Influence of the Jahn–Teller distortion on magnetic ordering in $TbMn_{1-x}Fe_xO_3$*

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The Jahn–Teller distortion plays an important role in determining the exchange interaction in rare-earth manganites. In this work we study the influence of the Jahn–Teller distortion on the magnetic structures of $TbMn_{1-x}Fe_xO_3$ ($x = 0$, 0.02, 0.05, 0.10, and 0.20) single crystals in the basal MnO_2 plane. The decrease in the quadruple splitting with the increasing Fe doping indicates the reduction of the Jahn–Teller distortion, which makes the nearest neighboring (NN) FM interaction dominant over the next nearest neighbor (NNN) AFM interaction. This alteration is favorable for the development of A-type AFM ordering instead of the spiral magnetic ordering, which collapses when $x \geq 0.05$. The analysis of dielectric data indicates that the ferroelectricity is arising from the peculiar spiral magnetic ordering.

Keywords: quadruple splitting, Jahn–Teller distortion, spiral magnetic ordering

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1. Introduction

Magnetoelectric multiferroic materials have gained enormous interest in recent years due to their potential applications in low-power spintronics devices as well as magnetic field sensors, microwave and magneto-optical devices, etc. based on the mutual control of magnetism and ferroelectricity.[1] In the last few years, much work has been done in exploring both single-phased[2−4] and the design[5−7] of materials with large magnetoelectric couplings. However, the mechanism underlying the magnetoelectric coupling is still an open question. It is meaningful to study this issue in the single-phased magnetoelectric material due to the perfect homogeneity in both crystal structure and physical properties.

The $TbMnO_3$ compound is of an orthorhombic perovskite structure, which shows *Pbnm* symmetry with the $GdFeO_3$-type distortion.[8] The Mn^{3+} ions form an incommensurate antiferromagnetic (AFM) structure at 42 K (T_N). This magnetic structure varies with temperature and develops a spiral magnetic ordering in the *bc* plane below 27 K (T_C), which accompanies a ferroelectric order along the *c* axis. The mutual control of magnetism and ferroelectricity in $TbMnO_3$ was reported in the previous studies below T_C. A magnetic field of several Tesla can switch the ferroelectric polarization from the *c* axis to the *b* axis by rotating the spin-spiral structure from the *bc* plane to the *ab* plane.[9] Otherwise, the spin helicity, clockwise or counterclockwise, can also be controlled by the polarity of the external electrical field.[4] A microscopic model has been proposed for the magnetoelectric coupling based on the spin supercurrent[10] for the spiral magnets. However, the internal mechanism for the unique magnetic structure as well as the magnetoelectric coupling is still not well understood.

The Jahn–Teller effect is one of the central problems in perovskite rare-earth manganites, which results in the staggered $d^2_{3x} - r^2/d^2_{3y} - r^2$-type orbital ordering within the MnO_2 basal plane in $TbMnO_3$ due to the co-existence of $GaFeO_3$-type distortion. This orbital order produces FM and AFM interactions for the nearest-neighbor (NN) and the next-nearest-neighbor (NNN) Mn^{3+} ions, respectively, according to the Goodenough–Kanamori rule.[11] The spiral magnetic ordering in $TbMnO_3$ is well reproduced by the frustration model based on the competition between the above two interactions.[12] The double-exchange model can also realize the spiral magnetic order by including the Jahn–Teller distortion term.[13] As a comparison, the iso-structural $TbFeO_3$, which excludes the Jahn–Teller distortion with the Fe^{3+} (e_g) orbital half occupied, shows entirely different magnetic prop-

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erties. The AFM transition in $TbFeO_3$ occurs at a much higher temperature $T_N \sim 692$ K, which has a weak transverse FM component due to the slight canting of spins. At low temperatures, $TbFeO_3$ exhibits many reorientation transitions.[14,15] Therefore, it is meaningful to investigate the magnetic ordering and the magnetoelectric coupling by controlling the distortion in $TbMnO_3$ by doping with non-Jahn–Teller Fe^{3+} ions.

In this work, we study the effect of the Jahn–Teller distortion on magnetic and dielectric properties in Fe-doped $TbMnO_3$ single crystals. The Mössbauer spectroscopy is used to make a direct observation of the gradual variation of the Jahn–Teller distortion.

