Magnetic short and long range order in a disordered perovskite

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PbFe\(_{1/2}\)Ta\(_{1/2}\)O\(_3\) belongs to the family of PbB\(_x\)B\(_{1-x}\)\(_3\)O\(_4\) which have inherent chemical disorder at the B-site. Due to this disorder, a complex magnetic phase diagram is expected in the material. In this paper, we report experimental results of magnetic properties in PFT through macroscopic characterization, neutron scattering and Mössbauer spectroscopy techniques. With these results we show for the first time that PbFe\(_{1/2}\)Ta\(_{1/2}\)O\(_3\) behaves very similar to PbFe\(_{1/2}\)Nb\(_{1/2}\)O\(_3\), i.e, it undergoes AF transition at 153 K and has a spinglass transition at 10 K, below which the antiferromagnetism coexists with spinglass. We believe that the mechanism which is responsible for such a non-trivial ground state can be explained by a speromagnet-like spin arrangement similar to the one proposed for PbFe\(_{1/2}\)Nb\(_{1/2}\)O\(_3\).

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I. INTRODUCTION

Studies of disordered materials have gained interest due to novel phases and phase transitions they exhibit.\(^{11\text{-}13}\) \(\text{AB}_x\text{B}_1-x\text{O}_3\) are complex perovskites which have inherent disorder at the B-site resulting in unusual properties. In particular, magnetic ion dilution at the disordered B-site leads to rich magnetic phase diagram and magnetic ground states ranging from simple antiferromagnet to incommensurate structure.\(^4\) Furthermore, spinglass properties have also been reported in some of the complex disordered perovskites.\(^5\) More recently, our studies of the disordered antiferromagnet PbFe\(_{1/2}\)Nb\(_{1/2}\)O\(_3\) (PFN ) demonstrated that long range antiferromagnetic order can co-exist with a spinglass state on the microscopic scale.\(^6\) Our model for this novel phase involved canting of \(\text{Fe}^{3+}\) moments. What remained unclear is whether the essential ingredients for such spin arrangement is disorder and magnetic dilution themselves or the particular magnetic ion at the disordered site. Previous studies of Pb(Fe\(_{1/2}\)Nb\(_{1/2}\))\(_{1-x}\)Ti\(_x\)O\(_3\) suggested that magnetic properties are indeed strongly affected by the type of non-magnetic ion present in the lattice.\(^{10}\) In the present work we make the next logical step, focusing on the fully substituted stoichiometric lead iron tantalate, PbFe\(_{1/2}\)Ta\(_{1/2}\)O\(_3\) (PFT ), a close relative of PFN considering the similarities in chemical properties of Ta\(_{5+}\) and Nb\(_{5+}\) ions. The chemical structures of both materials are essentially identical.\(^{11\text{-}12}\) Despite the strong structural similarities, magnetic properties of PFT are not very well understood in contrast to the generally accepted antiferromagnetic (\(\sim143\) K) and spinglass (12 K) transitions in PFN.\(^{11\text{-}13}\) One problem of PFT is that the temperatures where anomalies, indicative of magnetic transitions, appear in the \(dc\) magnetic susceptibility are strongly sample dependent. For example, various sources report anomalies in \(dc\) magnetization in the range of 130-180 K,\(^{15\text{-}19}\) signaling a transition into AF phase. Nonetheless, this transition is confirmed by the appearance of AF Bragg peak in neutron diffraction,\(^{20}\) suggesting a simple G-type structure with \(\sim3\mu_B\) magnetic moment per \(\text{Fe}^{3+}\) ion at base temperature.\(^{20}\) However, first principle calculations of the electronic structure of PFT suggest possibility of a second AF transition at 48 K which is claimed to be observed experimentally at \(\sim55\) K by Martinez et al.\(^{12}\) In addition, the \(dc\) susceptibility results show a maximum in ZFC data around 9 K which exhibits properties of a spinglass transition.\(^7\) Overall, there is uncertainty in the number and types of magnetic phases in PFT.

In the present work we seek to sort out the magnetic phase diagram of PbFe\(_{1/2}\)Ta\(_{1/2}\)O\(_3\). For this purpose, we employ bulk magnetization, neutron scattering and Mössbauer spectroscopy. Our results prove that PFT undergoes two magnetic phase transitions: an AF transition below \(T_N\) \(\sim153\) K and, a SG transition below \(T_{SG}\) \(\sim10\) K as observed by Falqui et al.\(^9\) Neutron scattering results suggest appearance of short-range magnetic correlations contributing to SG already below \(\sim50\) K. Combining the AF Bragg peak observed by neutron scattering with Mössbauer spectroscopy we show that the magnetic state of PFT below \(T_{SG}\) is a microscopically coexisting antiferromagnetic spinglass phase. These results, therefore, enable us to state that the magnetic phase diagram of PFT is identical to PFN despite having a different non-magnetic ion sharing Fe\(_{3+}\) ions.
II. SAMPLES & EXPERIMENTAL METHODS

PFT crystallizes in a cubic perovskite structure with Pb\(^{2+}\) ions residing at corners of the unit cell, while oxygen octahedra surrounds Fe\(^{3+}\)/Ta\(^{5+}\) ions as shown in Fig. 1. The Fe\(^{3+}\) and Ta\(^{5+}\) ions are believed to be randomly distributed over the B-site of the lattice. Upon lowering the temperature PFT undergoes several structural phase transitions. However, the distortions involved are rather insignificant\(^{16,22}\).

