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RESEARCH ARTICLE

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Monte Carlo simulations on magnetic behavior of a spin-chain system in triangular lattice doped with antiferromagnetic bonds

Abstract A three-dimensional Ising-like model doped with anti-ferromagnetic (AFM) bonds is proposed to investigate the magnetic properties of a doped triangular spin-chain system by using a Monte-Carlo simulation. The simulated results indicate that a steplike magnetization behavior is very sensitive to the concentration of AFM bonds. A low concentration of AFM bonds can suppress the stepwise behavior considerably, in accordance with doping experiments on $Ca_3Co_2O_6$. The analysis of spin snapshots demonstrates that the AFM bond doping not only breaks the ferromagnetic ordered linear spin chains along the hexagonal *c*-axis but also has a great influence upon the spin configuration in the *ab*-plane.

Keywords $Ca_3Co_2O_6$ compound, spin-chain, step-like magnetization

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1 Introduction

Many compounds with the general formula A'_3ABO_6 (A′ is Ca or Sr, while A and B are transition metal elements) have been synthesized and studied due to their quasi-one-dimensional structures and complex magnetic properties [1−5]. Among these, $Ca_3Co_2O_6$, as the only compound in which both A and B sites are occupied by the same metallic element, has attracted a lot of interest [6−11]. It is composed of parallel one-dimensional (1D) Co_2O_6 chains aligned along the hexagonal *c*-axis, separated by Ca^{2+} ions [7]. Each chain is surrounded by six equally spaced chains, forming a two-dimensional (2D) triangular (hexagonal) lattice in the *ab*-plane. Generally, the interchain distance is about double of the intrachain Co-Co distance, which ensures that the intrachain ferromagnetic (FM) interaction is much stronger than the interchain antiferromagnetic (AFM) one [6]. For this compound one of the most attractive features is the steplike magnetization (M) plotted against the magnetic field (h) applied along the chains [8, 9, 11]. As 10 K$<T<$25 K, with decreasing T the M-h relation gradually exhibits a $M_0/3$ plateau below $h \sim h_c \approx 3.6$ T, above which M jumps up to the saturated value M_0. When $T<10$ K, the $M_0/3$ plateau decomposes into three nonzero and equidistant substeps separated at $h_{S1} \approx 1.2$ T and $h_{S2} \approx 2.4$ T below $h_c \approx 3.6$ T.

In the field of experimental investigations, doping and substitution are effective methods to tune the interactions in the materials. Many experiments show that the physical properties of $Ca_3Co_2O_6$ can be modified by a suitable substitution at both the Ca [2,12] and Co sites [1,3,4]. Generally, introducing foreign elements to the Co site has more direct influence on the 1D Co_2O_6 chains, and consequently smoothens the magnetization steps [1,3,4]. In the work of Flahaut *et al*. [1], the experimental results indicates that the Cr^{3+} magnetic moments are antiferromagnetically coupled to their Co^{3+} neighbors, and the magnetization jumps, observed at low temperature, tend to be suppressed as the Cr^{3+} content increases. Recently, Jain *et al*. reported that the iron substitution reduces the one-dimensional characteristic of Ising spin chains because the iron doping breaks the ferromagnetically ordered linear spin chains along the hexagonal *c*-axis and produced an AFM exchange interaction between the Fe^{3+} ions [5]. Many experiments suggest that doping or substitution will introduce an AFM interaction in the spin chains, and accordingly take great effect on the magnetic properties of the materials. In this paper, based on the previous simulative investigation on triangular spin-chain sys-

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tem [13, 14], we perform a simulation on the 3D Ising model doped with the AFM bonds along the *c*-axis in a triangle lattice in order to comprehend further the effect of the doping on the magnetic behavior of the $Ca_3Co_2O_6$ compound.

2 Model and simulations

For $Ca_3Co_2O_6$ the strong Ising-like anisotropy of the spin interaction has been repeatedly confirmed both experimentally [9,10,15] and theoretically [16], which ensures that Ising models can be employed to describe the magnetic behavior of this compound [13, 14, 17]. Considering the 3D anisotropic spatial arrangement and ignoring the phase difference between the neighboring chains in $Ca_3Co_2O_6$, we may assume that the Co^{3+} ions are co-planar and then the lattice structure is composed of triangular 2D lattices stacked along the *c*-axis. The spin-chain is along the *c*-axis and the intrachain interaction is FM-type, namely $J_{\text{intra}} > 0$. The interchain interaction J_{inter} is AFM-type, namely $J_{\text{inter}} < 0$. The system Hamiltonian is then expressed as:

$$H = -\sum_{[m,l]} J^{\text{intra}} S_m S_l - \sum_{[m,n]} J^{\text{inter}} S_m S_n - h\mu_B g \sum_m S_m \quad (1)$$

