CHAPTER 6: Classification of Magnetic Spin Freezing of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ in Terms of Quantum Criticality

6.1 Introduction

In chapter 5, effect of structural distortions and magnetic perturbation on the spin dynamic of $Dy_2Ti_2O_7$ has been studied. It has been found that the Ising spin are strongly correlated and sensitive to the nature of neighboring magnetic ion's spins. In these materials, order of dipolar and exchange spin interactions are very small [48], [127]. Because of thermal/quantum fluctuations the rare earth ion's spin fluctuates via local transformation. These fluctuations force these correlated Ising spins to retain a liquid-like disordered phase even at low temperatures [16], [17], [22], [23], [65], [71]. As discussed in chapter 1, these materials posses two spin freezing at ~16 K (T_f) and ~4 K (T_{ice}) [61], [65], [69], [70]. It has been found that both T_f and T_{ice} strongly depend on the strength of the applied magnetic field. Further, spin ice freezing (T_{ice}) vanishes above an applied field of 1 T for both DTO and HTO [41], [57], [70]. Furthermore, in HTO spin dynamics are governed by the quantum fluctuation up to 30 K whereas in case of DTO it existed only up to ~12 K [61], [71]. The dependency of spin freezing on magnetic field and involvement of possible quantum fluctuations, DTO and HTO can be investigated in terms of "quantum criticality" of Quantum Phase Transitions (QPT). QPT follows the $(x\text{-}x_C)^{1/2}$ behavior with non-thermal parameters whereas in the classical region it follows $(x\text{-}x_C)$ type variation [76]–[78].Through the application of non-thermal control variables, such as pressure (P), composition(x), or magnetic field (H), one can obtain the Quantum Critical Point (QCP) as well as the region of quantum criticality of the materials. The discernment of quantum criticality and its associated

exotic phases in magnetically frustrated materials are one of the important problems of physics as well as from the application point of view [140], [141]. In this chapter, classification of the quantum critical region and control variables which affects the quantum critical point of HTO and DTO has been investigated.

6.2 Results and discussion

6.2.1 Magnetic analysis of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$

6.2.1.1 ac susceptibility and H-T Phase diagram of $Ho_2Ti_2O_7$

Figure 6.1 shows the temperature dependence of the real part (χ') of the ac susceptibility under different dc bias magnetic field in the range of 0 to 6 T measured at 500 Hz. For the sake of clarity, the field-dependent data has been splited into two parts. Figure 6.1 (a) shows the ac susceptibility response up to an applied field of 1 T. The inset of figure 6.1 (a) shows the changes in the freezing temperature more clearly. It has been found that in absence of field, no freezing is observed up to lowest measured temperature as shown in figure 6.1(a). On application of 0.35 T of external field, freezing belonging to T_{ice} appeared prominently, whereas the freezing corresponding to T_f has yet to develop. On further increase in the magnetic field i.e. 0.5 T, both freezing correspondings to T_f and T_{ice} are distinctly observed. On further increase in the applied magnetic field, the T_{ice} freezing gets suppressed whereas T_f freezing becomes pronounced and gradually shifted towards the higher temperature side.

