Disorder-Free Glass Transitions of Spins and Orbitals in a Frustrated Pyrochlore Magnet

Kota Mitsumoto[1], Chisa Hotta[2] and Hajime Yoshino[1,3]
[1] *Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*
Osaka University, Toyonaka 560-0043, Japan.
[2] *Department of Basic Science, University of Tokyo, Tokyo 153-8902, Japan*
[3] *Cybermedia Center, Osaka University, Toyonaka, Osaka 560-0043, Japan*

Abstract:

In this activity report, we present an overview of our recent extensive Monte Carlo simulations performed on the ISSP supercomputer (SYSTEM B) [1][2][3] to study our effective theoretical model for the disorder-free spin-glass transition observed experimentally in the pyrochlore oxide $Y_2Mo_2O_7$. By taking into account not only the spin but also the orbital degrees of freedom of the Mo ions, we found a new type of glass transition - spin-orbital glass transition.

1 Introduction

Glass is a generic state of matters which can be found in a diverse range of systems ranging from soft to hard condensed matters. Yet, unlike crystalline states with long-ranged ordering of periodic structures, the very mechanism(s) of the emergence of glasses remain quite elusive. The exceptional case is the family of disordered magnets with quenched disorder, i. .e. spin-glasses. In spin-glasses, the existence of thermodynamic glass transitions is established by experiments, theories and simulations (see for reviews [4, 5, 6, 7]). But apparently, glasses without quenched disorder is more ubiquitous in nature and in industrial materials. Understanding the mechanism of the emergence of glasses *without* quenched disorder remains as one of the most important unsolved problems in physics [8].

Majority of glassy systems without quenched disorder emerge from *supercooled liquids*. Typical examples are the structural glasses obtained by supercooling molecular liquids or making densely packed soft-matters like colloids. The most important basic question there is to clarify whether the so-called Kauzmann transition[9], which is a putative, idealized thermodynamic glass transition, can take place in the supercooled liquid state. Recently important progress was made on the theoretical side: a mean-field theory which combines the density functional theory of liquids [10] and the replica method used in statistical mechanics of disordered systems [11] established that the ideal glass transition exists (at least) in the large dimensional limit (see for a review [12]). However, the fate of ideal thermodynamic transition in *finite* dimensions is largely unknown [13]. The problem is difficult to solve precisely because of the glassiness: the extremely sharp increase of the relaxation time (viscosity) going deeper into the supercooled liquid state makes it very difficult to measure quantities in equilibrium. Another reason is that the super-cooled liquid state is a meta-stable state which should be replaced by the crystalline state in true equilibrium. A possible way out of these difficulties is to seek simple lattice models, which mimic the basic phenomenology of structural glasses, carefully designed to avoid crystalline transitions, and allow various simulation techniques developed for lattice models [14].

In principle, glass transitions similar to those found in the supercooled liquids can also take place in spin systems. Indeed one can show exactly that the ideal glass tran-

sitions can take place in spin systems without quenched disorder, by examing *supercooled paramagnetic states* in the large dimensional limit [15]. However, in reality, the metastability limit of the paramagnetic state toward long-ranged ordering of periodic structures (corresponding to the Kirkwood instability of liquids [16]) may preempt the ideal glass transition (see for instance [17]).

A very promising playground to explore glass physics is geometrically frustrated magnets on corner-shared lattices such as the Kagome lattice and pyrochlore lattice (see Fig. 1 (a)). In general, glassy states appear when periodic long-range ordering is avoided down to very low temperatures or high densities where strong interactions become important. Therefore frustration is a key ingredient for glass physics [18]. The most spectacular example is the pyrhoclore oxcide $Y_2Mo_2O_7$, which is known experimentally to exibit clear-cut spinglass transitions *without appreciable quenched disorder* [19, 20, 21, 22, 23, 24, 25]. Moreover, in sharp contrast to the structural glass transition mentioned above, the spin-glass transition emerges directly out of the paramagnetic state as a 2nd order transition much like the conventional spin-glass transitions[4, 5, 6, 7], without the need to go through the metastable 'supercooled' paramagnetic state. Actually, quite remarkably, the phenomenology of the spin-glass transition and even the critical exponents associated with the spin-glass transition [19, 20, 25] are nearly indistinguishable from that of the conventional, canonical spinglasses with quenched disorder.

