APPLICATION OF MICROCANONICAL TEMPERATURE TO THE SPIN CROSSOVER OF Fe-Co COMPOUNDS

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ABSTRACT

Using the Rugh's microcanonical approach to temperature we study the classical model of three dimensional spin-crossover of Fe-Co compounds. These compounds are characterized by magnetic ions that can be in a high-spin or low-spin state. We consider the case of diamagnetic low-spin state. The values of the magnetization average, and fraction of high-spin/low-spin are studied over a wide range of values for the system size, temperature, magnetic field, energy difference, nearest neighbor coupling and exchange interaction. We also address the metastability according to the relative values of interaction parameters and the phase diagram of the model.

Keywords: phase transition, dynamical temperature, spin crossover

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1. INTRODUCTION

The present study uses the Rugh's micro-canonical approach to temperature (Nurdin and. Schotte, 2002; Nurdin and Schotte, 2000; Khinchin, 1949; Huang, 1963; Rugh, 1997; and Rugh, 1998), to be taken into account in the classical model of three dimensional spin-crossover compounds. These compounds are characterized by magnetic ions that can be in a high-spin or low-spin state. We consider the case of diamagnetic low-spin state which are appropriate for Fe-Co compounds. Co-Fe is an attractive material owing to its two-way photo-switching, i.e., magnetic and non magnetic. Since the state of Co(II)-Fe(III) which is favorable at high temperature owing to its high degeneracy, we call it a high-temperature (HT) state and the Co(III)-Fe(II) state which is favorable at low temperature owing to its low energy, as a low-temperature (LT) state. In this material, the magnetic coupling between Co and Fe ions is anti-ferromagnetic. On the dynamics of spin-crossover solids the frontier works have pointed out the role of the interaction on the shape of relaxation curves, i.e. the time dependence of the metastable state fraction after photo-excitation of the system. In some octahedral coordinate iron complexes, a spin crossover (SC) may occur between a high-spin (HS) state and a low-spin (LS) state. An SC transition is induced by external stimulations such as temperature, photo-irradiation, and magnetic field (Goodwin, 1976; G¨utlich, 1981, G¨utlich, et.al., 1994; Renovitch and Baker, 1967).

The HS state is favorable at high temperature owing to its high degeneracy. On the other hand, the LS state is favorable at low temperature because it has a low energy with a low degeneracy. Interesting transitions between HS and LS states are provided by the

competition between entropy gain and energy gain. For SC transitions it has been pointed out that cooperative interactions are important. Smooth transition or discontinuous first order phase transition occurs in the SC transition according to the system parameters (Goodwin, 1976). Control between the HS and LS states has been realized by photo-irradiation as light-induced excited spin state trapping (LIESST) (Hauser, et.al., 1986,;Hauser, 1991; Decurtins, et.al., 1984; Guetlich, et.al., 1994; Hauser, 1995; Hauser, 1991; Renovitch and. Baker, 1967; Kahn and Martinez, 1998; Kahn, 1993; Decurtins, et.al., 1985; Hauser, 1991; L´etard, et.al., 1999) and the structure of the photo-induced metastable state of the systems has become an important topic (Hauser, 1995 ; Hauser, 1991 ; Romstedt, et.al., 1998, and Desaix, et.al., 1998). Wajnflasz-Pick (WP) model gave the theoretical basis of the mechanism of the cooperative transitions using an Ising model with degenerate states. The WP model and its extended models have explained successfully the static and dynamical properties of various cases of SC transitions (G¨utlich, 1981; G¨utlich, et.al., 1994; Renovitch and Baker, 1967; Kahn and Martinez, 1998; Kahn, 1993; Decurtins, et. al., 1985; Hauser, 1991). The metastable state can exist intrinsically at low temperature, which has been supported experimentally (Romstedt, et. al., 1998; Desaix, et. al., 1998). The effects of applying a magnetic field have been studied in some SC complexes (Renz, et. al., 2000; Nasu, 1997; Tayagaki and Tanaka, 2001; Miyashita, et. al., 2005; Tokoro, et. al., 2006; Wajnflasz and Pick, 1971). Since the magnetic moment in the HS state is larger than that in the LS state, the HS state is stabilized by applying a magnetic field. A shift in transition temperature under an applied magnetic field was confirmed experimentally (Renz, et. al., 2000; Nasu, 1997; Tayagaki and Tanaka, 2001).

