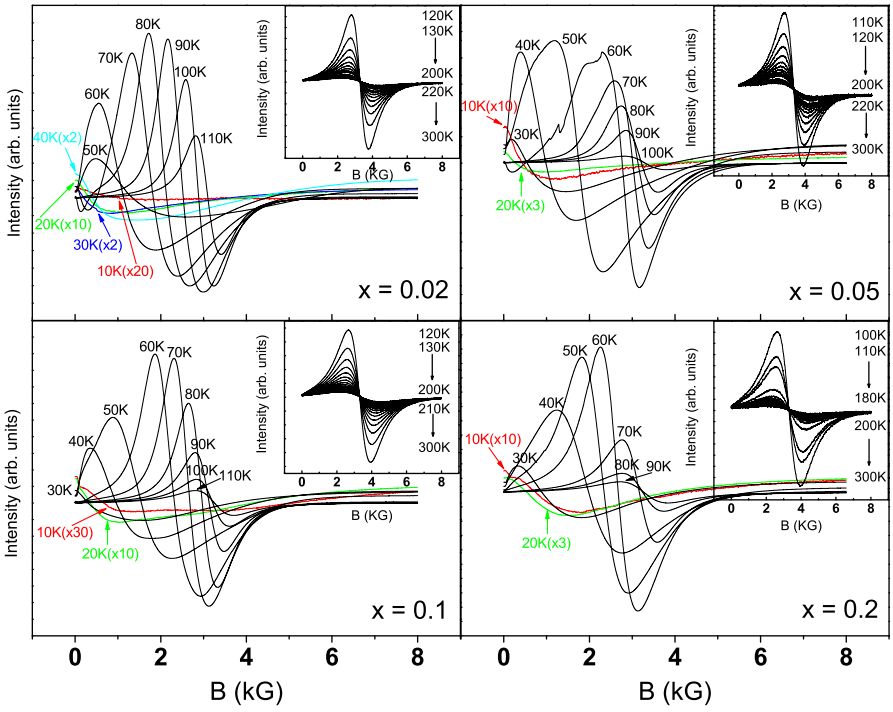

Fig. 2. Temperature dependence of the ESR spectra of $Nd_{0.6}Dy_{0.1}Sr_{0.3}Mn_{1-x}Ga_xO_{0.3}$ (x=0.02, 0.05, 0.1, and 0.2).

