Thermal hysteresis loop of the spin-state in nanoparticles of transition metal complexes: Monte Carlo simulations on an Ising-like model

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Theoretical investigation with Monte Carlo simulations predicts that thermal spin-switching hysteresis of transition-metal complexes appears even in nanoparticles, but the hysteresis width does not depend only on the interaction strength between molecules but also strongly on the shape and size of the particles.

The manufacture of 'functional nanoparticles' with potential applications is of current interest. Control of the particle state by an external field is a desirable functionality. Fe(II) spin-crossover complexes are attractive candidates,[1] because the spin-states of the crystal are controllable by external stimuli.[1–6] Actually nanoparticles of a Fe(II) complex were synthesized recently.[7] Thermal switching was observed for 60–200 nm nanoparticles. Nevertheless, switching properties of smaller particles are unknown. This study theoretically investigated the effects of the size and shape of the nanoparticles on their thermal spin-state switching behaviour.

Fe(II) complexes have low-spin (LS) and high spin (HS) states. Accompanying the spin-state switching between these states, various properties change: magnetism, optical properties and volume. The LS and HS states have different Fe–ligand distances, which engender the cooperative interaction between molecules. The cooperativity arises from synchronisation of the Fe–ligand distance through elastic interaction.

When that cooperative interaction is sufficiently large, thermal hysteresis appears: the HS-LS switching temperature in a heating process, $T_{c\uparrow}$, differs from that in a cooling process, $T_{c\downarrow}$. In the hysteresis region defined by $T_{c\uparrow} < T < T_{c\downarrow}$, both the HS and LS states survive as a bistable state. This thermal hysteresis is an important feature, where switching between the LS and HS states is realised by various stimuli such as irradiation,[4] an applied magnetic field,[5] and applied pressure.[6] Wide hysteresis around room temperature is desirable for applications. We focus in this paper on the thermal hysteresis in small particles.

To investigate the switching behaviour, we used Monte Carlo simulations on an Ising-like model, which have been used to analyse switching in crystals of the Fe(II) complexes.[8–12] In the Ising-like model, the stable states of each complex molecule and the cooperative interaction between molecules are regarded phenomenologically. A Fe(II) complex molecule is considered as a constituent unit called 'pseudospin'. The system energy is given with the pseudospin variables $\{S_i\}$ corresponding to the spin-states of molecules as

$$H = \tfrac{1}{2} \sum_i (\Delta - k_B T \ln g) S_i - \sum_{\langle i,j \rangle}^{n.n.} J S_i S_j,$$

where the two states $S_i = -1$ and $+1$ respectively represent the LS and HS states of the molecule i. The first term contains the internal energy difference between the LS and HS states in each molecule and the supplemental term proportional to $k_B T$ caused by the internal entropy effect.[13–15] The second term represents the cooperative interaction that only exists between the nearest neighbouring pairs.

The equilibrium state at each temperature is obtained using a Monte Carlo simulation technique with the Arrhenius algorithm for stochastic state-changing of each molecule. Calculation details are given in Refs. 15 and 16.

We treat these small particles, which consist of a simple cubic lattice of pseudospins. They are cubic particles with N units on an edge, denoted as C_N, and spherical particles with size N, denoted as S_N, are investigated for various N. For comparison, we also investigated cubes with three-dimensional periodic boundary condition (PBC), which have often been used for crystal analysis.

We calculated the fraction of the pseudospins in the HS state, n_H, in both heating and cooling processes. The transition temperatures are derived respectively by $n_H = 0.5$ in the heating process ($T_{c\uparrow}$) and in the cooling one ($T_{c\downarrow}$). The width of the thermal hysteresis ΔT_c is calculated by $\Delta T_c = T_{c\uparrow} - T_{c\downarrow}$

We used the following calculation parameters: $\Delta = 500$ K, $J = 70$ K, $k_B \ln g = 2.5$, which do not correspond to a specific material, but which suggest a typical $n_H(T)$ curve of $T_{c\downarrow} \sim 182$ K and $T_{c\uparrow} \sim 212$ K for the $N = 48$ cube with periodic boundary conditions (see Fig. 1). The activation energy between the LS and HS states in each molecule is set as $E_{A0} = 600$ K. $n_H(T)$ curves are calculated using the average of Monte Carlo samples so that statistical error may be sufficiently small, *e.g.* 50 samples are calculated for C_6.