2. Experiment

A series of $TbMn_{1-x}Fe_xO_3$ ($x = 0$, 0.02, 0.05, 0.10, 0.20) single crystals were grown in four atmospheric-pressure argon by using the floating zone method. Powder X-ray diffraction measurements at room temperature confirmed that all compounds investigated had the *Pbnm* symmetry. Single crystals were oriented by Laue X-ray diffraction patterns and cut into plates for magnetic and dielectric measurements. The magnetization was measured on a commercial superconducting quantum interference device (SQUID). The temperature-dependent dielectric measurement was conducted using an NF ZM2353 LCR meter at a frequency of 10 kHz under an alternating current (ac) electric excitation with an amplitude of 1 V. Mössbauer spectra were recorded by a Wissel system constant acceleration Mössbauer spectrometer with a ^{57}Co source. The values of velocities and the central shifts were calibrated using an α-Fe foil at room temperature.

3. Results and discussion

Figure 1 displays zero-field-cool (ZFC) and field-cool (FC) thermal magnetization curves from 5 K to 100 K under a magnetic field of 5 kOe (1 Oe=79.5775 A/m) along the c axis. The incommensurate AFM and the spiral magnetic transitions are confirmed to occur at $T_C = 42$ K and $T_N = 27$ K for the parent compound, which are consistent with the previous studies.[9] In the case of the $x = 0.02$ compound, both transitions move to lower temperatures, i.e., 39 K and 24 K, respectively. However, the $x = 0.05$ compound only exhibits one anomaly at 33 K, the transition at the lower temperature is lost. As the doping content is further increased, no anomaly can be identified in the curves. Noticeably, the spin or cluster glass behavior is induced by Fe^{3+} doping when $x \geq 0.05$, which is inferred from the splitting between ZFC and FC curves at low temperature.

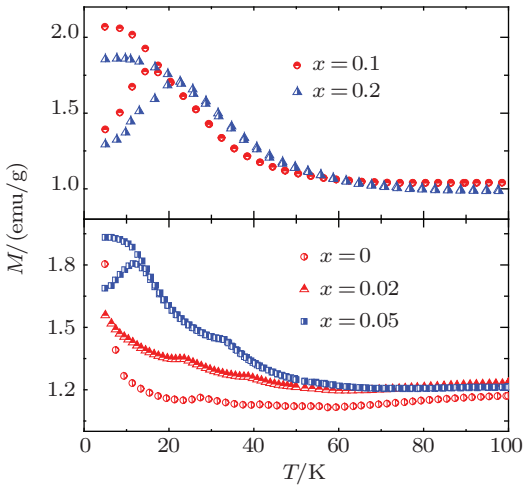


Fig. 1. (colour online) ZFC and FC thermal magnetization curves along the c axis for different Fe doping contents.

Due to the non-zero exchange field caused by $Mn(Fe)^{3+}$ subsystems with non-collinear magnetic structure, the Tb^{3+} moments in $TbMnO_3$ and $TbFeO_3$ compounds develop magnetic orderings at $T_N^{Tb} = 7$ K[16] and below 4.2 K,[17] respectively. Below T_N^{Tb}, a peculiar two-stage metamagnetic transition is trigged by the magnetic field along the b axis due to the spin reversal of the Tb^{3+} subsystem, which as a result causes the spin-reorientation of the Mn^{3+} subsystem.[9] Figure 2 displays the magnetization versus magnetic field along the crystallographic b axis for the doped compounds at 4 K. The two-stage metamagnetic transition remains when $x = 0.02$, blurs when $x = 0.05$, and disappears for higher Fe contents. We may infer from the collapse of the two-stage metamagnetic transition that the Fe-doped $TbMnO_3$ with $x \geq 0.05$ possibly develops a simple AFM structure instead of the spiral magnetic ordering, which is also observed in Na-doped $TbMnO_3$.[18]

The temperature-dependent dielectric behavior for $x \leq 0.05$ compounds along the c axis is displayed in Fig. 3. The dielectric anomalies, which indicate the ferroelectric transition, are observed in parent and $x = 0.02$ compounds. The anomalies appear in the vicinity of the spiral magnetic transition. We are therefore convinced that the ferrolectrictity arises

from the spiral magnetic ordering. However, no transition appears in the $x = 0.05$ compound, which reinforces our inference about the AFM magnetic ordering.

