Ising-like model for the two-step spin-crossover systems: Static properties with magnetic field effects using cluster variation method

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Abstract

We investigate the static properties of a two-sublattice Ising-like Hamiltonian for spin-crossover (SCO) systems [1-4] in the presence of an external magnetic field. Self-consistent equations are obtained using cluster variation method in the lowest approximation [5]. From the solutions of these equations, we present high-spin state fraction vs. temperature and magnetic field variations for various values of the degeneracy ratio between high-spin and low-spin states (*re*). It is shown that two metastable and one unstable (or saddle) branches in the SCO region are displayed in the *re* > 1 case while the metastable states disappear and only one saddle point occurs when *re* =1. However, only stable states are obtained at high temperatures outside the SCO region. The comparison of our results to other theoretical treatments is also given.

Introduction

In recent years, spin-crossover (SCO) materials have become attractive with potential application on many area such as memoris, sensors, switches and imaging systems. For this reason, studies focused on both spin-crossover (SCO) and magnetic order. These materials have become interesting in nature due to the phase transition behaviors that occur between the low-spin (LS) diamagnetic state and the high-spin (HS) paramagnetic state under induced such as temperature, pressure, magnetic field, and light.

We consider the two-equivalent sublattices which are coupled antiferromagnetically.

Both sublattices are in HS state at high temperature and in LS state at low temperature, but at intermediate temperature the sublattices have different state.

Model&Methods

Model Hamiltonian [1]

$$H=-J_1\sum_{\langle i,j\rangle}s_i^A s_j^A-J_1\sum_{\langle i,j\rangle}s_i^B s_j^B-J_2\sum_{\langle i,j\rangle}s_i^A s_j^B+\left(\frac{\Delta}{2}-\frac{k_BT}{2}\ln g\right)\sum_{\langle i,j\rangle}(s_i^A+s_j^B)+H_m\sum_{\langle i,j\rangle}(s_i^A+s_j^B)$$

Spin variable or order parameters:	$s^A, s^B=-1,\ +1$
Nearest-neighbour spins:	$\langle i,j\rangle$
Bilinear interaction (intrasublattice interaction), $J_1>1$ (ferro)) :	J_1
Bilinear interaction (intersublattice interaction), $J_2<1$ (antiferro) :	J_2
Ligand-field energy :	$\Delta=D_c$
External magnetic field :	H_m
Temperature :	T
Boltzmann constant :	k_B
Degeneracy :	g

Cluster Variation Method in the Lowest Approximation [5]

Free energy : $\Phi=\frac{\beta F}{N}=\frac{\beta}{N}(E-TS_E),\quad \beta=1/k_BT$

Internal energy :

$$\frac{E}{N}=-J_1\left(X_1^A-X_2^A\right)\left(X_1^A-X_2^A\right)-J_1\left(X_1^B-X_2^B\right)\left(X_1^B-X_2^B\right)-J_2\left(X_1^A-X_2^A\right)\left(X_1^B-X_2^B\right)+\left(\frac{\Delta}{2}-\frac{k_BT}{2}\ln g\right)\left[\left(X_1^A-X_2^A\right)+\left(X_1^B-X_2^B\right)\right]+H_m\left[\left(X_1^A-X_2^A\right)+\left(X_1^B-X_2^B\right)\right]$$

Entropy : $S_E=-Nk_B\left(\sum_{i=1}^{2}X_i^A\ln(X_i^A)+\sum_{j=1}^{2}X_j^B\ln(X_j^B)\right)$

The total number of lattice points : $N=N^A+N^B$

Internal variables : $X_1^A=+1, X_2^A=-1$; $X_1^B=+1, X_2^B=-1$

Order parameters can be expressed in terms of the internal variables: $s^A=X_1^A-X_2^A$, $s^B=X_1^B-X_2^B$

Equilibrium condition : $\partial\Phi/\partial X_i^A=0,\quad (i=1,2)$; $\partial\Phi/\partial X_j^B=0,\quad (j=1,2)$

