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Emergent order in the spin-frustrated system $Dy_xTb_{2-x}Ti_2O_7$ studied by ac susceptibility measurements

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We report the ac susceptibility study of $Dy_xTb_{2-x}Ti_2O_7$ with $x \in [0,2]$. In addition to the single-ion effect at T_s (single-ion effect peak temperature) corresponding to the Dy^{3+} spins as that in spin ice $Dy_2Ti_2O_7$ and a possible spin freezing peak at T_f ($T_f < 3$ K), a new peak associated with Tb^{3+} is observed in $\chi_{ac}(T)$ at nonzero magnetic field with a characteristic temperature T^* ($T_f < T^* < T_s$). T^* increases linearly with x in a wide composition range ($0 < x < 1.5$ at 5 kOe). Both application of a magnetic field and increasing doping with Dy^{3+} enhance T^*. The T^* peak is found to be thermally driven with an unusually large energy barrier as indicated from its frequency dependence. These effects are closely related to the crystal-field levels and the underlying mechanism remains to be understood.

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I. INTRODUCTION

Geometrically frustrated magnetic materials,[1–3] which are ordered systems with specific geometry that accommodates closely competing spin-spin interactions and therefore frustration, attract extensive interests because of their novel ground states. The pyrochlores[4] provide a variety of geometrically frustrated magnetic materials, including spin liquid,[5] spin ice,[6,7] and spin glass,[8–10] where magnetic exchange and dipolar interactions of the nearest-neighbor spins dominate the low-temperature magnetic property. Among these, two pyrochlores are of particular interests, spin ice $Dy_2Ti_2O_7$ (DTO), $Ho_2Ti_2O_7$ and spin liquid $Tb_2Ti_2O_7$ (TTO), which have completely different ground states while sharing essential similarities.

For the spin ice compound, spins upon each tetrahedron adopt the two-in-two-out configuration in the ground state, which is a direct analogy to the two-short-two-long proton bond configuration in water ice.[6] This results in the zero-point entropy.[11] Strong crystal-field (CF) splitting induces uniaxial anisotropy of Dy^{3+} spins giving rise to the Ising-type ground-state doublet, in DTO, with spins pointing along the local $\langle 111 \rangle$ axis, which lies more than 200 K below the first excited state.[12–14] Novel spin dynamics has been observed. The single-ion effect at 15 K and spin freezing into the ice state[15–18] (strictly, spins falling into compliance with the ice rule and freezing into disordered states) below 2 K are found to be responsible for the low-temperature dynamic properties. Moreover, it has been predicted[19,20] and most recently verified experimentally[21–23] that the dipole-dipole interactions give rise to magnetic monopoles, therefore a new wave of reconsideration of the equivalency of electricity and magnetism is invoked.

The spin liquid compound TTO has Ising-type spins similar to DTO but with a much smaller gap of 18.7 K between the ground and excited spin states,[24,25] which is one order of magnitude smaller than that of DTO. TTO remains in spin liquid state down to 50 mK despite a short-range antiferromagnetic (AFM) order.[25,26] With a Curies-Weiss temperature of −14 K (Ref. 24), the absence of an ordered ground state is unusual and has been attributed to the delicate balance between the AFM exchange and ferromagnetic dipolar interactions, which then places TTO right at the phase boundary according to the phase diagram by Hertog and Gingras.[27] This delicate balance, however, is vulnerable to external perturbations, such as pressure and magnetic fields. For example, TTO shows an AFM ground state with spin-liquid-like fluctuations under high pressure,[28] a long-range order with spin-wave excitations[29] and a spin-ice-like order with the $k=0$ propagation vector[30] under high magnetic fields along the [110] axis. It is also proposed that quantum fluctuations are responsible for the lack of an ordered ground state and TTO is argued to be in a quantum mechanically fluctuating spin ice state.[31,32]