The speed of temperature sweep in the heating/cooling process is $v_T = 10^{-5}$ K per Monte-Carlo step (MCS): the time unit in the simulation is MCS. Note that the thermal hysteresis is never observed in Monte Carlo simulations with infinite v_T, because the lifetime of the metastable state in the hysteresis region is very long but finite. We determined v_T so that the dependence of ΔT_c on v_T may be sufficiently small. Our method to determine v_T is the same as that in experiments. The relation between MCS and the actual time depends on the materials, *e.g.* 1 MCS = 1 s was used to analyse an LS-HS transition of [Fe (ptz)$_6$] BF$_4$ in our previous study.[10]

The fraction of the pseudospins in the state $S = +1$ (HS), n_H, is calculated as a function of temperature for various sizes. The cubic particle case (C_N) is shown in Fig. 1. For comparison, the n_H curve

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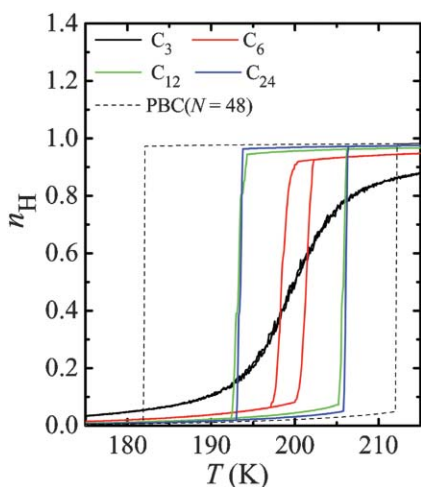
Fig. 1 The fraction of the unit in the HS state in an equilibrium state, n_H, for various sizes of cubic particles. For comparison, the result at $N = 48$ with the periodic boundary condition (PBC) is also shown.

for $N = 48$ with PBC is also shown. In the C_3 particle, n_H increases gradually as temperature increases. For the $N \leqslant 6$ case, in contrast, the drastic jump of n_H and thermal hysteresis appear even though the hysteresis loop is narrower than in the PBC case. Consequently, the thermal hysteresis loop appears even in small particles: e.g. the C_6 particle has only 216 molecules.

The width of the thermal hysteresis ΔT_c is shown in Fig. 2. The N-dependence of ΔT_c is divided into three regions as:

(a) $N \leqslant N_1$ ($N_1 = 4$ for cubes, $N_1 = 6$ for spheres)

Typical examples are C_3 in Fig. 1. In this region, ΔT_c is almost 0, indicating no hysteresis because of the low strength of the cooperative interaction.

(b) $N_1 < N \leqslant N_2$ ($N_2 = 12$ for both shapes)

Thermal hysteresis appears as C_6 and C_{12} in Fig. 1. ΔT_c arises as size increases, causing expansion of the thermal hysteresis. The ΔT_c of cubic particles is greater than that in spherical particles of the same N. This larger size is attributable to the difference in the total number of pseudospins included in the particles. There are more pseudospins in C_N, N^3, than in P_N, $\sim \pi N^3/6$. In this region, ΔT_c is approximately proportional to the number of units.
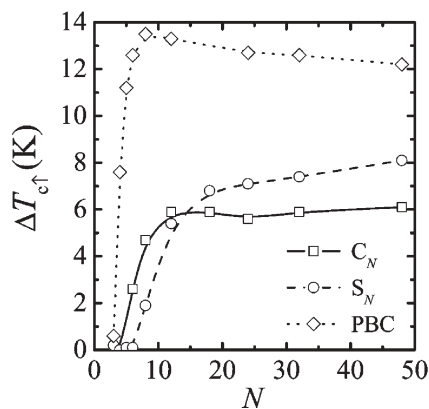
(c) $N < N_2$

Fig. 2 Size dependence of the width of the thermal hysteresis ΔT_c for cubic particles (C_N), spherical ones (S_N), and the PBC case.

In this region, the size-dependence of ΔT_c is smaller than those in region (b). More specifically, the cubic and spherical particles have different N-dependence. For the spherical particles, ΔT_c increases as N increases. In contrast, ΔT_c is almost independent of N in the cubic case. We should clarify the switching mechanism to elucidate the size-dependence. We investigated the dynamics in switching from the LS phase to the HS phase to clarify this phenomenon. Fig. 3(a) shows the time development of n_H in the process of the LS phase to the HS phase at $T = 208$ K, which temperature is slightly above $T_{c\uparrow}$. The 'inside' and 'surface' parts defined the units surrounded by six neighbours and the others, respectively. Switching to the HS phase initially proceeds in the surface region. Snapshots at each time marked in Fig. 3(a) are shown in Figs. 3(b)–3(d). The switching process has two stages: nucleation of the HS state and its growth. The nucleation initiates at the cubic particle vertices. The units at the vertices and those on the edges have only three and four neighbours, respectively, generating large fluctuations of the spin-states. Consequently, nucleations usually occur around the vertices.