The internal variables are found to be: $X_i^A=\frac{e_i^A}{Z^A},\quad X_j^B=\frac{e_j^B}{Z^B}$; $e_i^A=e^{\left(-\frac{\beta}{N}\frac{\partial E}{\partial X_i^A}\right)},\quad e_j^B=e^{\left(-\frac{\beta}{N}\frac{\partial E}{\partial X_j^B}\right)}$

Partition function : $Z^A=\sum_{i=1}^{2}e_i^A,\quad Z^B=\sum_{j=1}^{2}e_j^B$

Self-consistent equations :

$$s^A=\frac{e^{\beta(-2J_1s^A-J_2s^B+f+H_m)}-e^{\beta(2J_1s^A+J_2s^B-f-H_m)}}{e^{\beta(-2J_1s^A-J_2s^B+f+H_m)}+e^{\beta(2J_1s^A+J_2s^B-f-H_m)}}$$

$$s^B=\frac{e^{\beta(-2J_1s^B-J_2s^A+f+H_m)}-e^{\beta(2J_1s^B+J_2s^A-f-H_m)}}{e^{\beta(-2J_1s^B-J_2s^A+f+H_m)}+e^{\beta(2J_1s^B+J_2s^A-f-H_m)}}$$

Boltzmann statistics for two possible value of the fictitious spin is applied [4]:

$$s^A=\frac{-1+\frac{Z_{HS}^A}{Z_{LS}^A}}{1+\frac{Z_{HS}^A}{Z_{LS}^A}},\quad s^B=\frac{-1+\frac{Z_{HS}^B}{Z_{LS}^B}}{1+\frac{Z_{HS}^B}{Z_{LS}^B}}$$

$$Z_{LS}^A=g_{LS}e^{-\beta E_-^A},\quad Z_{HS}^A=g_{HS}e^{-\beta E_+^A}$$
$$Z_{LS}^B=g_{LS}e^{-\beta E_-^B},\quad Z_{HS}^A=g_{HS}e^{-\beta E_+^B}$$

Eigenvalues state:

$$\begin{cases}E_-^A=2J_1s^A+J_2s^B-f-H_m\\E_+^A=-2J_1s^A-J_2s^B+f+H_m\\E_-^B=2J_1s^B+J_2s^A-f-H_m\\E_+^B=-2J_1s^B-J_2s^A+f+H_m\end{cases}$$

$$f=\frac{\Delta}{2}-\frac{kT}{2}\ln g$$

$$s^A=\frac{-1+r_e e^{\left[-\beta\Delta E^A\right]}}{1+r_e e^{\left[-\beta\Delta E^A\right]}}$$

$$s^B=\frac{-1+r_e e^{\left[-\beta\Delta E^B\right]}}{1+r_e e^{\left[-\beta\Delta E^B\right]}}$$

