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SrFeO$_{3-\delta}$ belongs to the Ruddlesden-Popper class of systems exhibiting interesting electronic and magnetic properties. Ti^{4+}-doped, oxygen-deficient SrFeO$_{3-\delta}$ (SrFe$_x$Ti$_{1-x}$O$_{3-\delta}$; $x=0.9$ and 0.7) samples show canted antiferromagnetic spin ordering, in contrast to the undoped sample ($x=1$) which is known to exhibit a metallic behavior with a helical spin arrangement. ac susceptibility χ_{ac} (f,T) at $10 \leqslant T \leqslant 300$ K shows a frequency (100 Hz $\leqslant f \leqslant$ 10 kHz)-dependent temperature maximum, reminiscent of a spin-glass behavior. Increasing the Ti^{4+} content reduces the irreversibility, indicating a decrease in the frustration, which results in a diluted helical spin structure. Hysteresis loops can be associated with a gradual reorientation of spins in the field direction, indicating a canted type of spin arrangement. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2167050]

I. INTRODUCTION

The recent discovery of colossal magnetoresistance in aliovalent-doped LaMnO$_3$ has generated considerable interest due to their application potential in magnetic information storage and as read heads in computers.[1] Among the perovskites, SrFeO$_{3-\delta}$ has been under closer scrutiny due to the large negative magnetoresistance seen in its oxygen-deficient phases ($\delta \sim 0.15$).[2] SrFeO$_3$ is a helical antiferromagnet ($T_N = 134$ K) and has its propagation vector (Q) parallel to the crystallographic (111) plane.[3] SrFeO$_{3-\delta}$ ($\delta \sim 0.15$) is metallic at room temperature, and as $T \to 0$ K the metallicity increases with a sudden lowering in resistance around T_N, with samples showing a 20% change in magnetoresistance. Mössbauer spectra revealed the competing effects of paramagnetic (PM) and antiferromagnetic (AFM) interactions resulting in paramagnetic domains.[4] At $\delta > 0.15$, around the metal-insulator (MI) transition, a change of resistance up to 90% was observed in a field of 9 T. As $\delta \to 0.19$, a charge-ordered (CO) state appears around T_N, with a sharp rise in resistivity and hysteresis and a 90% positive magnetoresistance. These exotic properties are due to the disproportionation of Fe^{4+}/Fe^{3+} and spatial ordering.[2]

In a recent investigation on other oxygen-deficient samples of SrFeO$_{3-\delta}$,[5] we have identified compositions that lie on the boundary between MI and CO insulating states ($0.15 \leqslant \delta \leqslant 0.19$) and beyond $\delta > 0.19$. A strong frustration due to the competing FM and AFM phases of the helical structure is seen for the compositions $0.15 \leqslant \delta \leqslant 0.19$, which decreases as $\delta \to 0.19$. We also reported the observation of a high-temperature magnetic anomaly close to ~ 230 K.

It is possible to dilute helical structures seen in oxides such as SrFeO$_{3-\delta}$ by the use of pressure and strong magnetic field.[6] High pressures have been known to induce ferromagnetic ordering, breaking the helical spin arrangement and additional condition(s) which are the structural modifications of the unit cell. The modified exchanges could decrease the spin angle (Q), making the system a simple antiferromagnet. Such reduced complexity in the magnetic structure was earlier seen in Co^{3+}-doped SrFeO$_3$ (Ref. 7) and in others such as multiferroic BiFeO$_3$.[8]

It is the purpose of this paper to report on the possibility of inducing the collinear antiferromagnetism by introducing nonmagnetic ions into the lattice. A nonmagnetic ion such as Ti^{4+} helps reduce the complexity of the magnetic structure with a single magnetic ion, enabling a simpler understanding of the physics behind such transformations. We have also compared the results of the oxygen-deficient undoped SrFeO$_{3-\delta}$ with Ti^{4+}-doped systems. The results confirm that

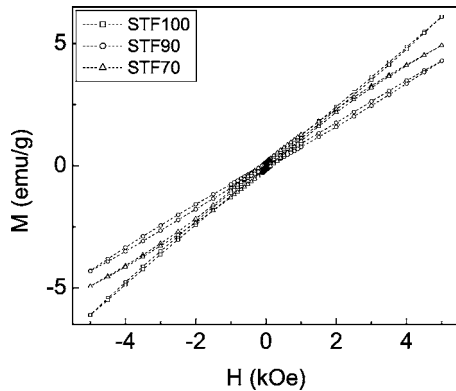[a)]Author to whom correspondence should be addressed; electronic mail: ssanyada@cas.usf.edu

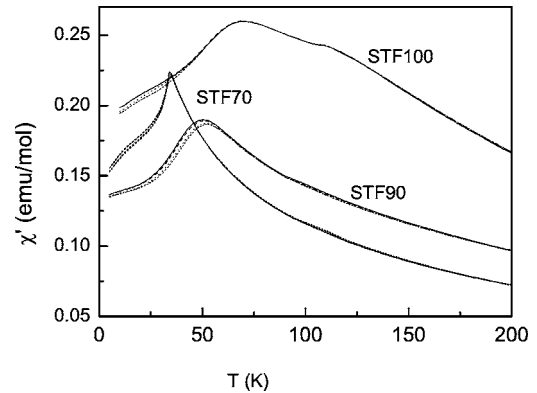FIG. 1. Hysteresis loops measured at 10 K for STF100, STF90, and STF70.

