Magnetization of mixed ferri-ferrimagnets composed of Prussian blue analogs $A1_xA2_{1-x}B$*

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(Received 21 October 2010; revised manuscript received 27 December 2010)

The magnetization of ternary metal Prussian blue analogues $A1_xA2_{1-x}B$, formed by three different sublattices $A1$, $A2$ and B, is studied by using the effective-field theory with self-spin correlations. Effects of the mole fraction x, the anisotropy and the transverse magnetic field on the magnetization are discussed.

Keywords: magnetization, orthorhombic crystal system, prussian blue analogs

PACS: 75.10.Hk, 75.10.Dg, 75.40.Mg **DOI:** 10.1088/1674-1056/20/5/057501

1. Introduction

It is difficult to have a rational design of conventional metal/intermetallics and metal–oxide magnets based on experimental findings because of the structural distortion engendered by substitutions of metals. Designs of magnets from a theoretical approach have not been very ideal, due to the existence of various types of exchange or superexchange interactions among spins. However, the design of molecular-based magnets within the framework of the molecular field theory is effective for the class of Prussian blue analogs. Molecule-based magnets are of considerable interest because of their characteristic features, such as electrical insulation, low density, transparency, high critical temperature and low fabrication temperature. They present several attributes unavailable in conventional metal alloys and metal–oxide magnets. Ohkoshi *et al.* have made progress in designing and synthesising a class of cyanide-bridged multimetal complexes: $A1_xA2_{1-x}[B(\mathrm{CN})_6]\cdot z\mathrm{H_2O}$ ($A1$, $A2$ and B are metal ions with unpaired electrons).[1,2] They have found an inverted magnetic hysteresis loop in the system of samarium (III) gadolinium (III) hexacyano-chromate (III). The magnetic properties of these complexes, such as saturation magnetization, coercive field, Curie temperature and compensation temperature, are controlled by changing the composition. Bobak *et al.* studied the compensation behaviour and magnetic susceptibility of a mixed ferro-ferrimagnetic ternary alloy of the type $AB(p)\mathrm{C}(1-p)$ on a cubic lattice by the use of Monte Carlo simulations. The relation of the studied model to ternary Prussian blue analogs has also been discussed.[3,4] The effects of single-ion anisotropies on the ferromagnet in an external magnetic field and nonlinear magnetization in a ferromagnetic nanowire and thin film have been studied in detail.[5–9] However, previous theoretical work only dealt with the face-centred cubic (fcc) structure of the Prussian blue analogs.[10,11] There has been no report dealing with the orthorhombic crystal system (such as $(\mathrm{Sm}_x^{\mathrm{III}}\mathrm{Gd}_{1-x}^{\mathrm{III}})[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_6]\cdot 4\mathrm{H_2O}$, abbreviated as $A1_xA2_{1-x}B$) by means of the effective-field theory with self-spin correlations. We shall focus on the magnetic properties of mixed ferri-ferrimagnetic orthorhombic crystal system, which can be described by a three-sublattice Ising system.

This paper is organized as follows. In Section

*Project supported by the Open Project of Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, China (Grant No. LZUMMM2010010), the Scientific Foundation of the Educational Department of Liaoning Province, China (Grant No. L2010390), the Natural Science Foundation of Liaoning Province, China (Grant No. 20102171), the Scientific Technology Plan of Shenyang, China (Grant No. F10-205-1-33), the Excellent Talents Program of the University of Liaoning Province, China (Grant No. LR201031), and the Hong Kong Polytechnic University through the University Research Grant, China (Grant No. A-PA8W).

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2, we derive the formulation within the effective-field theory with self-spin correlations for the Hamiltonian of the three-sublattice Ising model with formula of $A1_xA2_{1-x}B$. In Section 3, we present numerical results and discussions. Then, the conclusions are given in Section 4.

2. Formulation

Consider a magnet composed of three metallic ions, $A1$, $A2$ and B, where the A (either $A1$ or $A2$) and B ions are alternately connected. The magnetic couplings between the A and B ions are ferrimagnetic as shown in Ref. [1]. In Prussian blue analogs, there are only two types of superexchange interactions between the nearest neighbouring metallic ions considered, one for $A1-B$ and the other for $A2-B$. The B and $A1$ (or $A2$) ions, which are randomly distributed in the lattice, are linked in an alternating fashion. The Hamiltonian of the three-sublattice Ising system can be expressed as follows:

