Dynamical process for switching between the metastable ordered magnetic state and the nonmagnetic ground state in photoinduced phase transition

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We propose a dynamical mechanism of the two-way switching between the metastable state and the stable state, which has been found in experiments of photoinduced reversible magnetization and photoinduced structural phase transition. We find that the two-way switching with a non-symmetry breaking perturbation such as illumination is possible only in systems with appropriate parameters. We make it clear that the existence of two time scales in the dynamical process is important for the two-way switching.

Dynamics of the switching between the metastable state and the stable state is one of the most interesting topics of phase transitions. Photoinduced phase transition (PIPT) has currently attracted interests in the condensed matter physics. In spin-crossover complex several such phenomena have been reported. PIPT is accompanied by a structural phase transition as observed in TTF-CA or by a magnetic phase transition as observed in Co-Fe complex. Because the energy level of the low spin state of such a complex gets cross to that of the high spin state, the spin state can be changed between these states by stimulus due to changes of temperature, pressure, photoexcitation, etc. Among them, the cobalt-iron prussian blue analogs have been reported to be able to switch from the paramagnetic state to the ferrimagnetic state (or vice versa) by visible (or near-IR) illumination.

In order to study the switching mechanism, we consider a system which has a long-lived metastable ferromagnetic excited state. The transition process from the metastable magnetic state to the stable paramagnetic state can be realized by the nucleation process because the bulk free energy of the stable state is lower than that of the initial metastable state. Hereafter we refer to the metastable state as MS and to the stable state as SS. On the other hand, switching from SS to MS conflicts with the thermodynamic stability and it is considered to be difficult to realize as far as we apply only symmetric disturbance, e.g., illumination, although it is easy by using a uniform field which causes the symmetry breaking. Our interests is how the two-way switching is realized in a symmetric applied field. In our previous study, photon’s effect is attributed to the change of renormalized parameters \((D, T)\), where we chose these parameters in the phase diagram from a viewpoint of phenomenology.

In this letter we consider the condition for the two-way switching in terms of the transition probabilities among microscopic states. We find that the two-way switching cannot be realized when we introduce only a spin-pumping effect by photon. In addition to the pumping effect of photon, a suitable relation between transition probabilities among elementary processes is necessary to realize the two-way switching. Here we will extend the Glauber dynamics and introduce a more complicated relaxation process where the switching (SS \(\rightarrow\) MS) can be realized. Using this model we will study characteristics of the system which can show the two-way photoinduced transition.

As a typical model which shows the first-order phase transition, we adopt the Blume-Capel (BC) model in the simple cubic lattice,

\[
\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j + D \sum_i S_i^2,
\]

where \(S_i = \pm 1\) or 0 and \(\langle i,j \rangle\) denotes the nearest-neighbor pairs. Here \(S_i = \pm 1\) represents the high spin state with the magnetization \(\pm 1\), respectively, and \(S_i = 0\) represents the low spin state which is nonmagnetic. The excitation energy from the low spin state to the high spin state is \(D(> 0)\). We take \(J(> 0)\) as a unit of energy and set \(k_B = 1\).

Here we adopt a stochastic dynamics with multi-time scales as follows. Let \(P(S_1 \cdots S_k \cdots S_N, t)\) be the probability of the state \(\{S_1 \cdots S_k \cdots S_N\}\) at time \(t\). Using the transition probability per a unit time \(W_k(S_k \rightarrow S'_k)\) at the \(k\)-th site (Fig. (a)), the master equation is generally given by

\[
\frac{d}{dt} P(S_1 \cdots S_k \cdots S_N, t) = \sum_k \sum_{s_k \neq s'_k} W_k(S_k \rightarrow S'_k) P(S_1 \cdots S_k \cdots S_N, t) - \sum_k \sum_{s_k \neq s'_k} W_k(S'_k \rightarrow S_k) P(S_1 \cdots S_k \cdots S_N, t).
\]

Here, we assume that the time scale of the transition between \(S = \pm 1\) is much faster than that between \(S = 0\) and \(|S| = 1\), because the former is a simple spin flip process while the latter is accompanied by a structural change. Representing this situation, we introduce two transition processes: The first one is the standard Glauber type evolution,
The transition process between the high spin states $S \pm 1$ or $L \pm 1$, respectively. Blank circle denotes a nonmagnetic state.