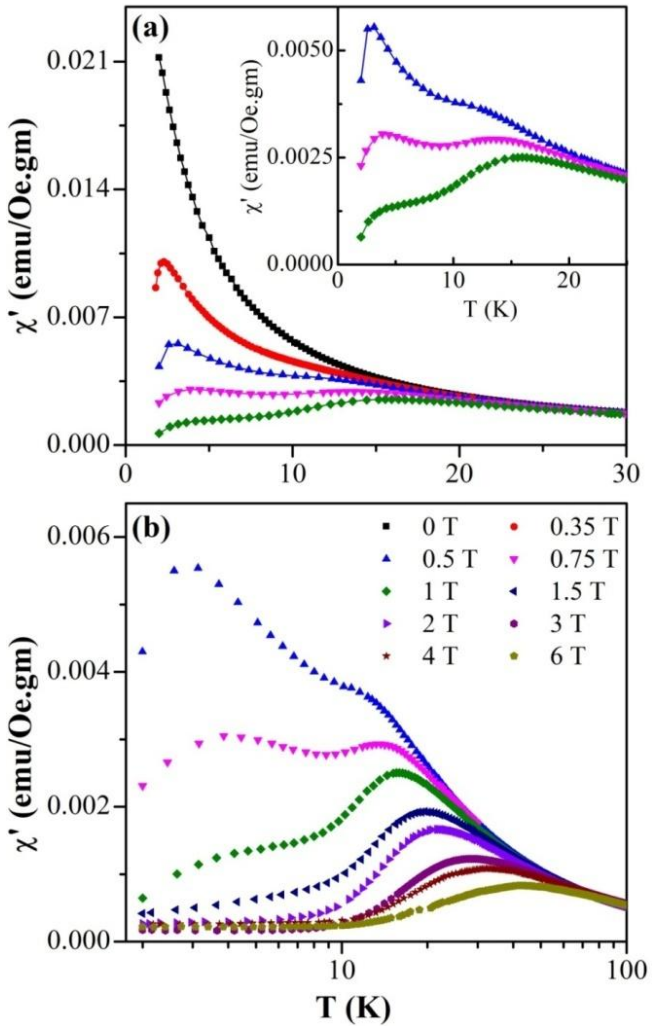

Figure 6.1: Temperature dependence of the real part of ac susceptibly measured at 500 Hz for dc bias field; (a) 0, 0.35, 0.5, 0.75 and 1 T and (b) 0.5, 0.75, 1, 1.5, 2, 3, 4 and 6 T for $Ho_2Ti_2O_7$ compound.

With the help of the obtained values of T_f with respect to H, T_f vs. H plot has been shown in figure 6.2 (a). As discussed above, in the quantum critical region, T_f follows $(H\text{-}H_C)^{1/2}$ variation whereas in the classical region it obeys a linear relation [76], [142], [143]. To investigate the type of dependency of T_f on H, observed T_f vs. H plot is fitted using $(H\text{-}H_C)^{1/2}$ expression in the field range 0.5-2 T and extrapolated. The value of the critical field (H_C) at QCP has been found 340± 35 Oe. The fitted curve is extrapolated up to 0 T to 7 T and shown by the pink color solid line in T_f vs. H plot (figure 6.2 (a)). The so obtained phase diagram

shows the deviation of T_f from $(H\text{-}H_C)^{1/2}$ variation at higher field. To obtain the deviation temperature, a linear fit has been performed in 3-6 T field range and extrapolated at the lower field (red line). The extrapolated curve shows a clear deviation from the liner behavior in the lower field region. The point of intersection of both fitted curve shows the crossover region at ~28.5 K temperature.