It is therefore interesting to ask how the ground state and magnetic interactions evolve if both Dy and Tb ions are introduced into the rare-earth (RE) sites. In a Brief Report,[33] both spin ice and liquid signatures are found in the ground state of $Ho_xTb_{2-x}Ti_2O_7$. Here, using the ac susceptibility study on $Dy_xTb_{2-x}Ti_2O_7$ (DTTO), we observed a new peak in $\chi_{ac}(T)$ at the characteristic temperature T^* ($T_f < T^* < T_s$). T^* is found to increase linearly with Dy composition x in a surprisingly wide range ($0 < x < 1.5$) for $H=5$ kOe. The phase diagram of the composition dependent T^* is obtained. The T^* peak is found to be thermally driven with an unusually large energy barrier as indicated from its frequency dependence. The observed peaks are closely related to the CF and possible origins are discussed using the composition and the field dependence of ac susceptibility.[34]

II. EXPERIMENTAL METHODS

Polycrystalline DTTO with $x \in [0,2]$ were prepared by the standard solid-state reaction method.[5,15] The x-ray diffraction data show that all samples are of single phase with a pyrochlore structure. The lattice constants (cubic phase, $a=b=c$) are shown in Fig. 1. For the two samples at the composition boundaries, lattice constants of 10.15(1) Å for

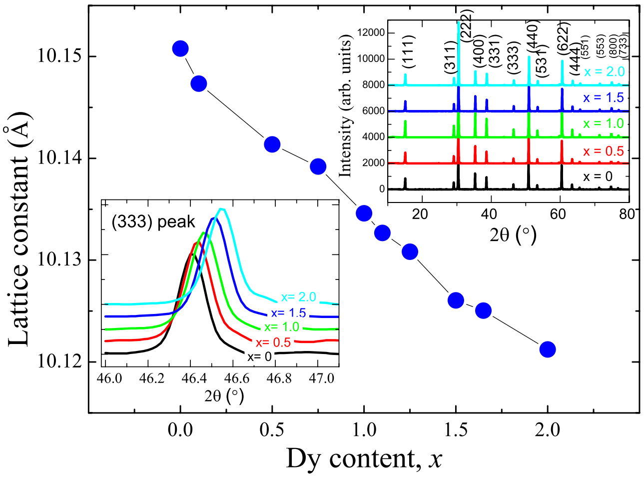

FIG. 1. (Color online) The lattice constant (cubic phase, $a=b=c$) of of $Dy_xTb_{2-x}Ti_2O_7$ as a function of x show a quasilinear decrease. (Upper inset) X-ray diffractions show single phase (pyrochlore structure) of all samples. (lower inset) Expanded XRD patterns show the peak shift with x(Dy), the full width at half maximum does not show increase, demonstrating the absence of phase separation.

TTO ($x=2.0$) and 10.12(1) Å for DTO ($x=0$) are in good agreement with previous reports,[3,5] Curie-Weiss temperatures by fitting to the dc susceptibility between 10 and 20 K are consistent with values reported.[34] As there are two spin species on the RE sites, it is important to address the issue of possible phase separation. As shown in the lower inset of Fig. 1, the full width at half maximum of the diffraction peaks does not show obvious increase with different x, which indicates that the system is free from phase separations. The quasilinear decrease in the lattice constants with increasing x further confirms the samples' quality. dc and ac susceptibilities are measured by a Quantum Design superconducting quantum interference device magnetometer and a physical properties measurement system (PPMS) using an excitation field of $H_{ac}=10$ Oe at frequency f ($10 \leq f \leq 10000$ Hz), respectively.

III. RESULTS AND DISCUSSIONS

In Fig. 2, we take sample $x=1.0$ as an example and show the real and imaginary parts of the ac susceptibility at varying magnetic fields. At $H=0$, $\chi'(T)$ increases monotonically with an increasing slope upon cooling for all excitation frequencies in study ($f=1$, 2, 5, and 10 kHz), which signals a canonical paramagnetic behavior.[17,35] The imaginary part $\chi''(T)$ in the lower panel shows a sharp increase as well, even when approaching our lowest available temperature 2 K. Therefore there should exist a strongly dissipative process at $T<2$ K. The zero-field ac susceptibility is qualitatively similar to that of TTO (Ref. 35) for all DTTO samples in study. The magnitude of $\chi'(T)$ at $H=0$ grows with increasing x, presumably due to the larger moment of Dy^{3+} spins. As the field increases to 5 kOe, a clear dip in $\chi'(T)$ appears around 8.5 K, leading to a local maximum in $\chi'(T)$ as well as a

