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2002 J. Phys.: Condens. Matter 14 2001

(http://iopscience.iop.org/0953-8984/14/8/327)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 2001–2009 PII: S0953-8984(02)26463-2

The possibility of two compensation points in a molecular-based ferrimagnetic material

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Received 3 July 2001
Published 15 February 2002
Online at stacks.iop.org/JPhysCM/14/2001

Abstract

A two-dimensional Ising system composed of ferrimagnetically ordered chains coupled weakly and ferromagnetically to each other is discussed by the use of differential operator technique, in order to clarify the possibility of two compensation points in a molecular-based ferrimagnetic magnetic material. For this possibility, we find that each chain must consist of at least three magnetic atoms with spin $\frac{1}{2}$ and integer spins as well as particular negative uniaxial anisotropy values. Two possible cases are proposed.

1. Introduction

A major advance in magnetism has been the discovery of molecular-based magnetic materials. Many bimetallic molecular-based magnetic materials in which two kinds of magnetic atom, A and B, alternate regularly have exhibited ferrimagnetic properties and seem to be rather well interpreted by the use of the mixed-spin (Heisenberg or Ising) model [1, 2]. Most of these ferrimagnetic materials have not exhibited a compensation point at which the sublattice magnetizations cancel out completely. However, some molecular-based compounds [3] whose structures are two-dimensional honeycomb networks have shown the complete cancellation of sublattice magnetizations at a finite temperature and the appearance of a compensation point in the compounds seems to be extremely characteristic, as discussed theoretically in [4, 5]. Furthermore, by mixing two Prussian blue analogues artificially Ohkoshi *et al* [6] have synthesized a new type of molecular-based ferrimagnetic material, whose spontaneous magnetization has for the first time shown the existence of two compensation points experimentally, although theoretically the possibility of two compensation points has been discussed in a variety of ferrimagnetic systems (see [7]).

Among these compounds, a particular interest has been paid to molecular-based ferrimagnetic chains coupled weakly to each other. Many theoretical studies have been directed to these low-dimensional systems and various magnetic properties of these systems have been examined (see [2]). However, it has not been discussed whether a compensation point may

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exist in such a low-dimensional ferrimgnetic system. As has been discussed in [8], on the other hand, the two-dimensional ferromagnetic Ising system composed of ferrimagnetically ordered chains with alternating spin-$\frac{1}{2}$ A and spin-S ($S > \frac{1}{2}$) B atoms may exhibit a compensation point when the anisotropy constant d (or $d = D_B/J$) of the spin-S atom is larger than $d = -1.0$ and the exchange interaction between spin-$\frac{1}{2}$ atomic pairs is strong in comparison with the exchange interaction between spin-$\frac{1}{2}$ and spin-S atomic pairs. As far as we know, however, it has not been clarified theoretically or experimentally whether two compensation points may exist in a low-dimensional molecular-based ferrimagnetic material.

The aim of this report is to propose a two-dimensional ferromagnetic system composed of ferrimagnetically ordered Ising chains coupled weakly, whose total magnetization may exhibit two compensation points at finite temperatures. In section 2, we propose a model system which may exhibit two compensation points and the formulation of the system is given within the framework of the Zernike approximation [9, 10]. In section 3, the numerical results are given for the two model systems.

2. Formulation

In [8], a two-dimensional ferromagnetic Ising system composed of ferrimagnetically ordered chains with alternating spin-$\frac{1}{2}$ and spin-S ($S > \frac{1}{2}$) atoms has been investigated by the use of the differential operator technique [9, 10]. However, the possibility of two compensation points could not be found in the system. For this possibility, therefore, it seems to be necessary for the chainlike system to include at least three magnetic atoms, spin-$\frac{1}{2}$ A atoms, spin-S B atoms and spin-S' ($S' > \frac{1}{2}$) C atoms. The spin structure of such a system is depicted in figure 1. The Hamiltonian of the system is given by

