Magnetic phase transitions and monopole excitations in spin ice under uniaxial pressure: A Monte Carlo simulation

Y. L. Xie,^{1,a)} L. Lin,² Z. B. Yan,¹ and J.-M. Liu¹

¹Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

²Department of Physics, Southeast University, Nanjing 211189, China

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In this work, we explore the spin ice model under uniaxial pressure using the Monte Carlo simulation method. For the known spin ices, the interaction correction (δ) introduced by the uniaxial pressure varies in quite a wide range from positive to negative. When δ is positive, the ground state characterized by the ferromagnetic spin chains is quite unstable, and in real materials it serves as intermediate state connecting the ice state and the long range ordered dipolar spin ice ground state. In the case of negative δ , the system relaxes from highly degenerate ice state to ordered ferromagnetic state via a first order phase transition. Furthermore, the domain walls in such ferromagnetic state are the hotbed of the excitations of magnetic monopoles, thus indicating that the uniaxial pressure can greatly increase the monopole density. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

The well-known frustrated magnetic system spin ices have been under intensive investigations for their fascinating ground states^{1–6} and fundamental spin excitations.^{7,8} They are discovered in pyrochlore oxide materials such as $\text{Ho}_2\text{Ti}_2\text{O}_7$,² $\text{Ho}_2\text{Sn}_2\text{O}_7$,⁹ $\text{Dy}_2\text{Ti}_2\text{O}_7$,¹⁰ and $\text{Dy}_2\text{Sn}_2\text{O}_7$.¹¹ The rare earth ions with large magnetic moments (about $10\mu_B$ for Ho^{3+} and Dy^{3+}) are sited on the vertices of the corner-shared tetrahedrons and can be treated as Ising spins,¹² pointing along the local $\langle 111 \rangle$ axis due to the huge crystal field.¹³ Spin ice is named for its unique ice states, in which each two spins point into the center of every tetrahedron and the other two points out. Such spin arrangement is reminiscent of the proton positions in water ice and called “ice rule.”¹ Magnetic moment at the i th site Ising spin formation $S_i = \mu s_i \sigma_i$, here, σ_i is the easy-axis unit vector, μ is the total moment, and its microstates can be described by the Ising variables $s_i = \pm 1$. The magnetic properties of spin ice can be well described by the Hamiltonian

$$H = J \sum_{\langle i,j \rangle} s_i s_j (\sigma_i \cdot \sigma_j) + \frac{D}{2} \sum_{i \neq j} s_i s_j \left[\frac{\sigma_i \cdot \sigma_j}{|r_{ij}|^3} - 3 \frac{(\sigma_i \cdot r_{ij})(\sigma_j \cdot r_{ij})}{|r_{ij}|^5} \right]. \quad (1)$$

The first term is the exchange interactions for the nearest neighbor spin pairs $\langle i, j \rangle$, while the second term is the long range dipolar interactions. Here, $r_{ij} = r_j - r_i$, where r_i is the location of the i th spin, $D = \mu_0 \mu^2 / (4\pi r_{nn}^3)$ is the dipolar coupling strength, where $r_{nn} = \sqrt{2}/4a$ (a is the lattice constant) is the distance between the nearest neighbor spins (see Fig. 1(a)). The system gradually enters the ice state at the crossover temperature $T \sim J_{\text{eff}}$ in an annealing process, here, $J_{\text{eff}} = -J/3 + 5D/3$

is the effective interactions between the nearest neighbor spins. The inter-rare-earth ions, like Dy^{3+} and Ho^{3+} , usually interact via very small J due to their active unfilled $4f$ orbitals shielded by the outer orbitals, while the rare earth ions have large magnetic moments (μ). As a result, we have $J_{\text{eff}} > 0$ and the nearest neighbor spins are ferromagnetically coupled.