where h is the magnetic field applied along the direction of up-spin; g is the Lande factor and μ_B is the Bohr magneton; $[m, l]$ denotes the summation over all the nearest-neighboring pairs in the chains; $[m, n]$ means the summation over all the nearest-neighboring pairs in the *ab*-plane; S_m is the moment of a lattice spin. It was revealed that the crystalline electric field splits the energy level of Co^{3+} ions into the high-spin ($S = 2$) and low-spin ($S = 0$) states [9, 16, 18]. Only the ions of high-spin ($S = 2$) contribute to the magnetic properties, so $S_m = \pm 2$ is chosen in the present simulation. In addition, the magnetic inhomogeneity of the interchain interaction is an important ingredient to induce the steplike feature of the magnetization below 10 K [14]. Therefore, a random exchange term $\Delta_{m,n}$ is taken into account in the interchain coupling. Then J^{inter} is replaced by $J^{\text{inter}}_{m,n}$,

$$\Delta_{m,n} = A \cdot R_{m,n} \quad (2)$$

$$J^{\text{inter}}_{m,n} = J^{\text{inter}} + J^{\text{inter}} \Delta_{m,n} \quad (3)$$

where $R_{m,n}$ is the random number in $[-1, 1]$, and parameter A represents the magnitude of random exchange interaction.

Based on the above model, considering the influence of substitution in materials, we randomly substitute a few AFM interactions with the value $-|J^{\text{intra}}|$ for intrachain FM coupling, namely a triangular Ising model doped with AFM bonds along c-axis is employed. The concentration of AFM bonds is denoted by p, which means the amount of intrachain AFM bonds divided by the total of intrachain bonds. The values of the parameters for the simulation are shown in Table 1. The values of J_{intra}, J_{inter} and A are judged from a quantitative comparison between the simulated results and the experimental data [13].

Table 1 System parameters chosen for the simulation.

Parameter	Value	Parameter	Value
μ_B /(J · T^{-1})	9.274×10^{-24}	k_B / (J · K^{-1})	$1.380\ 7 \times 10^{-23}$
g	2	A	0.15
J_{intra} /J	$8.284\ 2 \times 10^{-23}$	J_{inter} /J	$-5.522\ 8 \times 10^{-24}$

The simulation starts from an $L \times L \times L$ ($L = 40$) Ising lattice with periodic boundary conditions. In fact, the relaxation of the spins along the chains is much faster than that for the interchain spin relaxation in the *ab*-plane. Therefore, in our simulation, the mechanism of spin flipping includes flipping of several neighboring spins. The flip probabilities of one spin or several neighboring spins are calculated respectively according to the Metropolis algorithm, based on the change of energy resulting from the spin flips. Then the stochastic flipping of spins is approved based on these flip probabilities [13]. The procedure of simulation is described as follows. At a given T, the simulation starts from h=0 with a random spin configuration. The magnetization is evaluated after reaching equilibrium. Afterwards, h is raised and the simulation is performed on the state obtained before to reach a new equilibrium. This process is repeated until high field.

Figure 1 presents the simulated M as a function of h with p=0. When T is above 25 K, M as a function of h shows the paramagnetic behavior. In the T-range from 25 K to 10 K, the wide $M_0/3$ plateau appears gradually with decreasing T. As T is below 10 K, three substeps emerge at regular intervals of $h_{\text{int}} \approx 1.2$ T below $h_c \approx 3.6$ T, which is illustrated in the insert of Fig.1. These $M(h)$ curves without doping demonstrate the typical steplike magnetic behavior, in agreement with the experimental results of $Ca_3Co_2O_6$ [8, 9, 11]. The doping of the AFM bonds will influence these magnetic behaviors considerably.

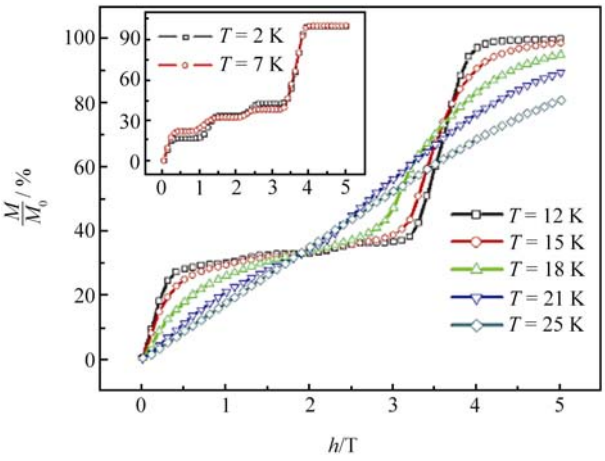

Fig. 1 M/M_0 as functions of h with $p = 0$ at different T. The insert gives M (h) curve at $T = 2$ K and 7 K.