$$\mathcal{H} = J\sum_{(im)}\mu_i^z S_m^z + J_1\sum_{(in)}\mu_i^z S_n^z - J_2\sum_{(i^\delta)}\mu_i^z\mu_{i+\delta}^z - J_3\sum_{(ij)}\mu_i^z\mu_j^z - D_B\sum_m (S_m^z)^2 - D_C\sum_n (S_n^z)^2, \tag{1}$$

where the first four summations run over the nearest-neighbour pairs. μ_i^z is the spin-$\frac{1}{2}$ operator for the A atoms. S_m^z and S_n^z are respectively the spin-S ($S > \frac{1}{2}$) operator for the B atoms and the spin-S' ($S' > \frac{1}{2}$) operator for the C atoms. D_B and D_C are the uniaxial anisotropy constants on B and C atoms. We assume that the inter-chain interaction J_3 is very weak in comparison with the intra-chain interactions J, J_1 and J_2.

The total magnetization of the system is given by

$$(M/nN) = \sigma_A + (m_B + m_C)/2 \tag{2}$$

with

$$\sigma_A = \langle\mu_i^z\rangle, \qquad m_B = \langle S_m^z\rangle, \qquad m_C = \langle S_n^z\rangle, \tag{3}$$

where N is the total number of A atoms in a chain and n is the number of chains. By the use of the differential operator technique [9, 10], as has been discussed in [4, 7, 8], the sublattice magnetizations m_B and m_C are exactly given by

$$m_B = -2\sigma_A F_B(J) \qquad \text{and} \qquad m_C = -2\sigma_A F_C(J_1), \tag{4}$$

where the function $F_n(x)$ (n = B or C) depends on the value of S (or S'). When $S = 1$ or 2, it is defined by

$$F_n(x) = \frac{2\sinh(\beta x)}{2\cosh(\beta x) + \exp(-\beta D_n)} \qquad \text{for } S = 1$$

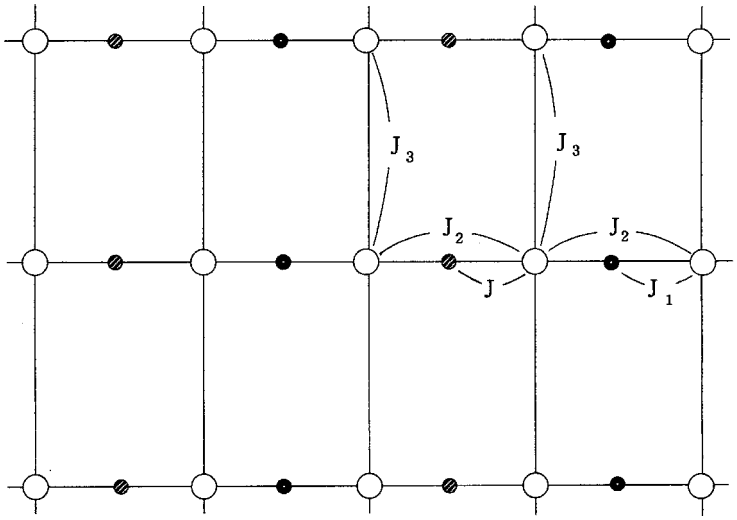

Figure 1. The spatial configuration of the ferrimagnetically ordered chainlike system composed of three magnetic atoms, like a molecular-based magnetic material. The white circles denote A atoms with spin $\frac{1}{2}$, the shaded circles represent spin-S ($S > \frac{1}{2}$) B atoms and the black circles are spin-S' ($S' > \frac{1}{2}$) C atoms.

or (5)

$$F_n(x) = \frac{4\sinh(2\beta x) + 2\exp(-3\beta D_n)\sinh(\beta x)}{2\cosh(2\beta x) + 2\exp(-3\beta D_n)\cosh(\beta x) + \exp(-4\beta D_n)} \qquad \text{for } S = 2,$$

where $\beta = 1/k_B T$. Substituting (4) into (2), the total magnetization can be rewritten as

$$(M/nN) = \sigma_A[1 - \{F_B(J) + F_C(J_1)\}]. \tag{6}$$

There may be a compensation temperature $T\kappa$ at which the total magnetization reduces to zero even though $\sigma_A \neq 0$. The compensation point in the system seems to be exactly given by