Here $\sum_{NN}$ denotes the summation over the nearest neighbor sites of $k$. We express this process by $\delta P(t) = \dot{L}_G(t)\mathcal{P}(t)$. The second one is a process of spin flip, $\dot{L}_S$, (Fig. 1 (b)),

$$W_k(S_k \rightarrow 1) = \frac{\exp(y)}{2\cosh y + \exp(\beta D)}$$
$$W_k(S_k \rightarrow -1) = \frac{\exp(-y)}{2\cosh y + \exp(\beta D)}$$
$$W_k(S_k \rightarrow 0) = \frac{\exp(\beta D)}{2\cosh y + \exp(\beta D)}$$

where $S_k = \pm 1$, 0(Fig. 1 (a)) and $y = \beta J \sum_{NN} S_i$. Here $\sum_{NN}$ denotes the summation over the nearest neighbor sites of $k$. We express this process by $\delta P(t) = \dot{L}_G(t)\mathcal{P}(t)$. The second one is a process of spin flip, $\dot{L}_S$, (Fig. 1 (b)),

$$W_k(\pm 1 \rightarrow 1) = \frac{\exp(y)}{2\cosh y}$$
$$W_k(\pm 1 \rightarrow -1) = \frac{\exp(-y)}{2\cosh y}$$
$$W_k(S_k \rightarrow S_k') = 0 \quad (\text{the other weights})$$

We study a combination of these two processes,

$$\dot{L}(t) = p_G\dot{L}_G(t) + p_S\dot{L}_S(t).$$

Here the parameters $p_G$ and $p_S$ ($p_G + p_S = 1$) describe the relative time scale of the processes. When $p_G/p_S$ is small, the relaxation among the high spin states ($S = \pm 1$) occurs more quickly than that between high and low spin states ($|S| = 1$ and 0). Because both $\dot{L}_G$ and $\dot{L}_S$ satisfy the detailed balance, it is warranted that with any combination of $p_G(\neq 0)$ and $p_S$ any initial state goes to the equilibrium state. Here we think that the ratio of $p_G$ and $p_S$ is given as an inherent property of individual materials. Under the process $\dot{L}_S$, the pumped spins tend to align before the system relaxes back to the state of $S = 0$. When the adequate balance of these two processes is realized, we expect that the reversible switching of the magnetization by illumination is possible.

Next we consider a process $\dot{L}_p$ for illumination. During the illumination, the pumping process is included. Photon excites a site which is either nonmagnetic or magnetic to a magnetic site. It is a natural assumption that the transition to up spin or to down spin has an equal probability and we take the transition probabilities (Fig. 1 (c)),

$$W_k(S_k \rightarrow \pm 1) = \frac{1}{2}.$$

The time evolution during the illumination is given by

$$\dot{L}(t) = p_G\dot{L}_G(t) + p_S\dot{L}_S(t) + p_P\dot{L}_P(t),$$

where $p_G + p_S + p_P = 1$. The magnitude of $p_P$ represents the strength of the excitation. Indeed in the experiments, two kinds of illuminations with different frequencies are used to realize the switching of magnetization.

We look for a suitable set of $p_G$, $p_S$ and $p_P$ with which the system can be switched between MS and SS. Let us study the dynamics of the system first within a mean field theory (MFT). We will then check the stability of the results of MFT by a Monte Carlo (MC) method.

In MFT, Eq. (2) is reduced to an equation of $p_1(t)$, $p_{-1}(t)$, and $p_0(t)$, which are respectively the probabilities for up spin state, down spin state, and nonmagnetic state on a site at time $t$. Furthermore, the equations of $p_1(t)$ and $p_{-1}(t)$ are reduced to an equation of the magnetization, and the equation is found to be expressed in the form of the Van Hove’s phenomenological equation.

$$\frac{d}{dt} m = \dot{p}_1(t) - \dot{p}_{-1}(t) = -\beta \frac{df(m,t)}{dm}.$$  

This $f(m,t)$ is regarded as the effective free energy, which is useful to visualize the thermodynamic force at a given time $t$. We obtain $f(m,t)$ by integrating the right hand side of Eq. (8) as to $m$.

$$f(m,t) = \frac{1}{2}Jzm^2 - \frac{1}{\beta}[\ln(2\cosh(\beta Jzm)) + \exp(\beta D)] - \frac{1}{\beta}[(1 - p_0(t = 0)\exp(-(p_G + p_P)t))] - \frac{p_G}{p_G + p_P}[(1 - \exp(p_G + p_P)t)]\ln(2\cosh(\beta Jzm))$$

In the case of no illumination ($p_P = 0$), the above free energy gives the equilibrium free energy $f_{eq}(m)$ in the limit $t \rightarrow \infty$ regardless of the parameters $p_G(\neq 0)$ and $p_S$. In Fig. 2 $f_{eq}(m)$ for $(D,T) = (3.2,0.6)$ is shown.

Because of the existence of metastable valleys, some initial states may relax to the MS instead of SS. In the case of $p_S = 0$ ($p_G = 1$), $f(m,t)$ is independent of time and takes the form of $f(m)$ in Eq. (8). When the value of magnetization is larger than the critical value $m_c (=
the case of spin ordering is expected to be enhanced. In spite of the system to relax to MS after the illumination, the magnetization of the stationary state in the illumination is much smaller than $m_c$, for any value of $p_P$. Therefore it is impossible to cause the transition SS $\to$ MS when $p_S = 0$