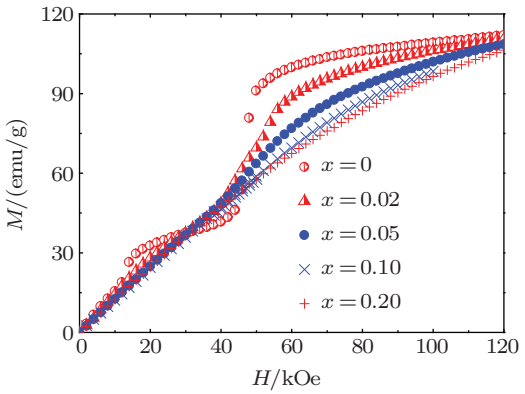


Fig. 2. (colour online) Initial magnetization curves for different Fe contents along the b axis at 4 K.

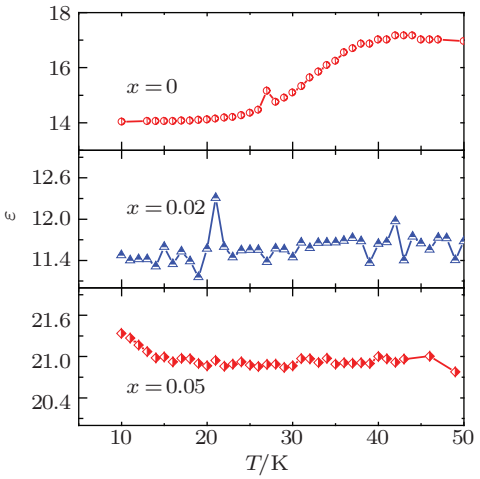


Fig. 3. The in-phase component of the dielectric permmitivity for $x \leq 0.05$ compounds.

Figure 4 shows the Mössbauer spectra for the $x \geq 0.05$ compounds at room temperature. A uniform doping will produce the identical chemical environment for Fe ions. However, the doping may produce slight Fe rich regions.[19] Consequently, we consider two possible chemical surroundings for Fe^{3+}. The data are fitted with two sets of Lorentzian curves. The fitted parameters are listed in Table 1 for clarity. The isomer shift spans the range of 0.221(35) mm/s–0.407(20) mm/s, which is typical for Fe^{3+}.[20] The linear relationship between the quadruple splitting and the Jahn–Teller distortion can be formulated as[21]

$$E_{\mathrm{JT}} = \frac{4\Delta(\mathrm{Fe}^{3+})}{7Q\left(1+\dfrac{\eta^2}{3}\right)^{1/2}} \left\langle r^2 \right\rangle_{3\mathrm{d}}, \qquad (1)$$

where E_{JT} is the energy degeneracy of e_{g} orbitals caused by the Jahn–Teller distortion, Q is the electric quadrupole moment of the ^{57}Fe nucleus, η is the asymmetry parameter, and r in $\left\langle r^2 \right\rangle_{3\mathrm{d}}$ is the radial distance of the 3d orbital from the nucleus. As seen in Table 1, the quadruple splitting decreases with the increasing Fe content for the dominant doublet, suggesting the reduction of the Jahn–Teller distortion.

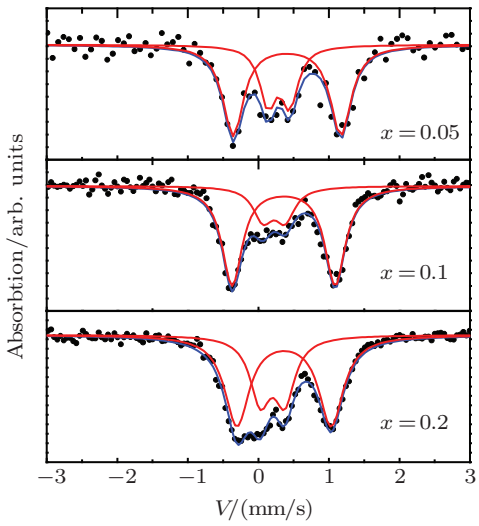


Fig. 4. (colour online) Mössbauer spectra for $x = 0.05$, 0.1, and 0.2 compounds. Both the fitting results and the experimental data are shown. The fitting parameters are listed in Table 1.