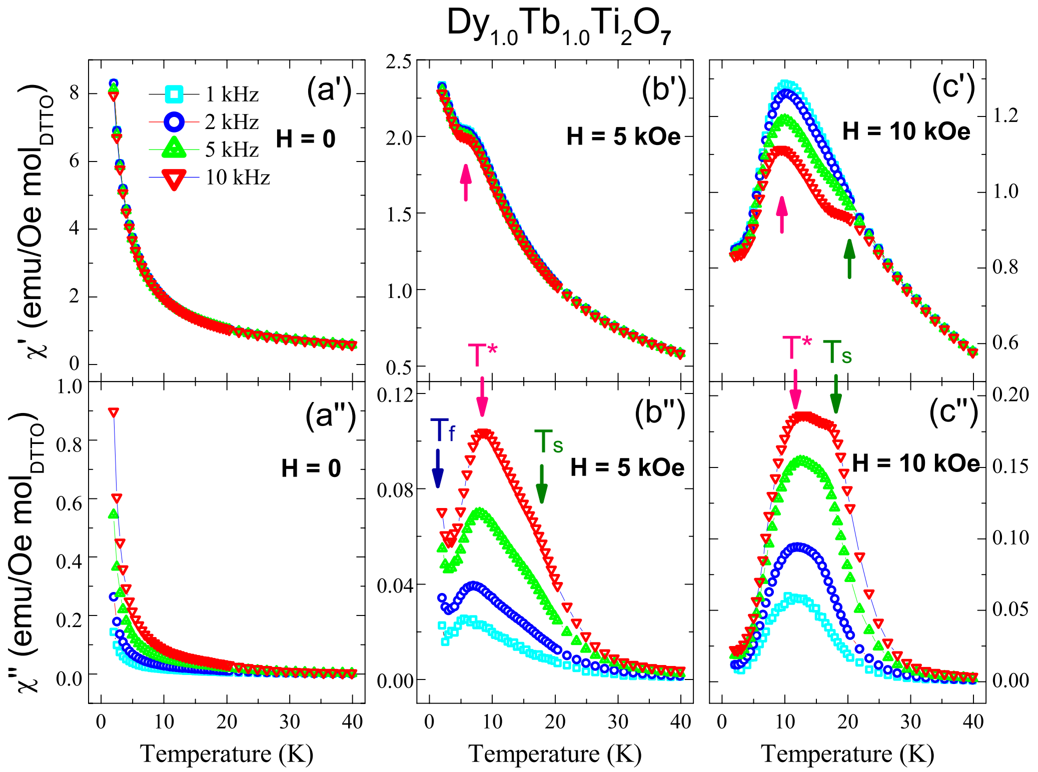

FIG. 2. (Color online) The real (upper panel) and imaginary part (lower panel) of ac susceptibility of $Dy_{1.0}Tb_{1.0}Ti_2O_7$ for several fields. Pointed by the arrows are: T_f peak, T^* peak, and T_s peak denoting the low-temperature freezing peak, the peak associated with Tb^{3+}, and the single-ion peak associated with Dy^{3+}, respectively, as discussed in Fig. 3 and corresponding text.