Effective degeneracy ratio : $r_e=\frac{g_{HS}}{g_{LS}}$

$$\Delta E^A=-4J_1s^A-2J_2s^B+2f+2H_m$$

$$\Delta E^B=-4J_1s^B-2J_2s^A+2f+2H_m$$

Fraction of n_{HS} molecules : $n_{HS}=\frac{m_F+1}{2}$

$$m_F=\frac{s^A+s^B}{2}$$

Results & Discussion

High-spin state fraction vs. temperature and magnetic field variations

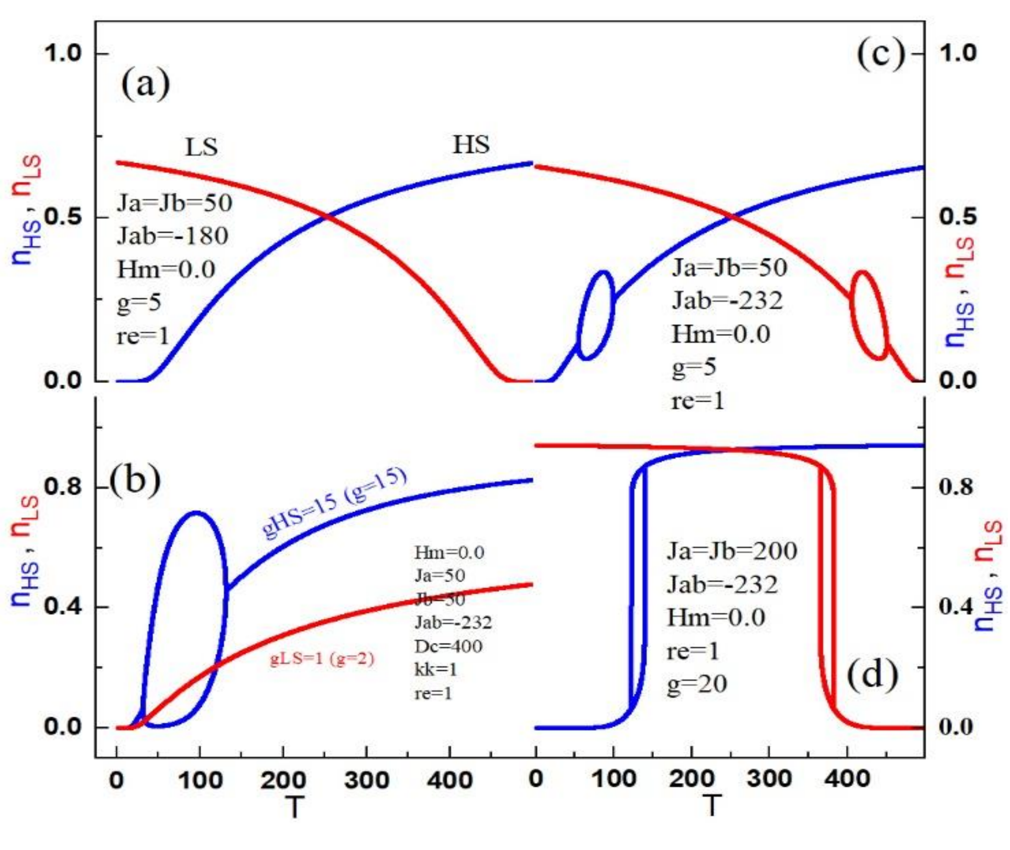

Fig. 1 Comparison of the n_{HS} and n_{LS} by temperature, (a) and (c) for different $J_{ab}=J_2$ (intersublattice interaction) value. (b) and (d) for different $J_a=J_1$, $J_b=J_1$ and g value. For all degeneracy figures ration between HS and LS is $r_e=1$.