Table 1. Fitting parameters of Mössbauer spectra for the $x \geq 0.05$ compounds, where δ is the isomer shift, and Δ is the quadruple splitting.

Fe content (x)	δ/mm·s^{-1}	Δ/mm·s^{-1}	Spectral weight
0.05	0.407(20)	1.525(42)	66.7(10)
	0.292(33)	0.309(54)	33.3(76)
0.1	0.359(10)	1.460(21)	76.2(66)
	0.221(35)	0.311(57)	23.8(55)
0.2	0.374(13)	1.168(31)	78.1(88)
	0.252(34)	0.387(63)	21.9(71)

As reported in $DyMn_{1-x}Fe_xO_3$, the static orbital ordering will last until the Fe doping ratio reaches 20% due to the strong Jahn–Teller effect of Mn^{3+} ions.[22] As a result, a slight Fe doping in $TbMnO_3$ will effectively influence the strength of the exchange interaction without changing the sign. In order to analyze the alteration in the exchange interaction, we should know the detailed information about the structural change with doping. The LHPM–Rietica was used to fit the powder XRD diffraction data. The lattice parameters and bond information obtained from the fitting are shown in Figs. 5(a) and 5(b), respectively. The gap between the a-axis and b-axis lattice constants decreases with increased doping. The c-axis lattice constant is elongated. In Fig. 5(b), S_{13} and S_{24} are the unequal O–O bonds in the basal MnO_2 plane as denoted in Ref. [18], which result in the anisotropic NNN interaction through the Mn–O–O–Mn paths. This anisotropic NNN interaction is demonstrated to play a key role in maintaining the spiral magnetic ordering.[12] However, the difference between S_{13} and S_{24} is narrowed by the increasing Fe doping, as a result of which the anisotropy in the NNN interaction is weakened. On the other hand, the reduced Jahn–Teller distortion favors the NN FM interaction.[23] In this case, the spiral magnetic ordering collapses due to the destroyed balance between the NN FM interaction and the NNN interaction. Instead, the A-type AFM structure is favored like in the light rare-earth manganite.[24] As the Fe content reaches $x \geq 0.05$, the enhanced NN FM interaction results in FM clusters, which exhibit the glassy behavior demonstrated in Fig. 1.

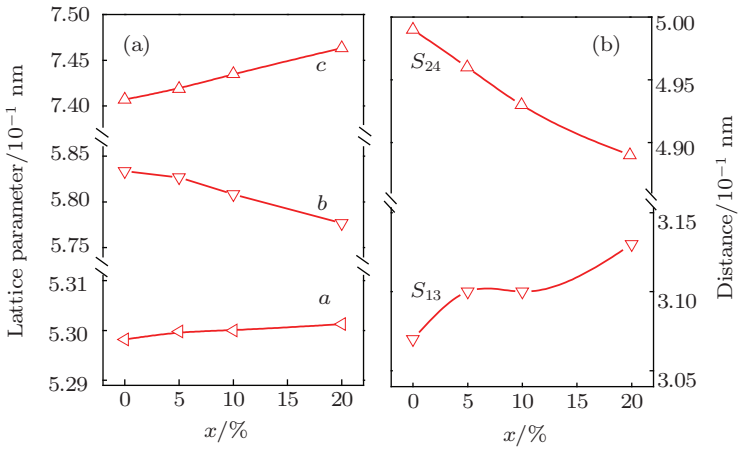


Fig. 5. (colour online) (a) Lattice constants and (b) unequal O–O bonds S_{13} and S_{24} each as a function of doping ratio.

4. Conclusion

In summary, the Jahn–Teller distortion is reduced by doping Fe^{3+} ions with a half occupied e_g orbital, which enhances the NN exchange interaction and weakens the NNN anisotropy in the basal MnO_2 plane. As a result, the spiral magnetic ordering is collapsed when $x \geq 0.05$. The ferroelectric ordering is confirmed to have arisen from the spiral magnetic ordering.

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