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2. DYNAMICAL TEMPERATURE

Starting from a micro-canonical ensemble, the entropy is a function of energy. It is defined as the logarithm of the number of different states which a physical system has with a given energy, that is $S = ln\ W$ with Boltzmann's constant set to unity. For a classical system with Hamilton function is proportional to the surface of constant energy in the phase space of canonical coordinates. More precisely it is the number of points between infinitesimal neighboring surfaces written in the form of a Gaussian surface integral. The direction of the infinitesimal surface element is normal to surface of constant energy coincides with the direction of the gradient. This quantity in general cannot be calculated directly for a mechanical system, but its logarithmic derivative with respect to energy can as has been pointed out by Rugh (Rugh, 1998; Hauser, et.al., 1986). Using Gauss' theorem the last integral in energy formula can be written as that is as an integral over all phase space where the energy is lower. The derivative with respect to energy is again a constant energy integral as for W. Using a pulsed high magnetic field, the creation of the HS state from the LS branch in the thermal hysteresis loop was observed and these results were interpreted using an Ising-like model Miyashita, et. al., 2005; Tokoro, et. al., 2006; Wajnflasz and Pick, 1971)

However, since both the HS and LS states in the SC complexes are paramagnetic, the study of the effects of applying a magnetic field has been performed only for the paramagnetic region. Both phenomenological mean field model and dynamic Monte Carlo simulation have been reported to describe the experimental data. The typical feature of self accelerated relaxation gives a sigmoidal shape was assigned to the effect of interaction. In addition a ‘tail’ was observed and attributed to the transient onset of correlations. This tail was not obtained in the mean field approach. The purely molecular aspect of relaxation has also received much attention, and the simple idea of thermally activated process in a large temperature interval (for instance 25 K) was developed for the examples of diluted complexes. Accordingly, the dynamic choice which was made to establish the first microscopic dynamic model of spin-crossover

solids was Arrhenius-like, rather than widely accepted Glauber choice (Hauser, et. al., 1986; Hauser, 1991; Decurtins, et. al., 1984; Guetlich, , et.al., 1994; Hauser, 1995; Hauser, 1991; Romstedt, et. al., 1998; Desaix, et. al., 1998). This choice was crucial to reproduce the experimental non-linear effects, i.e. sigmoidal relaxation curve in the range 30-60 K.

3. SPIN MODEL

Consider the phenomenon of a bipartite lattice Co-Fe, where one of the sublattices is occupied by Fe ions and the other is occupied by Co ions. The site of the Fe we call sublattice an A-site, and a site of the Co sublattice as B-site. The HT state consists mainly of Fe(III) and Co(II) ions. The LT state consists mainly of Fe(II) and Co(III) ions. Here, we consider the degeneracy of the spin degree of freedom. At an A-site, Fe(II) in the LT state is S = 0, whose degeneracy is 1, and Fe(III) in the HT state is S = 1/2 with a degeneracy of 2. At a B-site, the degeneracy of nB = 0 is 1 and that of nB = 1 is 4 because Co(III) in the LT state is S = 0, and Co(II) in the HT state is S = 3/2 with a degeneracy of 4. Besides the state site spin state n degeneracy spin degeneracy, the system has a degeneracy due to vibrational motions: g_{phonon}(HS) and g_{phonon}(LS). The degeneracy due to phonons is much larger than that of spin. However, in this study, we mainly use spin degeneracy, which is enough to provide the general aspects of the phase structure.