On the theoretical side, microscopic explanation of the disorder-free spin-glass transition remained a big challenge for more than 30 years. The principal magnetic interaction in the pyrochlore oxide $Y_2Mo_2O_7$ is the antiferromagnetic interaction between the magnetic moments of the Mo ions sitting on verticies of the pyrochlore lattice. It has been established that the purely antiferromagnetic Heisenberg spin model on the pyrochlore lattice exhibits no transitions down to $T = 0$ because of the very strong geometrical frustration [26, 27]. This is remarkable given that the system is three dimensional. Coming back to the experimental system, this observation means that the model is too crude to capture the real system which exhibits a spin-glass transition. In order to explain the spin-glass transition of the $Y_2Mo_2O_7$ system, previous theoretical studies assumed the presence of some amount of quenched disorder [28, 29]. However, from the mean-field theoretical point of view, disorder-free spin-glass transitions are possible [15]. Albeit in a somewhat artificial case with a highly non-linear interaction , where the model is built to describe an optimization problem like the graph coloring with continuous colors, a 2nd order disorder-free spin-glass transition involving full replica symmetry breaking emerges without passing through the super-paramagnetic phase has been found (See sec. 10 of [15]).

The purpose of the present work is to uncover the microscopic mechanism of the disorder-free spin-glass transition observed in the pyrochlore magnet. Our key observation in the present work [1], which is motivated by a recent experiment [23], is that in the pyrochlore oxides, not only the spins but also the orbitals (lattice displacements) exhibit glass transitions simultaneously - spin-orbital glass transition. In the following, we first explain our theoretical model and then present our results obtained by extensive Monte Carlo simulations at ISSP.

2 Model

We consider two kinds of dynamical variables associated with the $Mo^{4+}(4d^2, S = 1)$ ions which sit on the vertices $i = 1, 2, \ldots, N$ of the pyrochlore lattice. The first is the classical Heisenberg spin $\boldsymbol{S}_i = (S_i^x, S_i^y, S_i^z)$ normalized as $|\boldsymbol{S}| = 1$ which represents the magnetic moments of the Mo ion.

The second is the 'displacement' of the Mo ions $\boldsymbol{\sigma}_i = (\sigma_{i,x}, \sigma_{i,y}, \sigma_{i,z})$. The recent experiment [23] suggests that the pyrhocolore lattice is distorted by displacements of the Mo ions. The displacement of a vertex (the Mo ions) take place along the lines connecting the two tetrahedra that share the vertex. Thus the displacements of the vertices of a given tetrahedron are either pointing toward or away

