Magnetic field-induced switching of magnetic ordering in SrFeO$_{3-\delta}$

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Abstract The oxygen-deficient strontium iron oxide SrFeO$_{3-\delta}$ (SFO) exhibits richness in the phase diagram over a broad range of temperatures and for other external parameters. Room-temperature X-ray diffraction and Raman spectrum reveals that the structure of synthesized SFO system consists of two mixed phases, i.e., major orthorhombic and minor tetragonal phases. The low-temperature Raman and vibrating sample magnetometer measurements indicated a structural transition below 253 K. The magnetic property of the synthesized SFO for various external magnetic field (up to 5 T) reveals possible variation in oxygen stoichiometry. Also, the application of external $H$ increases Neel transition temperature ($T_N$), suppresses the hysteresis width ($W_H$), and thus weakens the first-order nature of the transition. Our analysis revealed the vanishing of hysteresis and the first-order antiferromagnetic transition becomes a crossover above a critical magnetic field $H_{CR} \approx 5$ T. Possible switching of magnetic ordering and oxidation state observed in same system enhances interest in related compounds which may be used in magnetic sensors and other magnetic switching devices.

1 Introduction

The perovskite oxides of the chemical form ABO$_3$, where A and B are cations, exhibit a host of interesting physical phenomena. Generally, the magnetic properties of strongly correlated transition metal oxide (TMO) compounds are closely related to the oxygen vacancies present in the system [1]. In this queue, oxygen-deficient strontium ferrite has been under examination for more than few decades, but still there are quite a lot of open problems for investigations. The unusual valence of Fe$^{4+}$ and Fe$^{3+}$ in SrFeO$_3$ along with oxygen deficiency as a result of homovalent doping is the reason for their interesting physical properties. So far, many studies have been made on the non-stoichiometric SrFeO$_{3-\delta}$ to stoichiometric SrFeO$_3$ systems [2].

Stoichiometric SrFeO$_3$ with cubic phase exhibiting metallic conductivity has Fe in rare valence of 4+ with high spin state [3]. It is a helical antiferromagnet with Neel transition at 130 K. The conversion of some of Fe$^{4+}$ ions into Fe$^{3+}$ ions and the resulting oxygen vacancies induce change in crystal structure from cubic to brownmillerate via tetragonal and orthorhombic in SrFeO$_{3-\delta}$ ($\delta > 0$). Depending on the deviation from their oxygen stoichiometry, it takes tetragonal ($\delta = 0.13$), orthorhombic ($\delta = 0.27$), and brownmillerite ($\delta = 0.5$) phases [4–7]. Any intermediate composition results in a mixture of two neighboring phases [8]. The compound in its defect state is so sensitive that even 1 % oxygen vacancy affects the metallic behavior and leads to semiconducting nature [4–8]. The magnetic phase diagram of SrFeO$_{3-\delta}$ is also much richer, and the enhancement of magnetic phases generated by oxygen vacancies in SrFeO$_{3-\delta}$ is interesting [9]. Li et al. [10] proved that the SrFeO$_3$ exhibits external field-induced ferromagnetism with $\sim 3.5$ $\mu_B$/Fe, which is basically antiferromagnetic system.
is well known that a perturbation such as magnetic field (H), pressure (P), irradiation, and substitution may change the physical properties dramatically or induce a phase transition [11–13]. Sarkar et al. [12] demonstrated that the controlling oxygen stoichiometry is a way of controlling the physical properties. Similarly, with the application of magnetic field, the nature of temperature dependence of lattice strain changes dramatically [13]. Although several reports are there to prove SrFeO$_{3-\delta}$ system is both pressure and defect sensitive, the reports on field-induced ordering of oxygen vacancy and its changes in magnetic properties are scare [10, 14, 15]. In this work, we prepared polycrystalline SrFeO$_{3-\delta}$ by solid-state reaction method to explore its magnetic properties under the influence of both external magnetic field (up to 5 T) and temperature (300–50 K).

2 Experiment details

SrFeO$_{3-\delta}$ powder was prepared by solid-state reactions from the starting materials of SrCO$_3$ and Fe$_2$O$_3$. The starting materials were weighed, thoroughly mixed with the help of agate mortar and pestle, and the mixed powders were fired at 1173, 1223, and 1273 K with intermediate grindings. The powders fired at 1273 K were grounded and pressed into pellets of 10 mm diameter. The pellets were sintered at 1473 K in flowing oxygen atmosphere. The phase purity of the prepared sample was examined by powder X-ray diffraction (PXRD) using X’Pert PRO PANalytical X-ray diffractometer with Cu-K$_\alpha$ radiation of $\lambda = 1.5418$ Å from 2$\theta = 10^\circ$ to 70$^\circ$ with a step size of 0.025$^\circ$. The Raman spectra were collected using a Renishaw InVia Reflex spectrometer having a 50 mW equipped with CCD camera. Green laser line (\(\lambda = 514.532 \text{ nm}\)) of Ar laser was used for the excitation in back scattering geometry. Magnetization measurements were carried out using a VSM with physical property measurement system. Quantum Design from the temperature range of 300–50 K and the magnetic field up to 5 T.