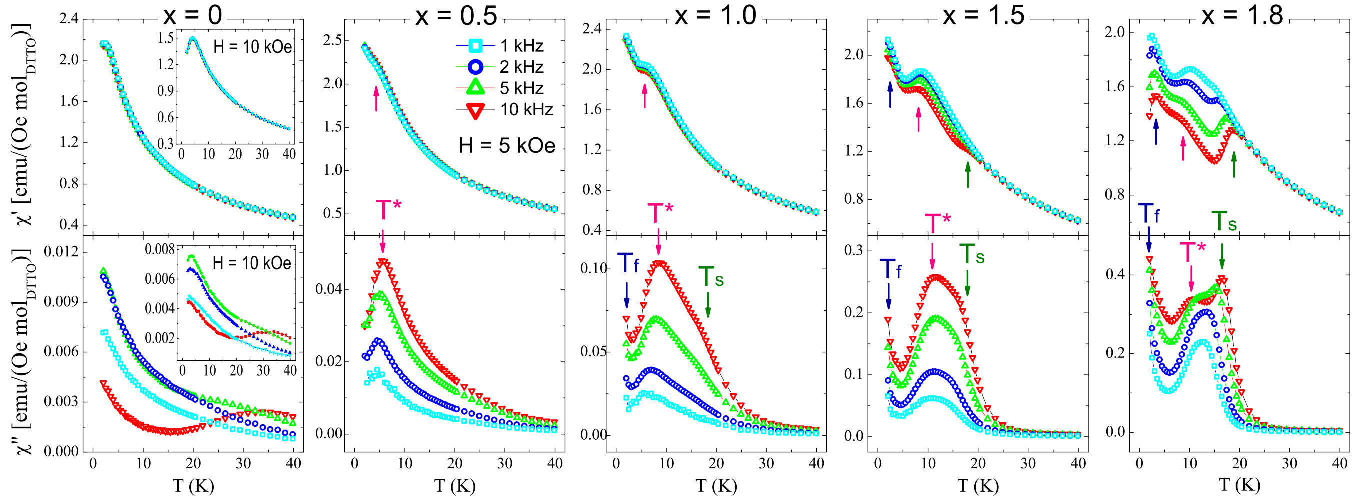

FIG. 3. (Color online) The real (upper panel) and imaginary part (lower panel) of ac susceptibility of $Dy_xTb_{2-x}Ti_2O_7$ ($x=0,0,5$, 1.25, 1.5, and 1.8) at $H=5$ kOe. Pointed by the arrows are: low-temperature freezing peak (T_f arrow), the single-ion effect peak associated with Dy^{3+} (T_s arrow), and the T^* peak (T^* arrow). Insets in the $x=0$ plots are the real (upper inset) and imaginary part (lower inset) of ac susceptibility of $Dy_xTb_{2-x}Ti_2O_7$ with $x=0$ at $H=10$ kOe.

correlated peak in $\chi''(T)$ dictated by the Kramers-Kronig relation. It is also notable that there is an emerging maximum on the right shoulder of the peak in $\chi''(T)$, which becomes prominent as the field increases. At $H=10$ kOe, $\chi'(T)$ shows two clear dips at 12 and 17.5 K, thereby two local maxima appear in $\chi''(T)$. As the frequency increases, the separation between the two local maxima increases [Fig. 2(c″)].

The two spin-freezing-like peaks cannot be attributed to a collective spin-glass transition although the random occupancy of rare earth sites by Dy^{3+} and Tb^{3+} is a likely source of spin glassiness. In contrast to the spin-glass transition, the dc susceptibility of DTTO shows simply a Curie-Weiss behavior, more strictly, a superposition of Curie-Weiss and Van Vleck terms,[24,35,36] with no freezing transition. Second, the application of a magnetic field enhances the characteristic temperature of the two freezing-like peaks, as opposed to the case of spin glass where the transition temperature is suppressed.[37] Furthermore, the interactions for Dy-Dy and Tb-Tb on the ground-state doublet in DTO and TTO cases are only of the order of 1 K, much lower than the temperature of the observed peaks. Therefore the freezing-like peaks are most likely not due to spin-glass transitions. With higher magnetic fields [$H=10$ kOe data shown in Fig. 4(b) and higher field data not shown here], the thermal spin contribution is suppressed at low and high temperatures, leaving only a broad peak in $\chi'(T)$ as observed in TTO and DTO.[35] Other samples with $0.5<x<1.5$ show qualitatively similar behaviors. The appearance of the two freezing-like peaks as well as their strong frequency dependence are reminiscent of the single-ion effect peak in pure DTO, i.e., $x=2.0$, and will be discussed in detail by examining the composition dependence below.