$$\begin{aligned} H = & -2J_{A1B}\sum_{i,j}\xi_{iA1}S^z_{iA1}S^z_{jB} \\ & -2J_{A2B}\sum_{i,j}\xi_{iA2}S^z_{iA2}S^z_{jB} \\ & -D_{\rm a}\sum_i\xi_{iA1}(S^z_{iA1})^2 \\ & -\Omega\Bigg[\sum_i\xi_{iA1}(S^x_{iA1}) \\ & +\sum_i\xi_{iA2}(S^x_{iA2})+\sum_j(S^x_{jB})\Bigg] \\ & -h\Bigg[\sum_i\xi_{iA1}(S^z_{iA1}) \\ & +\sum_i\xi_{iA2}(S^z_{iA2})+\sum_j(S^z_{jB})\Bigg], \end{aligned} \tag{1}$$

where J_{A1B} and J_{A2B} are the nearest-neighbouring exchange interactions. For the $(Sm^{III}_xGd^{III}_{1-x})[Cr^{III}(CN)_6]\cdot 4H_2O$ system, J_{A1B} (<0) and J_{A2B} (<0) are for the couplings between Sm–Cr and Gd–Cr, respectively, which are of a ferrimagnetic nature. The summation is made over all the nearest-neighbour pairs. The interactions between magnetic ions $A1$ and $A2$ are neglected, because the contributions from the second nearest (and farther) neighbours are neglected for simplicity. $D_{\rm a}$ is a uniaxial magnetic anisotropy from Sm^{III} ion. Ω and h are the transverse and longitudinal magnetic field, respectively. The spins of magnetic ions $A1$, $A2$ and B are $S_{A1}=5/2$, $S_{A2}=7/2$ and $S_B=3/2$. The Hamiltonian in the present work applied to the transverse field is different from that in Refs. [1] and [10].

Within the framework of effective-field theory with self-spin correlations, the average sublattice magnetizations are given by[11,12]

$$\begin{aligned} M_{A1} &= \langle\xi_{iA1}\langle S^z_{iA1}\rangle_{\rm O}\rangle_{\rm C}=\langle\xi_{iA1}\langle F_{A1}(E_{A1})\rangle_{\rm O}\rangle_{\rm C} \\ &= x\Bigg[\cosh(2J_{A1B}\eta_B\nabla) \\ &\quad +\frac{M_B}{\eta_B}\sinh(2J_{A1B}\eta_B)\Bigg]^{Z_{A1B}}F_{A1}(y)|_{y=0}, \end{aligned} \tag{2}$$

$$\begin{aligned} M_{A2} &= \langle\xi_{iA2}\langle S^z_{iA2}\rangle_{\rm O}\rangle_{\rm C}=\langle\xi_{iA2}\langle F_{A2}(E_{A2})\rangle_{\rm O}\rangle_{\rm C} \\ &= (1-x)\Bigg[\cosh(2J_{A2B}\eta_B\nabla) \\ &\quad +\frac{M_B}{\eta_B}\sinh(2J_{A2B}\eta_B)\Bigg]^{Z_{A2B}}F_{A2}(y)|_{y=0}, \end{aligned} \tag{3}$$

$$\begin{aligned} M_B &= \Big\langle\big\langle S^z_{jB}\big\rangle_{\rm O}\Big\rangle_{\rm C}=\langle\langle F_B(E_B)\rangle_{\rm O}\rangle_{\rm C} \\ &= \Bigg[x\cosh(2J_{BA1}\eta_{A1}\nabla) \\ &\quad +\frac{M_{A1}}{\eta_{A1}}\sinh(2J_{BA1}\eta_{A1})+1-x\Bigg]^{Z_{BA1}} \\ &\quad \times\Bigg[(1-x)\cosh(2J_{BA2}\eta_{A2}\nabla) \\ &\quad +\frac{M_{A2}}{\eta_{A2}}\sinh(2J_{BA2}\eta_{A2})+x\Bigg]^{Z_{BA2}}F_B(y)|_{y=0}, \end{aligned} \tag{4}$$

where M_{A1}, M_{A2} and M_B indicate the sublattice magnetizations per site. $\nabla=\partial/\partial y$ is the differential operator. $\langle\ \rangle_{\rm O}$ and $\langle\ \rangle_{\rm C}$ denote the thermodynamic average of spins and the configurational average, respectively. The effective fields E_{A1}, E_{A2} and E_B acting on the three sublattice sites are given by $E_{A1}=-2J_{A1B}\sum\limits_{i,j}\xi_{iA1}S^z_{jB}$, $E_{A2}=-2J_{A2B}\sum\limits_{i,j}\xi_{iA2}S^z_{jB}$ and $E_B=-2J_{A1B}\sum\limits_{i,j}\xi_{iA1}S^z_{iA1}-2J_{A2B}\sum\limits_{i,j}\xi_{iA2}S^z_{iA2}$; η_k ($k=A1,A2,B$) are obtained by