In the view of the dumbbell model,⁸ the tetrahedrons satisfying the ice rule are charge neutral, while the defects of the ice state with 3 in-1 out or 1 in-3 out spin configurations break the magnetic charge neutrality. Such defects, behaving similarly to the magnetic monopoles,¹⁴ have been receiving continuous attentions since they were detected experimentally.¹⁵ Usually, the monopoles are extremely distributed in the frozen ice state because it costs about $4J_{\text{eff}}$ energy to create a monopole-antimonopole pair. Thus, in this case, the monopoles are weakly correlated and behave as “free” particles in the lattice. The motion of these “free” monopoles in the lattice helps the system to approach true ground state of the dipolar spin ice.^{3,5,16} Recently, researches have focused on the case of high monopole density in spin ice.^{17,18} The high density monopoles are strongly correlated, and the onset of monopole-antimonopole dimer pairs has been observed experimentally.¹⁷ When the monopole fraction is up to $\sim 30\%$, the system undergoes a second-order transition into the staggered monopole ordered phase.¹⁶ To enhance the monopole density, reducing the monopole excitation energy is an efficient way.¹⁷ Zhou and collaborators used high-pressure synthesis to create a new spin ice $\text{Dy}_2\text{Ge}_2\text{O}_7$ with small lattice constant and remarkably reduced the monopoles’ chemical potential.¹⁸ Actually, applying physical pressure¹⁹ is a feasible approach to change the lattice constant and influence the ice state and the monopole excitations.

In this work, we perform a Monte Carlo (MC) study of the spin ice model under uniaxial pressure. Unlike the isotropic physical pressure, the uniaxial pressure reduces the crystal symmetry and gives rise to the splitting of the six-fold degenerate ice states.²⁰

^{a)}Author to whom correspondence should be addressed. Electronic mail: yunlongxie88@gmail.com.

FIG. 1. (a) The geometry of the spin ice model. The lattice constant is a , and the distance between two nearest spins is r_{nn} , $r_{nn} = \sqrt{2}a/4$. (b) The effective nearest neighbor interactions J_{eff} are split into $J_{eff} + \delta$ for bands (blue dashed lines) on (001) plane and J_{eff} otherwise (black solid lines). (c) The six ice states are split into two sets, two states with local magnetic moment m parallel to [001], the other four with $m \perp [001]$.

II. MODEL AND SIMULATION METHOD

Here, we use the nearest neighbor spin ice model to focus on influences of the uniaxial pressure on the ice states and the excitations of magnetic monopoles. As shown in Fig. 1(b), the uniaxial pressure along the [001] axis reduces the symmetry, and splits the nearest neighbor interactions into $J_{eff} + \delta$ for the bands on the (001) plane and J_{eff} otherwise. Thus, the Hamiltonian Eq. (1) is simplified as

$$H = J_{eff} \sum_{\langle i,j \rangle} S_i S_j + \frac{\delta}{2} \sum_i \sum_a S_i S_{i+a}, \quad (2)$$

where the first term is the energy summation for all the nearest neighbor bands, and the second summation covers only neighbors (S_{i+a}) on the same (001) plane as spin S_i , and the factor 1/2 is introduced to avoid repetitive counting. As mentioned above, $J_{eff} = D_{nn} - J_{nn}$, where $J_{nn} = J/3 > 0$ and $D_{nn} = 5D/3 > 0$. The interaction correction factor δ depends on the lattice constant, pressure intensity, and the rare earth ions. Table I lists the lattice constants and related magnetic parameters of the known spin ices.¹⁸ It can be clearly seen that both D_{nn} and J_{nn} increase correspondingly with the decreasing of the lattice

TABLE I. Lattice constant and the nearest neighbor interactions for spin ices.