$$1 = F_B(J) + F_C(J_1). \tag{7}$$

The problem is now how to evaluate the sublattice magnetization σ_A. For this aim, let us use the decoration–iteration transformation [11], in order to obtain the effective Hamiltonian for the anisotropic two-dimensional system described by

$$H_{\text{eff}} = -\sum_{(i^\delta)} J_\delta^R \mu_i^z \mu_{i+\delta}^z, \tag{8}$$

where J_δ^R can take three values depending on the direction. They are given by

$$\begin{aligned} J_\delta^R &= J_2 + J_{\text{eff}}^B \equiv J_B^R \qquad \text{for the interaction through a B atom,} \\ J_\delta^R &= J_2 + J_{\text{eff}}^C \equiv J_C^R \qquad \text{for the interaction through a C atom} \end{aligned}$$

and (9)

$$J_\delta^R = J_3 \qquad \text{for the interaction perpendicular to a chain.}$$

The two effective interactions J_{eff}^B and J_{eff}^C can be obtained easily by the use of the relation

$$\sum_{S_p^z} \exp[\beta J_{ip}(\mu_i^z + \mu_{i+\delta}^z)S_p^z + \beta D_P (S_p^z)^2] = A\exp[\beta J_{\text{eff}}^P \mu_i^z \mu_{i+\delta}^z], \tag{10}$$

where $J_{ip} = J$ or J_1 and $D_p = D_B$ or D_C, depending on whether p is selected as $p = m$ or $p = n$. The $J_{\rm eff}^P$ depends on the values of S and D_P (see [7, 8]).

Using the effective Hamiltonian and the differential operator technique [9, 10], the sublattice magnetization σ_A is given, within the framework of the Zernike approximation [12], in the form

$$\sigma_A = \left[\frac{1-2L_1}{8L_2}\right]^{1/2} \tag{11}$$

with

$$\begin{aligned} L_1 = (1/4)[&2f((J_B^R + J_C^R)/2 + J_3) + 2f((J_B^R + J_C^R)/2) \\ &+ f((J_B^R - J_C^R)/2 + J_3) - f((J_B^R - J_C^R)/2 - J_3)] \\ L_2 = (1/4)[&2f((J_B^R + J_C^R)/2 + J_3) - 2f((J_B^R + J_C^R)/2) \\ &+ f((J_B^R - J_C^R)/2 - J_3) - f((J_B^R - J_C^R)/2 + J_3)], \end{aligned} \tag{12}$$

where the function $f(x)$ is defined by

$$f(x) = (1/2)\tanh(\beta x/2). \tag{13}$$

The transition temperature T_C is then determined from the relation

$$1 = 2L_1. \tag{14}$$

3. Numerical results

For the following numerical calculations, let us first introduce the parameters defined by

$$a = J_1/J, \qquad b = J_2/J, \qquad c = J_3/J, \qquad d = D_B/J \qquad \text{and} \qquad \alpha = D_C/D_B. \tag{15}$$

We here assume that $c = 0.1$, while the value of c can of course take any value. Furthermore, after performing a number of numerical calculations for the relation (7) we have found that the values of S and S' must be integer numbers, such as the system with $S = 1$ and $S' = 2$, in order to find the possibility of two compensation points. In the following, we present the numerical results of the magnetic properties (phase diagram and magnetization curve) in two typical systems.

3.1. The ferrimagnetic system with $S = 1$ and $S' = 2$

In figure 2, the results of the compensation temperature T_κ obtained by solving (7) numerically for the system with $a = 0.75$, $S = 1$ and $S' = 2$ are plotted in the T–d space as solid curves, when the value of α is changed from $\alpha = 0.1$ to $\alpha = 1.0$. The curves labelled $\alpha = 0.2$ and 0.4 exhibit the reentrant behaviour (double values) in the special negative regions of d. In the figure, the results of the transition temperature T_C obtained by solving (14) numerically are plotted in the T–d space as dashed curves for the same system with the two values of b ($b = 5.0$ and 10.0), when the value of α is changed from $\alpha = 0.1$ to $\alpha = 1.0$. In order to get the physical meaning of a compensation point in the ferromagnetic system, each T_κ (solid) curve in figure 2 must take a value lower than the corresponding T_C (dashed) curve in the figure. Here, one should notice that the T_κ curve is the exact result but the T_C curve is the result of the Zernike approximation.

