Threshold Phenomena under Photo Excitation of Spin-crossover Materials with Cooperativity due to Elastic Interactions

Seiji Miyashita\textsuperscript{1,5}, Per Arne Rikvold\textsuperscript{2}, Takashi Mori\textsuperscript{1,5}, Yusuke Konishi\textsuperscript{3,5}, Masamichi Nishino\textsuperscript{4,5}, Hiroko Tokoro\textsuperscript{1,6}

\textsuperscript{1}Department of Physics, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113-8656, Japan
\textsuperscript{2}Department of Physics and Center for Materials Research and Technology, Florida State University, Tallahassee, Florida 32306-4350, USA
\textsuperscript{3}Solid State Theory Division, Institute of Materials Structure Science, KEK, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
\textsuperscript{4}Computational Materials Science Center, National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
\textsuperscript{5}CREST, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan
\textsuperscript{6}PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

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Photo-induced switching from the low-spin state to the high-spin state is studied in a model of spin-crossover materials, in which long-range interactions are induced by elastic distortions due to different molecular sizes the two spin states. At a threshold value of the light intensity we observe nonequilibrium critical behavior corresponding to a mean-field spinodal point. Finite-size scaling of the divergence of the relaxation time is revealed by analysis of kinetic Monte Carlo simulations.

Molecular solids whose molecules can exist in two electro-vibrational states, a low-spin ground state (LS) and a high-spin excited state (HS), are known as spin-crossover (SC) compounds. Due to higher degeneracy of the HS state, such materials can be brought into a majority HS state at low temperatures by several methods, including light exposure, known as Light-Induced Excited Spin-State Trapping (LIESST)\textsuperscript{3}. If the intermolecular interactions are sufficiently strong, this change of state can become a discontinuous phase transition such that the HS phase becomes metastable and hysteresis occurs. The different magnetic and optical properties of the two phases make such cooperative SC materials promising candidates for switches, displays, and recording media\textsuperscript{2}, and the cooperative properties of SC materials have therefore been studied extensively\textsuperscript{5}. In addition to SC materials, models with similar long-range interactions are relevant to a range of physical phenomena, including earthquake faults\textsuperscript{3} and phase transitions in polymers\textsuperscript{4}.

In a typical model of a SC material, the energy difference between the HS and LS states is taken as $D > 0$, while the degeneracy $g_{HS}$ of HS is larger than $g_{LS}$ such that HS is preferable at high temperature. We can express the HS (LS) spin state of the $i$-th molecule by $\sigma_i = +1$ ($-1$), giving the intra-molecule Hamiltonian,

$$\mathcal{H}_{\text{eff}} = \frac{1}{2} \sum_i (D - k_B T \ln g) \sigma_i,$$

where $g = g_{HS}/g_{LS}$. Here the difference of the degeneracies are expressed by a temperature dependent field. In order to provide the cooperative property in the SC transition, a short-range Ising-type interaction has previously been adopted\textsuperscript{2,6}. Recently, we pointed out an alternative mechanism with elastic interactions due to the volume difference between the LS and HS molecules\textsuperscript{7,8}. The elastic interaction mediates the effects of local distortions over long distances, and it has been found that the critical behavior belongs to the mean-field universality class\textsuperscript{3}.

Here, we study the dynamics under photo-excitation from the perfect LS state at low temperature. For a single molecule, we find a smooth increase of the HS fraction, and the saturated HS fraction is a smooth function of the irradiation intensity. On the other hand, if we include a cooperative interaction, a kind of threshold phenomenon appears. When the irradiation is weak, the system stays in the LS state. If the irradiation becomes stronger than a threshold value, the system jumps to the HS state. Thus, the stationary state suddenly changes from LS to HS at a threshold value of the irradiation intensity. This sudden change is analogous to the sudden change of magnetization at the coercive field in the hysteresis loop of a ferromagnet following reversal of the applied field, known as a “spinodal point.”

The dynamics of field-driven first-order phase transitions have previously been studied in detail for Ising/lattice-gas models with short-range interactions. In that case, the nucleation and growth of clusters play important roles, and different regimes have been identified, depending on the relative time scales of nucleation and growth\textsuperscript{10}. If the average time between nucleation events is long compared with the time it takes a single cluster to grow to a size comparable with the system, the transformation will happen stochastically in a Poisson process via a single cluster (single-droplet, or SD, regime), and the average lifetime of the metastable phase is inversely proportional to the system volume. If the average time between nucleation events is short compared with the growth time, many clusters nucleate while...
FIG. 1: (Color online) Time series of the order parameter \(M(t)\) under irradiation. Irradiation intensities \(a = 0.001, 0.002, 0.003, 0.004, \) and \(0.005\) from bottom to top. We plot 10 samples for each value of \(a\). The system size is \(L = 50\). The time \(t\) is measured in Monte Carlo steps per site (MCSS).

