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Monte Carlo simulation of Prussian blue analogs described by Heisenberg ternary alloy model

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ABSTRACT

Within the framework of Monte Carlo simulation technique, we simulate magnetic behavior of Prussian blue analogs based on Heisenberg ternary alloy model. We present phase diagrams in various parameter spaces, and we compare some of our results with those based on Ising counterparts. We clarify the variations of transition temperature and compensation phenomenon with mixing ratio of magnetic ions, exchange interactions, and exchange anisotropy in the present ferro-ferrimagnetic Heisenberg system. According to our results, thermal variation of the total magnetization curves may exhibit N, L, P, Q, R type behaviors based on the Néel classification scheme.

1. Introduction

Prussian blue analogs constitute an important class of molecular based magnets, and due to their potential in technological applications, investigation of their magnetic properties has attracted a considerable amount of interest. These magnetic structures can be regarded as a composition of three different spin sources originating from the presence of metallic ions in the form AB_pC_{1-p}. One of the most amazing properties of these materials is the observation of a photo-induced magnetization. For instance, cobalt–iron cyanide based Prussian blue analog $K_{0.2}Co_{1.4}[Fe(CN)_6{\cdot}6.9H_2O]$ exhibits an enhanced coercivity and critical temperature as a result of red light illumination [1]. Moreover, magnetization of this material can be decreased upon applying blue light, and the process could be repeated reversibly. Similarly, along with the observation of the same phenomenon for a $(Fe_xMn_{1-x})_{1.5}Cr(CN)_6$ system, it has also been reported that this material may exhibit a magnetic pole inversion (i.e. compensation behavior) by optical stimuli [2]. Furthermore, electro-deposited cyanide-based paramagnetic thin films order magnetically at 26 K upon illumination of visible light [3]. Besides, the saturation magnetization, critical temperature, coercivity, and even the color of them can be manipulated and controlled by changing the composition of the metal ions [4–6]. In addition, subsequent experiments showed that hexacyanochromate Prussian blue analogs exhibit large magnetocaloric effect near the ordering temperature [7].

Another remarkable property of these magnets (which also makes them potential candidates as magnetic recording media) is the observation of compensation behavior which is a direct consequence of different thermal dependencies of sub-lattice magnetizations. For instance, Ohkoshi and co-workers [8] showed that the Prussian blue $(Ni^{II}_{0.22}Mn^{II}_{0.6}Fe^{II}_{0.18})_{1.5}[Cr^{III}(CN)_6.7.6H_2O]$ exhibits magnetization reversals (compensation temperatures) at 35 and 53 K. Cador et al. [9] experimentally observed a multiple magnetic pole reversal behavior (two compensation points) in molecule based ferrimagnet containing three spin sources: $rad_2Ni_2Cu_3$ where organic radical rad_2 is the third spin source. Tang et al. [10] reported that the molecular based ferrimagnet $[N(n-C_4H_9)_4][FeFe(C_2O_4)_3]_n$ exhibits two compensation points observed between 5 K and room temperature, and found that coercivity is maximized at the compensation point T_{comp}.

From the theoretical point of view, these systems have been modeled as ternary metal compounds in the form AB_pC_{1-p}, and a variety of approximation schemes has been utilized including Bethe approximation (BA) [11], effective field theory (EFT) [12–14], Green function formalism (GFF) [15], mean field approximation (MFA) [16–23], and Monte Carlo (MC) simulations [24–33]. Except Ref. [15], these works are based on Ising type Hamiltonians, and due to the experimental facts [33], the pseudo spin variables were often proposed as $S_A = (\pm\frac{3}{2}, \pm\frac{1}{2})$, $S_B = (\pm 1, 0)$, and $S_C = (\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2})$ [11,16,18,21,25,31,33] which mimics the ternary molecular magnet $(Ni^{II}_pMn^{II}_{1-p})_{1.5}[Cr^{III}(CN)_6{\cdot}zH_2O]$. On the

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other hand, in Ref. [15] a model based on three-sub-lattice mixed-spin Heisenberg system has been introduced, but only magnetization profiles and hysteresis loops were investigated. Indeed, as far as we know, ferrimagnetic systems based on Heisenberg model have been rarely studied [34]. In this regard, a proper investigation of detailed phase diagrams of Heisenberg ternary alloy model in several planes deserves particular attention, and this fact inspired us for the present work.

