CHAPTER 7: Quantum Correlations and Its Associated Scrambled Quantum Information in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$

7.1 Introduction

In previous chapter it has been observed that in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ spin freezing lies in quantum critical region follows the $(H\text{-}H_C)^{1/2}$ behaviour. It has been well known that in quantum state, macroscopic properties of quantum materials are governed by ground state quantum fluctuations in which quantum information are propagated in a correlated manner with temporal evolution [79]–[81]. Due to quantum correlation, quantum materials have memory to distinguish their widely differing initial conditions i.e. properties of these materials depend on initial conditions. At finite temperature, thermalization phenomena erase the memory of these quantum systems by dephasing the quantum correlations [82]–[84] and put a limit for the experimental realization of quantum information. Recently, experimental realization of scrambled quantum information in atomic and bi-particle quantum systems triggered a new hope to study the exotic quantum behavior of other quantum materials [79], [81], [82]. Experimental findings reveal that in these quantum systems, due to the ergodic nature of microstate, thermalization phenomena of each microstate occurs individually though they are strongly correlated with each other [82], [85], [86]. It suggests that dephasing of quantum correlations are taking place at the microscopic level and for the study of exotic quantum behavior in materials, prevention of thermalization is mandatory, which remains a challenge. The unawareness of measurement protocol which set bound on thermalization to reach the system in thermal equilibrium and crucial variable of exotic quantum behavior further increases the puzzle.

The focus of the present chapter is dedicated to the experimental realization of exotic quantum behavior and their sensitivity on external stimuli in HTO and DTO quantum system. In previous studies it have been reported that in both HTO and DTO spin dynamics follow the thermally activated classical behavior even they lie in quantum critical region [61], [72]. However, the cause of classical behavior of spin in the quantum critical region in these compounds is still unknown and matter of investigation.

7.2 Results and Discussion

7.2.1 ZFCW, FCC and FCW of χ (T) measured at different magnetic field

To investigate the quantum correlations in HTO and DTO, static and dynamic magnetic properties has been performed in cooling and warming mode. Inset of figure 7.1 (a) shows the temperature-dependent zero field cooled warming (ZFCW) (solid line), field cooled cooling (FCC) (solid symbol) and field cooled warming (FCW) (open symbol) dc magnetization of HTO measured at several magnetic fields. In temperature-dependent magnetization, no difference has been observed in cooling down (FCC) and warming up (ZFCW and FCW) measurement for all external dc magnetic fields. This observation suggests that static properties of HTO do not depend on the cooling and warming measurements mode. A similar measurement protocol has been performed to study the dynamic properties of HTO in the presence of different external dc magnetic field. Figure 7.1 (a) shows the temperature-dependent ZFCW, FCW and FCC ac susceptibility of HTO measured at 200 Hz for different external dc magnetic field in temperature range 2-30 K. In ZFCW, FCC and FCW ac susceptibility performed in absence of external magnetic field, no thermal hysteresis has been observed in the measured range of temperature. Whereas, on the application of external dc magnetic field, along with the appearance of spin ice and single ion spin freezing, thermal hysteresises ($\Delta\chi'$) are observed and becomes pronounced at lower temperature. On increasing the external magnetic field strength, a variation in the magnitude of $\Delta\chi'$ has been observed. To get more insight information about the magnetic field induced thermal hysteresis, a similar study has been performed on DTO as well. Inset of figure 7.1 (b) shows the temperature dependent ZFCW, FCC and FCW magnetization measured at different magnetic field. In the static magnetic measurement of DTO, no thermal hysteresis has been observed in the measured range of temperature for all magnetic fields. Figure 7.1 (b) shows the temperature dependent ZFCW, FCC and FCW ac susceptibility of DTO measured at 200 Hz frequency for different external dc magnetic field. It has been found that similar to HTO in DTO as well, thermal hysteresis is emerged in the presence of an external dc magnetic field and varies with the strength of the external dc biased magnetic field.

These observations conclude that in both HTO and DTO magnetic field induced thermal hysteresis emerges in ac susceptibility measurements. To investigate the variation in the magnitude of $\Delta\chi'$ with external magnetic field strength, magnetic field dependent variation in $\Delta\chi'$ plot has been drawn at different temperature for both HTO and DTO as shown in figure 7.2 (a & b). It has been found that on the application of magnetic field $\Delta\chi'$ gets increases with the increasing magnetic field up to a critical field H_{max}. Above the value of H_{max}, a decrease in the value of $\Delta\chi'$ takes place in both HTO and DTO compounds. Furthermore, on increasing temperature, $\Delta\chi'$ gets suppressed with shifting in the peak maxima (H_m) towards higher magnetic field. Inset of figure 7.2 (a) shows the thermal variation in H_{max} for both HTO and DTO. It has been observed that in the case of HTO, thermal variation in H_{max} is very small in comparison to DTO. The thermal dependence of $\Delta\chi'$ and H_{max} suggest that thermal energy washes the field-induced thermal hysteresis in these compounds. The larger slope in temperature-dependent H_{max} of DTO further suggests the larger effect of thermal energy on the magnitude of $\Delta\chi'$ in comparison to HTO.