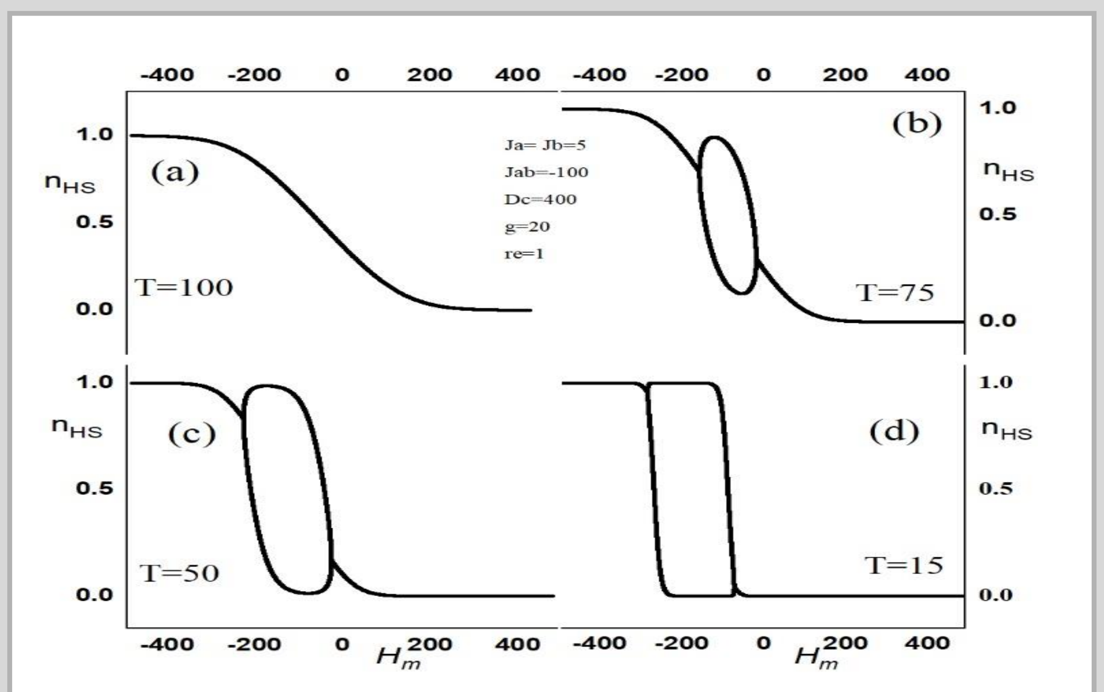

Fig. 2. Magnetic field evolution of the n_{HS} for different temperature T value. The degeneracy ration between HS and LS is $r_e=1$.

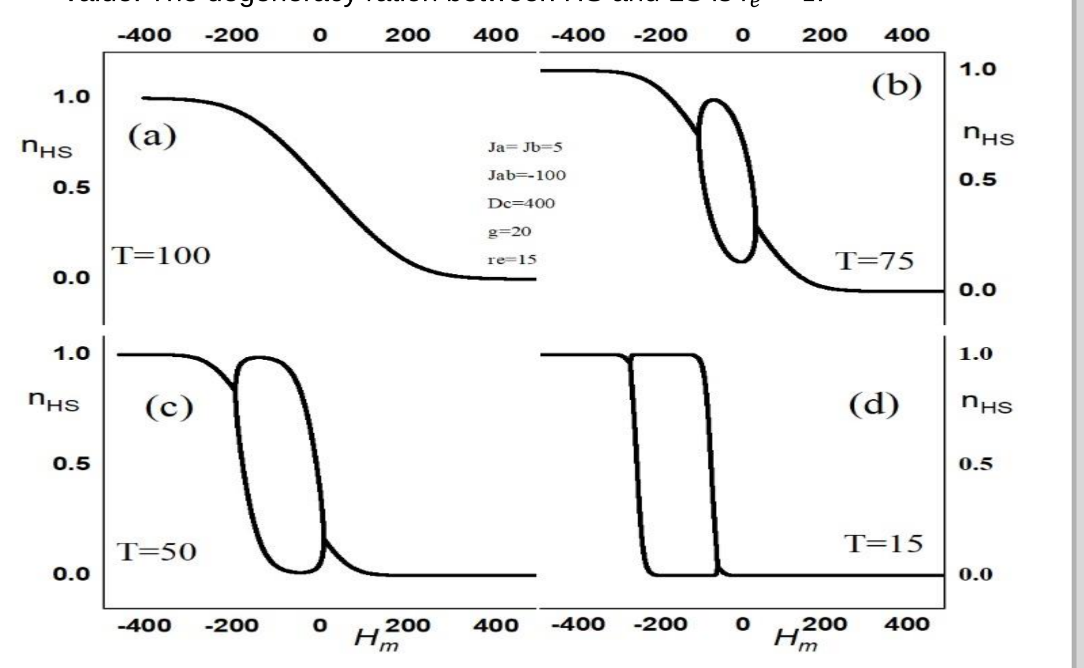

Fig. 3. Magnetic field evolution of the n_{HS} for different temperature T value. The degeneracy ration between HS and LS is $r_e=15$.

