AC Susceptibility of the Dipolar Spin Ice Dy$_2$Ti$_2$O$_7$: Experiments and Monte Carlo Simulations

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Experimental data of ac susceptibility $\chi_{ac}(\omega)$ of the dipolar spin-ice Dy$_2$Ti$_2$O$_7$ in zero magnetic field has been analyzed by Monte Carlo simulations, based on the single-spin-flip Metropolis algorithm. We have directly calculated $\chi_{ac}(\omega)$ and found that the simulated behaviors reasonably reproduce the experiments below about 1 K, where dilute magnetic monopoles diffusively move in the ice-rule obeying ground-state manifold. The conversion factors from the simulation time to real time, i.e., hopping rate of monopoles, strongly depend on temperature.

KEYWORDS: Dy$_2$Ti$_2$O$_7$, spin ice, ac susceptibility, Monte Carlo simulation

1. Introduction

Geometrically frustrated spin systems have attracted much attention for the realization of novel ground states and their exotic magnetic phenomena. One remarkable example is a spin-ice material such as Dy$_2$Ti$_2$O$_7$ (DTO), Ho$_2$Ti$_2$O$_7$, and Ho$_2$Sn$_2$O$_7$ where Dy or Ho atoms occupy a corner sharing network of tetrahedra. These compounds, a strong crystalline electric field forces the magnetic moments of rare earth ions to lie along the local (111) symmetry direction. Such an Ising anisotropy combined with the effective ferromagnetic nearest-neighbor-interaction $J_{\text{eff}}$, the order of 1–2 K, stabilizes the so-called 2-in-2-out structure, analogously to the ice rule of the proton configurations in water ice. The ground states of the spin ice are macroscopically degenerate, giving rise to the residual entropy. Recent theories pointed out that elementary excitations from such degenerate ground states can be viewed as magnetic point defects, i.e., monopoles. These excitations, created by flipping a spin, are fractionalized into two individual excitations and diffusively move in the ice-rule obeying ground state. Therefore, magnetic dynamics of the spin ice is an interesting problem, which enables us to study the monopole motion and relaxation.

The spin dynamics of the spin-ice materials studied by the ac susceptibility $\chi_{ac}(\omega)$ shows characteristic behavior associated with a single relaxation time $\tau$ which is a simple approximation but often use to describe the dynamics of these materials. Measurements of single- and poly-crystalline samples of DTO have revealed that the temperature dependence of $\tau$ exhibits a plateau-like behavior between 2 and 10 K and a rapid increase on cooling below 2 K. Numerical simulations reproduce such behavior of $\tau$ in $T > 2$ K, implying that the picture of creation and propagation of freely moving monopoles are thought to well explain the behavior of $\tau$. Recent Monte Carlo (MC) simulations and experiments also suggested that the hopping rate of monopoles depends strongly on temperature, giving rise to the marked increase of $\tau$ below 1 K.

In this work, we perform dynamical MC simulations for $\chi_{ac}(\omega)$ of the spin ice DTO, based on the single-spin-flip Metropolis algorithm for the dipolar spin-ice model, which simulates the diffusive dynamics of monopoles or spins. The purpose of the present work is to directly calculate $\chi_{ac}(\omega)$ in order to make direct comparison with experimental data of $\chi_{ac}(\omega)$ for DTO and explore the monopole dynamics. In particular, our main effort is devoted to investigate the frequency dependence of $\chi_{ac}(\omega)$. In this respect, the present results will support an analysis of $\chi_{ac}(\omega)$ of the spin ice materials, and provide a complementary investigation to already published experimental results.