$$\begin{aligned} \eta_{A1} &= \Big\langle\xi_{iA1}\big\langle(S^z_{iA1})^2\big\rangle_{\rm O}\Big\rangle_{\rm C}=\langle\xi_{iA1}\langle G_{A1}(E_{A1})\rangle_{\rm O}\rangle_{\rm C} \\ &= x\Bigg[\cosh(2J_{A1B}\eta_B\nabla) \\ &\quad +\frac{M_B}{\eta_B}\sinh(2J_{A1B}\eta_B)\Bigg]^{Z_{A1B}}G_{A1}(y)|_{y=0}, \end{aligned} \tag{5}$$

$$\begin{aligned} \eta_{A2} &= \Big\langle\xi_{iA2}\big\langle(S^z_{iA2})^2\big\rangle_{\rm O}\Big\rangle_{\rm C}=\langle\xi_{iA2}\langle G_{A2}(E_{A2})\rangle_{\rm O}\rangle_{\rm C} \\ &= (1-x)\Bigg[\cosh(2J_{A2B}\eta_B\nabla) \\ &\quad +\frac{M_B}{\eta_B}\sinh(2J_{A2B}\eta_B)\Bigg]^{Z_{A2B}}G_{A2}(y)|_{y=0}, \end{aligned} \tag{6}$$

$$\eta_B = \left\langle \langle (S_{jB}^z)^2 \rangle_{\rm O} \right\rangle_{\rm C} = \langle \langle G_B(E_B) \rangle_{\rm O} \rangle_{\rm C}$$
$$= \Big[x \cosh(2J_{BA1}\eta_{A1}\nabla) + \frac{M_{A1}}{\eta_{A1}} \sinh(2J_{BA1}\eta_{A1}) + 1 - x \Big]^{Z_{BA1}} \times \Big[(1-x)\cosh(2J_{BA2}\eta_{A2}\nabla) + \frac{M_{A2}}{\eta_{A2}} \sinh(2J_{BA2}\eta_{A2}) + x \Big]^{Z_{BA2}} G_B(y)|_{y=0}, \quad (7)$$

where Z_{KL} are the numbers of the nearest-neighbour K-site ions surrounding an L-site ion. The functions F_k and $G_k (k = A1, A2, B)$ are defined as

$$F_{A1}(y) = \frac{1}{\sum_{m=1}^{6} \exp(\beta\lambda_m)} \times \left[\sum_{m=1}^{6} \langle \phi_m | S_{iA1}^z | \phi_m \rangle \exp(\beta\lambda_m) \right], \quad (8)$$

$$F_{A2}(y) = \frac{1}{\sum_{n=1}^{8} \exp(\beta\lambda_n)} \times \left[\sum_{n=1}^{8} \langle \phi_n | S_{iA2}^z | \phi_n \rangle \exp(\beta\lambda_n) \right], \quad (9)$$

$$F_B(y) = \frac{1}{\sum_{p=1}^{4} \exp(\beta\lambda_p)} \times \left[\sum_{p=1}^{4} \langle \phi_p | S_{jB}^z | \phi_p \rangle \exp(\beta\lambda_p) \right], \quad (10)$$

$$G_{A1}(y) = \frac{1}{\sum_{m=1}^{6} \exp(\beta\lambda_m)} \times \left[\sum_{m=1}^{6} \langle \phi_m | (S_{iA1}^z)^2 | \phi_m \rangle \exp(\beta\lambda_m) \right], \quad (11)$$

$$G_{A2}(y) = \frac{1}{\sum_{n=1}^{8} \exp(\beta\lambda_n)} \times \left[\sum_{n=1}^{8} \langle \phi_n | (S_{iA2}^z)^2 | \phi_n \rangle \exp(\beta\lambda_n) \right], \quad (12)$$

$$G_B(y) = \frac{1}{\sum_{p=1}^{4} \exp(\beta\lambda_p)} \times \left[\sum_{p=1}^{4} \langle \phi_p | (S_{jB}^z)^2 | \phi_p \rangle \exp(\beta\lambda_p) \right], \quad (13)$$

where $\beta = 1/k_{\rm B}T$, $k_{\rm B}$ is the Boltzmann constant and T is the absolute temperature. Notice that, the eigenvalues λ_i and the eigenfunctions ϕ_i $(i = m, n, p)$ cannot be expressed analytically, but can only be given numerically.

