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Anisotropic spin glass pseudobrookite: Evidence for transverse freezing and possible implications

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We provide here clear evidence of transverse freezing in the anisotropic spin glass Fe_2TiO_5 from remanent magnetization studies. In addition, we find anomalous time dependences for zero field cooled and field cooled magnetizations below the transverse freezing temperature. An attempt is made to understand these results on the basis of possible separate time behaviors of f- and c-site magnetizations in the system.

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I. INTRODUCTION

Pseudobrookite (Fe_2TiO_5) is a well known anisotropic spin glass in which Fe^{3+} spin components along the c axis freeze, on cooling, at $T_{LF} \sim 51$ K (longitudinal freezing) and the spin components along the a and b axes continue to show paramagnetic behavior until $T_{TF} \sim 8$ K below which they too freeze (transverse freezing).[1,2] However, whereas the T_{LF} freezing is very clearly visible in ac susceptibility (χ) and dc magnetization (M) measurements, T_{TF} freezing has been seen, so far, only as a broad maximum, not very conspicuous, in M vs T (temperature) curves along the a and b axes.[2] Magnetic irreversibility (M_{irr}) data too fail to show a clear T_{TF} transition since M_{irr} along the a and b axes starts from T_{LF} itself, during cooling, presumably due to the presence of the Dzyaloshinsky-Moriya interaction in the system, which couples the longitudinal and transverse irreversibilities.[2,3] As a matter of fact, a powder measurement does not even report a T_{TF} freezing.[4] In this paper we give clear evidence of T_{TF} transition in Fe_2TiO_5 from remanent magnetization studies. In addition we report anamolous time (t) dependences for field cooled (FC) and zero field cooled (ZFC) magnetizations [M(FC), M(ZFC)] below T_{TF}. The implications of these results are examined.

II. EXPERIMENT

Like single crystal measurements,[1,2] our powder measurements (χ, M vs T) too show (a) a clear maximum at T_{LF} and (b) at T_{TF}, a broad maximum for M(ZFC), and mild change of slope for M(FC) (Fig. 1). These measurements were made using a commercial ac susceptometer [21 Hz, 0.5 Oe (rms) ac field] and vibrating sample magnetometer. The powder sample of Fe_2TiO_5 was prepared by the ceramic technique.[4,5] Starting from very high purity constituents and after repeated pelletization, grinding, and initial sintering, the sample was finally sintered at 1400 °C for 20 h. This resulted in sharp x-ray diffraction peaks that could be indexed in terms of the single-phase orthorhombic structure. The lattice parameters (± 0.02 Å) were $a = 9.80$ Å, $b = 9.97$ Å, and $c = 3.73$ Å, agreeing with the published data.[6] The sample was also char-