The first one is growing, resulting in an almost deterministic process (multi-droplet, or MD, regime), and the metastable lifetime is independent of the system volume (Avrami’s law) [10].

In this paper, we study the photo-induced transition in a model of SC materials with elastic interactions, which we have developed previously [8, 9]. In this model, we found that the appearance of large, compact clusters is strongly suppressed, and the system remains uniform near the critical point and also during simulations of field-driven hysteresis [9]. In the process of the photo-induced transition, we also expect to see effects of the effective long-range elastic interactions. Here, we therefore investigate the relaxation time near the threshold point and its dependence on the system parameters. We analyze the dependences from the viewpoint of the mean-field spinodal, which shows qualitatively different properties from field-driven phase transformation in short-range models [11, 12].

Here we use Monte Carlo (MC) simulations according to the constant-pressure method [8]. In addition, we include a process of photo-excitation by the following procedure. We choose a site randomly and change it to the HS state with a probability \(a\) if it is previously in the LS state. We denote \(a\) as the irradiation intensity.

The order parameter for the present model is the fraction of HS molecules, \(f_{\text{HS}}\), which is expressed by the “magnetization”

\[
M = \frac{1}{N} \sum_{i}^{N} s_i = \frac{1}{2} (f_{\text{HS}} - 1).
\]

Here we adopt the two-dimensional model of Ref. [9] with the same parameters, including \(g = 20\) and \(D = 0.5\).

In Fig. 1 we depict typical time series of the HS fraction under irradiation. We find a sudden change in the saturated values. For \(a \leq 0.003\) the system stays in the LS state, while it jumps to the HS state for \(a \geq 0.004\). In Fig. 2 we show the dependence of the saturated value on \(a\). Because of the cooperative interaction, the HS fraction remains low when the irradiation is sufficiently weak. On the other hand, it approaches unity when \(a\) exceeds a threshold value. This threshold value of \(a\) is estimated from Fig. 2 to be slightly below 0.004.

We also find a sudden change of \(M\) as a function of time. We depict an example of the relaxation process for \(L = 50\) in Fig. 3(a), which shows a sharp change around \(t = 5000\) Monte Carlo steps per site (MCSS). The HS fraction stays at an intermediate value \((M \simeq -0.2)\) for a while, and then it rapidly increases to the saturated value. This sudden change is reminiscent of a transformation via single-droplet nucleation from the metastable phase to the equilibrium phase. However, no visible clusters are observed. In Fig. 3(b) we depict a configuration at \(t = 6000\) MCSS, near the starting point of the sudden change. This absence of cluster structures is the same characteristic which we found previously in simulations of hysteresis in this model [8].

Next, we study the system-size dependence of the relaxation time. Here we define the relaxation time \(\tau\) as the time at which the average of \(\sigma_i\) reaches 0.5, correspond-
ing to a HS fraction of 0.75, starting from the perfect LS spin state ($\sigma_i = -1$). We perform $N_{\text{sample}}$ independent runs for each parameter set and average the results. In Fig. 1 we depict the size dependences of the relaxation times $\tau$ for $a \in [0.00365, 0.00400]$, obtained by averaging over the samples. Here, we plot the data as a function of $L^{2/3}$ because it is expected that the relaxation time diverges as $L^{2/3}$ at the spinodal point (see below).

We found the sudden change of the saturated value of $M$ around $a_{SP} \approx 0.0385$ in Fig. 2. Below this value, the relaxation times increase rapidly with $L$, while above it the relaxation times saturate for large $L$. As shown in Fig. 1 for $a < a_{SP}$ the times of the jump are widely distributed. This is a sign of stochastic nucleation, although we do not observe any clusters in Fig. 2(b). For $a > a_{SP}$, the transformation process becomes nearly deterministic.

It is also found that the size dependence of the standard deviation of the relaxation time $\sqrt{\langle \tau^2 \rangle - \langle \tau \rangle^2}$ is very different below and above the threshold. Below $a_{SP}$ the standard deviation is about the same as the mean value while it decreases with increasing $L$ above $a_{SP}$. The former suggests a kind of Poisson process in the SD region and the latter a kind of Gaussian process in the MD region. In Table I, we list typical examples.

It should be noted that the relaxation time increases with the system size. This system-size dependence of the relaxation time is qualitatively different from the behavior in systems with short-range interactions. In the latter case, the relaxation time is determined by the probability of creating a critical localized, compact droplet, whose free energy is independent of the system size. Droplets thus nucleate in a Poisson process of rate $L^{d}I$, where $d$ is the spatial dimensionality of the system (here, $d = 2$). Thus, the relaxation time becomes short when the size increases in both the SD and MD regions.

Compared to this dependence in short-range systems, the increase of the relaxation time in the present system with the system size is notable. The divergence when $L \to \infty$ indicates that the present threshold phenomenon is not just a crossover as in short-range systems, but a true critical phenomenon. Thus we will study its critical properties by analyzing the size dependence of the relaxation behavior.