The averaged total magnetization is then obtained by

$$M = m_{A1} + m_{A2} + m_B = g_{A1}M_{A1} + g_{A2}M_{A2} + g_B M_B. \quad (14)$$

3. Numerical results and discussion

Initially, the sublattices $A1(\mathrm{Sm^{III}})$ and $A2(\mathrm{Gd^{III}})$ have positive magnetizations and $B(\mathrm{Cr^{III}})$ has a negative one, because $|M_{A1} + M_{A2}|$ of nitrogen ends is larger than $|M_B|$ of carbon ends for this composition at low temperature. Let $Z_{A1B} = Z_{A2B} = Z_{BA1} = Z_{BA2} = 6$, $J_{A1B} = J_{BA1}$, $J_{A2B} = J_{BA2}$, $J_{A1B} = -0.32$ cm^{-1} and $J_{A2B} = -0.23$ cm^{-1}. Using these values, the magnetization is numerically calculated.

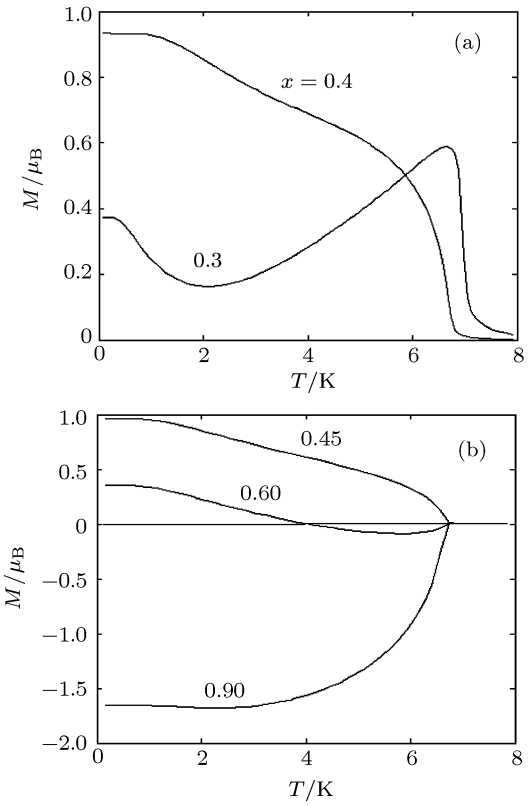


Fig. 1. Temperature dependence of the total magnetizations for (a) $x = 0.3$, 0.4, (b) $x = 0.45$, 0.6, 0.9. The number beside each curve is the value of the $A1$-ion mole fraction x.

In Figs. 1(a)–1(b), the magnetization vs temperature curves exhibit several different behaviours below $T_{\rm c}$, depending on $A1$-ion mole fraction x. For example,

the curves for $x = 0.45$ and 0.9 manifest a monotonically decreasing trend in magnetization with increasing T, while the curve for $x = 0.3$ in Fig. 1(a) exhibits two maxima and that for x =0.6 shows a compensation point in Fig. 1(b). This is observed due to the negative (positive) magnetization of the sublattice B ($A1$ and $A2$) with different temperature dependences. From our calculation, we know that the initial magnetizations (named by M_0) at nearly zero temperature change, depending on the sum of the sublattice magnetizations of Gd^{III} and Sm^{III} and the negative one of Cr^{III}. If the value of x ranges from 0 to 0.43 (or from 0.66 to 1), the value of M_0 increases with increasing x. In contrast, the value of M_0 decreases with increasing x in the range of $0.44 < x < 0.65$.

The effects of uniaxial magnetic anisotropy D_a and transverse field on the magnetization in mixed ferri-ferrimagnets composed of Prussian blue analogs $A1_xA2_{1-x}B$ are also calculated by solving Eqs. (2)–(7) numerically. All kinds of magnetization curves are plotted in Figs. 2 and 3 for several typical parameters. Figure 2(a) shows the thermal variations of M when $D_a = -1.5$, -3.0 and $x = 0.7$, 0.58, 0.4, 0.35. In order to investigate in detail the effect of the uniaxial magnetic anisotropy D_a on the magnetization of the system, we have calculated the thermal variations of M in Fig.2 (b) when the uniaxial magnetic anisotropy D_a and the $A1$-ion mole fraction x are selected as $D_a = -1$, –2, –3, –6, –10, and $x = 0.61$. As shown in the figure, the curve exhibits the compensation points when $D_a = -1.0$. A similar result has been presented in previous studies on the mixed spin ferromagnetic Ising model,[10,11] namely, the magnetization behaves as N-type curve in the Néel classification. According to the Néel theory, five typical curves of the magnetization in the magnetic system are classified as Q-, P-, N-, L- and M-types. However, the curves labeled $D_a = -3$, –6 and –10 manifest two compensation points in Fig. 2(b). This interesting result has not been predicted in the Néel theory, which originates from the competition between the effects of the uniaxial magnetic anisotropy D_a, the $A1$-ion mole fraction x and temperature on the spin configurations. Further investigation shows that two compensation points exist for $x = 0.61$ when $D_a < -1.9$. In Fig. 2, it also reveals that the magnetization curve is changed from L-type to M-type by increasing the absolute value of D_a from –1 to –2. Figure 3 shows typical temperature dependence of the magnetizations with different transverse fields at uniaxial magnetic anisotropy $D_a = -3.0$ and $A1$-ion mole fraction $x = 0.61$. It is also noted that the transverse field induces the decrease of transition temperature. In Fig. 3, the curve exhibits two compensation points at zero or low transverse field $\Omega = 0$, 0.5, and only one compensation point remains with increasing the transverse field to Ω = 1, 1.5. Finally, the compensation point disappears when the transverse field is sufficiently high, as is shown by the curve labeled by '2'.