Those vertex units are the reason for the N-independence of the thermal hysteresis loop in the cubic particles. For the cubic particles, the local structure around the vertices does not depend on the particle size. Therefore, nucleation at the vertices occurs in the same manner for all N. In contrast, for spherical particles, the thermal hysteresis loop widens as N increases. This increased width occurs because nucleation at the surface becomes difficult for large N particles due to the decreased surface curvature. As the curvature decreases, the density of the number of units having smaller neighbours decreases. As a result, the thermal hysteresis loop is expanded as N increases in the spherical particles.

In any regions of either particle shape, ΔT_c is smaller than that in the PBC case. This is attributable to nucleation of the ground
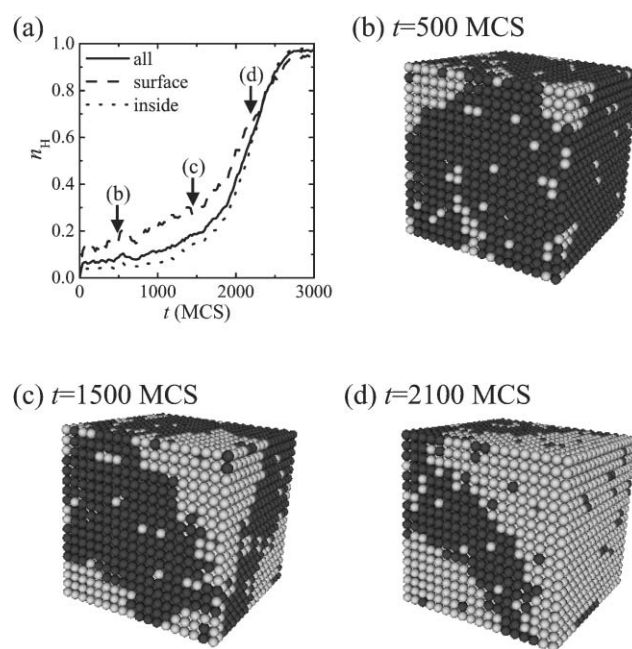

Fig. 3 Process of the phase transition from the LS phase to HS phase in the C_{18} particle at $T = 208$ K. (a) Fraction of the units in the HS state. (b)–(d) snapshots at times marked in (a). Black and white spheres respectively represent the units in the LS state and those in the HS state.
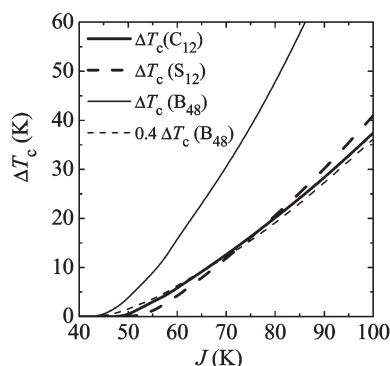
Fig. 4 Dependence of the width of the thermal hysteresis ΔT_c on the interaction strength J. C_{12} and S_{12} represent the cubic and spherical particles with $N = 12$, respectively. B_{48} indicates the $N = 48$ lattice with the periodic boundary conditions.

state, which occurs easily in the particles because of state fluctuations that are enhanced at the surface. In addition, it is important that T_c in the limit of $N \rightarrow \infty$ may differ for cubic and spherical particles. This difference indicates that the thermal hysteresis loop depends on the shape even in very large particles that are ordinarily considered as bulks.

Finally we investigated the effect of the interaction strength J on the width of thermal hysteresis ΔT_c. The interaction strength is known as a major criterion to determine ΔT_c in the crystals. In the nanoparticles, ΔT_c also depends on J strongly, as shown in Fig. 4. The $\Delta T_c(J)$ curves of the spherical and cubic particles almost overlap with the 0.4 times of the curve for the PBC case, *i.e.* the interaction dependence in the nanoparticles is qualitatively similar to the crystal, although its magnitude is suppressed.

In this study, we assume that cooperative interaction exists only among nearest neighbours because we have been successful in simulating observations on the crystals of Fe(II) complexes. However, introducing a long-range interaction may be required for precise simulation of observations. If we consider the long-range interaction of particles, suppression of the shape-dependence between the cubic and spherical particles is expected. That is, T_c of the cubic particles may depend to some degree on the size because the vertices' particularity is reduced by long-range interactions.

Our result is also applicable to spin switching in nanoparticles of cyano-bridged metal complexes such as cobalt hexacyanoferrate. Photo-induced and thermal-induced spin-state switching have been observed in crystals of this material.[17] A theoretical study of them using the similar model exists.[18] Syntheses of nanoparticles for various cyano-bridged complexes have also been reported,[19–27] but thermal spin-state switching has not been observed to date.

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