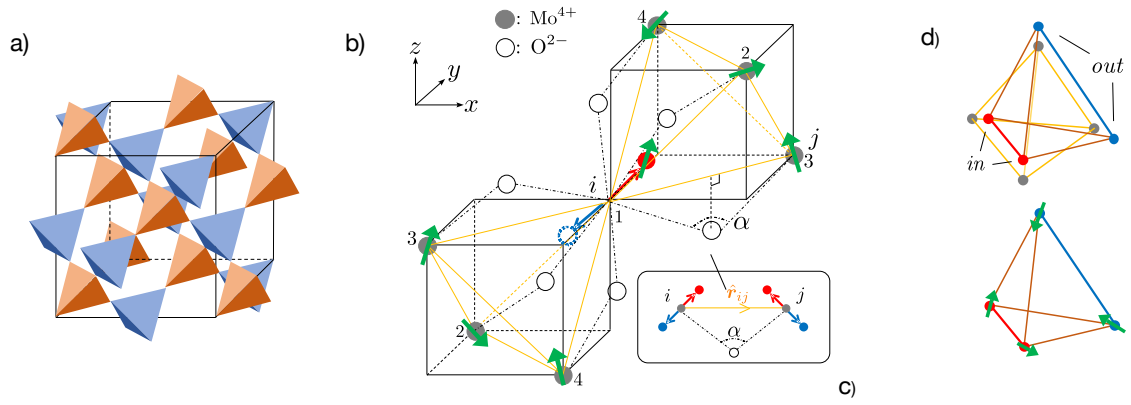

Figure 1: Spins on deforming pyrhoclore lattice. (a): Pyrhoclore lattice. (b): O^2 ions and magnetic Mo^{4+} ions around the i site, where the numbers $1-4$ are the sublattice indices of Mo^{4+} ions. Red and blue dashed circles represent the positions of the Jahn-Teller distorted i ion. Spins on a pair of Mo^{4+} ions (i,j) interact through the O^2 ion as shown in the inset panel, where alpha is the Mo-O-Mo angle and $\hat{r}_{ij}$ is the unit vector in the $i \to j$ direction. (c): Ice-type displacements of the Mo tetrahedron. The different color bonds represent different exchange interactions. (taken from [1, 2])

from the center of the tetrahedron. Furthermore, the experiment suggests that the displacements follow the 'ice-rule' [30] : the '2-in-2-out' structure (see Fig. 1 (d)). As suggested by the experiment, we parametrized the displacements as $\boldsymbol{\sigma}_i = \sigma_i \hat{e}_\nu$. Here we introduced an Ising variable $\sigma_i = \pm 1$ to represent 'in' and 'out' displacements depending on $\hat{e}_\nu$ which is a unit vector in the $[111], [1\bar{1}\bar{1}], [\bar{1}1\bar{1}]$ and $[\bar{1}\bar{1}1]$ directions respectively for the sub-lattices $\nu = 1, 2, 3, 4$ which the i-th spin belongs to (See Fig. 1.(b)). The microscopic mechanism of the peculiar displacements is presumably a Jahn-Teller effect: the displacements break the 3-fold rotational symmetry of the trigonal crystal field for the Mo ions resulting in the splitting of its e'_g orbital [3]. Thus we regard σ_i as the variable which represents the configuration of the orbital of the Mo ion.

Our effective model for the pyrhoclore magnet $Y_2Mo_2O_7$ is given by the following effective Hamiltonian,

$$H = \sum_{<ij>} J_{\boldsymbol{\sigma}_i,\boldsymbol{\sigma}_j} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \epsilon \sum_{<ij>} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \ (\epsilon > 0) \tag{1}$$

with

$$J_{\boldsymbol{\sigma}_i,\boldsymbol{\sigma}_j} = J[1 + \delta(\hat{\boldsymbol{r}}_{ij} \cdot \boldsymbol{\sigma}_i + (-\hat{\boldsymbol{r}}_{ij}) \cdot \boldsymbol{\sigma}_j)] \ (\delta > 0), \tag{2}$$

The 1st term of Eq. (1) describes the exchange interaction between the spins on the nearest-neighbour sites $< i, j >$ on the pyrhoclore lattice. The exchange interaction Eq. (2) between the spins on the i-th and j-th Mo ions, with the energey scale $J(> 0)$, is mediated by the O ion and depends on the angle α of the Mo-O-Mo bond. (see Fig. 1 (b)(c)) Thus the exchange interaction depends on the displacements $\boldsymbol{\sigma}_i$ and $\boldsymbol{\sigma}_j$ of the Mo ions. This form is constructed in a way to reproduce the values of the effective interactions derived microscopically from the perturbation process on a Kanamori-type of Hamiltonian [1, 2]. More-precisely we parametrize it as $J_{\boldsymbol{\sigma}_i,\boldsymbol{\sigma}_j} = (1 + 2\tilde{\delta})J\ (in,\ in), J\ (in,\ out), (1 - 2\tilde{\delta})J\ (out,\ out)$, where $\tilde{\delta} = \sqrt{6}\delta/3$.

The 2nd term of Eq. (1) represents the elastic energy of the Mo^{4+} displacements. The elastic energy is minimized if the ice-rule is satisfied.