This charge transfer phenomenon is expressed by an electron transfer between Fe and Co atoms. To express this transfer, we introduce the quantity n, which is 1 for Fe in the LT state (i.e., nA = 1) and 0 in the HT state (nA = 0). Correspondingly, it is 0 for Co in the LT state (nB = 0) and 1 in the HT state (nB = 1). Here, i(j) denotes A-(B-)sites. In this system, electrons are transferred between A and B sites. Here, D (> 0) is the difference in on-site energy between A- and B-sites, and J represents the magnetic interaction between A- and B-sites, and s denotes the spin. The external magnetic field is given by h. Since an Fe and Co pair has an electron of the total number of Co and Fe ions of the lattice. The magnetic states of the spins is introduced by s_A and s_B. When n_A = 1, S = 0 and thus s_A takes only 0, and when n_A = 0, S = 1/2 and thus s_A takes - 1/2 or 1/2. Similarly, when n_B = 0, S = 0 and s_B takes 0, and when n_B = 1, S = 3/2 and s_B takes - 3/2,- 1/2, 1/2 or 1/2. Specifying s_A and s_B, the degeneracy is taken into account naturally. In this model, electrons tend to stay at A-sites energetically, which denotes the LT state. When all the electrons are at A-sites, there is no energy cost due to D. We define this state as the perfect LT state. At high temperature, electrons tend to stay at B-sites owing to the difference in degeneracy mentioned above, which corresponds to the HT state.

4. PHASE TRANSITION IN MEAN FIELD THEORY

First, we study the properties of the system without magnetic interaction. The temperature dependences of the HT fraction (n(T)) obtained for the different values, the transition between HT and LT states is gradual and continuous.

For the higher value the transition becomes discontinuous and it shows a first-order phase transition. In this case, the transition temperature is 0.48 and the system has three solutions at Tc. Until the critical value, the transition is continuous. Energy profiles are depicted for various temperatures, where the metastable structure is at low temperature. The solutions with the largest and smallest HT fractions are stable states, whereas that with the intermediate HT fraction represents an unstable state. For large values, the local minimum of the HT state exists at all temperatures. The system possesses a HT metastable branch at low temperature in the case without the magnetic interaction (J = 0) as the temperature dependences of n are depicted with the parameters J = 0, 0.02, 0.04, and 0.06,. As the magnetic interaction is included, we find that the metastable branch is enlarged. In the case of J = 0.02, the HT fraction of the metastable HT state is increased. The HT fraction of the unstable solution is also affected.

The solution of J = 0 is not changed unless the magnetization has nonzero solution in the MF treatment.

The metastable solution and the unstable solution terminate at different temperatures T = 0.41 and T = 0.39, respectively, and are not connected to each other. This is due to the fact that the present model has three order parameters, i.e., (n, sA, sB). At T = 0.35, there are three solutions that are shown by closed circles for local minimum points and an open circle for a saddle point. When T is increased up to T = 0.4, the saddle point disappears, where two stable solutions correspond to points on the green solid line and black solid line denoting the LT state. At T = 0.42, the metastable point disappear and only one stable point remains, which gives a point on the black line. For large values of J, HT remains locally stable until T = 0, for J = 0.06.

Here, we point out a unique dependence of the stability of the ferrimagnetic state on J. If J < Jc = D/18, the ferrimagnetic state is metastable and not an equilibrium state at low temperatures. Here, Jc is obtained by the comparison of the energy of the complete ferrimagnetic state and the LT state.

Let us study the case where both thermal hysteresis and the HT metastable exist at low temperature. Consider the effect of the applied magnetic field h. The magnetic field dependence of magnetization at T = 0.1 is presented for various values of J (J = 0.02, 0.03, and 0.05). In the case of J = 0.02, the LT state is a stable state in the absence of a magnetic field. For a weak field, the system is always in the LT phase. The magnetization is suddenly induced up to nearly the saturated value at h = 0.338. The magnetization value of 2 indicates the ferromagnetic state of Fe (S = 1/2) and Co (S = 3/2) ions in the HT state. In the case of J = 0.04, a stable state in the absence of a magnetic field is still the LT state. The magnetization of 1 indicates an antiferromagnetic coupling between Fe and Co ions in the HT state, indicating that the plateau at the magnetization of 1 is the region of the ferrimagnetic state due to the antiferromagnetic interaction J. For the case of J = 0.06, the ground state is ferromagnetic even at h = 0. The magnetization is induced up to 2 in a strong magnetic field. These results indicate that the applied magnetic field can induce transitions between the three states: the LT state, the antiferromagnetic coupling HT state, and the ferromagnetic coupling HT state.

For temperature dependence of magnetization, in the case of T = 0.4, the system is in the LT state in a small field and the magnetization gradually increases until h = 0.175. Then the magnetization jumps to 0.87, and then gradually increases up to 2. The metastable state exists, indicating that the hysteresis loop can be observed. In the case of T = 0.47, the system is in the LT state in a small field and the magnetization increases up to 2 with a jump at h = 0.085.