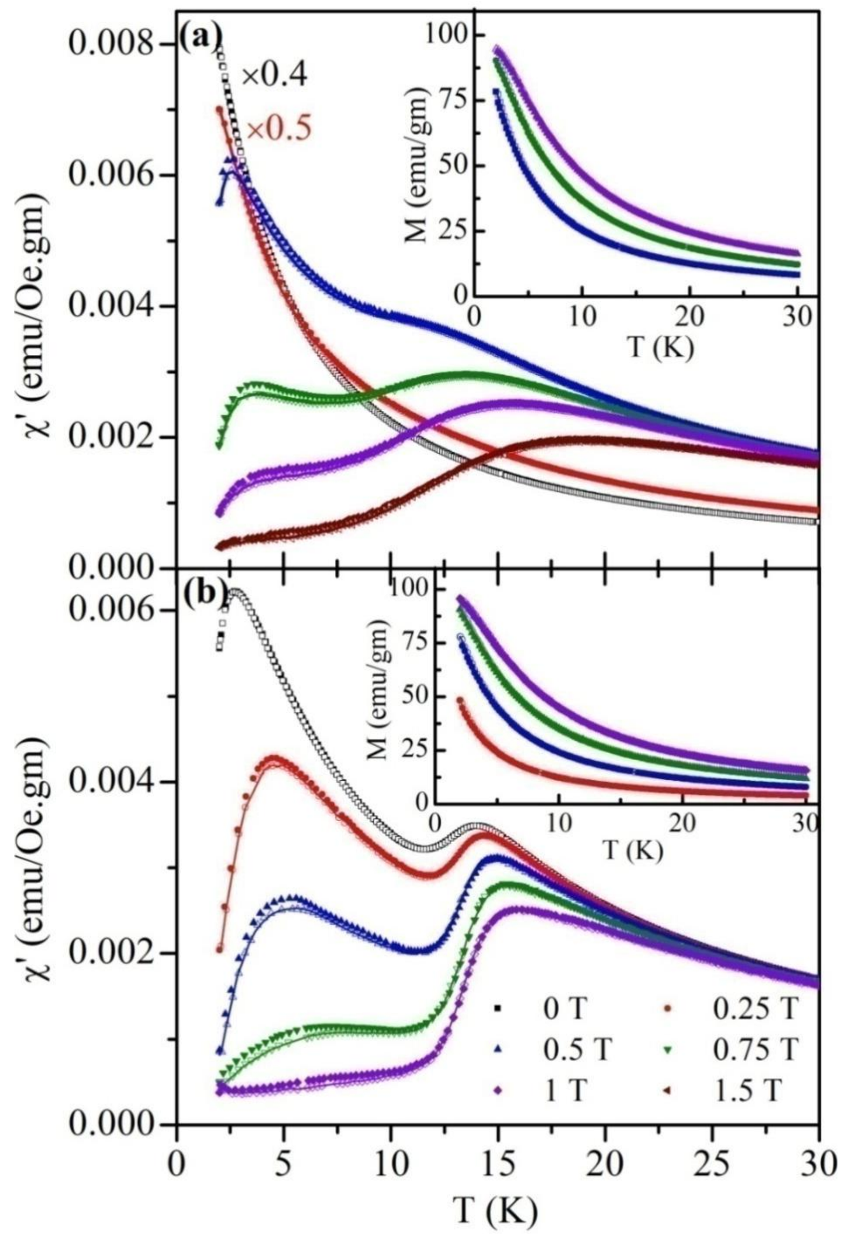

Figure 7.1: Temperature dependent ac susceptibility of (a) $Ho_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$ measured at different magnetic field in ZFCW, FCC and FCW measurement mode at frequency 200 Hz. Inset shows the temperature dependent dc magnetization of (a) $Ho_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$ in ZFCW, FCC and FCW measurement mode at different magnetic field.