Figure 3 shows the ac susceptibility of five representative samples with $x=0$, 0.5, 1.0, 1.5, and 1.8 at $H=5$ kOe. For $x=0$, there appears to be a peak below 3 K in $\chi'(T)$. The imaginary part of the sample with $x=0$ is clearly different from other doped samples regarding their frequency dependence. This is presumably related to the fact that the exchange coupling and the energy gap between narrowly spaced CF levels of TTO are of comparable energy scale and therefore both have non-negligible contributions to the susceptibility.[24,38] For samples with $0<x<0.5$ (data not shown here), the crystal-field contribution increases progressively as x increases, manifesting as the transition to the behavior of the sample with $x=0.5$. The sample with $x=0.5$ shows a single peak in $\chi''(T)$ (indicated by the T^* arrow). Additional peaks (indicated by the T_f and T_s arrows) start to emerge for $x=1.0$, and become more pronounced in $x=1.5$ and 1.8 samples. These additional peaks for $x\geq 1.0$ have the same origin as the two peaks in pure DTO. In pure DTO, two peaks are observed in $\chi''(T)$, a high-temperature peak corresponding to the single-ion effect, and a low-temperature peak associated with the spin freezing dictated by the ice-rule ground state.[15–18] For the sample with $x=1.8$, the position of the high-temperature peak (indicated by the T_s arrows) are in good agreement with the single-ion peak in DTO. Moreover, the frequency dependence of the high-temperature peak and the extracted energy scale corresponding to the crystal-field splitting are qualitatively similar to that of pure DTO, as discussed below. We therefore identify the high-temperature peak as the single-ion peak of Dy^{3+} spins. The low-temperature peak (indicated by the T_f arrow) also possesses a similar characteristic temperature with the spin-freezing peak in DTO,[18] the corresponding peak in $\chi''(T)$ should appear below 2 K, the limit of PPMS, thereby only a rapid increase in $\chi''(T)$ upon cooling below 5 K is observable, and a direct comparison with the DTO data is not allowed. Following the convention of previous reports, we define the characteristic temperature T_s as the high-temperature peak position in $\chi''(T)$ and similarly T_f for the low-temperature peak.

The most important new feature in all samples studied, is the presence of a third peak (indicated by the T^* arrow) between T_f and T_s. We define T^* ($T_f<T^*<T_s$) as the characteristic temperature for this third peak. T^* peak should root in the Tb^{3+} spins as it exists at regions with small x (including $x=0$ at $H=10$ kOe, see the insets in Fig. 3), where the peaks

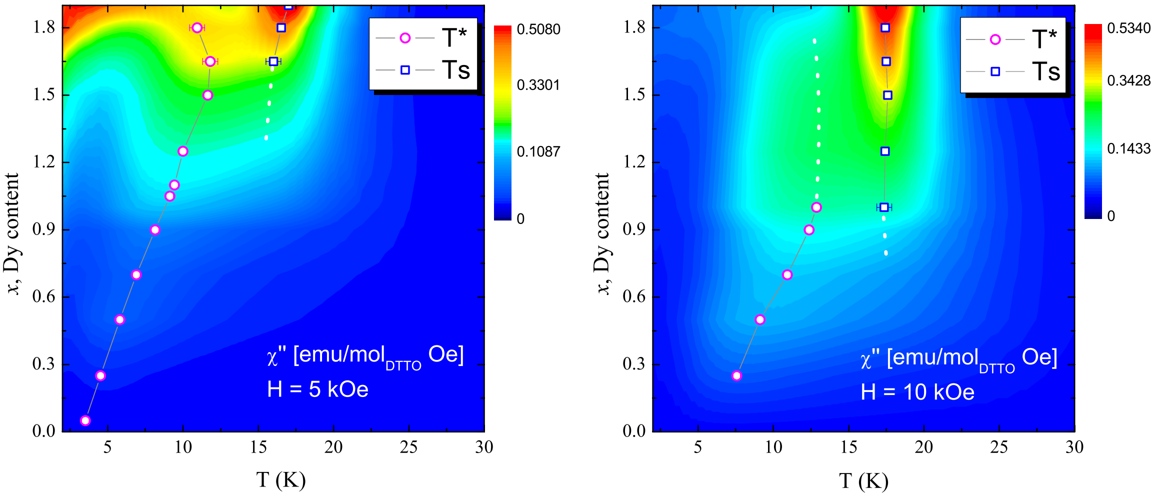

FIG. 4. (Color online) Contour plot of $\chi''(T)$ of samples with different x at $H=5$ and 10 kOe with $f=10$ kHz. Pink circles (blue squares) denote T^* (T_s). Dotted lines are guide to the eye where the peak positions are not well resolved.

associated with Dy^{3+} disappear and the effect of Dy^{3+} should play a minor role. Combined with the susceptibility of $Dy_{1.0}Tb_{1.0}Ti_2O_7$ at different fields shown in Fig. 2, it is interesting to note that the evolution of the ac susceptibility with increasing x (Fig. 3) is similar to that with constant x but increasing magnetic field (Fig. 2). In both cases, the increase in x or magnetic field leads to the appearance of the T^* peak and subsequently the T_s peak.