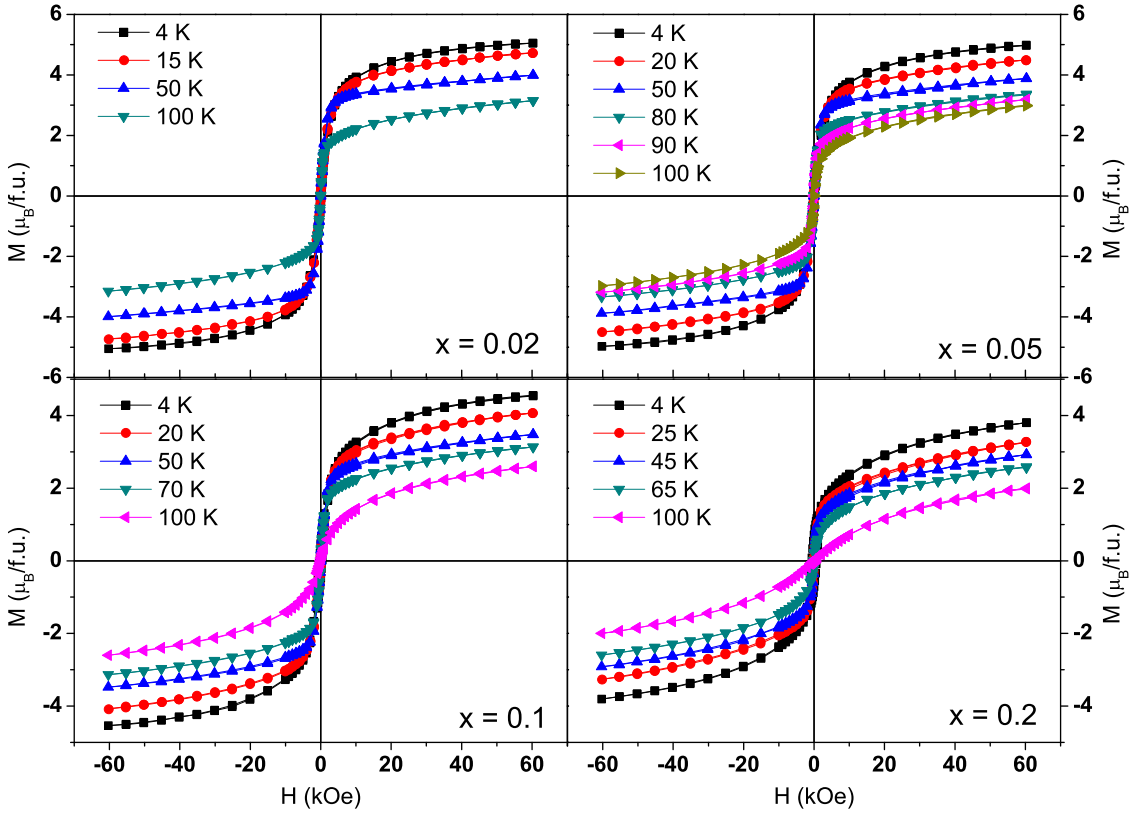

Fig. 3. Magnetic field response of the magnetization of $Nd_{0.6}Dy_{0.1}Sr_{0.3}Mn_{1-x}Ga_xO_{0.3}$ (x=0.02, 0.05, 0.1, and 0.2) measured under selected temperatures.

micro-magnetism behavior shown in the ESR spectra is consistent with the macro-magnetic behavior shown in the $M(T)$ curve.

We also studied the magnetic field response of the Ga-substituted compounds. Fig. 3 shows the isothermal magnetization curves as a function of the magnetic field for the doped samples. All curves show similar behaviors that exhibit a ferromagnetic characteristic below T_C. The magnetization increases significantly in the low field region (<5000 Oe), then it increases smoothly with the magnetic field. However, the magnetization does not become saturated in the highest field. At 4 K, the magnetization keeps increasing with the increasing field to quantities well above the value of the ordered moment of Mn^{3+} and Mn^{4+}. This result indicates that both the ferromagnetism of the Mn ions and the paramagnetism of the rare-earth ions contribute to the low temperature magnetization.

To probe the magnetic interaction between the 3d and the 4f electrons, the isothermal magnetization curves as a function of the magnetic field up to 16 T were measured at 4 K and 100 K. Fig. 4 shows that the magnetization is not saturated even at 16 T for both temperatures. A ferromagnetic manganese sublattice parallel to the rare-earth sublattice qualitatively explains the magnetization data. The obtained magnetization at 16 T and 4 K is $5.10\mu_B$, $4.98\mu_B$, $4.73\mu_B$, and $4.37\mu_B$ for the doped samples with $x=0.02$, 0.05, 0.1, and 0.2, respectively. However, these values are larger than the values derived from the full alignment of the magnetic moment of the Mn^{3+} and the Mn^{4+} ions ($3.62\mu_B$, $3.50\mu_B$, $3.30\mu_B$, and $2.90\mu_B$). The difference could come from the existence of the magnetic moment of rare-earth ions in addition to that of Mn^{3+} and Mn^{4+}. One notes that the magnetic moment of the free Nd^{3+} and Dy^{3+} ions are $3.5\mu_B$ and $10.6\mu_B$, respectively, and that the extracted value of the rare-earth ion moment $\sim 1.5\mu_B$ is rather low, which suggests that the rare-earth ion moments do not become fully ferromagnetically ordered at 16 T.

For the sake of comparison, the isothermal magnetization of $Nd_{0.6}La_{0.1}Sr_{0.3}MnO_3$ and $Nd_{0.6}Dy_{0.1}Sr_{0.3}MnO_3$ are also shown in Fig. 4. It can be observed that the magnetization behaviors of these compounds are similar to that of the Ga^{3+} doped samples. However, compared to the values of the Ga^{3+} doped samples, the high field slope in this case is smaller, and the extracted value of the rare-earth ion moment ($\sim 0.8\mu_B$) is about half. Why do the rare-earth ions show a stronger magnetism in the Ga^{3+} doped samples than in the parent compound? In the present system with the FM ground state, the coupling between the rare-earth ion moment and the Mn magnetic moments manifests itself below T_C, where the Mn-spin lattice polarizes the rare-earth magnetic sublattice. In the undoped samples, the Mn-sublattice establishes the FM coupling through the double-exchange interaction below the temperature T_C. This internal field acts on the magnetic moments of the rare-earth ions and polarizes it in the direction of the Mn-sublattice. It can be observed in Fig. 4 that the magnetization of the undoped samples increases sharply below 2 T and subsequently increases slowly with increasing magnetic field indicating that the magnetic moment of the rare-earth ions are polarized and pinned by the Mn-sublattice. Therefore, the magnetization is weakly dependent on the applied field in the high field region. However, in the Ga^{3+} doped samples, the high