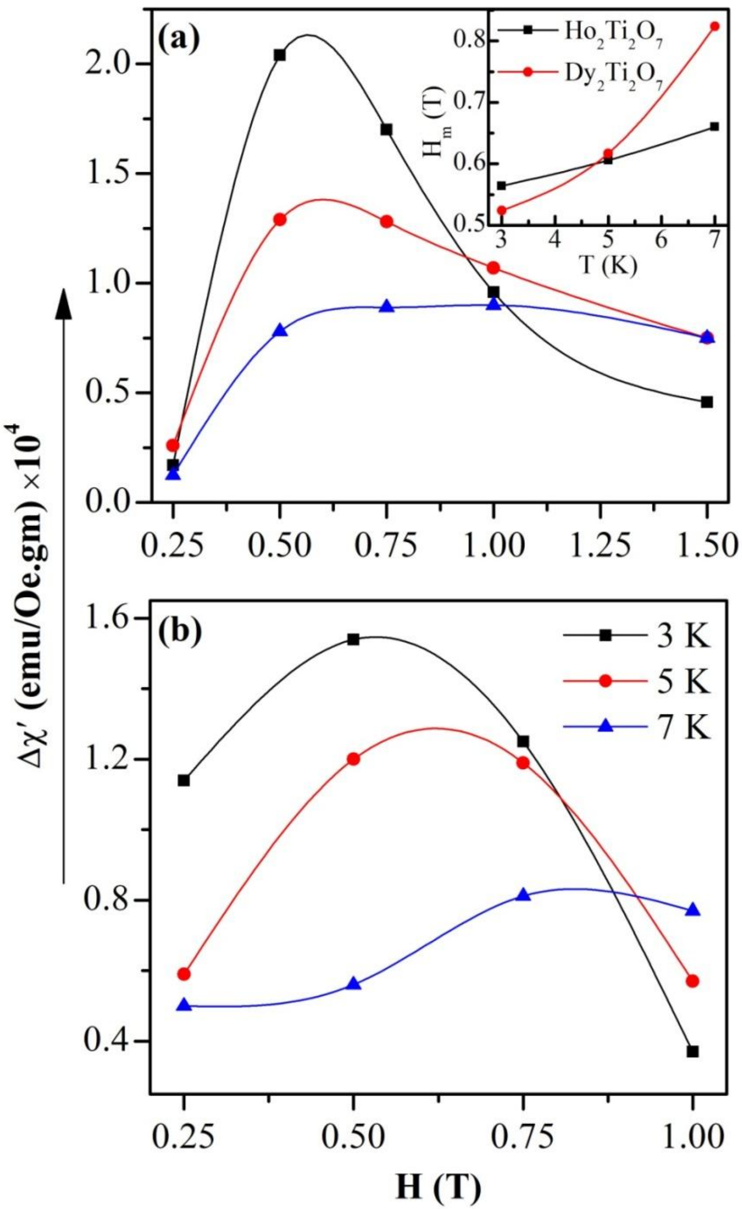

Figure 7.2: Variation of thermal hysteresis ($\Delta\chi'$) with external magnetic field for different temperature in (a) $Ho_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$. Inset shows the temperature dependent variation in peak maxima (H_m) for $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$.

The appearance of field-induced thermal hysteresis in ac susceptibility showing the individual coupling of spin with thermal bath [52], [145]. One needs to explore the possible role of external magnetic field as well. In HTO and DTO acting crystal field having strength of ~10^3 T, which is responsible for the Ising nature of Ho/Dy spin [137]. This means that applied external magnetic field can only increase the spin-flip time by splitting the degeneracy of Ising doublet state without affecting the Ising nature. Furthermore, due to the non-collinear spin structure, effect of applied magnetic field on the spin-flip time of individual Ising spins is different. Thus, an applied magnetic field breaks the ergodic nature of Ising spin into non-ergodic which increases the thermalization time i.e. time needed to reach the system in thermal equilibrium. On increasing magnetic field strength, the increment in the thermalization time increases until ordering of spins does not take place. After a critical field which enable the spin ordering, the role of thermalization processes will be minimal which in turn responsible for the suppression in the thermal hysteresis ($\Delta\chi'$) above the critical field H_{max}.

7.2.2 FCC and FCW χ (T) measured at different frequency

Since thermal hysteresis is observed only in the dynamic measurement of these frustrated compounds hence it will be interesting to know the sensitivity of $\Delta\chi'$ on measurement timescale. To investigate this temperature dependent ac susceptibility of HTO and DTO has been performed at different frequency in the presence of 0.75 T external magnetic field. It has been found that in both HTO and DTO the magnitude of $\Delta\chi'$ is rapidly decreasing with increasing frequency. In spite of this, it has been found that in case of HTO thermal hysteresis is observed in a wide temperature range ~25 K (fig. 7.3 a) whereas in DTO this hysteresis is observed only up to ~12 K (fig. 7.3 b). It has been reported for HTO that its quantum critical region is observed up to ~30 K whereas for DTO it is observed only up to ~12 K [61], [71]. In the measurements done in our case as well it has been noted that field-induced thermal hysteresis is also observed only in the quantum critical region where spin dynamics are governed by quantum fluctuations.