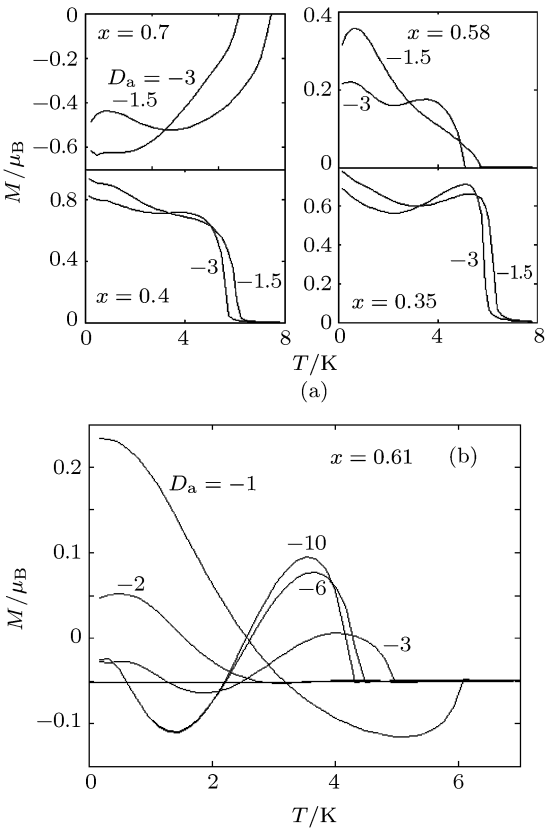


Fig. 2. Temperature dependence of the total magnetizations for (a) $x = 0.35$, 0.4, 0.58, 0.7; (b) $x = 0.61$. The number beside each curve is the value of the uniaxial magnetic anisotropy D_a.

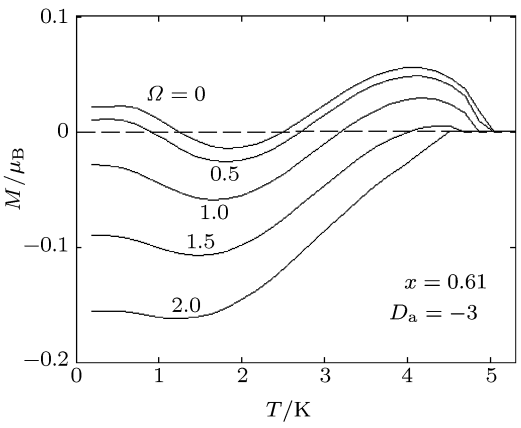


Fig. 3. Temperature dependence of the total magnetizations. The number beside each curve is the value of the transverse magnetic field Ω.

4. Conclusion

We have developed the effective-field theory with self-spin correlations for mixed ferri-ferrimagnets composed of Prussian blue analogs with the formula $A1_xA2_{1-x}B$, where $A1$, $A2$ and B are three different magnetic ions and form three different sublattices. The effects of the uniaxial magnetic anisotropy $D_{\rm a}$ and the transverse magnetic field on the magnetization are investigated in detail. The transverse field frustrates the existence of the compensation point. By increasing the absolute value of $D_{\rm a}$ from –1 to –2, the magnetization curve is changed from the L-type to the M-type. The orthorhombic crystal structure of the Prussian blue analogs maintains even when the rare-earth ions are substituted. Various types of the rare-earth and the conventional metal ions can be incorporated easily as spin centers. This method will be potentially useful for understanding the experimental results of mixed ferri-ferrimagnets rare-earth ions compound of Prussian blue analogs.

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