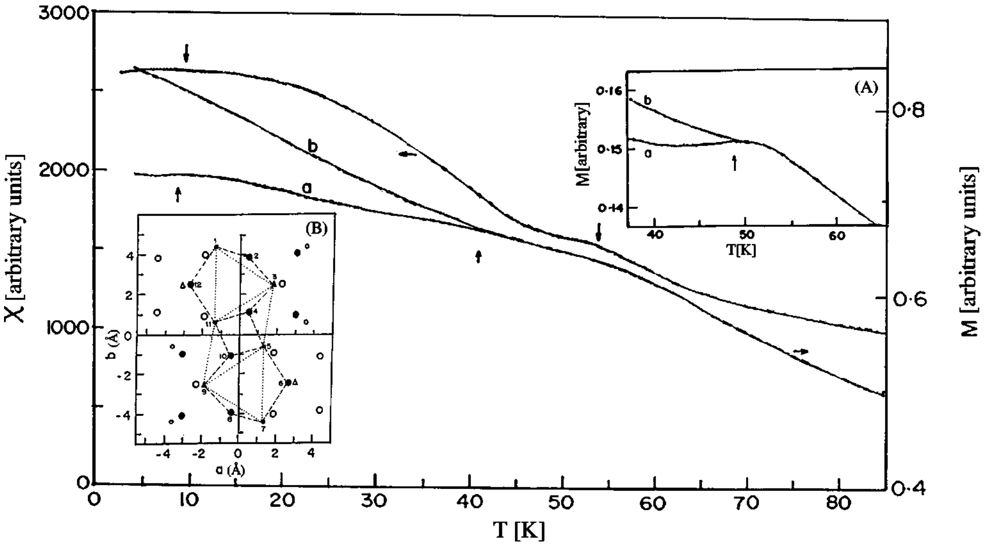

FIG. 1. Temperature (T) dependence of ac susceptibility (χ) and dc magnetization (M). Horizontal arrows indicate the y axes to which the curves belong and vertical arrows the transition temperatures. For the M-T variation, the external magnetic field $H = 5$ kOe and curve a [b] there belongs to the zero field cooled (ZFC) [field cooled (FC)] case. Inset (A) shows the magnetization variation for $H = 1$ kOe where curve a is for the ZFC case and curve b for the FC case. Inset (B) shows the ion positions in the Fe_2TiO_5 unit cell projected along the c axis. Details are described in the text.

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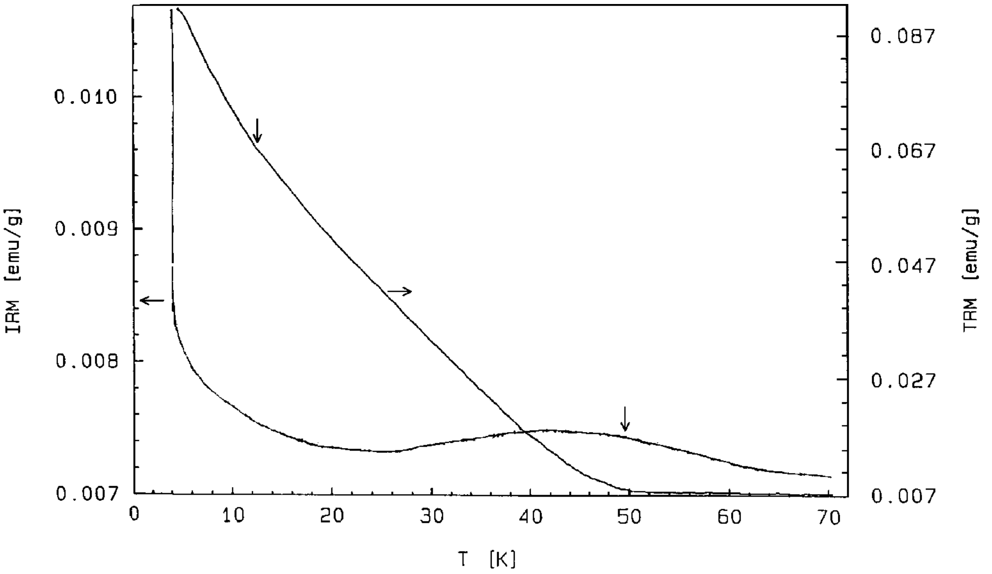

FIG. 2. Variation of the isothermal remanant magnetization (IRM) and thermoremanent magnetization (TRM) with temperature (T). Horizontal arrows indicate the y axes to which the curves belong and vertical arrows the transition temperatures. For the purpose of these measurements, an external magnetic field, $H=5$ kOe, has been applied and removed in the desired way. Details are described in the text.

acterized by Mössbauer spectroscopy and spectra similar to those given in Refs. 1 and 4 were obtained.