The results of $\alpha = 0.2$ and 0.4 in figure 2 clearly express that each system may exhibit the two compensation points when the value of d is selected in the reentrant (double-value) region of d. In order to confirm the prediction, the temperature dependences of $|M|$, σ_A, $|m_B|$

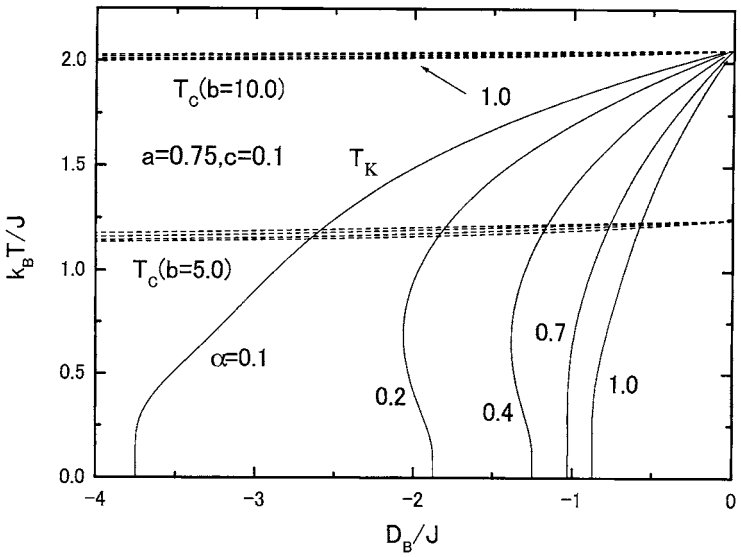

Figure 2. The phase diagram (T_C and T_κ) in the T–d plane of the system with $S = 1$ and $S' = 2$, when two values of b ($b = 5.0$ and 10.0) are selected and the value of α is changed from $\alpha = 0.1$ to $\alpha = 1.0$. T_C (dashed curve) and T_κ (solid curve) represent respectively the transition temperature obtained within the Zernike approximation and the compensation temperature obtained exactly. For the numerical calculations, the parameters a and c are fixed at $a = 0.75$ and $c = 0.1$. The dashed curves represent the five corresponding T_C curves obtained by solving (14) numerically. Within the negative region of d, the lowest value of T_C is obtained for the case of $\alpha = 1.0$, as noted in the figure. On the other hand, for the positive region of d, the lowest value of T_C is obtained for the case of $\alpha = 0.1$.

and $|m_C|$ are plotted in figure 3 for the two systems with $a = 0.75$, $b = 10.0$ and $c = 0.1$; $\alpha = 0.4$, $d = -1.3$ for curve γ and $\alpha = 0.2$, $d = -2.0$ for curve ζ. Each thermal variation of $|M|$ clearly represents the two compensation points below T_C and reduces to zero at $T = 0$ K. Such a thermal variation of $|M|$ originates from those of sublattice magnetizations, as shown in figure 3(b). The sublattice magnetization m_B takes the value of $m_B = 0.0$ (or the spin state $S_m^z = 0.0$) at $T = 0$ K, since in each case the value of d is lower than the critical value $d = -1.0$. With the increase of T, the sublattice magnetization m_B at first increases and then decreases to zero at $T = T_C$. The sublattice magnetization m_C takes the value of $|m_C| = 1.0$ (or the spin state $S_n^z = \pm 1.0$) at $T = 0$ K, since the value of d is in the region of $-1.0 < (D_C/J) < -(1/3)$. It at first shows a rapid decrease from the value at $T = 0$ K and then exhibits the normal thermal variation, while the sublattice magnetization σ_A represents the standard thermal variation. In particular, the possibility of two compensation points in $|M|$ originates from the characteristic behaviours of m_B and m_C. This fact indicates that the ferrimagnetic chainlike system composed from spin-$\frac{1}{2}$ A atoms, spin-2 B atoms and spin-2 C atoms may also exhibit the possibility of two compensation points, when the sublattice magnetizations m_B and m_C take forms similar to those of figure 3(b) by selecting the appropriate values for the five parameters a, b, c, d and α.