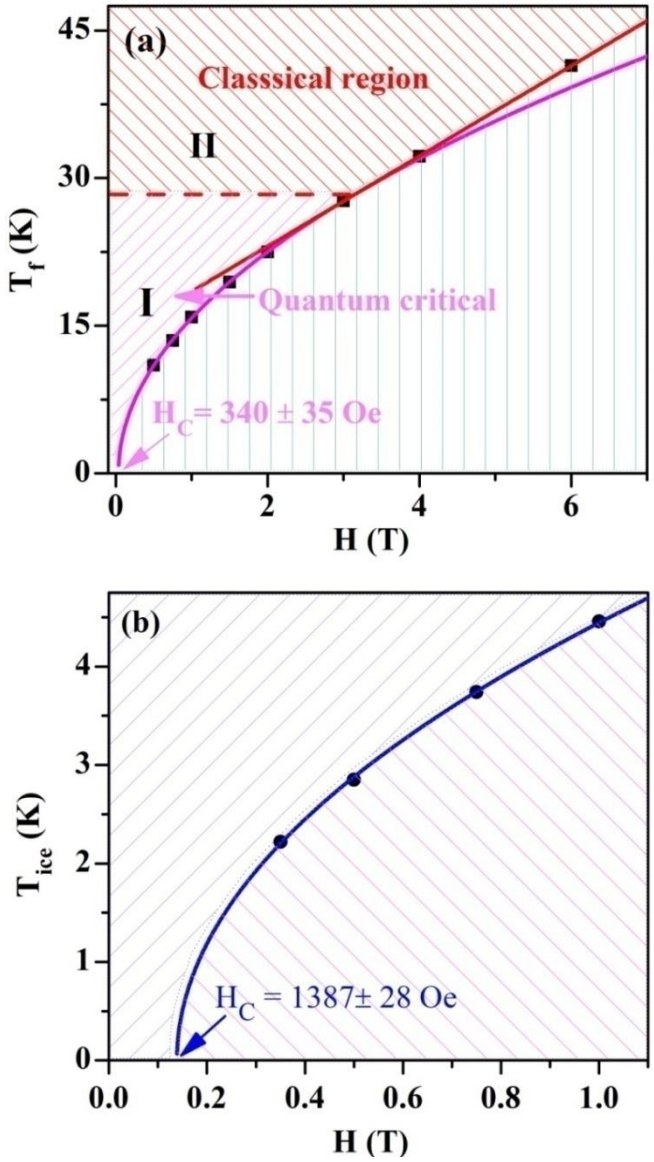

Figure 6.2: H-T phase diagram of the $Ho_2Ti_2O_7$ compound for (a) T_f and (b) T_{ice} freezing with deduced value of H_C. The $(H\text{-}H_C)^{1/2}$ fit is represented by solid pink and blue line whereas the linear fit is represented by a solid red line.

On the basis of observed fitting, H-T phase diagram is categorized into two distinct regions termed as-quantum critical and classical represented by I and II in the figure 6.2 (a). In regime I existed upto ~28.5 K, T_f vs. H plot follows $(H-H_C)^{1/2}$ relation. Above 28.5 K, (regime II), a crossover from quantum critical to classical region takes place, where spin dynamics is governed by classical thermal fluctuations. It has been noted that observed crossover temperature is almost same as obtained from neutron scattering measurement for this compound, thus further confirming the validity of the H-T phase diagram [70]–[72].

These experiments suggest that effect of magnetic field on T_{ice} is more prominent in comparison to single ion spin freezing T_f. M. Vojta has shown that, for these frustrated materials, there is a possibility that spin ice freezing may affect the value of the critical field at QCP [140]. For the spin ice freezing, T_{ice} vs. H plot is shown in figure 6.2 (b). The $(H-H_C)^{1/2}$ fitting yield critical field, H_C= 1387± 28 Oe at QCP which is larger than the critical field obtained for that of the single ion spin freezing (340Oe). The $(H-H_C)^{1/2}$-type variation of T_{ice} further confirms the formation of this exotic state in the quantum critical region.

6.2.1.2 ac susceptibility and H-T Phase diagram of $Dy_2Ti_2O_7$

To further confirm the validity of the H-T phase diagram, ac susceptibly measurement at different magnetic field has been performed on DTO as well. In the case of DTO, quantum fluctuations existed up to 12 K [61], [65]. This means that observed single spin freezing temperature (~16 K) will show the classical liner relation in $H-T_f$ plot whereas lower temperature spin ice freezing to shows $(H-H_C)^{1/2}$-type variation. Figure 6.3 shows the temperature dependence of the real part of ac susceptibility of DTO measured at 200 Hz frequency for different magnetic field. Unlike to HTO, in this compound, both T_f and T_{ice} freezing is observed in absence of an external magnetic field. However, on the application of

magnetic field, both freezing gradually shifted towards the higher temperature similar to HTO.

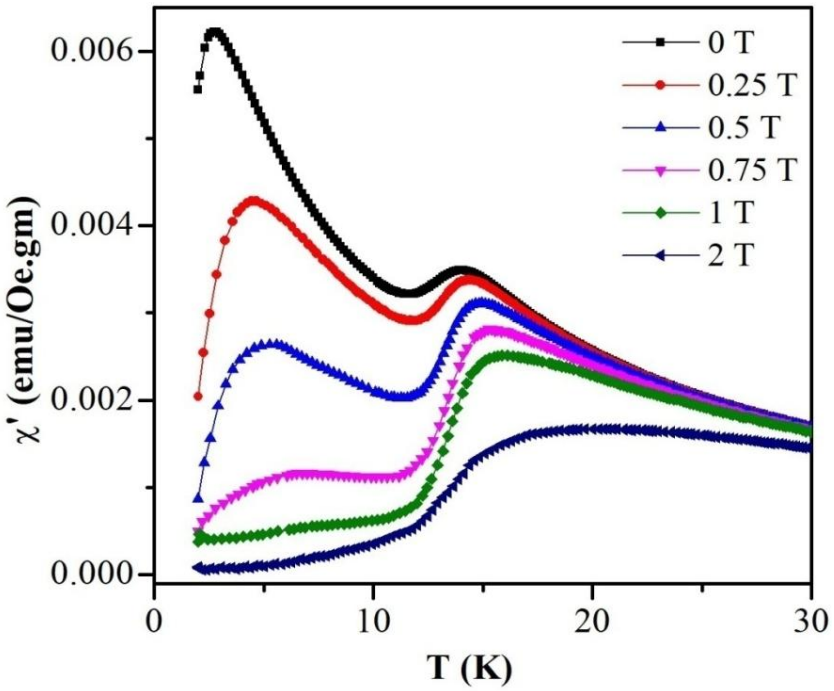

Figure 6. 3: Real part of magnetic susceptibility of $Dy_2Ti_2O_7$ compound measured at 200 Hz frequency for 0, 0.25, 0.5, 0.75, 1 and 2 T, dc bias magnetic field.