2. Formulation

In order to simulate a ternary alloy which simultaneously comprises ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions, it is necessary and sufficient to consider the exchange interactions between the nearest neighbor ions, and contributions from the second nearest neighbor sites can be neglected [6]. Depending on the orbital symmetries of the neighboring ions, exchange interactions can be either ferromagnetic or antiferromagnetic [35]. Based on these facts, the Hamiltonian describing a ferro-ferrimagnetic Heisenberg ternary alloy can be written as

$$\mathcal{H} = -\sum_{\langle ij\rangle} J_{AB}\zeta_i\zeta_j \mathbf{S}_i^A.\mathbf{S}_j^B - \sum_{\langle ij\rangle} J_{AC}\zeta_i\zeta_j \mathbf{S}_i^A.\mathbf{S}_j^C, \tag{1}$$

where $\mathbf{S}_i^A, \mathbf{S}_j^B, \mathbf{S}_j^C$ are the classical spin vectors with magnitudes $|\mathbf{S}_i^A| = 3/2$, $|\mathbf{S}_j^B| = 1$, $|\mathbf{S}_j^C| = 5/2$ (see Fig. 1). ζ_i and ζ_j are the site occupancy parameters which can take values zero or unity. If $\zeta_i = 1$ or $\zeta_i = 0$ then the lattice site i is either occupied by a magnetic ion A or nonmagnetic vacant site, respectively. If $\zeta_j = 1$ then the lattice site j is occupied by an ion B and it is the nearest neighbor of ion A at the site i. The interaction between ions A and B is of ferromagnetic type ($J_{AB} > 0$). Similarly, if $\zeta_j = 0$ then an ion C is placed on the lattice site j. In this case, ions A and C interact antiferromagnetically with each other ($J_{AC} < 0$). Spin vectors are placed on the nodes of a $L \times L \times L$ simple cubic lattice, and each ion A can interact with an ion X (X=B or C). For simplicity, we study on the systems with 1:1 lattice stoichiometry which means that there are no vacant sites on the sub-lattice A ($p_A = 1.0$) [25]. Concentrations of ions B and C are then given by p and $(1 - p)$, respectively with $0 \le p \le 1$. Hence, p is called the compositional factor. p=0 and p=1 special cases correspond to binary mixed ferrimagnetic and ferromagnetic structures, respectively.

We simulate systems with linear lattice dimension L=20 (we found more or less the same results for $L > 20$; see Appendix) using Metropolis Monte Carlo method with Marsaglia pseudo-random number sampling method [36], and apply periodic boundary conditions in all directions. At each Monte Carlo step, lattice sites have been sequentially swept. Data were collected over 10^5 Monte Carlo steps after discarding the first 25% for thermalization [37]. In order to reduce the statistical errors, 10 independent runs were also performed at each temperature.

Our program is capable of calculating the magnetic properties as follows: the components of instantaneous sublattice magnetizations are given by

$$\mu_A^\alpha = \frac{1}{N_A}\sum_{i=1}^{N_A} S_A^\alpha, \quad \mu_B^\alpha = \frac{1}{N_B}\sum_{j=1}^{N_B} S_B^\alpha, \quad \mu_C^\alpha = \frac{1}{N_C}\sum_{k=1}^{N_C} S_C^\alpha, \quad \alpha = x, y, z. \tag{2}$$

where $N_A = p_A L^3/2$, $N_B = pL^3/2$, and $N_C = (1 - p)L^3/2$. From Eq. (2), we can obtain the magnitudes of instantaneous sub-lattice magnetizations as

$$m_{A,B} = \sqrt{\sum_{\alpha=x,y,z} (\mu_{A,B}^\alpha)^2}, \quad m_C = -\sqrt{\sum_{\alpha=x,y,z} (\mu_C^\alpha)^2}. \tag{3}$$