3.2. The ferrimagnetic system with $S = 2$ and $S' = 2$

Figure 4 shows the phase diagram (T_C and T_κ versus d plot) of the ferrimagnetic chainlike system with $S = 2$ and $S' = 2$, when the parameters a and c are fixed at $a = 0.2$ and $c = 0.1$,

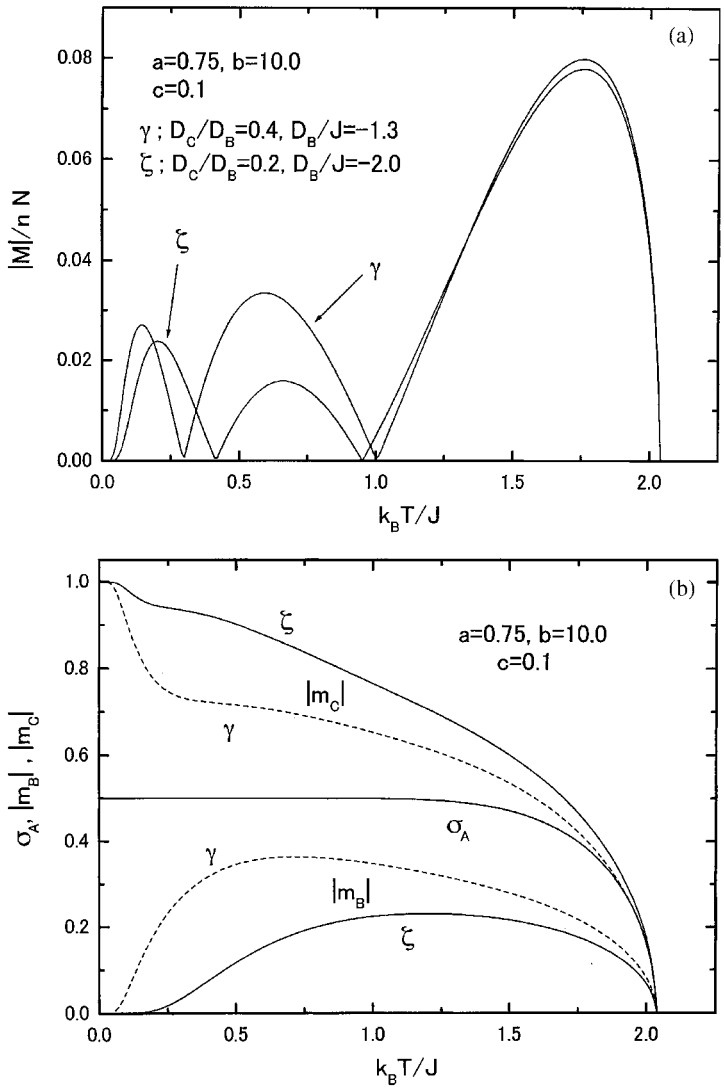

Figure 3. The temperature dependences of the spontaneous magnetization ($|M|/nN$ in (a)) and the sublattice magnetizations (σ_A, $|m_B|$, $|m_C|$ in (b)) in the system with $S = 1$ and $S' = 2$, when the two sets of d and α are selected and the other parameters are fixed at $a = 0.75$, $b = 10.0$ and $c = 0.1$. The sublattice magnetization curves (or σ_A) for γ and ζ take almost the same form and hence they cannot be distinguished within the present scale. The curves labelled γ and ζ in (b) represent the sublattice magnetization curves corresponding to the $|M|$ curves in (a).

two values of b ($b = 5.0$ and 10.0) are selected and the value of α is changed from $\alpha = 1.0$ to $\alpha = 4.0$. In order that the solid line obtained from (7) takes the real meaning of the T_κ value, each solid line must be lower than the corresponding dashed (or T_C) lines. In the figure, each dashed line actually represents the four T_C lines for the four values of α ($\alpha = 1.0$, 2.0, 3.0 and 4.0) obtained from (14) and within the scale in figure 4 they appear like one dashed line. The solid curve labelled 2.0 exhibits the reentrant (double values) behaviour in the vicinity of $d = -0.5$. This indicates that the two compensation points may be obtained in the $|M|$ curve, when one selects an appropriate value of d in the region.