2. Calculations and Experiments

The Hamiltonian used in the simulations is

$$\mathcal{H} = -\mu_{\text{eff}} \sum_{i,a} \mathbf{S}_i^a \cdot \mathbf{H} - \sum_{\langle i,a \rangle, \langle b \rangle} J_{i,a,j,b} \mathbf{S}_i^a \cdot \mathbf{S}_j^b + D \sum_{i,j,a,b} \left[ \frac{S_i^a S_j^b}{|R_{ij}|^3} - \frac{3(S_i^a \cdot R_{ij}^b)(S_j^b \cdot R_{ij}^a)}{|R_{ij}|^5} \right],$$

where $S_i^a$, with unit length $|S_i^a| = 1$, represents the spin vector parallel to the local (111) direction at the sublattice site $a$ in the unit cell of the fcc lattice site $i$. The first term represents the Zeeman interaction between the spins with the effective moment $\mu_{\text{eff}} = 9.866 \mu_B$ and the magnetic field $\mathbf{H}$. The second and third terms are the exchange and dipolar interactions, respectively. We used the nearest-, second-, and third-neighbor interactions of $J_1 = -3.41$ K, $J_2 = 0.14$ K, and $J_3 = -0.025$ K, respectively, and the dipolar interaction parameter $D = 1.32$ K. These parameters are known to reproduce well the experimental details of the spin-ice DTO, improving simulation results using two parameters of only $J_1$ and $D$. We also performed simulations with $J_1 = -3.72$ K and $D = 1.41$ K, in order to compare our results with previous work of Refs. [18] and [19].

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To obtain $\chi_{\text{ac}}(\omega)$, we performed the MC simulations based on the single-spin-flip Metropolis algorithm. In this simulation, the updates of spins are interpreted as the time evolution of the dipolar spin-ice model under an oscillating magnetic field $\mathbf{H}(t_{\text{MC}}) = \mathbf{H}_0 \sin(\omega t_{\text{MC}})$, where $\omega = 2\pi f$ and $f$ is frequency. $t_{\text{MC}}$ is the MC step and is regarded as time in the MC simulations. The real and imaginary components of $\chi_{\text{ac}}(\omega) = \chi'(\omega) - i\chi''(\omega)$ were calculated as,

$$\chi'(\omega)H_0 = \frac{1}{N_{\text{MC}}} \sum_{n=1}^{N_{\text{MC}}} M(t_{\text{MC}}) \sin(\omega t_{\text{MC}}),$$

$$\chi''(\omega)H_0 = \frac{1}{N_{\text{MC}}} \sum_{n=1}^{N_{\text{MC}}} M(t_{\text{MC}}) \cos(\omega t_{\text{MC}}),$$

where $N_{\text{MC}}$ is the number of total MC steps. We note that a similar method has been employed so far for calculating $\chi_{\text{ac}}$ of the spin glass.\(^{27}\) To compare the simulated $\chi'(\omega)$ and $\chi''(\omega)$ with experimental values, conversion factors from the MC time to real time, $A(T) \equiv t_{\text{MC}}/t_{\text{real}}$, were considered, since $t_{\text{MC}}$ is virtual time in simulations. These factors were estimated by comparing $\chi_{\text{ac}}(\omega)$ of simulations and experiments. We simulated the systems with a size of 2916 spins of $4 \times 10^5$ MC steps/spin for the periodic boundary condition. We typically used the strength of magnetic field of $|\mathbf{H}_0| = 100$ Oe. Although this value is larger than experimental $|\mathbf{H}_0|$,\(^{12-17,23,24}\) we confirmed that $\chi'(\omega = 0)$ is constant for $|\mathbf{H}_0| = 20, 50, 100, 200$ Oe at 0.6 K and 1 K. We also confirmed that $\chi_{\text{ac}}(\omega)$ is isotropic for field direction, which was tested by applying magnetic field along both [111] and [112]. This result is in fact consistent with experimental observations.\(^{14,15}\)