III. RESULTS AND DISCUSSION

In the present system the spin glass behavior arises due to the random distribution of Fe^{3+} and diamagnetic Ti^{4+} ions (cations) on the tetrahedral (or more correctly distorted octahedral) $8f$ and octahedral $4c$ crystallographic sites and the anisotropy arises owing to c-axis compression. Figure 1 (inset B) shows the ion positions in the Fe_2TiO_5 unit cell projected along the c axis; open symbols are for the $c=1/2$ plane, filled symbols for the $c=0$ plane, big circles represent O^{2-} ions, small circles f-site ions, and triangles c-site ions. For the $c=0$ plane, dashed lines show the interaction (superexchange) paths between the cations, via the O^{2-} ion, with favorable cation-O^{2-} distances and cation-O^{2-}-cation bond angles. The dotted lines there show various triangular lattices that get formed among the interacting cations and whose presence results in frustration and Fe^{3+} spin canting in the lattice. The random distribution of Fe^{3+} and diamagnetic Ti^{4+} ions on the f and c sites makes this spin canting random in the direction causing spin glass freezing.

Figure 2 shows the temperature dependence of isothermal remanent magnetization (IRM) and thermoremanent magnetization (TRM). For the IRM measurement, a sample was zero field cooled from room temperature to 4.2 K where a magnetic field (H) of 5 kOe was applied and removed. The remanent magnetization (IRM) vs T was then recorded. For the TRM measurement, the sample was field cooled in $H=5$ kOe from room temperature to 4.2 K. The field was then removed there and remanent magnetization (TRM) vs T measured. As seen in Fig. 2, IRM shows sudden enhanced value below ~ 10 K, giving a spectacular evidence of the existence of a transverse freezing transition. The T_{LF} transition appears only as a broad maximum around 50 K in IRM vs T curve. However, this transition is seen, again spectacularly, in TRM vs T curve, which shows a sudden strong enhancement in the TRM value below T_{LF}. The T_{TF} transition appears as a change in slope of the TRM vs T curve.

Figure 3 shows the time dependence of IRM and TRM at (a) $T=30$ K and (b) $T=4.2$ K. As seen in Fig. 1, at $H=5$ kOe, $T_{LF}\sim 40$ K (measured from the start of M_{irr} on cooling) and $T_{TF}\sim 8$ K [measured from M(ZFC) maximum]. Thus for $T=30$ K, $T_{TF}<T<T_{LF}$ and for $T=4.2$ K, $T<T_{TF}$. For the IRM measurement, the sample was zero field cooled from room temperature to the measurement temperature [i.e., 30 K for Fig. 3(a) measurement and 4.2 K for Fig. 3(b) measurement] and $H=5$ kOe was applied and removed at that temperature. The IRM vs t measurement was then carried out. For the TRM measurement the sample was field cooled from room temperature, in $H=5$ kOe, to the measurement temperature [30 K for Fig. 3(a), 4.2 K for Fig. 3(b)]. H was removed there and TRM vs t measured. As seen in Fig. 3, IRM and TRM show a fast initial decrease that is followed by a slow decrease with t. Such behavior has been observed in other spin glass systems also. However, the exact nature of t dependence varies from system to system, being exponential or algebraic or logarithmic or stretched exponential or a combination of these.[7–11]

Figure 4 shows the t dependence of M(ZFC), M(FC) at (a) $T=30$ K and (b) $T=4.2$ K. The reason for choosing these temperatures is already mentioned above. For the M(ZFC) measurement, the sample was zero field cooled from room temperature to the measurement temperature (30 K [Fig. 4(a)], 4.2 K [Fig. 4(b)]) and a field of $H=5$ kOe applied there. This field remained present throughout the M(ZFC) vs t measurement. For the M(FC) measurement, the sample was field cooled from room temperature, in $H=5$ kOe, to the desired temperature (30 K [Fig. 4(a)], 4.2 K [Fig. 4(b)]) and M(FC) vs t measured with the field present. It may be men-