	a (Å)	J_{nn} (K)	D_{nn} (K)	J_{eff} (K)
Dy ₂ Ge ₂ O ₇	9.93	1.80	2.47	0.67
Dy ₂ Ti ₂ O ₇	10.10	1.15	2.35	1.20
Dy ₂ Sn ₂ O ₇	10.40	0.99	2.15	1.16
Ho ₂ Ge ₂ O ₇	9.90	0.87	2.49	1.62
Ho ₂ Ti ₂ O ₇	10.10	0.63	2.35	1.72
Ho ₂ Sn ₂ O ₇	10.37	0.56	2.17	1.61

constant a or the distance between rare earth ions r_{nn} , noting that J_{nn} is more sensitive to the changes of a . As $J_{eff} = D_{nn} - J_{nn}$, the function of J_{eff} vs the lattice shrinkage Δa is closely dependent on the lattice constant a . When a is reduced to 1.68% from Dy₂Ti₂O₇ to Dy₂Ge₂O₇, J_{eff} is dramatically decreased up to 44.2%. On the contrary, for the case of Dy₂Sn₂O₇ to Dy₂Ti₂O₇, only 3.45% J_{eff} is increased with 2.88% reduction of a . Therefore, pressure introduces a negative δ for spin ice with larger lattice constant (Dy₂Sn₂O₇, Ho₂Sn₂O₇) and a positive δ for small lattice constant (Dy₂Ge₂O₇, Ho₂Ge₂O₇). In addition, both 1% lattice shrinkage of Ho₂Ti₂O₇ (Ref. 20) and Dy₂Ti₂O₇ (Ref. 19) are successfully realized by applying physical stress. Hence, it is expected that the 1% lattice shrinkage may give rise to considerable variation of J_{eff} . In our model, J_{eff} has been set to 1 for simplification. The pressure is applied along [001] axis and the interaction correction factor δ varies from -0.2 to 0.2 .

As shown in Fig. 1(c), the six ice states are split into two sets, type I with the net magnetic moment of the tetrahedron $m \parallel [001]$, and type II with $m \perp [001]$. Their energies are expressed as $E_1 = 2\delta - 2J_{eff}$ and $E_2 = -2\delta - 2J_{eff}$, respectively. For $\delta < 0$, we have $E_1 < E_2$, which illustrates that the net magnetic moment of local tetrahedron is parallel to [001] in the ground state, implying the standard three-dimensional Ising universality class. Therefore, the phase transition at the critical temperature is expected to be first order. For the case $\delta > 0$, $E_1 > E_2$, the ground state of the system is also highly degenerate, as the type II set is quad degenerate.

Our MC simulation process is divided into high temperature part ($T > 0.5$) and low temperature part ($T < 0.5$). In

FIG. 2. (a) T vs δ phase diagram for spin ice model under uniaxial pressure. At high temperature, the system exists in PM phase, and gradually reaches the ice phase below T_S (red double-dotted dashed line). For $\delta < 0$, the system finally relaxes to a FM state via a first order phase transition at T_M (blue dashed line). And for $\delta > 0$, the system exists in the unstable “CO” state below T_P (black dotted dashed line). The sketch of FM state (b) and the CO state (c).

the high temperature range, each MC step contains N single spin updates; here, N is the spin number of the system. In our model, each unit cell contains 16 spins,²¹ and the lattice is composed of $L \times L \times L$ cells, yet we have $N = L \times L \times L \times 16$. While in low temperature range, one MC step contains $N/2$ single spin flips as well as $N/2$ loop spin updates.²² The long loop update can change the total magnetization without breaking the ice rule. Moreover, it is quite efficient to overcome the anisotropic barrier, which prevents the spins from free single flipping.

III. RESULTS AND DISCUSSION

In Fig. 2(a), we first present the contour plot of the specific heat (C) with different δ and T . It can be seen that the phase plane is divided into four phases. The high temperature line labeled as T_S (the red double-dotted dashed line) corresponds to the paramagnetic (PM) phase to spin ice phase transition. Below T_S , the system gradually approaches to the 2 in-2 out ice state, which is further classified as three phases: ferromagnetic (FM) phase, chain ordered (CO) phase, and typical spin ice phase. Under this ice state, the relaxation time increases rapidly and the dynamics of the system are driven by the trace amounts of monopoles.²³