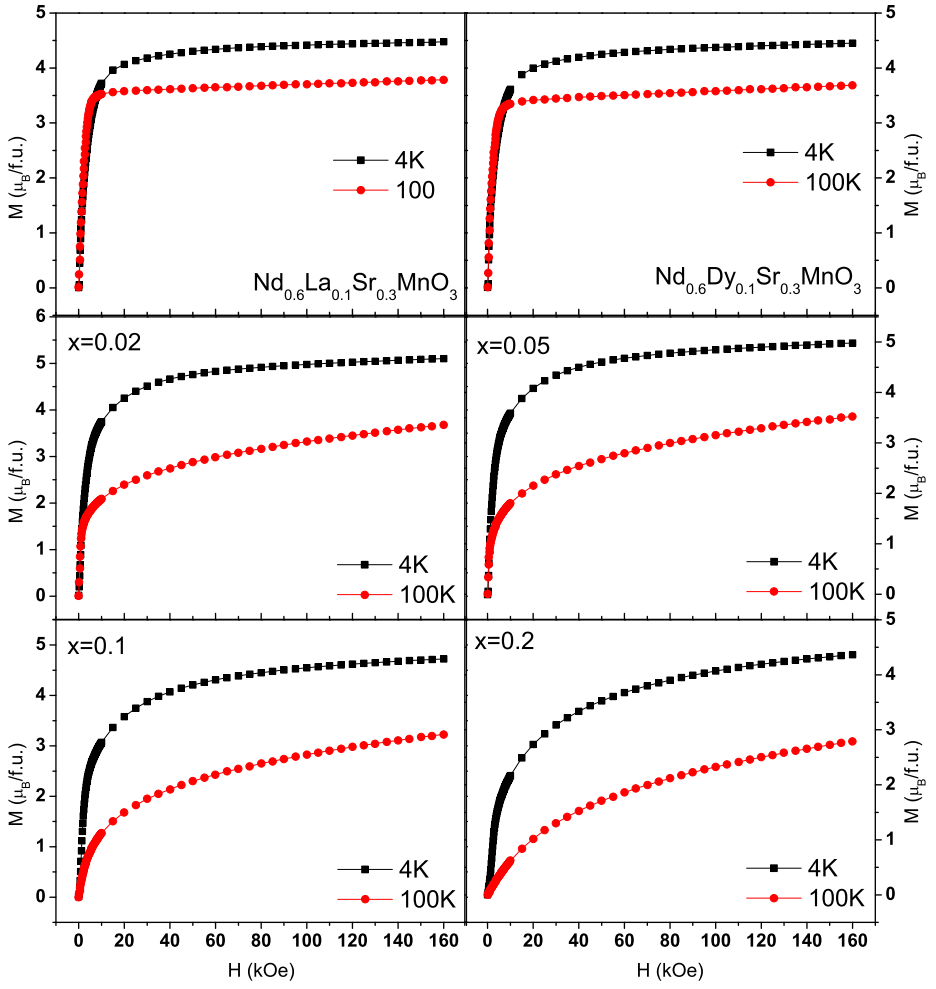

Fig. 4. Magnetic field response of the magnetization of $Nd_{0.6}Dy_{0.1}Sr_{0.3}Mn_{1-x}Ga_xO_{0.3}$ ($x=0.02$, 0.05, 0.1, and 0.2) measured under 4 K and 100 K.

field dependence of the magnetization is enhanced with the increase of Ga^{3+} content. As it was previously highlighted, the Mn–Mn interaction strength, J_{Mn-Mn}, is weakened by the doping of Ga^{3+}. One can conclude that the effective field acting on the rare-earth ion moments from the Mn-spin lattice is indeed reduced by Ga substitution. Consequently, the interaction strength between the Mn magnetic sublattice and the rare-earth magnetic sublattice, J_{Mn-R}, should also be reduced. Therefore, the pinning force, which affects the rare-earth ion moments in the Mn magnetic sublattice, is weakened, and the rare-earth ion moments show a PM-like behavior in response to the applied field. These results unambiguously show that J_{Mn-R} is an important ingredient for rare-earth magnetic ordering below T_C.