3 Results and discussion

The powder X-ray diffraction (PXRD) pattern of a sample sintered at 1473 K shown as Fig. 1a shows the reflection planes (1 1 0), (1 1 1), (2 0 0), (2 1 1), (2 2 0) and (3 1 0). The enlargement of diffraction peaks shown as Fig. 1b reveals that there is a splitting in (1 1 1), (2 2 0) and (3 1 0) peaks, which indicates the presence of possible lower symmetry with major orthorhombic phase. Further, the presence of diffraction peak (1 1 0) indicates the presence of tetragonal phase [3, 16, 17]. Due to the unusual valence state of Fe, some Fe$^{4+}$ reduces to Fe$^{3+}$ to maintain the charge neutrality leading to oxygen vacancy. This induces considerable strain in the lattice, making the structural transformation toward possible lower symmetry.

Raman spectrum shown in Fig. 2a is in agreement with the assumption that mixed phase exists in SrFeO$_{3-\delta}$. It is noted that a cubic perovskite structure has no Raman active modes [18, 19]. Indeed, our mixed-phase sample has peaks at 130, 220, 330, 430, and 620 cm$^{-1}$ as shown in Fig. 2a. Factor group analysis on tetragonal phase SrFeO$_{2.85}$ revealed 31 Raman active modes out of which 11 are doubly degenerated [18, 19]. However, experimental room-temperature Raman spectrum of tetragonal phase exhibits only three modes around 130, 330, and 430 cm$^{-1}$ out of the 31 active modes and at lower temperature several weak intense Raman bands appeared [18, 19]. Further, the factor group analysis on orthorhombic phase Sr$_4$Fe$_4$O$_{11}$ indicated 21 non-degenerate Raman active modes. Earlier Raman studies on the orthorhombic phase SrFeO$_{2.75}$ indicated very strong Raman peak at around 330 cm$^{-1}$, medium strong at 430 cm$^{-1}$, medium intense band at 620 cm$^{-1}$ and sharp weak band at around 220 cm$^{-1}$ [18, 19]. In addition to these major peaks, minor bands were appeared from 50 to 200 cm$^{-1}$. Interestingly, the temperature-dependent Raman spectra measured from the temperature range 4–300 K for the orthorhombic phase showed no major structural transition [17].

The presence of Raman peaks at 130, 220, 330, 430, and 620 cm$^{-1}$ in the room-temperature Raman spectrum of the investigated sample indicates the mixture of major orthorhombic and minor tetragonal phase. In order to study the eventual change of the crystal structure at temperature below 300 K, we performed low-temperature Raman measurements on the prepared polycrystalline sample, and the recorded temperature-dependent Raman spectra are shown in Fig. 2b. This indicates major shift in the 330 and 430 cm$^{-1}$ at below 253 K. The shift in the Raman bands, broadening, and disappearance of the Raman band at 220 cm$^{-1}$ implement the possible transition at around 253 K.

Figure 3 shows the temperature-dependent magnetization of SrFeO$_{3-\delta}$ measured for different magnetic fields from 0.01 to 5 T in field cooling and heating runs. Our low-field magnetization result confirms the composition is approx nearer to SrFeO$_{2.73}$, which exhibits major orthorhombic phase at room temperature [16]. Cubic-to-orthorhombic distortion with a strong split in the reflections is reported to occur for $\delta = 0.27$ (SrFeO$_{2.73}$) and matches with our PXRD result [16, 17]. For 0.01 T, the onset of antiferromagnetic order with thermal hysteresis at 70 K ($T_{N1}$) is observed together with a small cusp of the susceptibility at 235 K ($T_{N2}$). With the increase in field, the 235 K transition disappears and the 70 K transition slowly moves toward the higher temperature with the reduction in
hysteresis width. Further, for high field (5 T), there is no visibility of thermal hysteresis as shown in Fig. 3.

Application of higher magnetic field increases the order of the magnetic transition with a reasonable shift toward higher-temperature regime. The application of $H$ increases $M$ and shifts $T_{N1}$ toward the higher temperature at the rate of 3 K/T (Fig. 3). The width of the thermal hysteresis at $H = 0.01$ T is about 1.5 K, which narrows progressively with increasing $H$ and completely disappears at a critical field of 5 T (Fig. 4). The width of the thermal hysteresis in $M$ gradually decreases with $H$ and the heating–cooling curves merges to one another at a critical field, $H_{CR} = 5$ T with the corresponding critical temperature ($T_{CR}$) is 120 K (Fig. 4).

In the region between warming and cooling cycles, the magnetic state of the system is determined by the way through which the sample arrives at this region, i.e., by the increase or decrease in temperature. This confirms that the investigated SrFeO$_{2.75}$ has a critical end-point $H_{CR}$ of 5 T at 120 K, which indicates the crossover from first-order AFM transition ($T_N$) to second-order AFM transition as shown in Fig. 4. Close-field observations are needed to find out the exact critical field with more precision.