With the help of obtained values of T_f and T_{ice} with respect to H, H-T phase diagram for both freezings has been plotted and shown in figure 6.4. A linear fit for T_f vs. H plot is shown by red color in figure 6.4 (a) thus depicting the classical liner relation. A similar variation in the T_f with H has been obtained by shi et al. in ac susceptibility studies of the single crystal of DTO [144]. The linear variation of T_f with respect to field confirming the classical nature of observed freezing. On the other hand, variation of T_{ice} freezing with magnetic field shows the $(H-H_C)^{1/2}$ variation having QCP at H_C = -1558± 48 Oe. The $(H-H_C)^{1/2}$ variation of spin ice freezing confirms that this freezing lies in the quantum critical region.

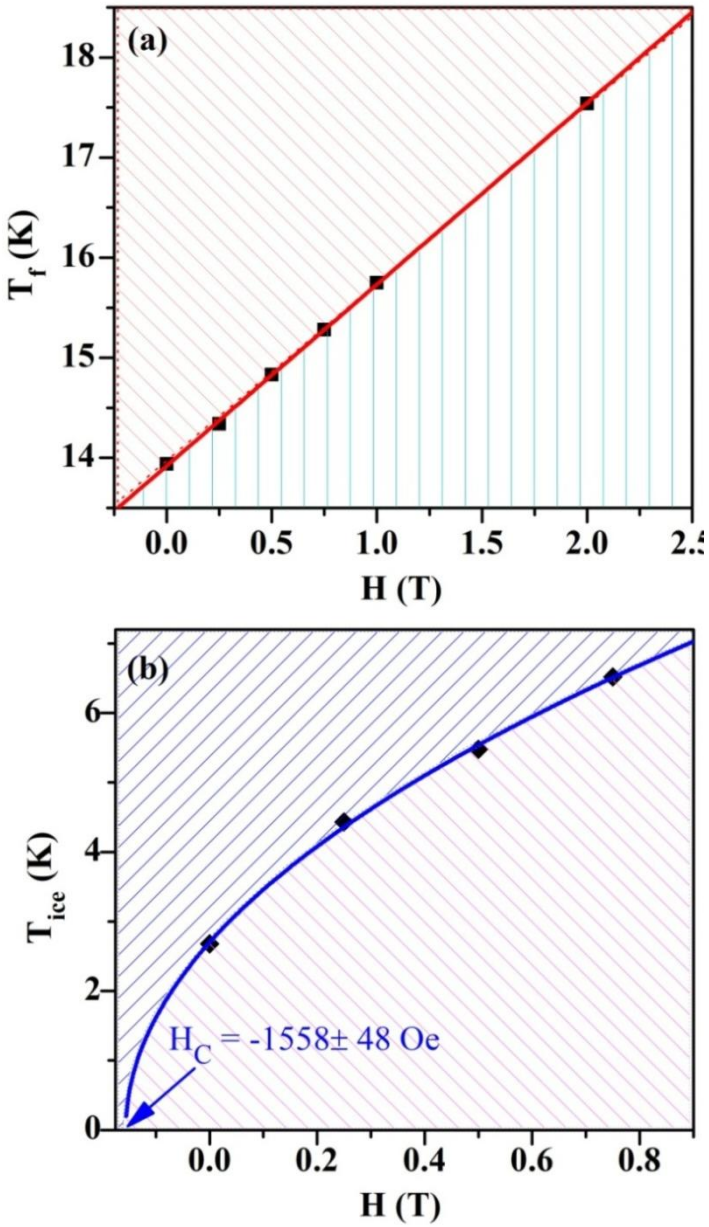

Figure 6.4: H-T phase diagram of $Dy_2Ti_2O_7$ compound for (a) T_f and (b) T_{ice} freezing with deduced value of H_C.