FIG. 2. ac magnetic susceptibility as a function of temperature for STF100, STF90, and STF70 measured at 500 Hz, 1 kHz, 5 kHz, and 10 kHZ from top to bottom.

Ti^{4+} addition to the lattice reduces frustration, making the structure simple antiferromagnetic at higher doping levels.

Earlier studies were only confined to identifying T_N and explaining the magnetic properties and did not attempt to investigate from the perspective of the helical spin structure dilution.[9] Our systematic ac and dc magnetic measurements clearly establish that Ti^{4+} doping indeed destroys the helical spin structure in $SrFeO_{3-\delta}$.

II. EXPERIMENT

Ceramic samples of $SrFe_xTi_{(1-x)}O_{3-\delta}$ [$x=1$, where x corresponds to the mole% of Fe (STF100) $x=0.9$ (STF90), and $x=0.7$ (STF70)] were prepared using solid-state reactions. Stoichiometric amounts of $SrCO_3$, Fe_2O_3, and TiO_2 were mixed thoroughly and fired in air at 900 °C (STF100) or at 1200 °C (STF70/90)for 4 h. These powders were pressed into cylindrical pellets (12×2 mm^2) in an isostatic pressure of 150 bars and were again sintered at 1400 °C for 2 h in flowing O_2 (STF100). In the case of STF70 and STF90, the pressure was applied uniaxially. Sintering was conducted for 3 h at either 1300 °C (STF70) or 1400 °C (STF90) in air. Phase identification was done using x-ray diffraction (XRD), which confirmed the presence of a single $SrFeO_{3-\delta}$ phase. Oxygen stoichiometry estimated using the thermogravimetry (TG) for STF100 is $\delta=0.205$.

χ_{ac} (f,T) and bulk magnetization (M_{dc}) both in zero-field-cooled (ZFC) and field-cooled (FC) conditions were measured using a physical property measurement system (PPMS model 6000, Quantum Design) at the temperature range of $10 \leqslant T \leqslant 300$ K, magnetic fields of $0 \leqslant H \leqslant 6$ T, and frequencies 10 Hz $\leqslant f \leqslant 10$ kHz.

III. RESULTS AND DISCUSSION

Figure 1 shows the *M-H* loops of STF100 and those of Ti^{4+}-doped samples, STF90 and STF70, measured at 10 K. For STF100, magnetization shows an increase with increasing field, and no saturation is seen even at fields as high as 50 kOe. This unsaturated linear-field-dependent loop is indicative of a system having helical antiferromagnetism. A 10 mole % addition of Ti^{4+} in $SrFeO_{3-\delta}$ (STF90) did not appear to change the magnetic structure significantly, and the *M-H* data continues to show a linear unsaturated loop. However, on further increase in Ti^{4+} content in STF70, a nonlin-

earity is observed at high fields, with enhanced magnetization as compared to STF90. This indicates that there are at least some spins that have saturated by aligning in the direction of the magnetic field, implying the onset of a collinear antiferromagnetic ordering.

The χ_{ac} (f,T) curves for STF100, STF90, and STF70 are shown in Fig. 2. In the case of STF100, χ_{ac} (f,T) increases gradually with increasing temperature, reaching a maximum T_{max} at 68 K (tetragonal T phase); another at 110 K is related to the cubic C phase.[2] An additional transition was observed at 230 K, a possible magnetic anomaly.[5] There is a small frequency dispersion to higher temperatures of the χ_{ac} at T_{max}, which indicates the presence of frustrated magnetic interactions strongly coupled to the exchange between neighboring spins.

The χ_{ac} (f,T) curves of STF90 and STF70, on the other hand, (Fig. 2), although they resemble that of STF100, show a frequency dispersion around the T_{max} that decreases with increasing Ti^{4+} doping. With increasing temperature, susceptibility increases gradually and reaches a maximum at 50 K for STF90 and 33 K for STF70. The broad maximum seen in STF100 and STF90 gives way to a sharp transition in STF70. The broad maximum and frequency dispersion in STF90, reminiscent of spin-glass systems, due to the increased impurity levels cannot sustain the strong forces that bind the helical spin structure. This causes the helical structure to break down, thus giving rise to a system with clusters that are antiferromagnetic. The absence of frequency dispersion and a sharp transition in STF70 could be due to the emergence of a simple antiferromagnetic phase. This also explains the nonlinearity seen for STF70 in the hysteresis loops (Fig. 1).