There are three parameters in this system; $\tilde{T} = k_B T/J$ is the dimensionless temperature, $\tilde{\epsilon} = \epsilon/3J$ the ratio of the energy scales between the exchange interaction and the elastic energy

of the displacement, and $\tilde{\delta} = \sqrt{6}\delta/3$ is the amplitude of the displacement (hereafter we call them simply as T, ϵ, δ). At $\epsilon \to \infty$, the lattice distortion becomes static.

Finally let us note what happens if we switch off the coupling between the spins and orbitals (lattice displacements) $\delta = 0$. Then our system is decoupled into (1) the spin part with purely antiferromagnetic interactions [26, 27] and (2) the orbital (lattice) part with pure 'spin-ice' type interaction [30, 31]. Both of them have essentially flat energy landscape so that the two degrees of freedom remain disordered down to $T = 0$.

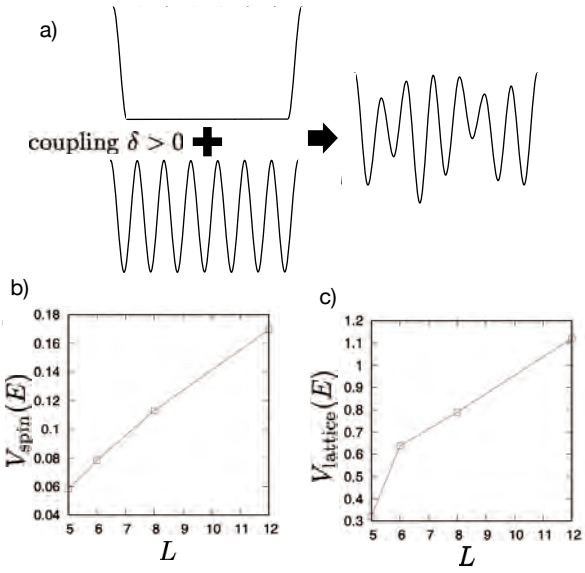

Figure 2: Energy landscape. (a): Schematic picture of energy landscape. The essentially flat energy landscapes (with many energetically degenerate minima) of the spins (left/top) and orbitals (left/bottom) in the absence of the coupling $\delta = 0$ change into a complex one in the presence of the coupling $\delta > 0$ (right). (b),(c) variance of the energy between different energy minima obtained by quench experiments (taken from [2])

3 Simulation Methods

In order to perform simulations in equilibrium, we combined the following methods in our Monte Carlo simulations.

Single spin update: The usual single spin updates by the conventional Metropolis algorithm is employed for the Ising variables $\sigma_i = \pm 1$ $(i = 1, 2, \ldots, N)$.

Loop update method: We also adopted a nonlocal update method called the loop update algorithm, used to simulate spin-ice systems [32], to for the Ising variables σ_i.

Monte Carlo reflection method: For the Heisenberg spins $\boldsymbol{S}_i$ $(i = 1, 2, \ldots, N)$, we used the single spin updates by the Metropolis reflection method [33].

Over-relaxation method: We also used the over-relaxation method to update the Heisenberg spins. [34]

Replica exchange method: On top of the above methods we used the replica-exchange method [35] to accelerate the equilibration of the whole system.

We consider the periodic systems of cubic geometry consisting of L^3 unit cells with totally $N = 16L^3$ spins, and perform 120 statistically independent runs for the system size $L = 4, 5, 6, 8$, evaluating the averages and mean-squared errors of observable. In the following analysis, we mainly focus on a representative system at $\delta = 1.5, \epsilon = 0.6$.

4 Results

4.1 A simple analysis of the energy landscape

As we mentioned at the end of sec. 2, the energy landscape of our system becomes essentially flat (with many energetically degenerate minima) if we switch off the coupling between the spins and orbitals (lattice displacements) , i. e. $\delta = 0$. Here let us show the result of a simple quench experiment which provides some insights on how the energy landscape changes in the presence of the coupling $\delta > 0$. First we generated 'spin-ice' configurations of σ_i's randomly. Note that any of them minimizes the 2nd term of the Hamiltonian Eq. (1). Second, we performed a simple energy descent simulation with respect to the 1st term of the Hamiltonian Eq. (1) by zero