The negative value of critical field suggests that this compound have very large energy barrier to flip the Ising spin from one direction to another. This energy barrier associated with the local internal magnetic field (H_{int}) induced by crystal field, spin-lattice and magnetic interactions and have exponential relationship with spin flip time. On application of external

perturabation (magnetic field in this case), this underlying energy barrier increases linearly. As the spin-flip time, follows the Arhenius like behaviour, it increases exponetially, which in turn reflected through emergence and shifting in freezing temperature. This means that positive or negative value of critical field represents the magnitude of the magnetic field needed to obtain the spin freezing at absolute zerotemperature via enhancement or suppressionin the internal field-induced energy barrier through external variables giving an important physical parameter to control the quantum critical limits.

In the case of HTO, it has been found that T_{ice} freezinghavea larger value of critical field than the T_f freezing. The increment in the critical field of T_{ice} freezing indicates that underlying magnetic interaction responsible for this freezing also affecting the energy barrier similar to the magnetic field. To see the effect of magnetic interaction on energy barrier, B-site Mn substituted $Ho_2Ti_{1.9}Mn_{0.1}O_7$ and $Dy_2Ti_{1.9}Mn_{0.1}O_7$ samples have been synthesized. Due to strongly interacting nature of magnetic Mn ion, it is supposed that this substitution will alter the internal field induced energy barrier.

6.2.2 Structural analysis of $Ho_2Ti_{1.9}Mn_{0.1}O_7$ and $Dy_2Ti_{1.9}Mn_{0.1}O_7$

The diffraction pattern shown in the figure 2.2 and 2.3 in chapter 2 has been analyzed using Rietveld refinement. Through the Rietveld refinement, $Fd\bar{3}m$ space group and site occupancy of Ho, Dy and Ti/Mn ions at 16c and 16d sites of HTMO and DTMO samples have been confirmed. The obtained fit is remarkably good and shown in figure 6.5. The obtained reliable fitting parameters R_p, R_{wp}, R_{exp} and lattice constant are shown in the table 6.1. It has been found that in HTMO and DTMO a decrease in the lattice constant takes place without affecting the cubic $Fd\bar{3}m$ crystallographic phase.