The PFT samples used in the present study were synthesized with the same procedure as employed for PFN\(^{19,23}\). The essential difference is that the sintering temperatures for PFT are 1100 °C, 1250 °C for ceramics and single crystals respectively.

Macroscopic measurements were made on ceramics and single crystals of PFT using a Physical Property Measurement System (PPMS). Conventional Mössbauer absorption spectroscopy experiments were conducted with the help of He-flow cryostat in transmission geometry on a powder of PFT with natural abundance of \(^{57}\)Fe. Neutron scattering experiments were performed at the cold 3-axis spectrometer TASP (SINQ, Switzerland). A high-quality single crystal of PFT (see Fig. 1b) wasaligned in the \(<hh0>/ <00l>\) scattering plane in cubic notation so that the AF Bragg peak at the \(Q_{AF} = (\frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2})\) position is reachable. Most of the neutron data were collected using \(k_f = 1.55 \text{ Å}^{-1}\) and a collimation of open-8\(^0\)-sample-80\(^0\)-80\(^0\). Higher resolution results were obtained with collimation of open-20\(^0\)-sample-20\(^0\)-20\(^0\). A liquid nitrogen cooled Be-filter was used to suppress higher order contaminations. For polarized neutron diffraction, the MuPAD setup\(^{23}\) was employed with a spectrometer configuration \(k_f = 1.97 \text{ Å}^{-1}\), leading to effective collimation open-8\(^0\)-sample-80\(^0\)-open. All the neutron data are analyzed by convoluting the respective scattering function with resolution of the spectrometer using ResLib package\(^{24}\). The calculated resolution reproduces the measured Bragg peaks (110) and (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)) leading to effective sample mosaicity values of 12\(^\circ\) and 20\(^\circ\) respectively in 20\(^\circ\)-collimation and 80\(^\circ\)-collimation setups. The effective mosaicity that is obtained for polarized data is 27\(^\circ\).

FIG. 1. a) Perovskite unit cell of PbFe\(_{1/2}\)Ta\(_{1/2}\)O\(_3\); b) a photo of PFT single crystal (1x0.5x0.3 cm\(^3\)) used in the neutron scattering experiments.

III. RESULTS

A. Bulk Magnetization

Two magnetic phase transitions of PFT are immediately detected in macroscopic experiments. Fig. 2 shows the \(dc\) magnetic susceptibility of PFT powder taken in field-cooled (FC) and zero-field-cooled (ZFC) protocols as a function of temperature. At \(T_N \sim 153\) K, PFT undergoes paramagnetic (PM) to AF transition\(^{19,22}\), while the low-temperature anomaly seen as a splitting of ZFC and FC data around 10 K suggests a second transition from AF into SG phase\(^{19,22}\). The SG nature of this transition is further verified by gradual frequency dependence of \(ac\) susceptibility. Inset of Fig. 2 shows a rounded peak around \(T_{SG}\) whose maximum shifts to higher temperatures upon increasing the field frequency. Additional measurements performed on collections of small single crystals of PFT give essentially the same results with \(T_N \sim 158\) K and \(T_{SG} \sim 9\) K. So we conclude that the PFT samples with very different metallurgy have similar macroscopic properties.

Macroscopic methods alone are insufficient to properly explore the magnetic phases of PFT. The development of short range magnetic correlations and the very presence of AF long-range order (LRO) in the SG state is best probed with neutron scattering.

B. Neutron Scattering

As mentioned earlier, long-range AF order presents itself as a Bragg peak at \(Q_{AF} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) position in neutron diffraction. Fig. 3 shows a color map of this Bragg peak measured in a high-resolution setup above and be-
low $T_{SG}$. As depicted in the figure, we observe a sharp resolution limited AF Bragg peak intensity that remains undisturbed while passing through SG transition. Meaning, the true LRO persists into the SG phase.

In addition to the LRO, short-range correlations can also be observed by neutron diffraction in the form of diffuse scattering (DS). In our material, these short-range correlations give rise to a broad peak under the sharp AF Bragg reflection as shown in Fig. 3.