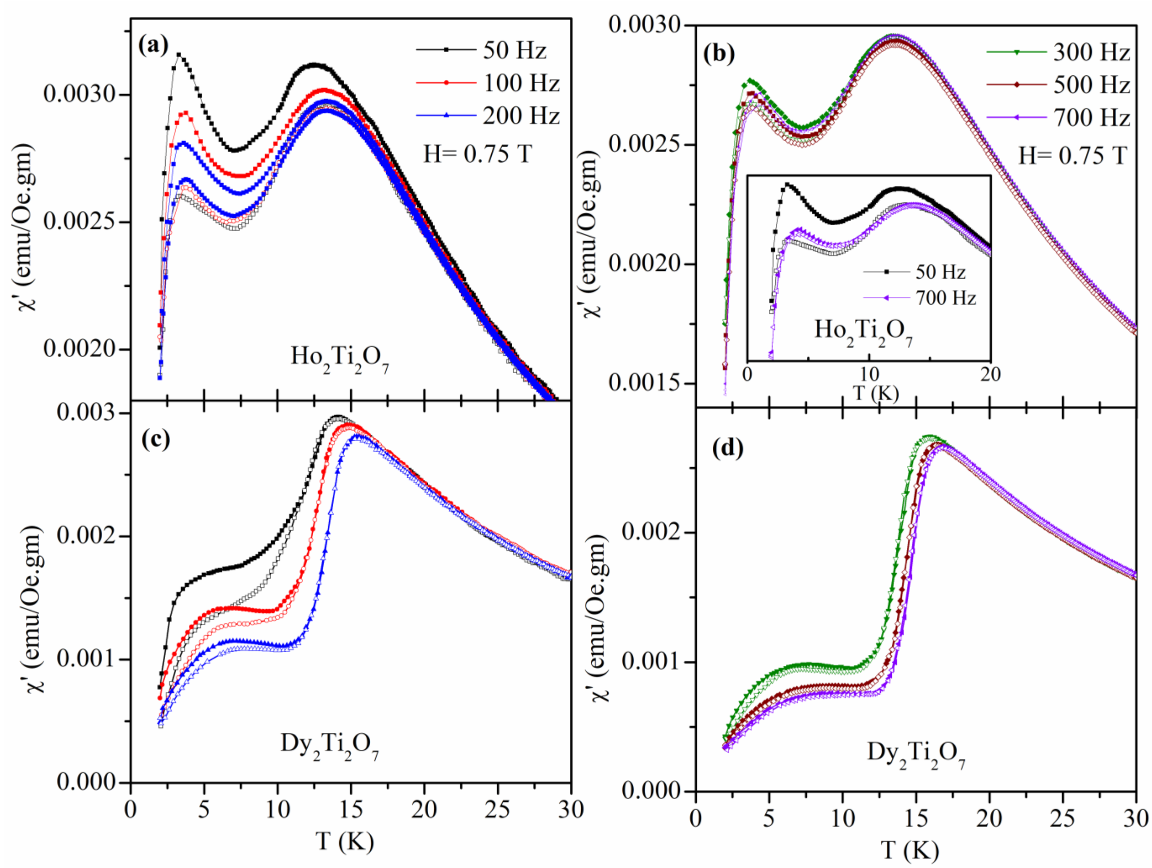

Figure 7.3: Temperature dependence of ac susceptibility (χ') of (a, b) $Ho_2Ti_2O_7$ and (c, d) $Dy_2Ti_2O_7$ measured at different frequency in FCW and FCC measurement mode at an external magnetic field 0.75 T. Inset of figure 7.3 (b) shows the variation in thermal hysteresis for 50 Hz and 700 Hz.

This observation suggests that observed field-induced thermal hysteresis in HTO and DTO is reflecting the scrambled quantum information of quantum correlations, which is anomalously sensitive to external stimuli.

7.2.3 Variation in thermal hysteresis $\Delta\chi'$ with frequency

To investigate the effect temperature and measurement timescale on $\Delta\chi'$, frequency dependence of $\Delta\chi'$ has been plotted at different temperature for both HTO and DTO, as shown in figure 7.4. It has been found that $\Delta\chi'$ follows exponential decay like behavior with applied frequency. In literature, it has been found that the decaying of quantum information with measurement timescale follows the exponential law given as [79].

$$F_{\phi}(\tau) = \sum_{m=-N}^{N} I_m(\tau) \exp(-im\phi) \tag{7.1}$$

Where, $F_{\phi}(\tau)$ represents the average over the magnetization of each spin in the array whereas $I_m(\tau)$,τ and ϕ represents the multiple quantum intensity, time and variable angle, respectively. In this context equation 7.1 can be rewritten as

$$\Delta\chi'(T) \propto I(T) \exp(-R(T)\times f) \tag{7.2}$$

Where, I(T) and R(T) are the intensity and decay rate of the quantum information at a constant temperature. The so observed exponential decay of $\Delta\chi'$ with frequency leads us to conclude that effect of applied ac-field frequency, which exponentially dephases the quantum correlations, is similar to temperature. Such a crucial dependency of scrambled quantum information on measurement time scale showing the sensitivity of quantum information on the measurement condition.

To understand the effect of temperature and underlying magnetic interaction on the intensity of this scrambled quantum information, which is associated to the difference in the susceptibility in this case, and its decay rate, temperature dependent I(T) and R(T) has been plotted for HTO and DTO and shown in figure 7.5. It has been found that in both HTO and DTO, I(T) and R(T) follow similar trends with temperature which indicates that both compounds exhibit a similar kind of mechanism. Temperature-dependentvariation in I(T) and R(T) of HTO and DTO shows non-monotonic temperature dependent behavior in different temperature regions. It has been found that on decreasing temperature up to ~6 K in HTO and ~5 K in DTO, I(T) increases gradually with a rapid decrease in the R(T) whereas on further lowering temperature both I(T) and R(T) rapidly increases up to ~3.5 K and ~3 K in HTO and DTO, respectively. Below this temperature, a rapid decrease in I (T) and R(T) takes place. In general it can be possible that on decreasing temperature quantum information I(T) gradually increases with simultaneous decrease in rate R(T) but a simultaneous rapid increase and decrease in both I(T) and R(T) in both compounds suggests that formation of low temperature spin ice state significantly affect the quantum information and its decay rate.