In order to investigate the origin of the T^* peak, we studied a series of samples with $x\in[0,2]$, and track T^* and T_s in all samples when observable. A global view of $\chi''(T)$ with different x is shown in the contour plot in Fig. 4. It is clearly seen that the T^* peak exists in a wide range of x. Most interestingly, $T^*(x)$ increases linearly with increasing x in a wide range of x, both at 5 and 10 kOe. At $H=10$ kOe, the low-temperature upturn is strongly suppressed compared with the 5 kOe case, as mentioned above. The linearity of $T^*(x)$ persists in a wide x range, from $x=0$ to 1.5, obvious deviation from the linearity occurs when $x>1.5$. The characteristic peak temperature of T_s is also shown in Fig. 4, with a slight decrease as x becomes smaller.

A clear deviation from linearity in T^* for $x\geq 1.5$ is also an indication for its Tb^{3+} origin. The pyrochlore structure of DTTO consists corner-shared tetrahedrons, by assuming that Dy^{3+} and Tb^{3+} spins in DTTO occupy the lattice randomly therefore uniformly, there are two critical values of x(Dy) where large change in local environment (i.e., tetrahedron that consists of only one spin species: all Dy^{3+} or all Tb^{3+}) emerges: for $x>1.5$ ($x\leq 0.5$), tetrahedrons of Dy^{3+}-only (Tb^{3+}-only) spins appears, while Tb^{3+} (Dy^{3+}) still lies in the uniform neighborhood coordinated with six Dy^{3+} (Tb^{3+}) spins. The deviation from the linearity in $T^*(x)$ can be understood as a direct consequence of the critical value of $x=1.5$. It is important to note that there is no such deviation at the Tb end. The presence of the deviation at $x=1.5$ as well as the lack of that at $x=0.5$ is a strong indication of the asymmetric roles of Tb^{3+} and Dy^{3+} spins in the origin of T^* peak, consistent with our argument that the T^* peak is associated with Tb^{3+}.

To see the nature of T^*, we show in Fig. 5(a) the phase diagrams of the $T_s(x)$ and $T^*(x)$ with different ac excitation frequencies (1, 2, 5, and 10 kHz) at $H=10$ kOe. The quasilinear increase in $T^*(x)$ is preserved at $H=10$ kOe at different frequencies. The frequency dependence of both T^* and T_s behaves according to the Arrhenius relation, as shown in Fig. 5(b). One note that to achieve a reliable fitting with the exponential function $f=f_0\exp(-E_A/k_BT)$, data with frequencies spanning over several decades are necessary. In our case, however, at frequencies lower than 1 kHz, T^* and T_s peaks are indistinguishable, making the data at lower frequency range inaccessible. Thus we only focus on the data above 1 kHz. From the fitting of $f=f_0\exp(-E_A/k_BT)$, where f_0 is taken to be the physically reasonable values of 1 GHz,[14,15] the energy barrier E_A can be extracted. The extracted energy barrier E_A is shown in Fig. 5(c), including E_A by fitting with $f_0=0.5$ and 5 GHz to verify the reliability of the fittings. The validity of the fitting by Arrhenius law indicates that in the presence of a magnetic field the spin relaxation is thermally driven.[15] In pure DTO, E_A has been found to be 200 K (Ref. 16). This energy barrier has been interpreted as the gap between the lowest-lying crystal-field levels of Dy^{3+}. In DTTO, it can be seen that E_A associated with T_s changes only slighly from 193 K for $x=1.25$ to 200 K for $x=1.8$, a value very close to the energy barrier in pure DTO. This again proves our understanding that T_s peak is associated with the single-ion effect of Dy^{3+}. On the other hand, E_A associated with T^* (attributed to Tb^{3+} above) increases rapidly from 85 K for $x=0.25$ to 154 K for $x=1.0$. These values are unusually high since the crystal-field gap of ground-state doublets for TTO is only O(20 K). Similar fittings with data at 5 kOe cannot be performed since the T^* and T_s peaks are not well resolved for low frequencies.