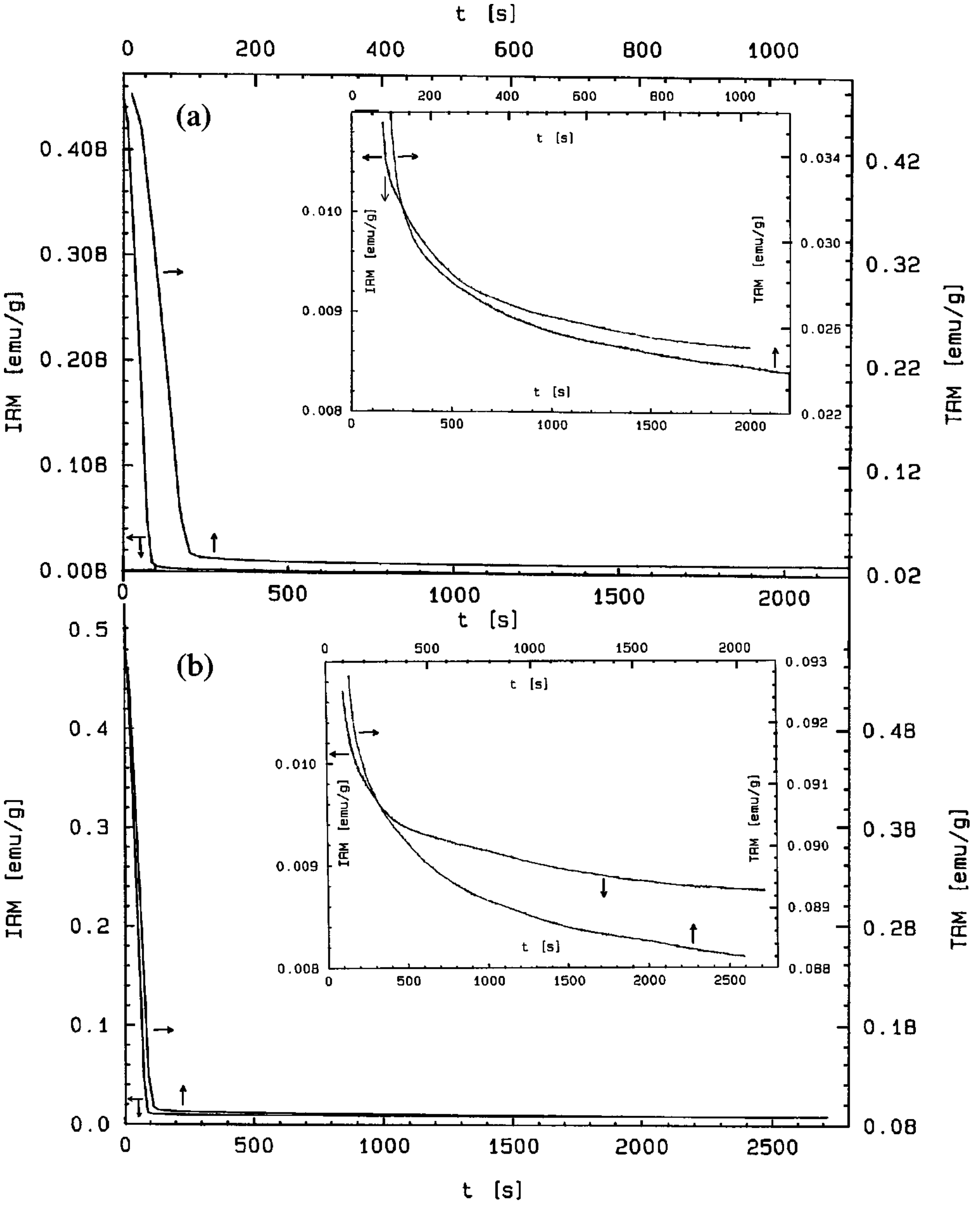

FIG. 3. Time (t) dependence of the isothermal remanent magnetization (IRM) and thermoremanent magnetization (TRM) at (a) $T=30$ K and (b) $T=4.2$ K. Horizontal (vertical) arrows indicate the y axes (x axes) to which the curves belong. Insets show an enlarged view of the large t portion of the curves that is not visible in the main figure. For the purpose of these measurements, an external field, $H=5$ kOe, has been applied and removed in the desired way. Details are described in the text.