Now, let us start with the discussion of spin ice state (below T_S). For the case $\delta < 0$, the system relaxes to the ferromagnetic phase as temperature drops below the critical temperature T_M (the blue dashed line), where the phase changes from the short range ice state to the long range ordered state. Fig. 2(b) presents a slice of the ground state of FM phase on (010) plane, which has also been obtained by applying [001] magnetic field.² For each tetrahedron, the local magnetic moment points along [001] axis. As mentioned above, a first order transition occurs at T_M . Here, we present our Monte Carlo simulation results to demonstrate this feature. The behaviors of specific heat at T_M are important evaluation criteria for a first order transition. At the critical temperature, one has

$$\begin{aligned} C_{\text{peak}}(L) &= \alpha + \beta L^d, \\ T_{\text{peak}}(L) &= T_C + \gamma L^{-d}, \end{aligned} \quad (3)$$

where C_{peak} and T_{peak} are the maximum value of specific heat C and the corresponding temperature T . d is the dimension of

FIG. 3. The specific heat data (C) as a function of T , for $L = 2, 3, 4, 5, 6$ and $\delta = -0.04$. The upper and lower insets show the $C_{\text{peak}}-N$ curve and $T_{\text{peak}}-1/N$ curve, respectively.

the model, and L^d can be replaced by the total spin number N in our model. α , β , and γ are constants. And T_C is the critical temperature of an infinite system $T_C = T_{\text{peak}}(\infty)$.

Fig. 3 shows the specific heat data as a function of temperature (T) for different lattice size L at the fixed interaction correction $\delta = -0.04$. As the lattice size L increases, the peak of the specific heat becomes sharper, and the transition point shifts to high temperature. The upper and lower insets to Fig. 3 further show the function of C_{peak} versus N and T_{peak} versus $1/N$, respectively, where each data point is an average over ten independent simulations. Then, we have tried out best to do a line fit of Eq. (3) to the data, and the results are as follows:

$$\begin{aligned} C_{\text{peak}}(L) &= 0.31 + 0.0021N \\ T_C &= 0.23 \\ T_{\text{peak}}(L) &= T_C - 2.4N^{-1}. \end{aligned} \quad (4)$$

It can be clearly seen that such finite size scaling is well consistent with that expected first order phase transition. The first order phase transition corresponds to a sudden drop of system energy below the critical temperature T_C , then, the system may be trapped into metastable states when it undergoes a rapid annealing process. Especially in our model, the spins are all frozen in its ice state; hence, it is hard for the system to relax to a perfect ferromagnetic state without the loop spin flip Monte Carlo steps in the simulations. Therefore, the system is more likely to rest on a state with magnetic domains. Fig. 4(b) shows the sketch of a possible metastable state with two domain walls, which should be a perfect interface and parallel to [001] confined by the “ice rule.” Now suppose that the domain wall has defects on it (Fig. 4(c)), the “ice rule” is broken and a pair of magnetic monopoles is produced at the two ends of the domain wall defects. Actually, the domain walls have higher energy than somewhere else. As shown in Fig. 4(b), the energy of each

FIG. 4. (a) The δ ($\delta < 0$) dependent monopole density curves at $T = 0.03$ and $T = 0.1$. Each data point is the statistic average of 10^5 independent simulations. (b) The sketch of domains in ferromagnetic state. (c) The excited monopoles on the domain walls.

tetrahedron on the domain walls is $-2\delta - 2J_{\text{eff}}$ ($\delta < 0$), which is 4δ higher than other tetrahedrons with energy $2\delta - 2J_{\text{eff}}$. Hence, the tetrahedrons on the domain walls have a higher probability to excite monopoles, which implies that the defects are more likely to spread along the domain walls. Especially, the motion of the domain walls is closely associated with the spread of monopoles. Thus, one is expected that once the metastable states with domain walls approach to the ground state, the domain walls will absorb certain monopoles. Besides, one can also expect that the monopole density increases with the decreasing of δ .