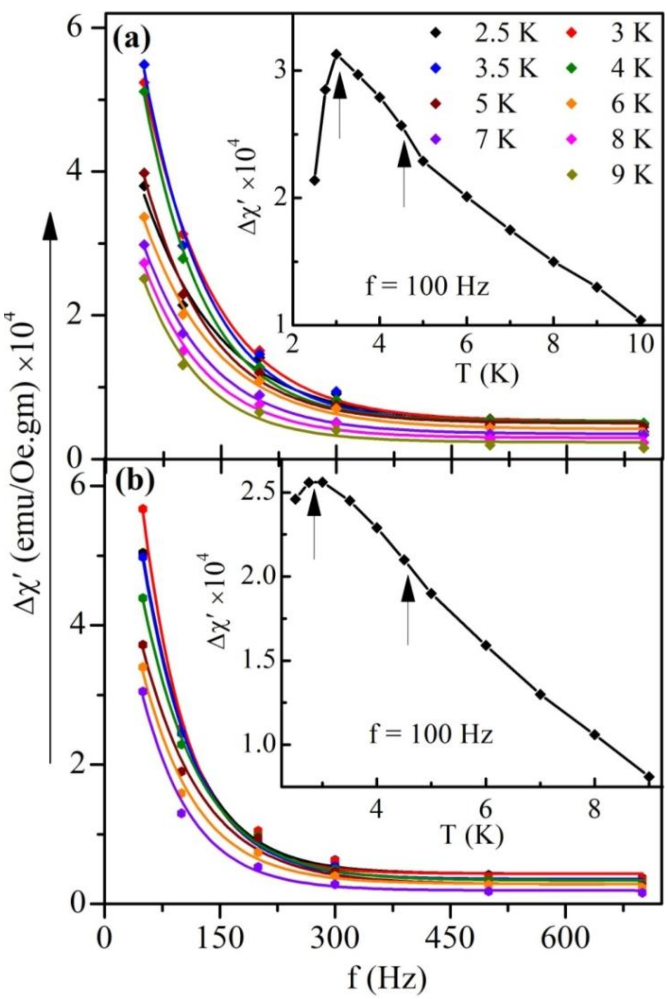

Figure 7.4: Exponential fit of frequency dependent thermal hysteresis ($\Delta\chi'$) of (a) $Ho_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$ for different temperatures. Inset shows the temperature variation in thermal hysteresis ($\Delta\chi'$) for 100 Hz frequency for both compounds.

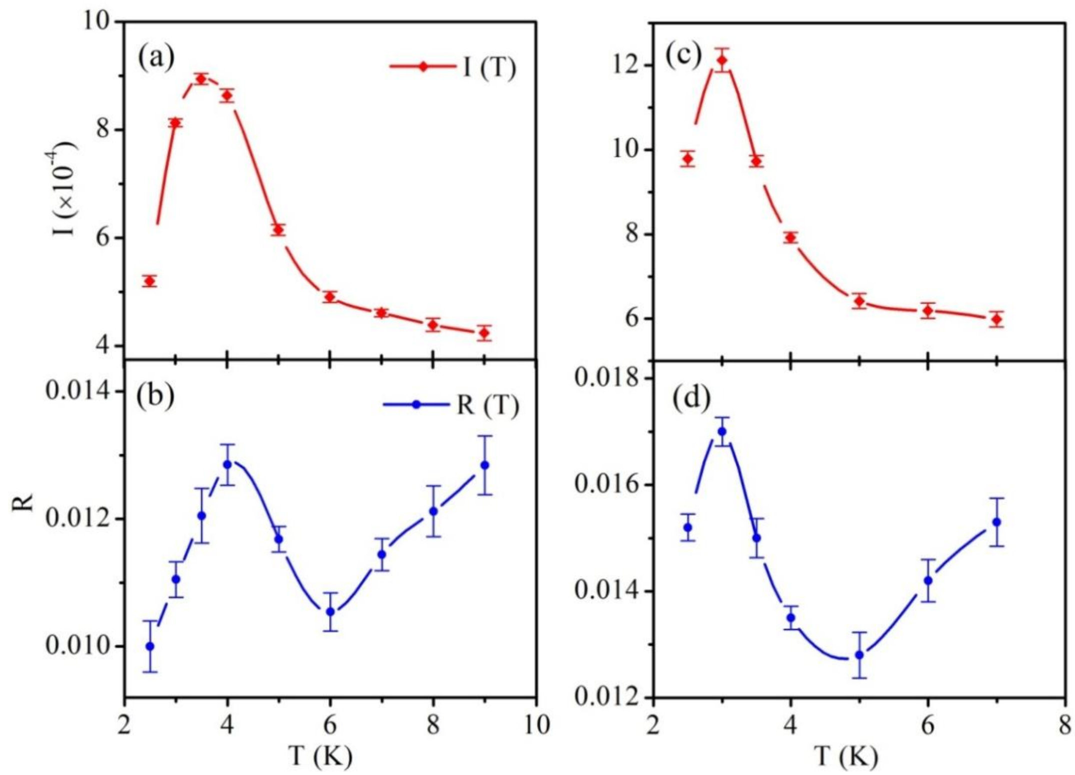

Figure 7.5: Temperature dependent variation in I(T) and R(T) parameters for (a) $Ho_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$ as obtained from exponential fit of frequency dependent thermal hysteresis($\Delta\chi'$).