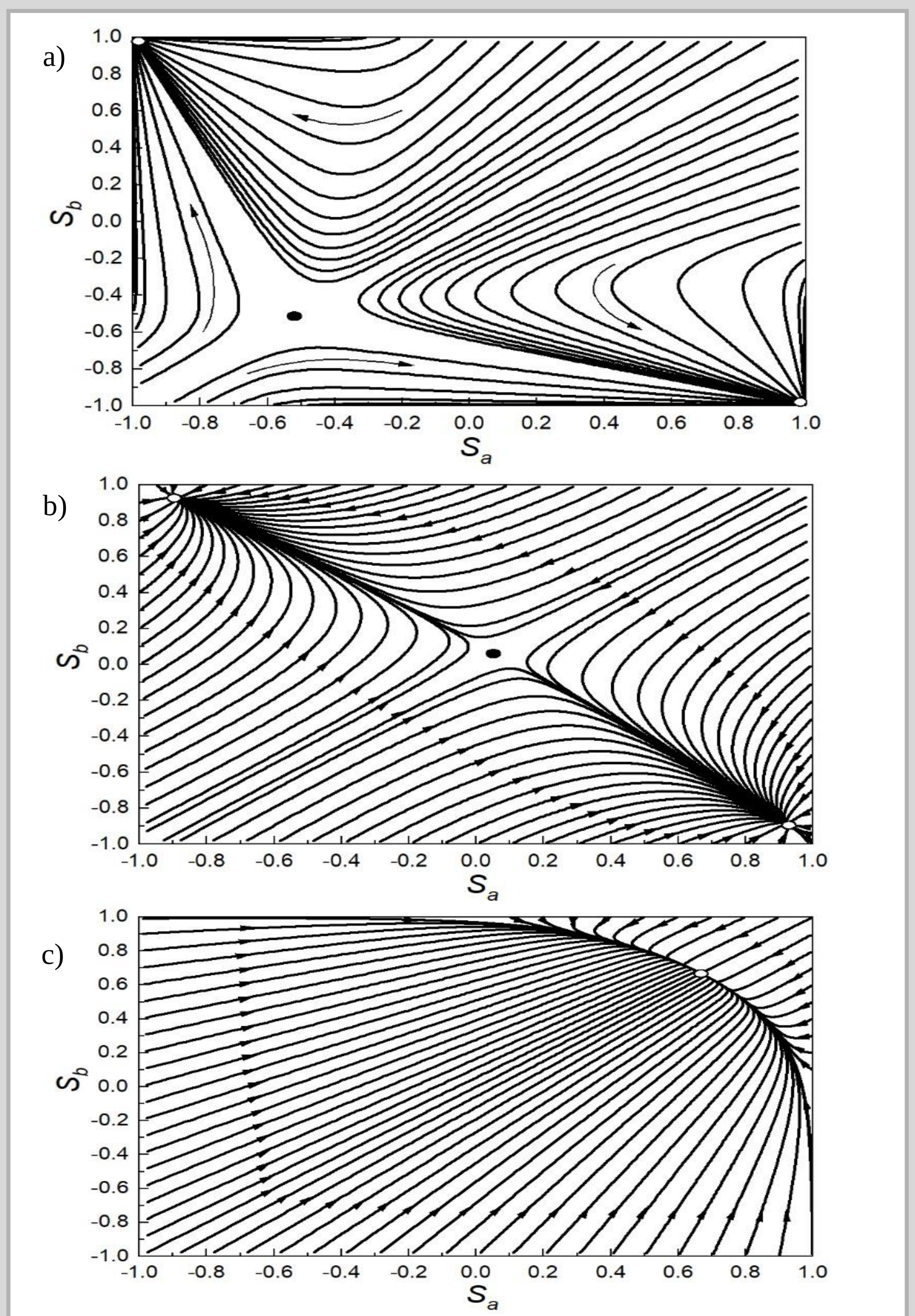

Fig. 4a. The flow diagram of S_a and S_b, and temperature $T=58K$. The open circle corresponds to the stable state and filled circle corresponds to the unstable state.

Fig. 4b. The flow diagram of S_a and S_b, and temperature $T=300K$. The open circle corresponds to the stable state and filled circle corresponds to the unstable state.

Fig. 4c. The flow diagram of S_a and S_b, the open circle corresponds to the stable state and temperature $T=300K$ for the degeneracy ratio $re=15$.

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