By comparing the temperature-dependent magnetization results (Fig. 3) with the reported results [20–24] elucidates that our 0.01 T data match with the SrFeO$_{2.75}$ and our 5 T data match with the SrFeO$_{2.85}$. From this observations roughly, we can summarize that applied magnetic field plays the role of change in possible oxygen stoichiometry in SrFeO$_{3-d}$. Further, Adler et al. [21, 23] also observed a hump around 235 K for SrFeO$_{2.75}$ sample which is well matched with our 0.01 T result, and it corresponds to the orthorhombic phase. However, further investigations needed to confirm this precisely. Our present investigation indicates that possible magnetic field-induced structural phase change starting from orthorhombic (SrFeO$_{2.75}$ for 0.01 T) to tetragonal phase SrFeO$_{2.85}$ with higher magnetic field. Also, the field increment reduces the thermal hysteresis width toward zero confirming the collapsing of orthorhombic phase at 5 T. Similar behavior is observed in
manganites and especially in Sr-based manganite, i.e., Sm_{0.52}Sr_{0.48}MnO_3 \cite{11}. By applying external magnetic field or pressure or by doping, the magnetic transition becomes second order in nature, or it becomes a crossover \cite{13, 25}. This behavior is considered to result from the transition from an antiferromagnetic spin structure to a canted spin structure induced by the applied magnetic field. However, SrFeO_{3-δ} undergoes a canted metamagnetic or a spin-flop mechanism, in which the spins, initially antiferromagnetically ordered, tend to align parallel to the applied magnetic field. These doubled the order of the magnetic moment by increasing applied magnetic field.

Mossbauer measurements of earlier reports show that SrFeO_{2.73} contains Fe ions both in +3 and +4 oxidation states in equal proportions \cite{3, 26–28}. It was shown that the Fe^{3+} sublattice is magnetically ordered below the Neel temperature of around 230 K, while Fe^{4+} remains disordered down to the lowest measured temperatures. Further, the transition at 70 K is due to the presence of Fe^{4+} sublattices (tetragonal phase). The AFM transition at 70 K is more pronounced compared to the 230 K transition due to the Fe^{3+} ions being masked by Fe^{4+} ions from 230 K onwards. Both 70 and 230 K transitions are present at low field confirms that the two mixed phases are present in our

Fig. 2 a) Room-temperature Raman data of SrFeO_{3-δ}. b) Low-temperature Raman data for different temperature varies from 130 to 403 K.

Fig. 3 Magnetization versus temperature M(T) results for various magnetic fields from 0.01 to 5 T shows the suppression of thermal hysteresis due to induction of Fe^{4+} ions by increasing magnetic field.

Fig. 4 Hysteresis width (W_H) and T_N versus H phase diagram.

Strong coupling transitions at low field confirms that the two mixed phases are present in our
composition which reflects our XRD and Raman observations. Further increase in field suppresses the orthorhombic phase and made the domains more Fe\(^{3+}\) (tetragonal). In a tetragonal crystal field, the degenerate 3d state of Fe\(^{3+}\) ion splits into relatively narrow four doublet states, and the energy splitting was estimated as about 70 K. There is thus the possibility of mixing energy levels and implementing field-induced conversion of Fe\(^{3+}\) to Fe\(^{4+}\) ions associated with the suppression of magnetic transition in a high-magnetic-field regime. It is clear that external magnetic field induces more Fe\(^{4+}\) ions and switches the system from orthorhombic to tetragonal structure (major orthorhombic + minor tetragonal to major tetragonal + minor orthorhombic) as shown in Fig. 3. Also, the inducing Fe\(^{4+}\) ions by external magnetic field transit the SFO system from first-order to second-order magnetic transition. Switching of oxidation states from Fe\(^{3+}\) to Fe\(^{4+}\) takes places in both temperature and magnetic field. These structural switching and magnetic order switchings by external magnetic field and temperature suggest the possibility of controlling lattice parameters by external perturbations. Several studies have shown the strong dependence of properties on external \(H\) and suggest that the magnetic and structural order parameters are coupled to each other [29, 30].

4 Conclusion
We investigated the effect of magnetic field and temperature on the nature of antiferromagnetic phase transition of SrFe\(_{3-x}\)O\(_3\) system. The strong hysteretic behavior of magnetization with temperature and the decrease in the value of magnetization below 70 K (\(T_N\)) suggest that the AFM transition is discontinuous first order in nature. Increasing external magnetic field increases \(T_N\) and suppresses the first-order character of the transition. We have identified a critical end-point of the first-order AFM transition and is given approximately by \(H_{CR} = 5\) T and \(T_{CR} = 120\) K. From our results, we found that the system exhibits changes in the order of magnetization with the increase in magnetic field. The observed relation is not reported yet in this class of ferrites. It is found to be very new for SrFe\(_{3-x}\)O\(_3\) perovskite, and it opens up a broad range of possible applications with temperature and magnetic field as controlled parameter. However, further detailed in situ structural studies are essential to understand the nature of mixed phases and the origin of the observed properties.

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References
25. M. B. Salamon, M. Jaime, Rev. Mod. Phys. 73, 583 (2001)