To get more insight information temperature dependent variation in Δχ' for 100 Hz frequency has been plotted for both HTO and DTO as shown in the inset of Fig. 7.4 (a) and (b). It has been found that both compounds show the similar nature of variation in Δχ' with temperature which is well corroborated with I(T) and R(T) behaviour. In both HTO and DTO, Δχ' vs. T plot shows a linear increase in Δχ' up to ~5 K whereas below ~5 K to ~3 K, a further increment in their slope has been observed. With further decrease in temperature below ~3 K, a decrease in Δχ' has been observed. The so observed increase and decrease at ~5 K and ~3 K in both compounds is also corroborated with the temperature variation in I(T) and R(T). In literature, it has been reported that long-range dipolar correlations in these compounds existed up to ~10 K whereas spin ice state is formed below ~4 K by nearest neighbor effective ferromagnetic interaction [50], [127], [133]. This observation suggests that strengthen spin-spin correlation through dipolar interaction would be responsible for the anomalous increments in I(T), R(T) and $\Delta\chi'$. Whereas spin constraints by the underlying effective nearest neighbor interaction suppress the I(T), R(T) and $\Delta\chi'$.

7.2.4 ZFCW, FCC and FCW χ (T) of $Ho_2Ti_{1.9}Mn_{0.1}O_7$

To further confirms the effect of spin correlation and magnetic interactions on the intensity of quantum information, ac susceptibility of Ti-site substituted $Ho_2Ti_{1.9}Mn_{0.1}O_7$ (HTMO) compound has been measured. Due to insertion of the extra magnetic ion at non-magnetic Ti-site (Mn in this case) strengthen the interaction and correlation between the spins as observed for $Ho_{2+x}Ti_{2-x}O_{7-\delta}$ stuffed spin ice [72], [146]. Figure 7.6 (a) shows the ac susceptibility of $Ho_2Ti_{1.9}Mn_{0.1}O_7$ measured at different external magnetic field. It has been found that the spin ice freezing which does not appear in HTO without dc magnetic field appears even absence of external magnetic field. The appearance of spin freezing suggests that Mn substitution significantly alters the underlying spin interactions. Further, temperature dependent ZFCW, FCC and FCW ac susceptibility performed at different external magnetic field, shows thermal hysteresis in the presence of external magnetic field. This observation suggests that thermal hysteresis can be induced only by the application of an external magnetic field. Figure 7.6 (b) shows the temperature-dependent FCC and FCW ac susceptibility of HTMO and HTO measured at 100 Hz frequency in presence of 0.75 T magnetic field. In HTMO, a significant change the thermal hysteresis has been observed. To analyze the change in thermal hysteresis, temperaturedependent variation in $\Delta\chi'$ has been plotted for both HTO and HTMO as shown in the inset of Fig. 5 (b). It has been found that in case of HTMO, decrease in $\Delta\chi'$ takes place at ~5 K in spite of 2.75 K whereas above 5 K, $\Delta\chi'$ shows a small increment in comparison to HTO. This observation suggests that this change might be due to the change in the altered magnetic interactions because of Mn presence. It is mandatory to know that observed field-induced thermal hysteresis is associated with the ground state or by high to low entropy crossover.