To simulate the formation of domain walls, the Monte Carlo simulation is performed in a rapid annealing process. We use 10^4 MC steps to cool the system from $T=3$ (paramagnetic phase) down to the target temperature (lower than T_M), and the system size is chosen as $L=4$. Fig. 4(a) shows the δ dependence of magnetic monopole density under selected temperature $T=0.03$ and $T=0.1$. As expected above, the monopole density should increase with the decreasing of δ for both cases. However, the two cases seem a little different. The thermal excitations at extreme low temperature $T=0.03$ should be greatly frozen. On this occasion, some free monopoles are absorbed by the domain walls, thus leading to a saturation below -0.09 .

The case $\delta > 0$ is an unique case here. In the phase diagram (Fig. 2(a)), the system relaxes to a partial ordered phase below the temperature T_p , where T_p is the temperature that C undergoes a peak. Here, we intuitively call it “chain ordered” phase, where the ground state is composed of uncorrelated ferromagnetic chains (Fig. 2(c)). As a result, such ground state is also highly degenerate with the residual entropy per spin of the system $\Delta S \sim 1/L$. For an infinite system, ΔS should approach to 0. Actually, CO state is an unstable. In real systems, the existence of the long range dipolar interactions and the next-nearest neighbor exchange interactions make the chains arranged in ferromagnetic order or in antiferromagnetic order. When the spin chains arrange in ferromagnetic order, it is precisely the FM phase, as shown in Fig. 2(b), while long range ordered dipolar spin ice ground state for the case $q=(0, 0, 2\pi/a)$ is established when the chains arrange in antiferromagnetic order. In other words, the stress on spin ice can help the system to relax to the true ground state of the dipolar spin ice, which may extend our scope to explore such ordered state experimentally.^{6,24}

IV. CONCLUSION

In summary, we have simulated the spin ice model under uniaxial pressure. Rich phase transitions are carried out by the stress. For the spin ice with small lattice constant, like $\text{Ho}_2\text{Ge}_2\text{O}_7$ and $\text{Dy}_2\text{Ge}_2\text{O}_7$, the stress brings in a positive interaction correction (δ). The intermediate states characterized by the ferromagnetic spin chains link up the ice state and the long range ordered dipolar spin ice ground state, and it is hopeful to explore such ordered state in experiment by applying uniaxial pressure. While in the case of the spin ice with large lattice constant ($a > 10.10 \text{ \AA}$, $\text{Ho}_2\text{Sn}_2\text{O}_7$, and $\text{Dy}_2\text{Sn}_2\text{O}_7$), the uniaxial pressure causes a negative interaction correction, which allows the system relaxing from

highly degenerate ice state to ordered ferromagnetic state via a first order phase transition. Furthermore, the domain walls in such ferromagnetic state can generate magnetic monopoles. The simulation results have revealed that the stress can greatly increase the monopole density in the lattice.