Our observations including the field, composition and frequency dependence of T^* raise the question of its underlying mechanism. Knowing the exchange and dipolar interaction in both DTO and TTO [for TTO, nearest-neighbor exchange $J_{nn}=-0.88$ K, nearest dipolar interaction $D_{nn}=0.8$ K (Ref. 39), for DTO $J_{nn}=-1.2$ K, $D_{nn}=2.35$ K (Ref. 27)], it is hard to imagine that certain combinations of interactions between Dy and Tb spins (i.e., Dy-Dy, Tb-Tb, and Dy-Tb) can give rise to a characteristic temperature T^* with its energy barrier

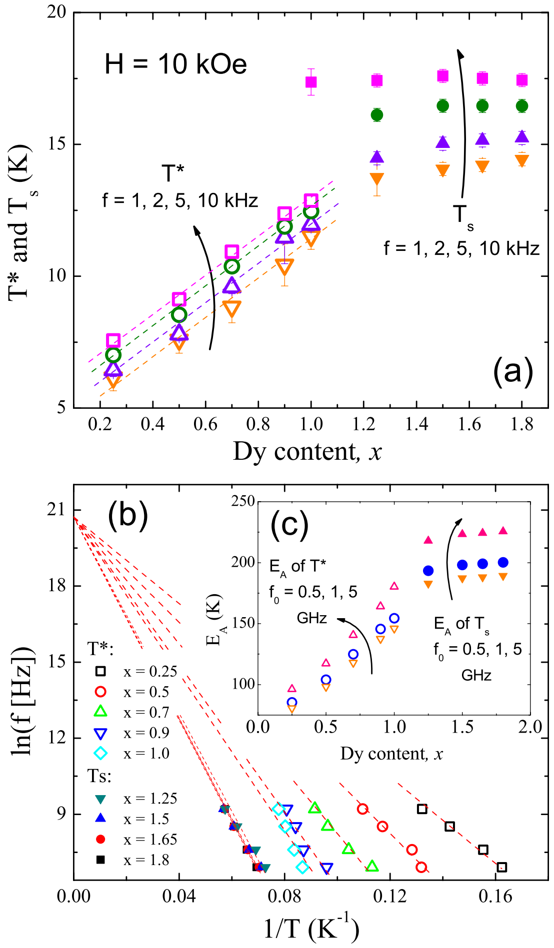

FIG. 5. (Color online) (a) At $H=10$ kOe, T^* (empty symbols) and T_s (solid symbols) as a function of x(Dy) at different frequencies. Dash lines are guide to the eye to show the quasilinear increase in T^*. (b) Fittings by $f=f_0\exp(-E_A/k_BT)$ with f_0 taken to be the physically reasonable value of 1 GHz. (c) The extracted energy barrier E_A for T^* (open symbols) and T_s (solid symbols) with fitting parameter $f_0=0.5$, 1, and 5 GHz.