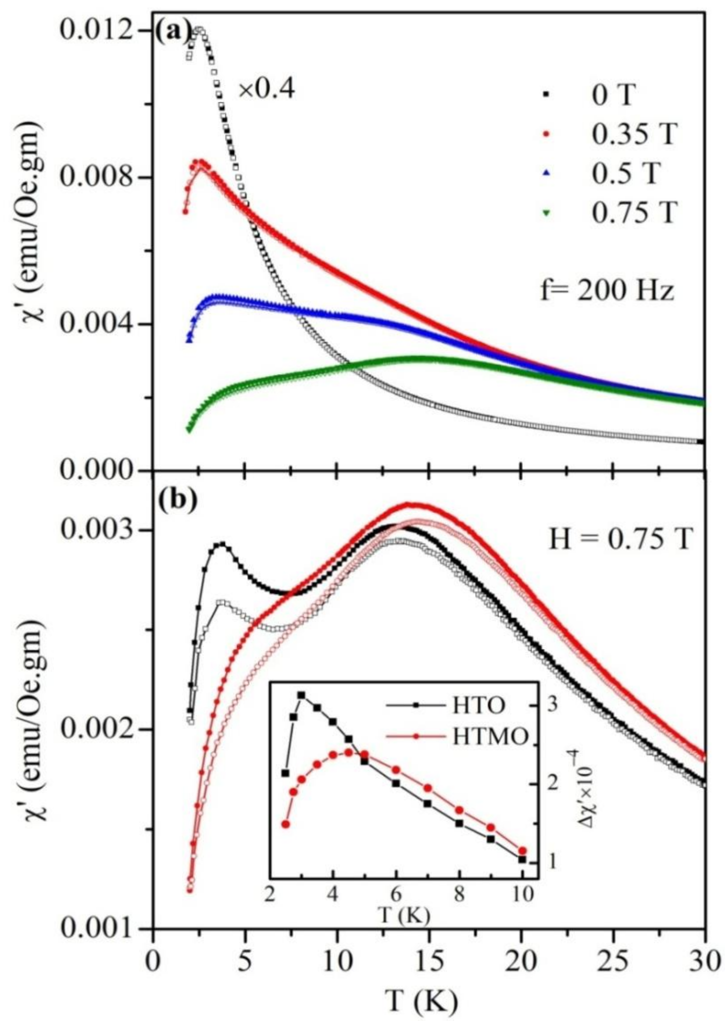

Figure 7.6: For $Ho_2Ti_{1.9}Mn_{0.1}O_7$; (a) temperature dependent real part (χ') of ac susceptibility measured at different external magnetic field in ZFCW, FCC and FCW measurement mode at a constant frequency 200 Hz. Inset shows the ZFCW, FCC and FCW of temperature dependent magnetization measured at different magnetic field. (b) Temperature dependent χ' for $Ho_2Ti_2O_7$ and $Ho_2Ti_{1.9}Mn_{0.1}O_7$ at 100 Hz frequency and 0.75 T magnetic field for FCC and FCW measurement mode. Inset shows the variation in thermal hysteresis ($\Delta\chi'$) for both compounds.

7.2.5 Effect of magnetic field on thermalization time

To confirm the possible origin of thermal hysteresis, cooling and warming measurement of HTO has been performed in 30 K to 9 K, i.e. the system remains in high entropy state throughout the measurement and 30 K to 2 K i.e. the system go through a change from high entropy state to low entropy state, and shown in figure 7.7. The value the 9 K has been selected as 9 K is well above the temperature where all the spin ordered states are equally probable as reported by Jubert et al. [133].

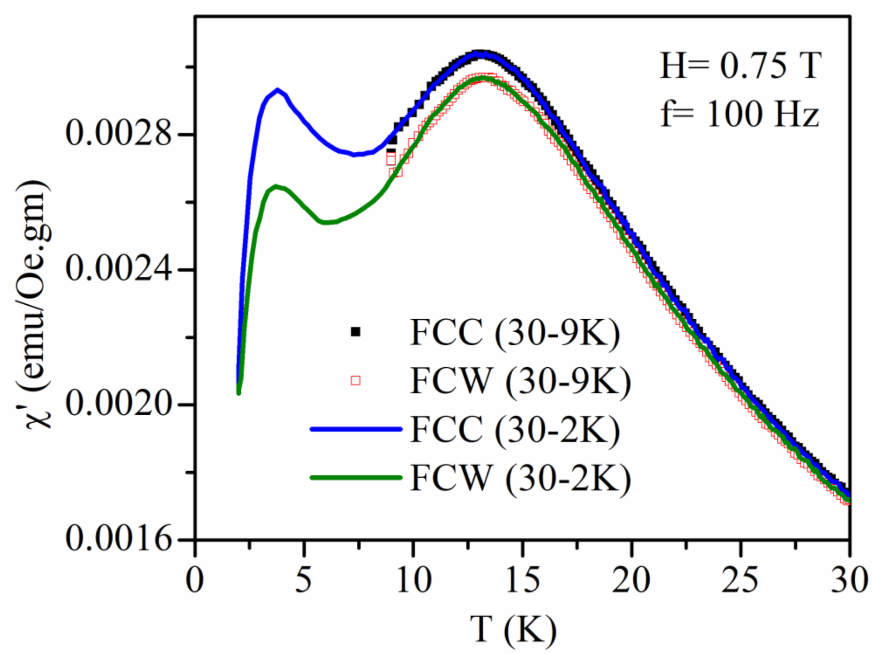

Figure 7.7: FCC and FCW of temperature dependent real part (χ') of ac susceptibility measured in 2-30 K(solid line) and 9-30 K(dot symbol) temperature range at 100 Hz frequency in presence of 0.75 T external magnetic field for $Ho_2Ti_2O_7$.

It has been found that in both set of measurements, there is no difference in FCC and FCW susceptibility. This means that observed field-induced thermal hysteresis is governed by with quantum fluctuations and role of spin microstate is non-significant. Further, in the case of 30-9 K temperature range measurement, at 9 K where temperature stabilized, both FCC and

FCW data points merge at $\Delta\chi'/2$ when sufficient time has been provided for thermalization. The merging of FCC and FCW shows that after a certain time interval system is thermalized i.e. attains thermal equilibrium where quantum correlations are dephased. This observation leads us to conclude that the external magnetic field increases the thermalization time of the system and bring it to measurement time scale. Due to increment in thermalization time because of externally applied magnetic field, scrambled quantum information associated with quantum correlation is partially maintained which reflected in the form of thermal hysteresis in ac susceptibility measurement. This means that in the thermalized state system behave classically whereas in the non-thermalized state quantum correlations are partially maintained and the so-called quantum information is not totally dephased. In the quantum correlated state, system pertains the memory of its initial conditions and able to respond to the changes, where it goes from high entropy classical region or low entropy quantum region.