temperature, greedy Monte Carlo updates of the spins with orbitals σ_i being fixed. Repeating this procedure we obtained a large number of energy minima of various energies E. In Fig. 2 (b) we display the variance of the energy $V_{\rm spin}(E) = \overline{\langle E^2 \rangle} - \overline{\langle E \rangle}^2$ between different realizations of the spins with a common orbital (lattice) configuration (averaged over different realizations of such orbitals). Here $\langle \ldots \rangle$ represents the average over different realizations of the spins with a common orbital (lattice) configuration and $\overline{\ldots}$ the average over different realizations of the orbitals. In Fig. 2 (c) we show the corresponding one to measure the fluctuation between different realizations of the orbitals (lattice) $V_{\rm lattice}(E) = \overline{\langle E^2 \rangle} - \overline{\langle E \rangle}^2$. Both (b) and (c) show that the variance grows with the system size L suggesting lugged, complex energy landscape.

4.2 Critical slowing down without long-ranged ordering

By lowering the temperature we observed that the dynamics of both the spins and orbitals (lattice displacements) slow down significantly. In Fig. 3 (a)-(b) we display the time autocorrelation functions of the spins $C_s(t)$ and orbitals $C_\sigma(t)$ plotted against time t. Here we used 'single spin updates' for the spins and orbitals to measure the dynamical observables, starting from the initial configurations equilibrated using all protocols listed in sec 3. As shown in (c)-(d), the relaxation times grow in lowering the temperature following a power law. The independent power-law fits on the two observables suggest a common critical temperature $T_{\rm c} \sim 0.07$ with different exponents $z\nu \sim 4.2$ (orbital) and $z\nu \sim 3.5$ (spin). As shown in (e)-(f) the auto-correlation functions follow scaling laws in terms of scaled times. We have checked that finite-size effects of the auto-correlation function is negligible within the temperature and time scales shown in the Figure. We have found that the same type of scaling holds for $\epsilon = 0.65$, with $T_{\rm c} \sim 0.086$ and almost the same exponents as obtained above [2, 3].

As shown in Fig. 4, the structure factor of the spins S_s and orbitals (lattice displacements) S_σ show no hints of long-range ordering. Some pinch points can be seen in S_σ, for example at $(1/2, 1/2, 1/2)$, at low temperatures as well known in spin-ice systems [31].

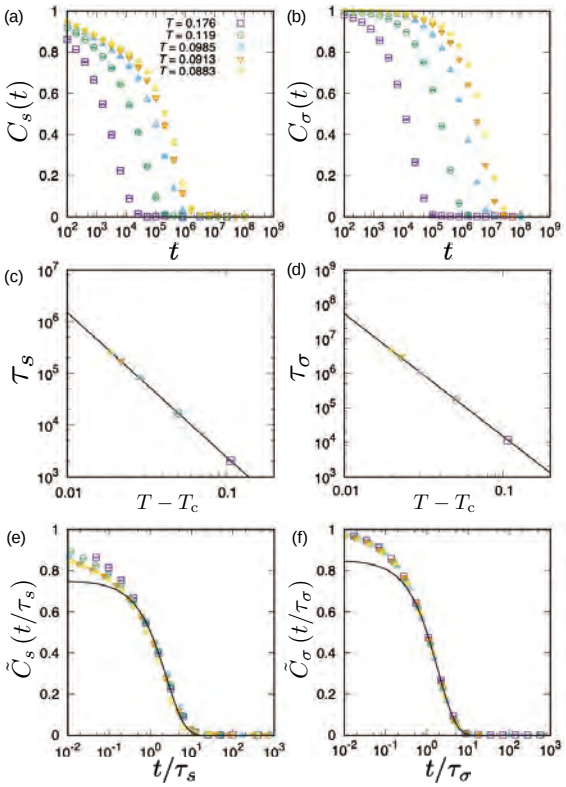

Figure 3: Autocorrelation functions and relaxations times of the spins and orbitals. $L = 6$, $\epsilon = 0.6$. (taken from [1])

To summarize the above observations suggests a simultaneous, 2nd order glass transitions of the spins and orbitals (lattice displacements) at a common temperature, into a new glass phase - spin-orbital glass phase, which emerges directly from the high temperature paramagnetic (liquid) phase.