It should be noted that a temperature independent factor $A(T)$ was used in Refs. [18] and [19] to compare experimentally observed $\tau$ and calculated $\tau$ by MC simulations, where autocorrelation of magnetization was used.\(^{18,19}\) It was argued that the $T$-independent factor $A(T)$ means that all the monopole or spin dynamics are taken into account by the MC simulation which uses the Metropolis algorithm with a single-spin-flip dynamics, where monopoles move diffusively. While we need to use $T$-dependent $A(T)$, implying that there are some other mechanisms not taken into account by the MC simulation. Roughly speaking, the values of $A(T)$ were evaluated from peak positions of $\chi''(\omega)$: $A(T) = f_{p,\text{exp}}/f_{p,\text{MC}}$, where $f_{p,\text{MC}}$ and $f_{p,\text{exp}}$ are the peak positions of $\chi''(\omega)$ of MC-simulations and experiments, respectively. These peak positions are related to $\tau$ under the single-\(\tau\) approximation: $\tau_{\text{MC}} = 1/2\pi f_{p,\text{MC}}$ and $\tau_{\text{exp}} = 1/2\pi f_{p,\text{exp}}$. A similar method for estimating such a conversion factor has been used in the recent work.\(^{16}\)

We performed measurements of $\chi_{\text{ac}}(\omega)$ on a single crystalline sample of DTO, because there is a slight discrepancy in previous experimental results between single crystals and polycrystals at about 2 K (Fig. 1). We used a rectangular shape of a crystal, cut into a thin plate with a size of approximately $3 \times 5 \times 0.2$ mm$^3$ and mass of 19.6 mg. A wide plane of the sample includes the [111] and [112] directions. The demagnetization factors for these directions were as small as $N = 0.08$ and $N = 0.05$, respectively,\(^{28}\) and the demagnetization correction was not performed. $\chi_{\text{ac}}(\omega)$ was measured by using a commercial SQUID magnetometer (Quantum Design MPMS) down to 1.8 K and with a mutual inductance method below 2 K in a $^3$He refrigerator. The ac magnetic field $H_{\text{ac}}$ with the strength of 0.1, 1 or 5 Oe-rms was applied along the [112] direction. $\chi_{\text{ac}}(\omega)$ at different frequencies ranging from 1 Hz to 1.5 kHz was measured and the background signal was subtracted.

### 3. Results

#### 3.1 Temperature dependence of $\chi_{\text{ac}}(\omega)$ in the dc limit

In Fig. 1, we present temperature dependence of calculated and observed $\chi''$. Compared with previous results, the dc limit of $\chi''(\omega = 0)$ of simulations agrees reasonably with experimental results. It also exhibits the same behavior of the zero-field susceptibility $\chi_0 \propto \langle M^2 \rangle/T$ calculated by simulations, where $\langle M^2 \rangle$ represents fluctuations of magnetization. We confirmed that $\chi''(\omega = 0)$ of our single crystal matches the behavior of previous results of single crystals, smoothly varying at about 2 K. These results ensure the reliability of simulations and experiments at a first step.

#### 3.2 Frequency dependence of $\chi_{\text{ac}}(\omega)$

Figure 2 presents the frequency dependence of $\chi_{\text{ac}}(\omega)$. We confirm that calculated $\chi_{\text{ac}}(\omega)$ reasonably agrees with observations at temperatures below about 1 K, where the spin-ice correlations strongly develop and the monopole picture is a good description for DTO.\(^{3,4,11}\) We can thus expect that our simulations reproduce well the monopole dynamics in $\chi_{\text{ac}}(\omega)$. One can see that there is a slight discrepancy above 1.2 K, which becomes more obvious in the behavior of $\chi''(\omega)$. In Fig. 3, we present a comparison between calculated and observed frequency dependence of $\chi''(\omega)/\chi'(\omega = 0)$ in higher temperatures above 1.8 K. The discrepancy between simulations and observations becomes clearer at higher temperatures.
The temperature dependence of the conversion factor $A(T)$, estimated using experimental data of Refs. [12, 14, 15], is plotted in Fig. 4(a). $A(T)$ shows a crossover behavior; it is constant between 2 and 10 K and rapidly changes on cooling. In particular, it exhibits an Arrhenius-type temperature dependence $A(T) \propto \exp(-\Delta/T)$ below 1 K. The activation energy $\Delta$ is roughly obtained as $\Delta = 4$ K, which is consistent with the previous result.\(^{16}\) These imply that the dynamics not taken into account by the MC simulation becomes crucial for the anomalous increase of $\tau_{\text{exp}}$ below 1 K. In Fig. 4(b), $\tau_{\text{MC}}$ scaled by $A(T)$ and $\tau_{\text{exp}}$ evaluated from several work were summarized. Note that the data of Ref. [13] is adjusted by multiplying a factor of 0.5 since demagnetization effects cause a slight discrepancy of the data of Ref. [13] as is also observed in Fig. 3.\(^{13,15}\)