7.2.6 Role of time in quantum correlated state

According to the previous study performed on atomic and bi-particle quantum systems, the physical properties of quantum systems varies with the evolution of time [84], [147]. To study the time evolution effects in non-equilibrium state, ac susceptibility of the HTO has been performed after a time interval of 48 hours using same measurement protocol and shown in figure 7.8. Inset of figure 7.8 shows the ac susceptibility of HTO performed in the absence of an external magnetic field after 48 h. Both ac susceptibility measured in absence of external magnetic field, do not show any difference in the measured range of temperature. On the other hand, in presence of 0.75 T external magnetic field, the measurement performed after 48 h follows the similar trends with a slightly higher values of χ' in 15-4 K temperature range in both FCC and FCW measurement. However, in spite of this difference in the values of χ', there is no noticeable difference in the magnitude of Δχ' has been observed.

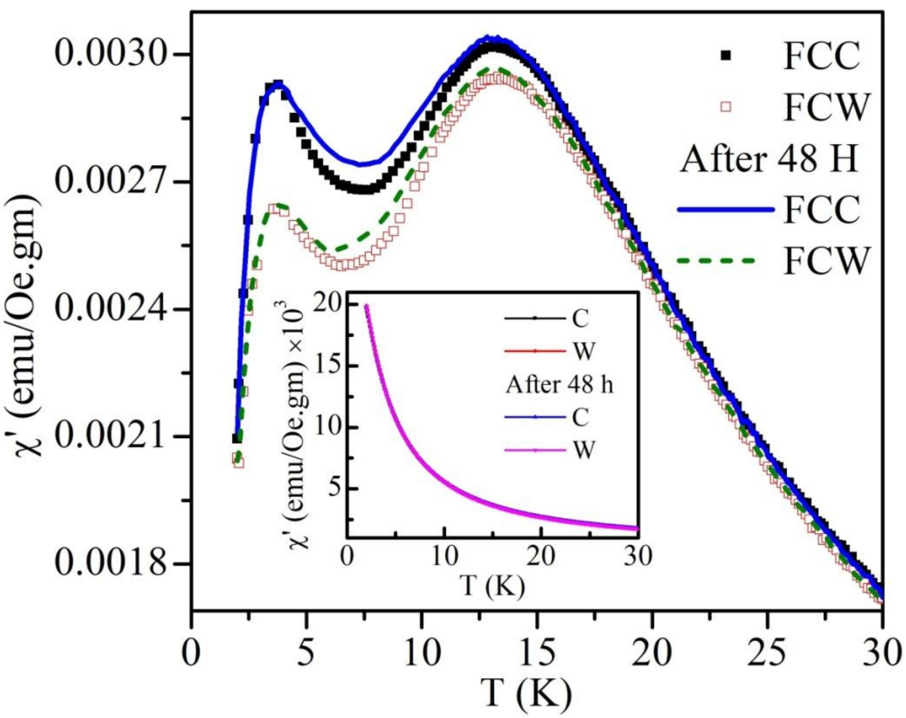

Figure 7.8: FCC and FCW of temperature dependent χ' measured at two different time having time interval 48 hour at 100 Hz and 0.75 T external magnetic field. Inset shows the FCC and FCW of temperature dependent χ' in absence of external magnetic field.

7.3 Conclusion

To summarize, in these strongly spin correlated frustrated magnetic systems, due dynamic nature of spin, which is taking place by local transformation ease the quantum fluctuation to maintain the quantum correlation between Ising spins. However, due to the ergodic nature of spin, thermalization phenomena dephases the quantum correlations which in turn responsible for the classical nature of spin in the quantum critical region. An external magnetic field set bound on dephasing of quantum correlations by increasing the thermalization time and bring it to the measurement time scale. Due to increment in thermalization time, scrambled quantum information associated with quantum correlations are partially maintained as observed in the form of thermal hysteresis in ac susceptibility measurement. Exponential decay of $\Delta\chi'$ with applied frequency evident that applied frequency also dephases the quantum correlations similar to thermalization phenomena and works as a control variable for quantum and classical nature of spin in these compounds. The analysis of temperature-dependent variation in $\Delta\chi'$, I(T) and R(T) conclude that strengthen in spin correlation enhances the quantum correlation whereas magnetic interaction induced spin constrained suppress the quantum correlations. It has been found that unlike to classical behavior where macroscopic properties are stationary and universal with respect to widely differing initial conditions, in quantum-correlated state, macroscopic properties are depending on the initial conditions and varies with temporal evolution. The anomalous sensitivity of quantum correlation on external stimuli (magnetic field and frequency), provides an effective tool to control the classical and quantum behavior of these compounds. The so observed control over macroscopic properties of these quantum materials suggests them to study in more depth for future applications. Further, these findings open a new approach to study the exotic quantum behavior of other quantum magnetic materials in terms of quantum correlations.