The simulated M (h) curves with different p at T=12 K and 2 K are presented in Fig. 2 (a) and (b) respectively. It is demonstrated that only a low concentration of the AFM bonds doping in spin chains have great influence on the

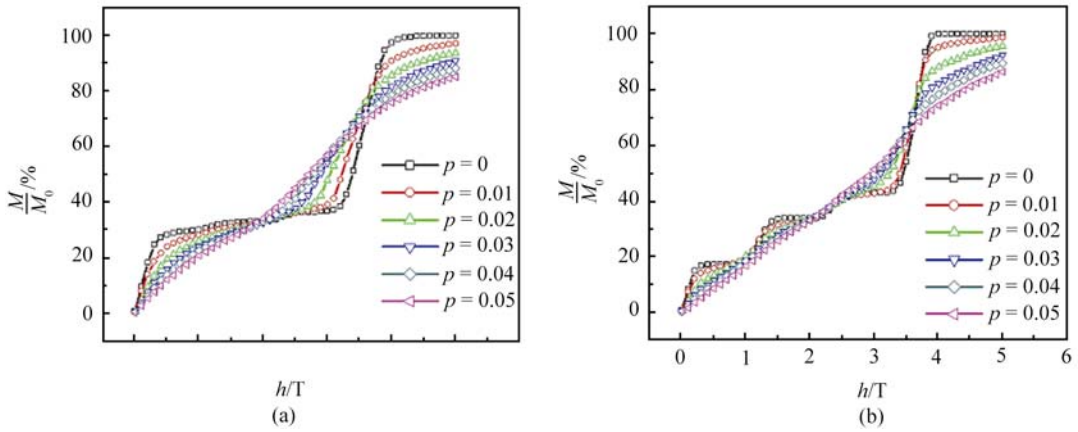

Fig. 2 M/M_0 as functions of h for different p at **(a)** 12 K and **(b)** 2 K.

magnetic behavior of this system at low temperature. At about 12 K, the $1/3M_0$ plateau smear out gradually as p increases and a gradual growth of M with increasing h is established when p is about 0.05. The magnetic field values, necessary to induce the ferrito-ferromagnetic transition, decrease as p increases. When T = 2 K, the increasing value of p also seems to melt the three substeps. Finally for the sample with p = 0.05, no steps can be observed. It is consistent with the experiments, indicating that the AFM coupling introduced by doping or substitution really smoothens the magnetization steps.

The effect resulting from the AFM doping can be studied by spin configuration. Since the AFM couplings are doped into the intrachain interactions, they will affect the intrachain FM ordering directly. The sectional snapshots along the c-axis at h = 0 are demonstrated in Fig. 3, where the snapshots in the left column are for T=2 K and those at T=12 K are correspondingly illustrated in the right column, with p = 0, 0.02, 0.04 from the top down. The black and grey-white solid squares represent spin-up and spin-down respectively, and the spin up along the direction of h. It is observed that at p = 0, all the spins in one chain align in the same direction at T = 2 K [Fig. 3 (a)], and for most of chains all spins aligned in the same direction at T=12 K [Fig.3 (b)]. When p = 0.02 the snapshots in Fig. 3 (c) and (d) show that the spins in some chains do not maintain the same orientation, which indicates that the doping of the AFM coupling break the FM ordering in some chains. As p=0.04 [Fig.3 (e), (f)], the spins of many chains have different spin orientations, namely the long-range intrachain FM ordering is destroyed, and consequently the one-dimensional character of Ising spin chains is suppressed partially.

Though the doping of the AFM bonds is along the c-axis, they also have a great effect on the spin configurations in the ab-plane. Figure 4 shows the sectional spin snapshots in the ab-plane with different p at T = 12 K, as h = 1.8 T on the 1/3 M_0 plateau of magnetization, where the black and grey-white solid circles represent spin-up and spin-down respectively. When p = 0, shown in Fig. 4 (a) the spin configuration in the