4. Conclusion

In this work, the influence of the Mn-magnetic ordering on the rare-earth magnetic sublattice is investigated experimentally in manganite $Nd_{0.6}Dy_{0.1}Sr_{0.3}MnO_3$ with an FM ground state by substituting Ga for Mn. The results show that the Ga for Mn substitution not only weakens the double-exchange interaction of the Mn-sublattice, which leads to a sharp decrease of T_C, but also significantly affects the rare-earth magnetic ordering. Our results confirm that substituting nonmagnetic ions for magnetic ions in one sublattice can change the magnetism in the other sublattices.

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References

[1] C.N.R. Rao, B. Raveau (Eds.), Colossal Magnetoresistance, World Scientific, Singapore, 1998.
[2] M.B. Salamon, M. Jaime, Rev. Mod. Phys. 73 (2001) 583;
J.M.D. Coey, M. Viret, S. von Molnar, Adv. Phys. 48 (1999) 167.
[3] S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, L.H. Chen, Science 264 (1994) 413.
[4] E. Dagotto, T. Hotta, A. Moreo, Phys. Rep. 344 (2001) 1.
[5] M. Fäth, S. Freisem, A.A. Menovsky, Y. Tomioka, J. Aarts, J.A. Mydosh, Science 285 (1999) 1540.
[6] J. van den Brink, G. Khaliullin, D. Khomskii, Phys. Rev. Lett. 83 (1999) 5118.
[7] P.G. Radaelli, D.E. Cox, M. Marezio, S.W. Cheong, Phys. Rev. B 55 (1997) 3015.
[8] R. Mahesh, R. Mahendiran, A.K. Raychaudhuri, C.N.R. Rao, J. Solid State Chem. 114 (1995) 297.
[9] H.Y. Hwang, S.W. Cheong, P.G. Radaelli, M. Marezio, B. Batlogg, Phys. Rev. Lett. 75 (1995) 914.
[10] A. Maignan, Ch. Simon, V. Caignaert, B. Raveau, Solid State Commun. 96 (1995) 623.
[11] L.M. Rodriguez-Martinez, J.P. Attfield, Phys. Rev. B 54 (1996) 15622.
[12] F. Damay, C. Martin, A. Maignan, B. Raveau, J. Appl. Phys. 82 (1997) 6181.
[13] A. Maignan, C. Martin, F. Damay, B. Raveau, Chem. Mater. 10 (1998) 950.
[14] J. Hemberger, S. Lobina, H.A. Krug von Nidda, N. Tristan, V.Yu. Ivanov, A.A. Mukhin, A.M. Balbashov, A. Loidl, Phys. Rev. B 70 (2004) 024414.
[15] R.M. Thomas, V. Skumryev, J.M.D. Coey, S. Wirth, J. Appl. Phys. 85 (1999) 5384.
[16] F. Millange, V. Caignaert, G. Mather, E. Suard, B. Raveau, J. Solid State Chem. 127 (1996) 131.
[17] F. Fauth, E. Suard, C. Martin, F. Millange, Physica B 241–243 (1998) 427.
[18] J. Hemberger, S. Lobina, H.A. Krug von Nidda, N. Tristan, V.Yu. Ivanov, A.A. Mukhin, A.M. Balbashov, A. Loidl, Phys. Rev. B 70 (2004) 024414.
[19] G.J. Snyder, C.H. Booth, F. Bridges, R. Hiskes, S. Dicarolis, Phys. Rev. B 55 (1997) 6453.
[20] Y. Sun, M.B. Salamon, W. Tong, Y. Zhang, Phys. Rev. B 66 (2002) 094414.
[21] H. Terashita, J.J. Neumeier, Phys. Rev. B 63 (2001) 174436.
[22] L.E. Hueso, J. Rivas, P. Sande, A. Fondado, F. Rivadulla, M.A. Lopez-Quintela, J. Magn. Magn. Mater. 238 (2002) 293.
[23] J. Fan, L. Ling, B. Hong, L. Zhang, L. Pi, Y. Zhang, Phys. Rev. B 81 (2010) 144426.