two orders of magnitude higher than the energy scale set by the interactions. Instead, the large energy gap extracted from the frequency dependence of T^* suggests that single-ion effects may play an important role. The CF levels for pure TTO and DTO have been studied in detail previously.[12,24,25] For the DTTO samples, there exist two sets of CF schemes associated with Dy^{3+} and Tb^{3+}, respectively, with their CF level structures determined by the local chemical environment. The zero-field E_A in pure DTO is around 200 K. With $H=10$ kOe, E_A associated with Dy^{3+} in DTTO also stays around 200 K as is shown in Fig. 5(c). Thus one may expect that the single-ion peak temperature T_s corresponding to the CF of Dy^{3+} in DTTO should be robust against the change in magnetic field. However, according to the ac susceptibility data at zero field, e.g., Figs. 2 (a′) and 2(a″), none of the sample with $x \leq 1.5$ show signs of a single-ion peak above 2 K, implying narrowly spaced CF levels similar to that in TTO. Moreover, the field dependence of T^* and T_s in Fig. 2 indicate a dominant impact on their respective CF gap by the field. The possible field dependence of the CF levels is unusual and deserves further investigation. Here with the current limited data, we discuss possible mechanisms that may give rise to the field dependence. It is known that with the application of a magnetic field, the Zeeman splitting of the spin states may cause changes in the CF scheme. Take Dy^{3+} ions as an example,[40] $g_J J \sim O(10)\mu_B/\mathrm{Dy}$. With the magnetic field of 1 T, the Zeeman energy is $g_J JH \sim O(10)$ K, which is one order of magnitude smaller than the experimental E_A value. We therefore reason that there should be some interactions beyond the CF interaction that contribute to the magnetic field dependence. Previous studies on TTO and similar geometrically frustrated systems revealed the softening of the crystal field gap due to the presence of the spin-spin correlation.[5,41] The spin-spin correlation can significantly alter the CF in TTO since its energy gap is only O(10) K. It is therefore possible that the interplay between CF interaction and spin-spin correlation dominate the magnetic field dependence of the single-ion peaks. At zero field, the gap of CF is softened due to the spin-spin correlation between Dy^{3+} and Tb^{3+}, causing the disappearance of the T_s and T^* peak. With the presence of a field, the spin-spin correlation is dramatically altered, the gap of CF is again activated and thus the peaks appear. However, the spin-spin interactions are orders of magnitude smaller than the gap observed here, thus may not cause sizable softening of the gap. Another possibility is the presence of magnetoelastic coupling.[28,42,43] A giant magnetostriction has been reported in TTO (Ref. 43), indicating strong coupling between spin and lattice degree of freedom. In $Dy_xTb_{2-x}Ti_2O_7$, it is possible that similar magnetoelastic coupling act in a way that the magnetic field may change the chemical environment of the RE ion and tune the crystal field effectively. However, such a strong effect on crystal field (change by several tens of Kelvin) by a moderate magnetic field (1 T) is still surprising. The detailed mechanism remains to be explored.

At $H=10$ kOe, with E_A associated with Dy^{3+} attaining its zero-field value of 200 K, the composition dependence of the T^* peak can be understood as a consequence of the change in the crystal field with Dy^{3+} doping. The crystal-field scheme is intimately related to the structural parameters of the system,[24] including the lattice constants and the positional parameters of the eight oxygen surrounding the RE ion. Dy^{3+} doping leads to a systematic change in the structure and the corresponding changes in the crystal-field levels. A very recent specific-heat measurement on the same system[34] shows that for small concentration of Dy, a high-temperature peak corresponding to the first excited CF level of Tb^{3+} moves to higher temperature, indicating a modification of the CF of Tb^{3+} site, which is consistent with our understanding. Also, the linearity of $T^*(x)$ can be understood as a consequence of the monotonic increase in $E_A(x)$ by the Arrehnius relation with suitable parameters. Another possibility for the composition dependence of T^* peak is the crystal field-phonon coupling as suggested in TTO,[44] as Dy^{3+} doping alters the phonon spectrum and thus the CF level scheme.

The aforementioned similarity between the evolution of the ac susceptibility with increasing Dy doping x and that with constant x but increasing magnetic field now has a plausible interpretation. In both cases, the change in crystal-field levels dominates the behavior of the ac susceptibility: in the former case, the Dy doping changes the structure and alters the crystal field directly; in the latter case, the magnetic field affect the crystal field possibly through the magnetoelastic coupling.

IV. CONCLUSION

To conclude, we have systematically studied the ac susceptibility of $Dy_xTb_{2-x}Ti_2O_7$. A new peak associated with single-ion Tb^{3+} (T^* peak) is observed, together with another peak associated with that of Dy^{3+} (T_s peak). The phase diagram of both $T^*(x)$ and $T_s(x)$ is presented showing the characteristic temperature increasing linearly with x. Both T_s and T^* peaks show strong frequency dependence, suggesting that the transition is thermally activated. We interpret the origin of the energy barrier to be associated with the gap in the lowest-lying CF levels of Dy^{3+} and Tb^{3+}. However, the extracted energy barrier for the T^* peak is an order of magnitude higher than that of TTO and comparable to that of DTO. Furthermore, despite the large energy barrier, O(100 K), these characteristic temperatures are strongly influenced by applied magnetic field. Further neutron experiments and theoretical calculations may help to fully understand the system.

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