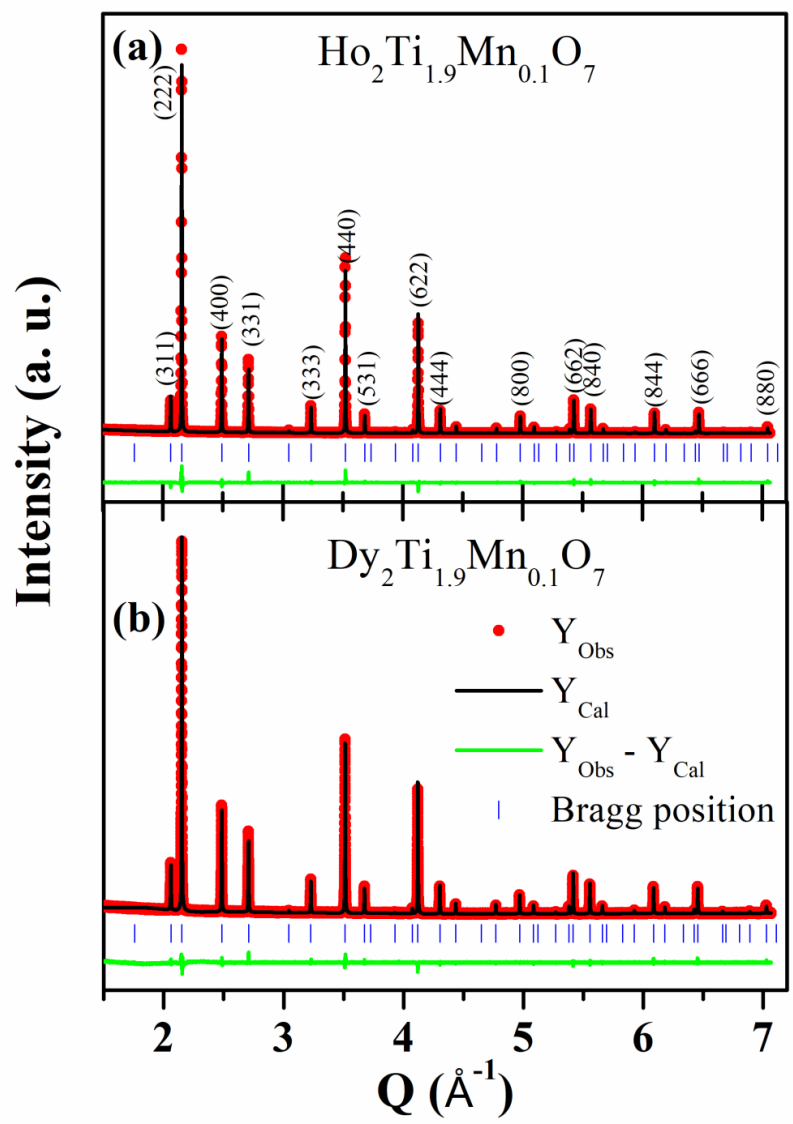

Figure 6.5: Rietveld refinement of x-ray diffraction pattern of polycrystalline; (a) $Ho_2Ti_{1.9}Mn_{0.1}O_7$, and (b) $Dy_2Ti_{1.9}Mn_{0.1}O_7$.

Table 6.1: Details of refinement as obtained from high-resolution x-ray diffraction. Compound, lattice constant, variable coordinate x of 48f-site, R-factors (R_p, R_{wp} and R_e) and goodness of fit χ^2.

Compound	a (Å)	x (48f)	R_p	R_{wp}	R_e	χ^2
$Ho_2Ti_{1.9}Mn_{0.1}O_7$	10.0913(4)	0.329(1)	12.2	12.4	7.56	2.70
$Dy_2Ti_{1.9}Mn_{0.1}O_7$	10.0804(1)	0.327(1)	25.2	16.8	14.81	1.29

6.2.2.1 ac susceptibility of $Ho_2Ti_{1.9}Mn_{0.1}O_7$ and $Dy_2Ti_{1.9}Mn_{0.1}O_7$

To investigate this phenomenon, field dependent ac susceptibility of HTMO and DTMO has been measured. Figure 6.6 shows the temperature dependence of the real part of the ac susceptibly measured at 200 Hz for 0 T, 0.5 T and 0.75 T applied magnetic fields for both the compounds. It has been found that the spin ice freezing which does not appear without a magnetic field in HTO appears in HTMO even in absence of applied magnetic field (fig. 6.6 (a)). On application of an applied dc magnetic field, this freezing shows a shifting towards the higher temperature side. In case of DTMO, T_{ice} shifts towards higher temperature whereas T_f shifts towards the lower temperature side (see figure 6.6 (d)). On application of external magneticfield, T_{ice} freezing disappeared whereas T_f freezing shifted towards the higher temperature (figure 6.6 (e & f)). These observations suggest that altered magnetic interaction in HTMO and DTMO, spin freezing lies in the quantum critical region shifted towards the higher temperature whereas thermal classical spin freezing shifted towards the lower temperature. The appearance and shifting of spin freezing lie in the quantum critical region suggest alteration in energy barrier. Due to this alteration in energy barrier, a prominent change in the spin ice freezing takes place. This change in the spin ice freezing also follows the $(x\text{-}x_C)^{1/2}$ variation further confirming the dominance of quantum fluctuation in these systems. The change in T_{ice} suggests that effect of altered effective energy barrier on the spin freezing closer to the quantum critical point is much significant due to $(x\text{-}x_C)^{1/2}$ variation.