tioned here that in all measurements described in this paper, after zero field cooling of the sample, H is applied without any waiting (i.e., waiting time $t_w=0$). As seen in Fig. 4(a), at $T=30$ K M(ZFC) increases with t towards M(FC), which itself, after an initial increase, shows very little time dependence. This is similar to that observed in other spin glass systems where a weak time dependence of M(FC) has been interpreted as indicating its closeness to the equilibrium magnetization (i.e., the magnetization of a possible equilibrium state) of the system. However, the time dependence of M(ZFC) and M(FC) at 4.2 K [Fig. 4(b)] is quite complex and to our knowledge has not been reported for any other spin glass system so far. Instead of showing a monotonic increase with t, M(ZFC) passes through a maximum at ~ 1000 s after which it shows a slow decrease. The behavior of M(FC) is more complex, which shows an oscillatory dependence on t.

We have tried to understand the above-mentioned time behaviors on the basis of the unit cell ion positions shown in Fig. 1 (inset B). As shown there, there are f and c sublattices that are coupled by the f-O-c (O is the oxygen ion) antiferromagnetic superexchange interaction. The f-O-c is stronger than the c-O-c and the f-O-f interactions owing to the favourable f-O-c bond angles. Thus the observed magnetization $M=M_f-M_c$ can have a variety of variations with t depending on how the f-site and c-site magnetizations, M_f and M_c, vary with t. Owing to the anisotropic spin glass freezing, M_f vs t and M_c vs t can be quite complex. As