4.3 Non-linear susceptibilities

The signatures of the spin-orbital glass can be detected by observing non-linear susceptibilities of the two degrees of freedom. As shown in Fig. 5, the non-linear susceptibilities computed using fluctuation formulae (see [1] for the details) at lower temperatures grow *negatively* rapidly when increasing the system size L. This observation provides an interesting suggestion for experiments: by observing not

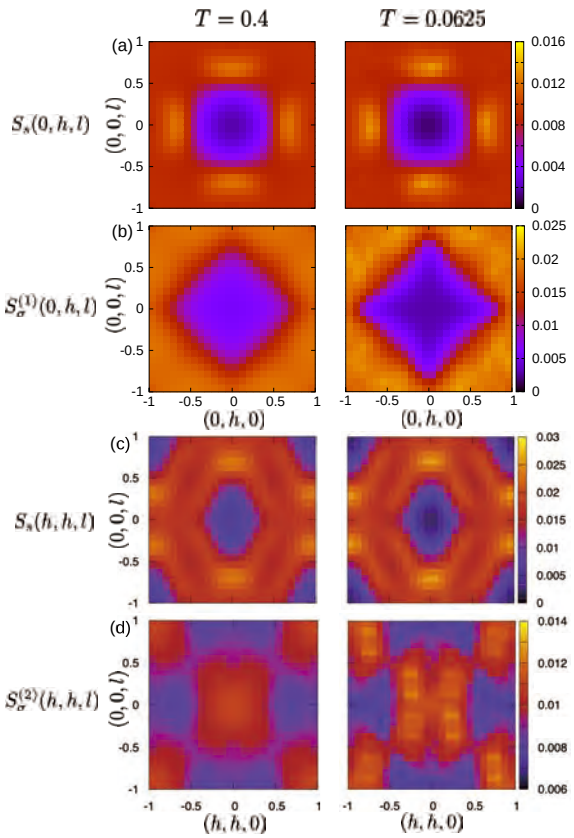

Figure 4: Heat maps of the structure factors of the spins and lattice displacements. $L = 6$, $\epsilon = 0.6$ above T_c ($T = 0.4$) in the left side and below T_c ($T = 0.0625$) in the right side. (taken from [1])

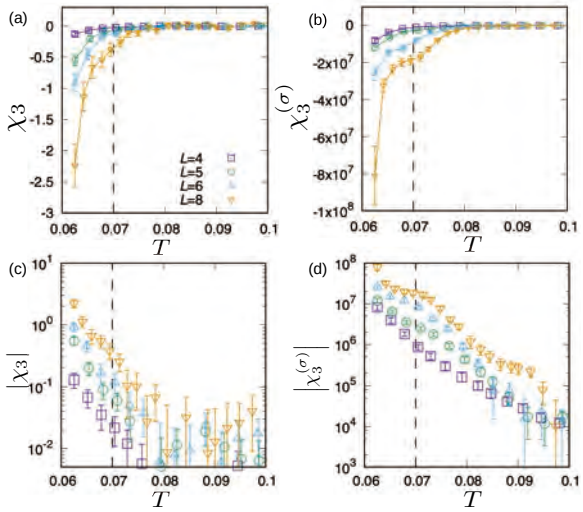

Figure 5: Non-linear susceptibilities of the spins and orbitals (lattice displacements). $\epsilon = 0.6$. Panels (a),(c) display the non-linear susceptibilities of the spin while (b),(d)display the non-linear susceptibilities of the lattice displacements (orbitals). (taken from [1])

only the usual magnetic non-linear susceptibility, which is used often to study conventional spin-glasses [4, 6, 7], but also dielectric non-linear susceptibility, the simultaneous spin-orbital glass transitions suggested by the present work may be detected experimentally.

4.4 Static or dynamic distortions?

In our study we regard the lattice distortions (orbitals) as *dynamical* degrees of freedom rather than as frozen-in, static quenched disorder. But by increasing the energy scale of the lattice displacements given by the parameter ϵ in Eq. (1), one would wonder whether the lattice displacements can freeze independently from the spins at higher temperatures. If this happens, the spin-glass transitions of a conventional type, i. e. the one due to *quenched* disorder, may take place at a lower temperature.