The simple van Hove type dynamics using the mean-field approximation implies that the waiting time before a jump over the free-energy barrier for $a < a_{SP}$ has the form

$$\tau \sim \exp(cN),$$  \hspace{1cm} (3)

where $N = L^d$ is the volume of the system and $c$ is positive. The present case appears similar. Indeed, the present threshold behavior is essentially the same as the sudden phase change near a mean-field spinodal point, and we expect that the parameter dependence is the same as that near the spinodal point of the Ising ferromagnet with weak long-range interactions (the Husimi-Temperley model), with the irradiation strength $a$ here playing the role of the magnetic field. Thus, the relaxation time for $a > a_{SP}$ should diverge as

$$\tau \propto (a - a_{SP})^{-1/2},$$  \hspace{1cm} (4)

independent of $L$. At the spinodal point, the relaxation time diverges with the system size as

$$\tau \propto N^{1/3},$$  \hspace{1cm} (5)

where $N$ is the total number of spins.

We plot the relaxation times for various values of $a$ as functions of $N^{1/3} = L^{2/3}$ in Fig. 4. The relaxation times at $a = 0.00385$ are seen to follow a straight line, consistent with the properties of the mean-field spinodal point. The relations (3), (4), and (5) can be combined into a scaling form,

$$\tau \propto L^{d/3} f(L^{2d/3}(a - a_{SP})),$$  \hspace{1cm} (6)

where $f$ is a function.

### Table I: List of average and the standard deviation of the distribution of the relaxation time.

| $a$   | $L$   | $N_{\text{sample}}$ | $\langle \tau \rangle$ | $\sqrt{\langle \tau^2 \rangle - \langle \tau \rangle^2}$ |
|-------|-------|----------------------|-------------------------|--------------------------------------------------|
| 0.00375 | 20   | 200                  | 12174.045               | 8189.569                                         |
| 0.00375 | 40   | 200                  | 105239.460              | 96223.716                                       |
| 0.00375 | 60   | 400                  | 4608237.905             | 4343268.886                                    |
| 0.00400 | 20   | 200                  | 4281.680                | 1321.136                                        |
| 0.00400 | 40   | 200                  | 5394.570                | 1111.389                                        |
| 0.00400 | 60   | 200                  | 5905.740                | 945.039                                         |
| 0.00400 | 80   | 200                  | 6245.863                | 727.554                                         |
| 0.00400 | 100  | 350                  | 6475.271                | 591.310                                         |

FIG. 4: (Color online) Dependence of the relaxation time $\tau$ on system size $L$ and irradiation strength $a$. Shown as $\tau$ vs $L^{2/3}$ for $a = 0.00365, 0.00370, 0.00375, 0.00377, 0.00378, 0.00379, 0.00380, 0.00381, 0.00382, 0.00383, 0.00384, 0.00385, 0.00386, 0.00397, 0.00399, 0.00395 and 0.00400 from above to below. Straight-line behavior consistent with (3) is seen for $a = 0.00385 \approx a_{SP}$. 

FIG. 3: (Color online) Size dependence of the distribution of the relaxation time.

FIG. 2: (Color online) Initial relaxation times as a function of the HS fraction $\sigma_i$.
where the scaling function $f(x)$ has the following asymptotic dependences on the scaling variable $x = L^{4/3}(a - a_{SP})$:

$$f(x) \sim \begin{cases} 
\exp(|x|^{3/2}) & \text{for } x \ll -1 
\end{cases}$$

$$x^{0} & \text{for } |x| \ll 1 
$$

$$x^{-1/2} & \text{for } x \gg 1 
$$

In Fig. 5, we plot the scaling function $f(x) = \frac{\tau}{L^{2/3}}$ on logarithmic scale vs $|x|^{3/2}$ in order to have all the data including the large relaxation times at small values of $a$ in one figure. We find that all the points collapse onto a scaling form, which shows the asymptotic behavior given in (7). This scaling form has been found for the spinodal phenomenon in the Husimi-Temperley model as well [10].

We also study the finite-size scaling of the standard deviation of the distribution of the relaxation time. Above $a_{SP}$, the distribution of the relaxation time is narrowly localized, and the standard deviation decreases with increasing system size. On the other hand, far below $a_{SP}$, the distribution is exponential, so that the standard deviation is of the same order as the average. In Fig. 6 we show the ratio of the standard deviation to the mean of the relaxation time vs the scaling variable $x$. The results collapse quite well onto a scaling function.

In conclusion we note that the present spin-crossover model with elastic interactions displays a sharp spinodal point with critical properties consistent with those of the mean-field universality class. We hope that this truly critical nonequilibrium phenomenon soon will be experimentally observed during photo-irradiation of SC materials.

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