With the help of Eq. (3), thermal and configurational averages of total and staggered magnetizations are defined by [25]

$$M_T = \langle m_T\rangle = \langle N_A m_A + N_B m_B + N_C m_C\rangle/N, \tag{4}$$

$$M_S = \langle m_S\rangle = \langle |N_A m_A + N_B m_B - N_C m_C|\rangle/N, \tag{5}$$

where $N = N_A + N_B + N_C$. Finally, direct and staggered susceptibilities can be calculated via fluctuation-dissipation theorem

$$\chi_{M_T} = \frac{N}{k_B T}\left(\langle m_T^2\rangle - \langle m_T\rangle^2\right), \tag{6}$$

$$\chi_{M_S} = \frac{N}{k_B T}\left(\langle m_S^2\rangle - \langle m_S\rangle^2\right). \tag{7}$$

The location of the transition temperature has been estimated by examining the thermal variation of staggered susceptibility which exhibits a prominent peak at $T = T_c$. In the calculations, we set $k_B = 1$ for simplicity.

3. Results and discussions

3.1. Isotropic case

In this subsection, we assume that the exchange interactions between adjacent ions are spatially identical as described in Eq. (1). In the limiting cases, ternary alloy model reduces to ferromagnetic binary Heisenberg mixtures with spin vectors $|\mathbf{S}_i^A| = 3/2$ and $|\mathbf{S}_j^B| = 1$ for p=1.0 whereas for p=0.0, we have ferrimagnetic mixed Heisenberg system with $|\mathbf{S}_i^A| = 3/2$ and $|\mathbf{S}_j^C| = 5/2$ sub-lattices. Some results regarding the critical temperatures of corresponding mixed $(\frac{3}{2}, 1)$ and $(\frac{3}{2}, \frac{5}{2})$ Ising systems have been reported in the literature. For instance, MFT and EFT calculations predict

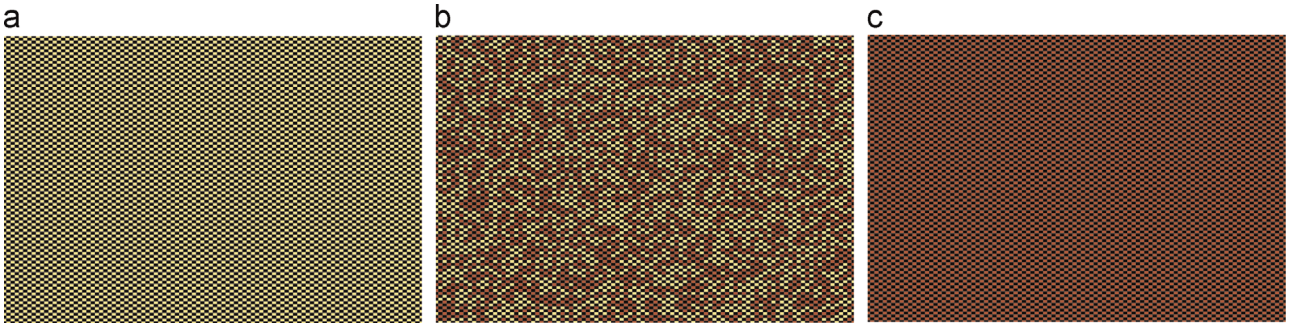

Fig. 1. Schematic representations of Heisenberg ternary alloy model of the chemical formula AB_pC_{1-p}. (a) Binary mixed AC ferrimagnet with p=0.0, (b) ferro-ferrimagnetic ternary alloy with p=0.5, (c) binary mixed AB ferromagnet with p=1.0. Black, red and yellow nodes represent A, B, and C ions, respectively.