**3.3 Temperature dependence of $\tau_{\text{MC}}$**

In Fig. 5, we present $\tau_{\text{MC}}$ as a function of temperature, which is estimated from peak positions of $\chi''(\omega)$ using the relation $\tau_{\text{MC}} = 1/2\pi f_{p,\text{MC}}$. We found that $\tau_{\text{MC}}$ continuously change on cooling, and approximately varies with the inverse of monopole density $n$ which is calculated from the number of 3-in 1-out spin configurations per tetrahedron in the 2-in 2-out ground-state manifold. As clear from Fig. 5(b), one can see a linear relation between $1/\tau_{\text{MC}}$ and $n$ at temperatures below about 2 K where monopole density $n$ becomes small. It is noted that such a linear relation is theoretically predicted for the single-spin-flip Metropolis dynamics.\(^{10,29}\)

We found that $\tau_{\text{MC}}$ is slightly different between the simulations under parameters of $J_1$-$J_2$-$J_3$-$D$ and of only $J_1$-$D$. This discrepancy becomes apparent at temperatures below 2 K and suggests that additional parameters of $J_2$ and $J_3$ cause the quantitative behavior of $\tau_{\text{MC}}$. In fact, it is known that these parameters are important to describe the ground state in magnetic field.\(^{22,26}\) Nevertheless we note that the change in $A(T)$ is much larger in $T < 2$ K [Fig. 4(a)], which implies that the other mechanism is more crucial than the difference between these additional exchange parameters and play an important role.
role for the rapid increase of $\tau_{\text{exp}}$ below 1 K.

We confirmed that the temperature dependence of $\tau_{\text{MC}}$ reasonably agrees with the results of Refs. [18] and [19]. The slight discrepancy is probably due to influence of estimation of $\tau_{\text{MC}}$: it was extracted by fitting multiple relaxation times in the autocorrelation function,\(^{18,19}\) whereas $\tau_{\text{MC}}$ was evaluated from peak positions of $\chi''(\omega)$ as a single-τ in our simulations [Fig. 2(b)]. This discrepancy is also negligibly small for the change in $A(T)$, and therefore we expect that both $\tau_{\text{MC}}$ extracted from $\chi''(\omega)$ and from the autocorrelation function can be useful for the estimation of τ in simulations.

4. Discussion

The frequency dependence of $\chi_{\text{ac}}(\omega)$ of DTO was analyzed by MC simulations based on the single-spin-flip Metropolis algorithm. It is realized that observed $\chi_{\text{ac}}(\omega)$ was adequately characterized by simulated behaviors, in particular below 1 K, where the spin-ice correlation develops. This means that the diffusive motion of monopole defects dominates the dynamics, giving rise to the nearly single-τ frequency dependence of $\chi_{\text{ac}}(\omega)$. In contrast, $\chi_{\text{ac}}(\omega)$ at higher temperatures deviates from simulations, which is apparent in a temperature range of 2–10 K. This result is likely due to dynamics not taken into account in the simulations. It is considered that in an actual material, some other complex motions can appear at $T > 2$ K which causes the distribution of $\tau_{\text{exp}}$ and spread the frequency dependence of $\chi_{\text{ac}}(\omega)$. In fact, the density of all-in and all-out double defects tends to increase above 4 K.\(^{19}\) Such contributions may lead to additional effects and interactions to the diffusively moving defects, which influences relaxation processes and time.

Further improvement for the estimation of precise value of τ beyond the single-τ model should be needed in this temperature region.