Having observed these short-range correlations, the first step is to verify their magnetic origin. For this, we make use of polarized neutron scattering with neutron polarization vector parallel to the scattering vector $\mathbf{Q}$. In this geometry, scattering due to magnetic moments flips the direction of polarization whereas, the polarization state is retained if the scattering is of coherent nuclear origin. In PFT, the entire AF and DS intensity is observed in the spin-flip channel as shown in Fig. 5. There is nearly no scattering in non-spin-flip channel as indicated in the inset of Fig. 5a. Therefore, we conclude that these short-range correlations are of magnetic origin. To obtain the time scale of the short-range correlations we have measured several inelastic scans through magnetic DS around AF Bragg peak. We find that the fluctuations corresponding to short-range correlations happen within the timescale of $10^{-11}$ s and therefore refer to quasi-static nature. Having established that the short-range correlations are magnetic and essentially static, we further assumed that they decay exponentially ($e^{-|\mathbf{Q}|/\xi}$) with distance with some characteristic correlation length $\xi$. An exponential decay implies a lorentzian-squared form for the structure factor of the diffuse scattering. The total structure factor for quasielastic scattering is then written as:

$$ S(Q, T) = S_{AF}(Q, T) + S_{DS}(Q, T) \quad (1) $$

$$ S_{AF}(Q, T) = A(T)\delta(Q - Q_{AF}) \quad (2) $$

$$ S_{DS}(Q, T) = B(T) \frac{\kappa}{[(Q - Q_{AF})^2 + \kappa^2]^2} \quad (3) $$

where $S_{AF}(Q, T)$ and $S_{DS}(Q, T)$ are the Bragg and DS contributions, respectively. $A(T), B(T)$ are temperature dependent integrated intensities of the AF and DS contributions respectively and $\kappa$, inverse correlation length of DS such that $\kappa = \frac{1}{\sqrt{\frac{Q^2}{2} - \frac{1}{\xi^2}}}$.

The best fits of the data to the resolution convoluted scattering function defined above are shown by solid lines in Figs. 4b, 5.

Performing this analysis at each temperature we get T-dependence of the inverse correlation length $\kappa$, as well as the intensities of the Bragg and diffuse components (Fig. 6). Intensity of the AF Bragg peak remains nearly unchanged in the covered temperature range as shown in Fig. 6a. The intensity of DS is weak and remains nearly constant for $T \geq 50$ K. However, it increases rapidly upon lowering the temperature below 50 K. The width of the DS remains almost constant as shown in Fig. 6b, and the corresponding average correlation length is $\sim 10 \pm 2$ Å.
FIG. 5. Polarized neutron elastic scans from PFT around \( q_{AF} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) demonstrating magnetic origin of the Bragg peaks and DS intensity. i.e, the intensity in non spin-flip channel (inset of a)) is negligible compared to that observed in spin-flip channel (a)). c)-d) highlight the respective DS intensity in a)-b). Solid lines are fits to the functions Eq. 1-3 as described in the text. Red lines correspond to the best-fit results, shaded areas refer to AF Bragg peak, and the black lines emphasize contribution from magnetic DS.

C. Mössbauer spectroscopy

While neutron scattering provides information on spatial correlations of magnetization, microscopic techniques give a more precise measurement of the distribution of local magnetization. Specifically, in our previous studies of PFN, a clear proof of coexisting AF and SG order parameters was obtained in Mössbauer spectroscopy experiments. In this work we used a similar approach for PFT.

Fig. 7 shows representative \(^{57}\)Fe Mössbauer spectra of PFT above and at several temperatures below \( T_N \). The spectrum taken above Néel temperature, at \( T = 300 \) K, is shown in Fig. 7a. It exhibits a single, although complex, line with its center of weight shifted to \( \delta = 0.3 \) mm/s. This is known as chemical shift and in PFT it clearly corresponds to the Fe\(^{3+} \) valency state. The spectrum in Fig. 7a has a doublet shape due to quadrupolar splitting produced by a non-spherical charge distribution around Fe\(^{3+} \) ion. This is not surprising, as PFT is in ferroelectric phase at room temperature and an additional deviation from the spherical approximation can be induced by different formal charges of Fe\(^{3+} \) and Ta\(^{5+} \) ions. Furthermore, attempts to fit the spectrum of Fig. 7a using a single component lead to unsatisfactory description as the resulting \( \chi^2 \) was too high and an excessive broadening had to be assigned for this line. Instead, an adequate description of the Mössbauer spectra is achieved by assuming two contributions with different quadrupolar splittings \( \Delta E_1, \Delta E_2 \) as shown in Fig. 7b. These two components are probably caused by the disorder present at Fe\(^{3+} \)/Ta\(^{5+} \) site in PFT. Ratio of the areas of two components in the spectra is found to be \( 0.56(\pm 0.01):0.44(\pm 0.01) \).