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- ¹A. P. Ramirez, A. Hayashi, R. J. Cava, R. Siddharthan, and B. S. Shastry, *Nature* **399**(6734), 333 (1999).
- ²M. J. Harris, S. T. Bramwell, D. F. McMorrow, T. Zeiske, and K. W. Godfrey, *Phys. Rev. Lett.* **79**(13), 2554 (1997).
- ³R. Melko, B. Hertog, and M. Gingras, *Phys. Rev. Lett.* **87**(6), 067203 (2001).
- ⁴T. Fennell, O. A. Petrenko, G. Balakrishnan, S. T. Bramwell, J. D. M. Champion, B. Fak, M. J. Harris, and D. McK Paul, *Appl. Phys. A* **74**(0), s889 (2002).
- ⁵D. Pomaranski, L. R. Yaraskavitch, S. Meng, K. A. Ross, H. M. L. Noad, H. A. Dabkowska, B. D. Gaulin, and J. B. Kycia, *Nat. Phys.* **9**(6), 353 (2013).
- ⁶C. Krey, S. Legl, S. R. Dunsiger, M. Meven, J. S. Gardner, J. M. Roper, and C. Pfeleiderer, *Phys. Rev. Lett.* **108**(25), 257204 (2012).
- ⁷L. Balents, *Nature* **464**(7286), 199 (2010); H. Kadowaki, N. Doi, Y. Aoki, Y. Tabata, T. J. Sato, J. W. Lynn, K. Matsuhira, and Z. Hiroi, *J. Phys. Soc. Jpn.* **78**(10), 103706 (2009).
- ⁸C. Castelnovo, R. Moessner, and S. L. Sondhi, *Nature* **451**(7174), 42 (2008).
- ⁹H. Kadowaki, Y. Ishii, K. Matsuhira, and Y. Hinatsu, *Phys. Rev. B* **65**(14), 144421 (2002).
- ¹⁰M. J. Harris, S. T. Bramwell, P. C. W. Holdsworth, and J. D. M. Champion, *Phys. Rev. Lett.* **81**(20), 4496 (1998).
- ¹¹K. Matsuhira, Y. Hinatsu, K. Tenya, H. Amitsuka, and T. Sakakibara, *J. Phys. Soc. Jpn.* **71**(6), 1576 (2002).
- ¹²R. Siddharthan, B. S. Shastry, A. P. Ramirez, and A. Hayashi, *Phys. Rev. Lett.* **83**(9), 1854 (1999).
- ¹³S. Rosenkranz, A. P. Ramirez, A. Hayashi, R. J. Cava, R. Siddharthan, and B. S. Shastry, *J. Appl. Phys.* **87**(9), 5914 (2000).
- ¹⁴S. T. Bramwell, S. R. Giblin, S. Calder, R. Aldus, D. Prabhakaran, and T. Fennell, *Nature* **461**, 956 (2009).
- ¹⁵Z. Fang, N. Nagaosa, K. S. Takahashi, A. Asamitsu, R. Mathieu, T. Ogasawara, H. Yamada, M. Kawasaki, Y. Tokura, and K. Terakura, *Science* **302**(5642), 92 (2003).
- ¹⁶R. A. Borzi, D. Slobinsky, and S. A. Grigera, *Phys. Rev. Lett.* **111**(14), 147204 (2013).
- ¹⁷H. D. Zhou, S. T. Bramwell, J. G. Cheng, C. R. Wiebe, G. Li, L. Balicas, J. A. Bloxson, H. J. Silverstein, J. S. Zhou, J. B. Goodenough, and J. S. Gardner, *Nat. Commun.* **2**, 478 (2011).
- ¹⁸H. D. Zhou, J. G. Cheng, A. M. Hallas, C. R. Wiebe, G. Li, L. Balicas, J. S. Zhou, J. B. Goodenough, J. S. Gardner, and E. S. Choi, *Phys. Rev. Lett.* **108**(20), 207206 (2012).
- ¹⁹M. Mito, S. Kuwabara, K. Matsuhira, H. Deguchi, S. Takagi, and Z. Hiroi, *J. Magn. Magn. Mater.* **310**(2), E432 (2007); I. Mirebeau and I. N. Goncharenko, *Physica B* **350**(1–3), 250 (2004).
- ²⁰L. D. C. Jaubert, J. T. Chalker, P. C. W. Holdsworth, and R. Moessner, *Phys. Rev. Lett.* **105**(8), 087201 (2010).
- ²¹R. Melko and M. Gingras, *J. Phys.: Condens. Matter* **16**(43), R1277 (2004).
- ²²G. T. Barkema and M. E. J. Newman, *Phys. Rev. E* **57**(1), 1155 (1998).
- ²³L. D. Jaubert and P. C. W. Holdsworth, *J. Phys.: Condens. Matter* **23**(16), 164222 (2011); J. Snyder, B. G. Ueland, J. S. Slusky, H. Karunadasa, R. J. Cava, and P. Schiffer, *Phys. Rev. B* **69**(6), 064414 (2004).
- ²⁴J. P. Morgan, A. Stein, S. Langridge, and C. H. Marrows, *Nat. Phys.* **7**(1), 75 (2011).