We confirmed that $A(T)$ is temperature dependent. In particular, such a T-dependent $A(T)$ appears at temperatures below 1 K. This result suggests that the diffusive motion of monopoles depends on temperature, i.e., the diffusion constant is temperature dependent. It is reminiscent of a fact that strong field associated with spin-ice correlations affects flipping a spin, or impurities confine the motion of monopoles, which result in temperature-dependent hop rate of monopoles.\(^{16}\) This is characterized by the Arrhenius-type behavior below 1 K [Fig. 4(b)]. It is worth noting here that such type of diffusion constant is recently found in a vortex dynamics in superconducting films, which show an exponential decay of the diffusion constant, possibly originating in pinning of vortex cores.\(^{30}\)

We realized that $A(T)$ in our simulations exhibits approximately the same behavior of the conversion factor given in Ref. [16] in which $\tau_{\text{MC}}$ was also computed by MC simulations based on the single-spin-flip dynamics, while the open boundary condition and the surface and impurity effects were considered.\(^{16}\) In our simulations, the periodic boundary condition was used and the surface and impurity effects were not taken into account. We thus think that within the single-spin-flip dynamics and our simulation accuracies, the qualitative behavior of $A(T)$ is not so sensitive to those conditions and effects. Those are, however, important to describe the detailed behavior of $\chi_{\text{ac}}(\omega)$ in the dc limit.\(^{16}\)

Finally, it is also worth noting here that given an ac magnetic response in simulations matching experimental behavior below 1 K implies that the motion of magnetic monopoles in the spin ice originates in diffusion, as suggested in several work,\(^{11,18,29,31}\) since the single-spin-flip dynamics simulates the diffusive motion of monopoles or spins. It is reminiscent of a nearly single-τ curve of the frequency-dependent relative permittivity in respect of the electron-gas-like behavior of H$_3$O$^+$ and OH$^-$ ionic defects in water ice,\(^{32}\) which is analogously to the behavior of monopole and anti-monopole simulated in our MC simulations. Therefore, a hallmark of the diffusive motion of monopoles in $\chi_{\text{ac}}(\omega)$ can be seen in the simulated curve of $\chi''(\omega)$ which reasonably reproduces the experimental results.

5. Conclusion

We have investigated frequency dependence of ac susceptibility $\chi_{\text{ac}}(\omega)$ of Dy$_2$Ti$_2$O$_7$ by Monte Carlo (MC) simulations based on a single-spin-flip Metropolis algorithm. We demonstrated that calculated $\chi_{\text{ac}}(\omega)$ reproduces well observed $\chi_{\text{ac}}(\omega)$ below 1 K where the spin-ice correlations develop. We consider T-dependent conversion factors of simulation time to real time, in order to reproduce the marked increase of relaxation time below 1 K. This means that there are some mechanisms for the dynamics not taken into account in the simulations, suggesting that the diffusion constant or hop rate of monopoles strongly depend on temperatures. This study complementarily support analysis of $\chi_{\text{ac}}(\omega)$ of the spin

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Fig. 5. (Color online) Temperature dependence of relaxation time in MC simulations $\tau_{\text{MC}}$. Results under parameters of $J_1$-$J_2$-$J_3$-$D$ and of only $J_1$-$D$ slightly deviate from each other. This is significant at temperatures below 2 K. Instead, both $\tau_{\text{MC}}$ show the same behavior of the temperature dependence of the inverse of monopole density $n$: the dashed line is for the result of the $J_1$-$J_2$-$J_3$-$D$ calculation, and dotted line is for the result of the $J_1$-$D$ calculation. In order to compare with the results of Refs. \(^{18}\) and \(^{19}\), the y axis of $\tau_{\text{MC}}$ is shifted by multiplying a constant determined at 2K. The same constant is used for both results of the $J_1$-$J_2$-$J_3$-$D$ and $J_1$-$D$ calculations. (b) $1/\tau_{\text{MC}}$ as a function of $n$ per tetrahedron. The linear relation is realized at temperatures below about 2 K.
ice at the low-$T$ state, which is now considered to be a playground of fractionalized magnetic monopoles.

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