To get some insight into this issue within the available computational resources, we analyzed the heat capacity C and the fraction P of the tetrahedra which satisfies the ice rule at various values of ϵ. At $\epsilon = 0.6, 0.65$, for which we have determined the critical temperature of the spin-orbital glass transition, we found that the heat-capacity exhibit a peak at slightly higher temperatures, similarly to the case of the conventional spin-glasses [4] and the experimental result in the $Y_2Mo_2O_7$ system [36]. We have checked that the finite-size effects of the heat capacity are very weak [1]).

As shown in Fig. 6, the heat-capacity exhibit an additional peak at a higher temperature at larger values of $\epsilon > 1.0$. The peak at the higher temperatures appears to follow the peak of dP/dT. This observation suggests that at larger values of ϵ, the liquid state of the lattice distortions exhibits a smooth crossover from purely random one to more spin-ice like one at higher temperatures. On the other hand, the other peak of the heat capacity located at

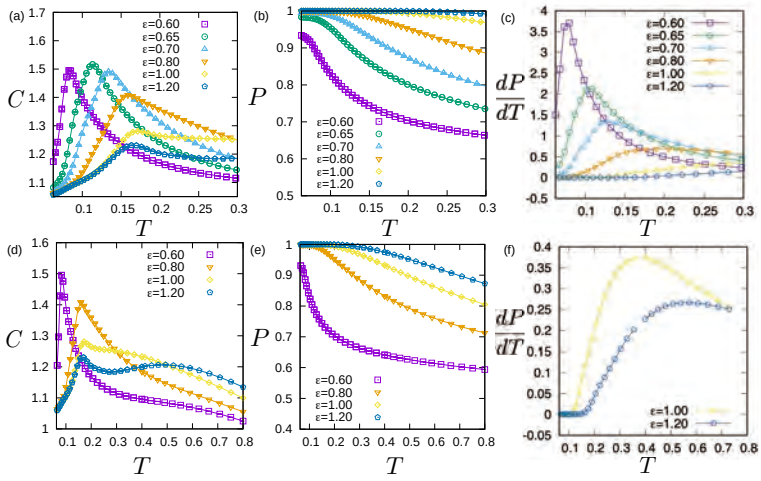

Figure 6: Heat capcity C and fraction P of tetrahedra which satisfy the ice-rule. $L = 5$. (a)-(c) for $0 < T < 0.3$ (d)-(f) for a wider temperature range $0 < T < 0.8$. (taken from [1])

the lower temperatures tend to saturate to a finite temperature $T \sim 0.16$ by increasing ϵ. Very importantly we confirmed that the orbital degrees of freedom remain dynamically fluctuating between the intermediate temperatures between the higher and lower peak temperatures of the heat-capacity [2, 3]. This means that the orbitals do *not* produce the putative static quenched disorder for spins but remain dynamical. We consider that the spin and orbital degrees of freedom interact cooperatively at the energy scale corresponding to the lower peak temperature and exhibit the simultaneous glass transition at that energy scale.

5 Summary and Outlook

To summarize we constructed a theoretical model to describe the spontaneous glass transition observed in the pyrochlore oxide $Y_2Mo_2O_7$ and performed extensive Monte Carlo simulations of the model. Our results strongly suggest a new type of glass transition - spin-orbital glass transition.

There are numerous possibilities for further works. Exploration of the parameter space, especially along the ϵ-axis, should be done to clarify to what extent our present scenario holds. Construction of a mean-field theory [37] would provide a useful guideline in this respect. The criticality of the spin-orbital glass transition and its universality, consistency with the experimental results [19, 20, 25], should be examined by approaching more closer to the critical temperatures.

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References

[1] Kota Mitsumoto, Chisa Hotta, and Hajime Yoshino. *Physical Review Letters*, 124(8):087201, 2020.

[2] Kota Mitsumoto, doctoral thesis, Osaka Univ., 2020.