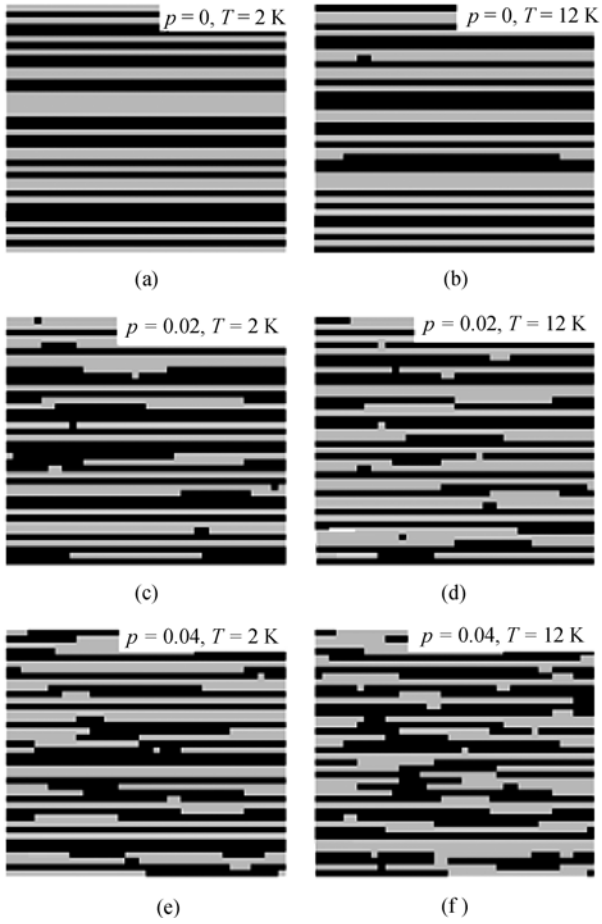

Fig. 3 Sectional snapshots along c-axis at **(a)**, **(c)**, **(e)** 2 K and **(b)**, **(d)**, **(*f*)** 12 K without external magnetic field for different p (from the top down, p = 0, 0.02, and 0.04).

ab-plane is mostly homogeneous, showing a regular ferrimagnetic structure, namely one of the three spin chains takes spin down, while the other two take spin up, leading to M~ $M_0/3$. With doping of the AFM interaction, when p = 0.02 in Fig.4 (b), some small disordered paramagnetic areas appear. When p = 0.04 [Fig.4 (c)], more regions in the spin configu-

ration show disordered paramagnetic feature. Therefore it is indicated that the AFM coupling doping results in the appearance of disordered regions in the *ab*-plane.

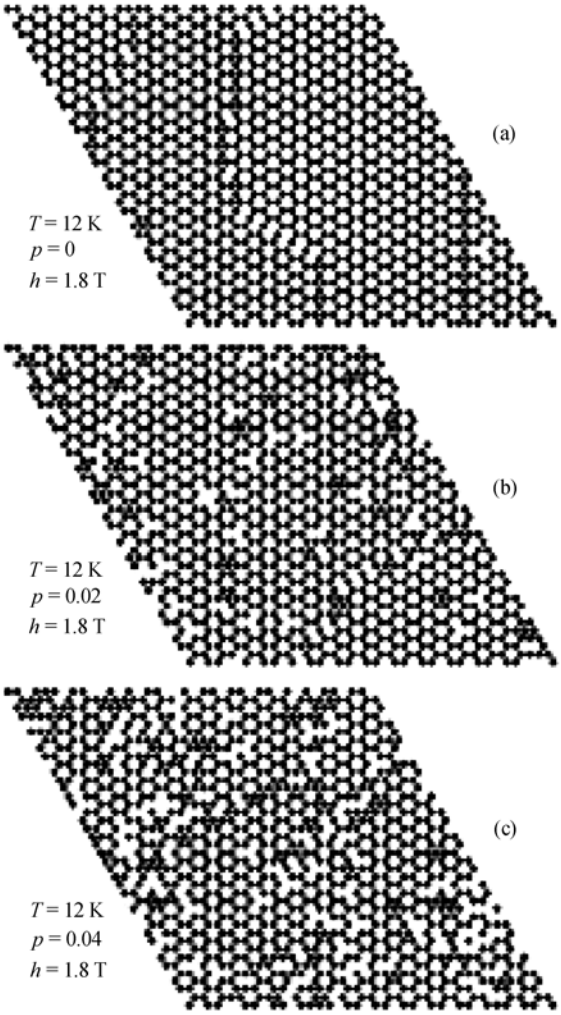

Fig. 4 Sectional snapshots in the *ab*-plane at T =12 K with h=1.8 T for different p (from the top down, p = 0, 0.02, and 0.04).

3 Conclusions

In summary, the magnetic properties of a doped spin-chain system in a triangular lattice are investigated by Monte Carlo simulation in an Ising-like model with the AFM bonds doped. The results show that the low concentration of AFM bonds can modify the magnetic properties of the system, namely the stepwise magnetic behavior is suppressed by the doping considerably, consisting with experimental observations on the doped $Ca_3Co_2O_6$. Through the investigation of the spin snapshots, it is demonstrated that the doping of AFM bonds breaks the FM ordering along the spin chains and introduces disordered regions in the spin configuration of the *ab*-plane.

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