Below the Néel temperature (Figs. 2b-d), the Mössbauer spectra of PFT exhibit a conventional sextet. This is to be interpreted as a direct evidence of Zeeman splitting of \(^{57}\)Fe nuclear levels induced by the sponta-
FIG. 7. Mössbauer absorption spectra of PFT taken (a) above and (b)-(d) below $T_N$. Red lines are fits to the spectra as described in the text. Two components of the spectrum shown in Fig. 7(a) result from different quadrupole splittings $\Delta E_1$, $\Delta E_2$ detected in PFT.

FIG. 8. Temperature dependence of the model parameters obtained from fits of the Mössbauer spectra of PFT. Here, $B_{hf1}$, $B_{hf2}$ are the maximum values of hyperfine fields, and $\sigma_{hf1}$, $\sigma_{hf2}$: are the widths of two Gaussian hyperfine field distributions. The lines are guide to the eye.

The sextet contribution itself is noticeably broadened at higher temperatures. At base temperature this broadening vanishes and sharp absorption lines are observed, indicating static and rather uniform local fields around Fe$^{3+}$ sites.

To obtain more quantitative information from Mössbauer data, the spectra taken below $T_N$ were fitted with hyperfine fields having Gaussian distributions (see Fig. 7(b)-(d)). It turned out that a consistent fit for all the spectra can be obtained with two distributions of the hyperfine fields in the same ratio as was inferred from paramagnetic phase. Fig. 8a shows the temperature dependences of the amplitudes of both hyperfine fields $B_{hf1}$, $B_{hf2}$. $B_{hf}$ for the two contributions increases smoothly on cooling from $T_N$ down to $\sim 50$ K. Below 50 K a faster increase of $B_{hf}$ is observed, and both finally reach essentially the same value of $\sim 50$ T at 4 K. This value is very close to the saturated hyperfine field in other Fe-containing oxides and thus suggests that Fe$^{3+}$ in PFT recovers a full moment at base tempera-
ture. The widths $\sigma_{hf,1}$, $\sigma_{hf,2}$ of the two hyperfine field distributions are shown in Fig. 3 and clearly exhibit non-monotonic temperature evolution. For both contributions, $\sigma_{hf}$ gradually increases upon cooling through $T_N$ and exhibits a plateau between $\sim 120$ K and $\sim 50$ K. Below $T \sim 50$ K, the distribution widths rapidly decrease to the very small value at $T_{SG} \sim 10$ K. This pronounced temperature dependence of $\sigma_{hf,1}$, $\sigma_{hf,2}$ clearly suggests that the dynamic effects dominate the broadening of the Mössbauer lines of PFT. The nearly zero value of $\sigma_{hf,1}$ and $\sigma_{hf,2}$ obtained at 4 K implies vanishing contribution from static fluctuations in $B_{hf}$.

The features of the Mössbauer spectra below $T_{SG}$ unambiguously confirm a homogeneous environment for all Fe$^{3+}$ ions in the system, and a uniformity of the magnitude of the moments at saturation. Since neutron scattering demonstrated an increase of short-range correlations in this regime, we conclude that the disorder at low temperature is purely orientational. This, in turn, supports the same scenario for the AFSG phase, that we previously suggested for PFN.

IV. SUMMARY

In summary, we have shown that the magnetic properties of PFT are essentially identical to those of PFN. PFT undergoes only two magnetic phase transitions: one of which is AF ($T_N \sim 153$ K) and the other is SG ($T_{SG} \sim 10$ K), contrary to the previous claims of two Néel temperatures, namely $T_{SG} \sim 160$ K and $T_{SG} \sim 18$ K. Our experiments allow us to associate the latter temperature with the enhancement of magnetic short-range correlations in the sample which are further developed as $T_{SG}$ is approached. These correlations are revealed by an increase of the integrated intensity of DS scattering (Fig. 5), a similar feature also observed in PFN. In PFT, the measured correlation length $10 \pm 2$ Å corresponds to nearly two lattice constants which clearly suggests that magnetic interactions beyond first nearest-neighbor are important.

Through temperature evolution of Mössbauer spectra, we observe that the fluctuations in hyperfine field slow down as $T_{SG}$ is approached, in accordance with increasing intensity of short-range correlations. The sharp absorption lines in the Mössbauer sextet below $T_{SG} \sim 10$ K point to ultimate freezing of the fluctuations.

To conclude, the nature of the magnetic phases and specifically the microscopic coexistence of long range AF and orientational SG order are a generic feature of stoichiometric disordered PbFe$_{1/2}$B$_{1/2}$O$_3$ materials. Which actual non-magnetic ions are substituted on the B site to dilute the magnetic Fe ions and induce disorder, appears to be largely irrelevant.