[3] Kota Mitsumoto, Chisa Hotta, and Hajime Yoshino. *in preparation.*

[4] John A Mydosh. *Spin glasses: an experimental introduction.* CRC Press, 2014.

[5] M Mézard, G Parisi, and M Virasoro. volume 9. World Scientific Publishing Company, 1987.

[6] K Binder and AP Young. *Reviews of Modern physics*, 58(4):801, 1986.

[7] H Kawamura and T Taniguchi. volume 24. Elsevier, 2015.

[8] PW Anderson. *Science*, 267:1615, 1995.

[9] W. Kauzmann. *Chem Rev*, 43:219–256, 1948.

[10] Jean-Pierre Hansen and Ian R McDonald. *Theory of simple liquids*. Elsevier, 1990.

[11] M. Mézard, G. Parisi, and M. A. Virasoro. *Spin glass theory and beyond*. World Scientific, Singapore, 1987.

[12] Giorgio Parisi, Pierfrancesco Urbani, and Francesco Zamponi. *Theory of Simple Glasses: Exact Solutions in Infinite Dimensions*. Cambridge University Press, 2020.

[13] Ludovic Berthier and Giulio Biroli. *Reviews of Modern Physics*, 83(2):587, 2011.

[14] Yoshihiko Nishikawa and Koji Hukushima. *arXiv preprint arXiv:2003.02872*, 2020.

[15] Hajime Yoshino. *SciPost Phys*, 4:040, 2018.

[16] J. G. Kirkwood. *in in Phase Transitions in Solids, edited by R. Smoluchowski, J. E. Mayer, and A. Weyl (Wiley, New York, 1951)*.

[17] Leticia F Cugliandolo, Laura Foini, and Marco Tarzia. *Physical Review B*, 101(14):144413, 2020.

[18] Gilles Tarjus, Steven A Kivelson, Z Nussinov, and Pascal Viot. *Journal of Physics: Condensed Matter*, 17(50):R1143, 2005.

[19] MJP Gingras, CV Stager, BD Gaulin, NP Raju, and JE Greedan. *Journal of applied physics*, 79(8):6170–6172, 1996.

[20] MJP Gingras, CV Stager, NP Raju, BD Gaulin, and JE Greedan. *Physical review letters*, 78(5):947, 1997.

[21] JS Gardner and et al. *Physical review letters*, 83(1):211, 1999.

[22] HD Zhou, CR Wiebe, A Harter, NS Dalal, and JS Gardner. *Journal of Physics: Condensed Matter*, 20(32):325201, 2008.

[23] PMM Thygesen and et al. *Physical review letters*, 118(6):067201, 2017.

[24] CH Booth and et al. *Physical Review B*, 62(2):R755, 2000.

[25] N Hanasaki and et al. *Physical review letters*, 99(8):086401, 2007.

[26] JN Reimers, AJ Berlinsky, and AC Shi. *Physical Review B*, 43(1):865, 1991.

[27] R Moessner and JT Chalker. *Physical review letters*, 80(13):2929, 1998.

[28] TE Saunders and JT Chalker. *Physical review letters*, 98(15):157201, 2007.

[29] H Shinaoka, Y Tomita, and Y Motome. *Physical review letters*, 107(4):047204, 2011.

[30] L Pauling. volume 260. Cornell university press Ithaca, NY, 1960.

[31] ST Bramwell and MJP Gingras. *Science*, 294(5546):1495–1501, 2001.

[32] Roger G Melko, Byron C den Hertog, and Michel JP Gingras. *Physical review letters*, 87(6):067203, 2001.

[33] S Große Pawig and K Pinn. *International Journal of Modern Physics C*, 9(05):727–736, 1998.

[34] JL Alonso and et al. *Physical Review B*, 53:2537–2545, 1996.

[35] K Hukushima and K Nemoto. *Journal of the Physical Society of Japan*, 65(6):1604–1608, 1996.

[36] NP Raju, E Gmelin, and RK Kremer. *Physical Review B*, 46(9):5405, 1992.

[37] Kota Mitsumoto and Hajime Yoshino. *in preparation*.