Next we consider the case of $p_S \neq 0$, where the process of spin ordering is expected to be enhanced. In spite of the case of $p_S = 0$, the form of $f(m, t)$ depends on $t$ and $p_0(t = 0)$. In Fig. 3 we show a kind of phase diagram of the initial values $(p_0, m)$ for the cases of (a)$p_G/p_S = 0.667$, (b)$p_G/p_S = 0.163$ and (c) $p_G/p_S = 0.429$. Because of the condition $p_1 + p_{-1} + p_0 = 1$ and $0 \leq p_1, p_{-1}, p_0 \leq 1, p_0 + m \leq 1$ must be satisfied. The open circles denote the boundary between the region of $(p_0, m)$ from where the state goes to MS and the region from where the state goes to SS. There the values $(p_0, m)$ of the stationary state of the illumination process ($p_P \neq 0$) are also plotted by closed circles for various values of $p_P$ keeping the ratio of $p_G/p_S$. That is, in the case of $p_P = 0.5$ and $p_G/p_S = 0.667$, $p_G = 0.2$ and $p_S = 0.3$.

If a closed circle for a value of $p_P$ is located below the critical line linking open circles, the initial state with the values $(p_0, m)$ denoted by this closed circle relaxes to SS (para). By the illumination the system becomes to the state denoted by this closed circle, and then after the illumination it relaxes to SS. In the case of (a) the point $(p_0, m)$ of the stationary state with any value of $p_P$ is located below the critical line as shown in Fig.3 (a), and thus all states after the illumination give the initial state for SS. On the other hand, if a closed circle for a value $p_P$ is located above the critical line, the state relaxes to MS. By this illumination the system becomes to the state denoted by this closed circle, and then after the illumination it relaxes to MS (ferro). In the case of (b) the point of the stationary state with any value of $p_P$ is located above the critical line as shown in Fig.3 (b), and thus all states after the illumination give the initial state for MS. In order to realize the two-way switching (MS$\to$SS) the system has to have both cases for different values of $p_P$. That is, the closed circles are located on both sides of the critical line as shown in Fig. 3(c).

With the present observation we find that the two-way switching is not possible in every system but in only limited materials which have a peculiar property that the boundary (open circles) crosses with the line of closed circles. On the other hand, we also find that such situation can be actually exist in some appropriate condition.

Now we demonstrate how the switching of the magnetization is realized. According to the results in Fig. 3, we choose the ratio $p_G/p_S=0.429$. As an initial state we take the equilibrium state of the parameter $(D, T) = (3.2, 0.6)$ where $m = 0$ and $p_0 = 0.99$. We make the system in the illumination of $p_P = 0.7$ for a period $t_0 < t < t_1$ (process I), and then we turn off the illumination and let the system relax, i.e. $p_P = 0$ for a period $t_1 < t < t_{11}$ (process II). The change of the effective free energy $f(m, t)$ in the process I is shown in Fig. 4 (a), at the end of the process $f(m, t)$ almost reaches the form of its stationary state where $f(m, t)$ has two minima and $m = \pm 0.18$. In the second process $f(m, t)$ changes as shown in Fig. 4 (b). Because the final state of the process I $(p_0, m) = (0.11, 0.18)$ locates in the region to go to MS (ferro), the system relaxes to the metastable state. Thus we have the switching SS $\to$ MS. We see that the magnetization increases with time in the process II.
Next, let us consider a procedure for the switching MS → SS. Now we illuminate the system with another light of $p_F = 0.9$ for a period $t_{III} < t < t_{IV}$ (process III), where $f(m,t)$ changes as shown in Fig. 4 (c). The $f(m,t)$ at the final state ($t = t_{IV}$) is parabolic and the system has almost no magnetization. Thus after turning off the light the system relaxes to the stable paramagnetic state as shown in Fig. 4 (d) (process IV). The time evolution of magnetization of the whole processes is shown in Fig. 5 (a). In the process III we could choose $p_F$ to be 0.4 instead of 0.9 to realize MS→SS because the closed circle for $p_F = 0.4$ is also located below the critical line.

We have shown that the two-way switching is realized by the processes I ~ IV in MFT. In order to check whether the switching process is stable against fluctuations, we study the processes by a Monte Carlo (MC) method. Of course quantitatively MC and MFT gives different results. But, qualitatively the same features of the dynamics as obtained in MFT are also found in MC. Namely, when $p_S = 0$, the switching SS → MS is not observed for any value of $p_F$. On the other hand we can realize the two-way switching by tuning the parameters as $p_C/p_S = 0.289$, $p_F = 0.096$ for the process I and $p_F = 0.24$ for the process III. The time evolution of magnetization per site is shown in Fig. 5 (b) (simple cubic lattice with 1000 sites in periodic boundary condition). Strictly speaking, in MC the true stationary state of the process II is the paramagnetic state, but the relaxation MS → SS is very slow and thus practically the same behavior as in MFT is reproduced. We confirmed that this switching of magnetization can be repeated reliably, and we conclude that the two-way switching provided by the processes I - IV is stable even in systems with short range fluctuations. In the MC simulation, the switching dynamics depends very sensitively on the ratio of parameters as well as in the MFT case.
is possible. This implies that only materials which satisfy such conditions can show the photoinduced switching phenomena.

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