5. MONTE CARLO CALCULATION

In this section, we study the model by Monte Carlo simulation and confirm the results obtained in the previous section. Then we study dynamical properties and the metastability of the model.

The system size is 16×16×16, which is large enough to study thermal properties. At each step, we performed 7000 MCSs for transient steps and 10000 MCSs to measure the physical quantities. We heat the temperature up to T = 1 and then cool it down to the original temperature. The changes in n(T) and m(T) starting from the initial states of n = 1 and m = 1, respectively, which correspond to the photoinduced HT saturated state at very low temperature. In the case of J = 0, we found a smooth n(T) in Monte Carlo simulation, we find that the HT phase exists down to T = 0 as a metastable state that causes the first-order phase transition at some temperature. This fact indicates that in MC, different types of n(T) appear for the same set of parameters, which is naturally expected. Nevertheless, in MC, we find a similar trend of n(T).

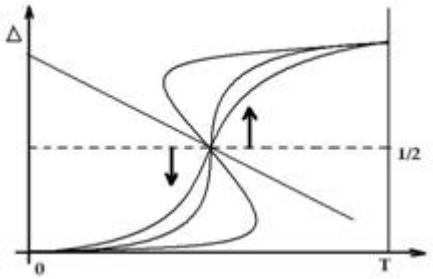

Figure 1. First order transition as J increase

Because we sweep the temperature, the result depends on sweeping rate. However, we find that the position of the transition from metastable HT to stable LT changes little with sweeping rate, which suggests that the state is stable or metastable and is rather well defined by the system parameters. We find n(T) at high temperature, where the state is paramagnetic, is also caused by J. When J = 0.025, n(T) changes from that for J = 0, although the system is paramagnetic in both cases. If we increase J further, the system shows a first order phase transition as in Figure 1.

We study the relaxation processes from the metastable HT to LT states by MC simulation. The structure of the metastable state e.g., the local minimum of this metastable HT state exists at low temperature. In the field of photoinduced phase transition, the existence or nonexistence of the metastable phase is a significant issue because whether the photoinduced HT phase is a metastable phase or a photogenerated thermodynamically unstable phase. We adopt here the initial state of n near 1 where the positions of HT sites are chosen randomly. Such a state can be produced by rapid cooling or light irradiation where the HT sites locate uncorrelatedly. We study the system using (D, J, h) = (1, 0.025, 0) at T = 0.1 for different HT fractions. The system size is 64×64×64. When the HT fraction is smaller than 0.9, the relaxation curves show monotonic decreases. In contrast, when n is larger than 0.90, the relaxation curves increase initially. This is a particular phenomenon due to the existence of a local minimum of the HT state. After that, the states relax to the LT state with sigmoidal shapes.

6. DISCUSSION

A model we take into account is the fact that charge transfer occurs between Co and Fe ions that are ordered antiferromagnetically at low temperatures. The spin states and magnetic properties of antiferromagnetic Co-Fe were studied. The effects of magnetic interaction and an external magnetic field on the structure of the metastable states. A systematic change in the temperature dependence on the parameters of the system, was found as in the previous study. The magnetic interaction induces a magnetic order and enhances the ordering of the metastable states. The low-temperature metastable HT branch is enlarged and even connected to the HT branch. The solution of the metastable states disappears discontinuously, which causes a discontinuous transition. The external magnetic field causes a change in a similar sequence to that found for magnetic interaction. The direction of initial relaxation can be upwards or downwards when the metastability exists depending on the initial. The qualitative features of the effect of magnetic interaction obtained using the MF approximation were confirmed by MC simulation, although in the MC method we found that the magnetic interaction has an effect even in the paramagnetic states. Temperature dependence of nsp, similar to that of the unstable solution.

In the present calculation, we take into account details of microscopic structure changes, such as dynamical temperature, spin values in the HT structure, and thus the formalism will be useful to study the combined phenomena of magnetic ordering, spin-crossover and charge transfer in a wide range of materials. Not only those belonging to Fe-Co but also more general materials in which charge transfer and spin-crossover induce phase transitions, the magnetic properties obtained in this study, particularly the trend of the changes in the temperature dependences of n and m on system parameters will be useful for classifying various materials.

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