Figure 3 shows the ZFC and FC $M_{dc}(T)$ in the temperature range of $5 \leqslant T \leqslant 300$ K for STF100, STF90, and STF70 (bottom panel). For STF100, ZFC qualitatively shows all the features that are observed in the ac magnetic susceptibility with a broad maximum around 110 K. The most remarkable result is the divergence of FC and ZFC susceptibility at low temperatures ($\sim$45 K), below the T_{max} (68 K). Even though the high-temperature anomaly is not evident, its signature is clearly visible as a slope change in $1/\chi_{dc}$ versus temperature.[5]
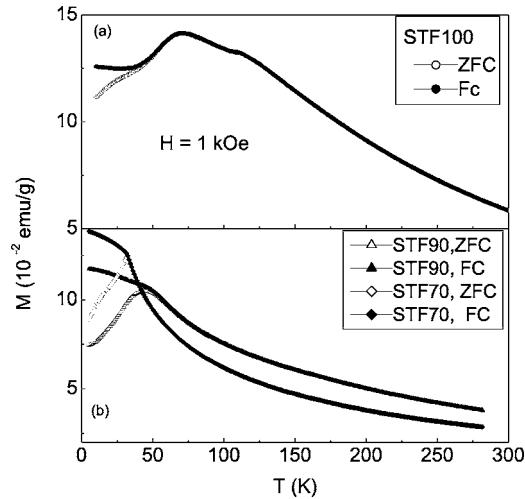
FIG. 3. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization measured at 1 kOe for (top) STF100, (bottom) STF90, and STF70.

TABLE I. Magnetic parameters of $SrFe_xTi_{1-x}O_{3-\delta}$ [$x = 1$, 0.9, 0.7].

Composition	μ_{eff} (μ_B)	θ_p (K)	T_{max}
$SrFeO_{3-\delta}$ (STF100)	4.90	20	68.0
$SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ (STF90)	4.36	−53	45.5
$SrFe_{0.7}Ti_{0.3}O_{3-\delta}$ (STF70)	3.75	−49.7	32.0

The ZFC curves of Ti^{4+}-doped samples resemble that of STF100, reaching maxima at ∼50 K (STF90) and at ∼33 K (STF70). In the case of FC, the susceptibility decreases right from the lowest temperature and merges with the ZFC curve at T_{max}. The high-temperature anomaly seen in STF100 is not prominent in either STF90 or STF70. The bifurcation of the ZFC and FC data clearly indicates the presence of magnetic frustration in the sample, albeit reduced with increasing Ti^{4+} content. The decrease in the broadness of the peak with increasing Ti^{4+} itself is indicative of the reducing frustration in the system. This could be a result of the melting of the cycloidal spin arrangement. The melting of the helical spin arrangement allows spins to move freely in the direction of the applied magnetic field, as in the case of STF70, giving rise to a reduced frustration. The observed nonlinearity in the hysteresis loops of STF70 confirms this assumption, where the antiferromagnetically aligned spins on the neighboring ions are not perfectly 180°. This gives rise to canting of at least some of the spins, which are forced by the magnetic field to turn to its direction.

The high-temperature paramagnetic data at $T > 230$ K for all the samples fit well in the Curie-Weiss law. The fit gives an effective magnetic moment (μ_{eff}) of $4.9\mu_B$ and a paramagnetic Curie temperature (θ_p) of 20 K for STF100, which is close to the spin-only value of Fe^{4+}. In this case, a dominant contribution to the magnetic properties arises from Fe^{4+}. With the addition of Ti^{4+}, however, μ_{eff} gradually decreases from the spin-only value of Fe^{4+}, from $4.9\mu_B$ in STF100 to $4.36\mu_B$ in STF90 and to $3.75\mu_B$ in STF70. The negative θ_p values, −53 and −49 for STF90 and STF70, respectively, indicate predominant antiferromagnetic exchange interactions (Table I), which are different from those seen by Adler and Eriksson.[9] This unexpected and intriguing result can be explained because of the interaction between Fe^{4+} [high spin (HS)]−O−Fe^{4+} [low spin (LS)], on one hand, and Fe^{4+} (HS)−O−Fe^{3+} (LS), on the other. There are several perovskites such as $CaFeO_3$ with Fe^{4+} which transform into a LS state from a HS state as a function of pressure and temperature.[10] Further investigations in this direction using x-ray photoemission spectroscopy, neutron diffraction, and Mössbauer spectroscopy are underway.

In conclusion, it can be said that the spiral spin arrangement in $SrFeO_{3-\delta}$ could be melted by the addition of a nonmagnetic cation such as Ti^{4+} in varying proportions. The results also point to the presence of Fe^{4+} in its LS state, making it one of the few perovskites where such magnetic interactions can be found.

ACKNOWLEDGMENTS

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