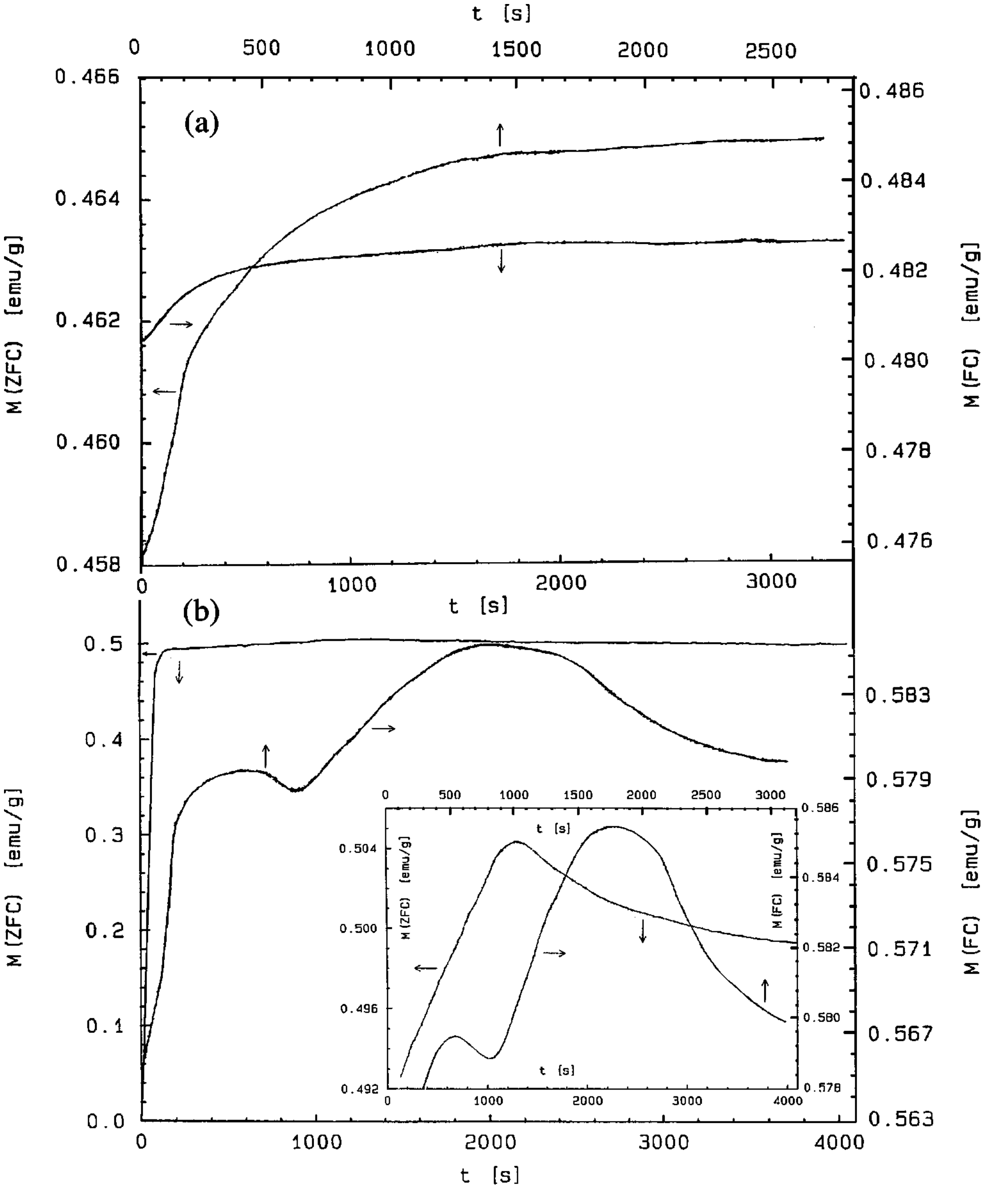

FIG. 4. Time (t) dependence of zero field cooled magnetization, M(ZFC), and field cooled magnetization, M(FC), at (a) $T=30$ K and (b) $T=4.2$ K. Horizontal (vertical) arrows indicate the y axes (x axes) to which the curves belong. The inset shows an enlarged view of the large t portion of the curves that is compressed in the main figure. For these measurements, external field, $H=5$ kOe, has been applied in the desired way. Details are described in the text.

mentioned before, various types of time dependences, such as algebraic, exponential, logarithmic, stretched exponential, or a combination of these, are possible for M_f and M_c. Thus a complex M vs t may occur. In Fig. 5 we have shown some possible calculated variations of M. For instance, in Fig. 5(A) curve c shows a situation where M is time independent after initial increase and c' where M increases with t. Corresponding M_f, M_c time variations are shown by the curves a, b and a', b', respectively. Similarly in Fig. 5(B), curve c shows a situation where M has a maximum in its t dependence and c' where M vs t is oscillatory. Corresponding M_f, M_c variations are given there by the curves a, b and a', b', respectively.

The calculated variations of Fig. 5 match those shown in Fig. 4. Mathematically, assuming exponential t dependences for M_f and M_c,

$$M(t)=M_f(t)-M_c(t)=[M_f(\infty)-M_c(\infty)]-[M_f(\infty)-M_f(0)]e^{-\zeta_f t}+[M_c(\infty)-M_c(0)]e^{-\zeta_c t}, \qquad (1)$$

where $M_f(0)$, $M_c(0)$ and $M_f(\infty)$, $M_c(\infty)$ are the $t=0$ and $t=\infty$ values of M_f, M_c. ζ_f and ζ_c, respectively, represent the growth rate of M_f and M_c with time. Various forms of M given in Fig. 5 are generated for different values of ζ_f, ζ_c. For instance, a $\zeta_f=\zeta_c$ situation yields almost time independent M after an initial increase, $\zeta_f\neq\zeta_c$ makes M monotonically increase with t or go through a maximum, and a time dependent ζ_f, ζ_c [i.e., $\zeta_f(t)$, $\zeta_c(t)$] yield oscillatory M vs t.