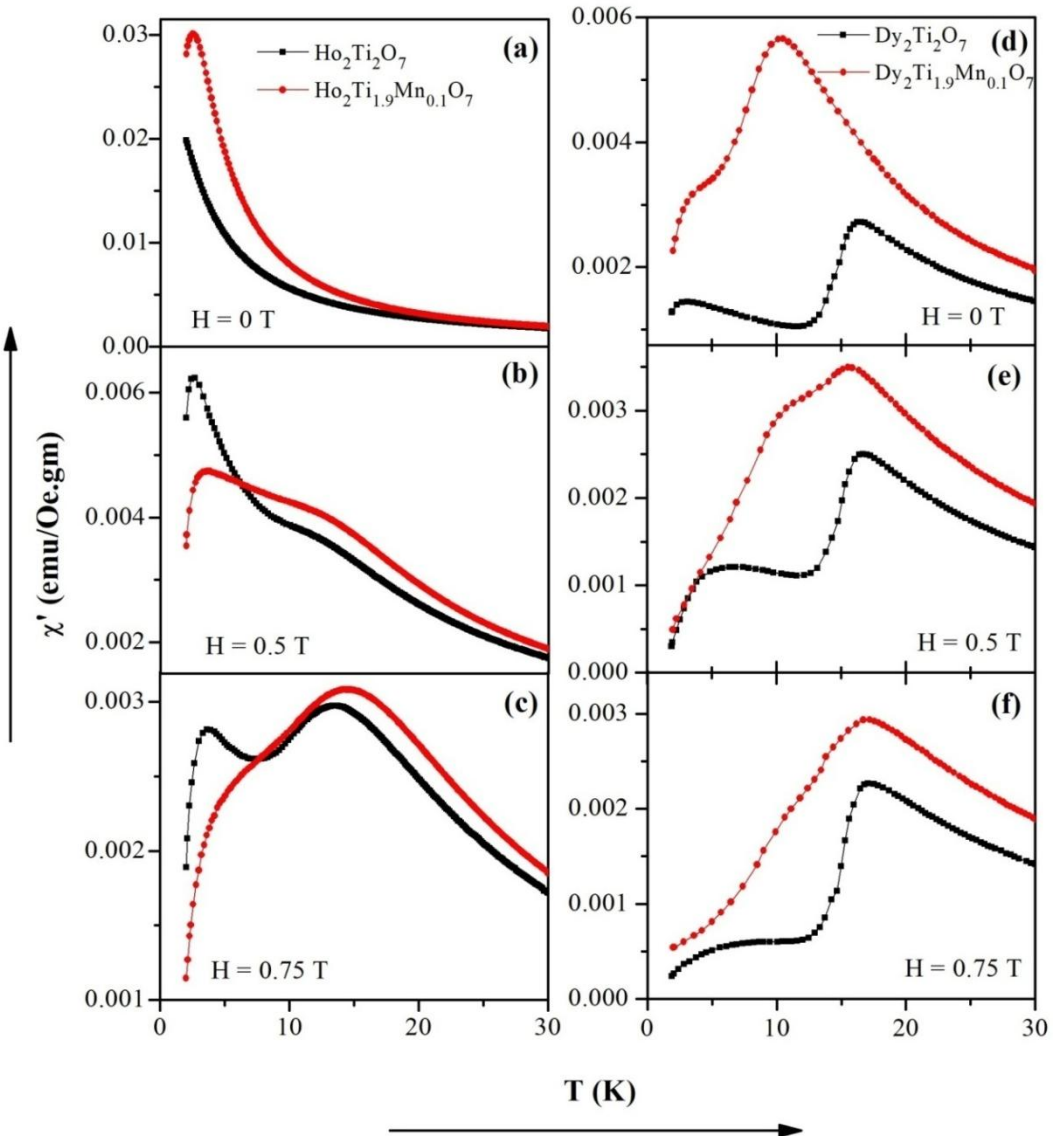

Figure 6.6: Temperature dependence of the real part of ac susceptibly measured at the 200 Hz frequency for $Ho_2Ti_2O_7$ and $Ho_2Ti_{1.9}Mn_{0.1}O_7$ (a, b, & c) and for $Dy_2Ti_2O_7$ and $Dy_2Ti_{1.9}Mn_{0.1}O_7$ (d, e, & f) at different DC bias field.

6.3 Conclusion

These results can be sumarise as: in $Ho_2Ti_2O_7$ both single ion spin freezing temperature (T_f) and spin ice freezing temperature (T_{ice}) lies in the quantum critical region whereas in $Dy_2Ti_2O_7$ only T_{ice} lies in the quantum critical region. The obtained values of critical field at quantum critical point suggests higher effective energy barrier for spin relaxation in DTO in

comparison to HTO. The value of critical field represents magnitude of the magnetic field needed to influence spin freezing at absolute zero temperature. ac sucessptibilty study of B-site Mn substituted $Ho_2Ti_{1.9}Mn_{0.1}O_7$ and $Dy_2Ti_{1.9}Mn_{0.1}O_7$ shows that these substitutions affect T_{ice} freezing in more prominent way in comparasion to the single ion freezing T_f in these componds, which means that competing magnetic interactions acting in different temperature regime are one of the preliminary factors responsible for the alteration in quantum critical point in these compounds. This observed dependencies of the low temperature phases on non-thermal external variable, open a new route to investigate the underlying physics of geometrically frustrated magnetic materials in terms of quantum criticality at non-zero temperatures.