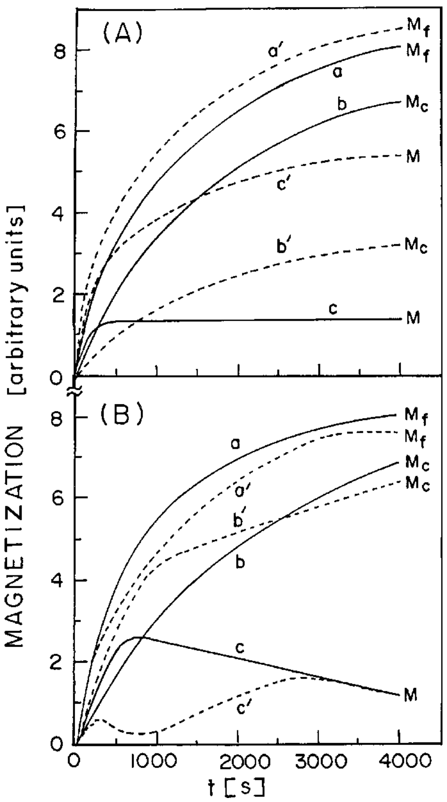

FIG. 5. Typical time (t) variation of magnetization (M) calculated for various possible time behaviors of f- and c-site magnetizations, M_f and M_c. Details are described in the text.

Thus in Fig. 4(a) ($T=30$ K) an increase of M(ZFC) with t shows $\zeta_f \neq \zeta_c$. This is possible since as shown in Fig. 1 (inset B), in the $c=0$ plane, where strong superexchange interaction paths are present (due to favorable cation-O-cation bond angles), for a given f-site ion, there are two f-site ions and two c-site ions as neighbors. Out of these neighbors, only one c-site ion is strongly interacting. On the other hand, for a c-site ion in the $c=0$ plane, there are four f-site ions as neighbors, two strongly interacting and two weakly. This makes the behaviors of f- and c-site ions different, making $\zeta_f \neq \zeta_c$. The situation in the $c=1/2$ plane is same. However, between $c=1/2$ and $c=0$ planes, interaction is very weak owing to the absence of favorable cation-O-cation bond angles. We now try to understand the M(FC) curve of Fig. 4(a). In the field cooled state, the magnetization time dependence becomes very slow since, as mentioned before, field cooled magnetization is close to the equilibrium value. This gives rise to almost time-independent $M_f(t)$, $M_c(t)$, i.e., ζ_f, $\zeta_c \rightarrow 0$, which is same as the $\zeta_f = \zeta_c$ situation. This explains the presence of almost time-independent M(FC), after an initial increase, as seen in Fig. 4(a).

In Fig. 4(b) ($T=4.2$ K), M(ZFC) vs t is similar to curve c of Fig. 5(B), which is the $\zeta_f \neq \zeta_c$ case. However, M(FC) vs t is complex, indicating a time dependent ζ_f, ζ_c [Fig. 5(B) curve c']. For the field cooled state this time dependence can be understood as follows. A spin glass system has many ground states and the system drifts from one ground state to the other, as it moves towards some equilibrium ground state.[7,12–14] The rate of drift, which in the present context decides ζ_f, ζ_c, depends on Δ_B/kT where Δ_B is the energy barrier separating two ground states. At lower temperatures, when kT is small, any small difference in Δ_B between different ground states will make Δ_B/kT time dependent as the system drifts, causing ζ_f, ζ_c to become time dependent. The presence of H during cooling in the field cooled case makes Δ_B unequal between different ground states owing to the preferential anisotropy, which develops along $\vec{H}$. Thus drift rate from one ground state to the other and, consequently, ζ_f, ζ_c, become time dependent. It may be noted that even without field cooling it is possible to have time-dependent ζ_f, ζ_c if the frustration-induced exchange anisotropy effect on barrier heights is comparable to kT.

IV. CONCLUDING REMARKS

To summarize, we have given in this paper clear evidence of the T_{TF} freezing in anisotropic spin glass Fe_2TiO_5. Further, we have also reported complex time dependences of field cooled, zero field cooled, and remanent magnetizations. These could be understood on the basis of the time behaviors of f-site and c-site magnetizations.

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