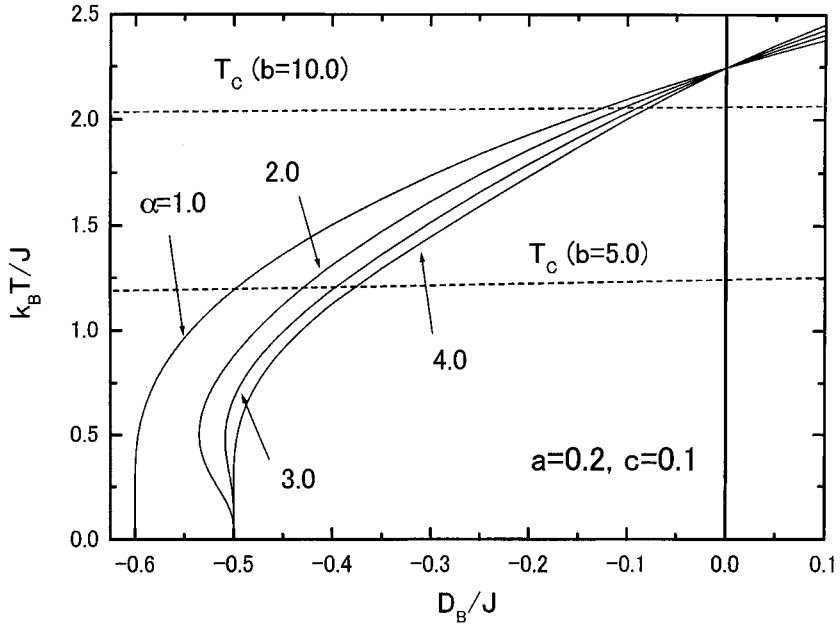

Figure 4. The phase diagram (T_C and T_κ) in the T–d plane of the system with $S = 2$ and $S' = 2$, when the two parameters are fixed at $a = 0.2$ and $c = 0.1$, the two values of b are selected as $b = 5.0$ and 10.0 and the value of α is changed from $\alpha = 1.0$ to $\alpha = 4.0$. Each dashed line represents the four T_C curves obtained by changing the four values of α, but within the present scale they are plotted as one dashed line. The solid curve below the corresponding T_C line denotes the real compensation temperature T_κ.

In figure 5, the temperature dependences of the total magnetization ($|M|/nN$) and the sublattice magnetizations (σ_A, $|m_B|$ and $|m_C|$) are plotted for the system with $a = 0.2, b = 5.0$ and $c = 0.1$, selecting the values of $d = -0.525$ and $\alpha = 2.0$. Their thermal variations are very similar to those in figure 3. $|M|/nN$ clearly shows two compensation points below T_C, as predicted in figure 4.

4. Conclusions

In this work, we have studied the possibility of two compensation points in a two-dimensional ferromagnetic system composed of ferrimagnetically ordered chains by the use of the differential operator technique. The chain consists of spin-$\frac{1}{2}$ A atoms, spin-S ($S > \frac{1}{2}$) B atoms and spin-S' ($S' > 1/2$) C atoms. We have examined the phase diagram and the magnetization curve in the system with a weak interchain interaction (or $c = 0.1$), in order to simulate the experimental data of molecular-based magnetic materials. As discussed in section 3, we have found the possibility of two compensation points in two chainlike systems; one is composed of $S = 1$ and $S' = 2$ and another is composed of $S = 2$ and $S' = 2$. The possibility is rather restricted in the two systems, since one has to select special values of uniaxial anisotropy constants, in order that the sublattice magnetizations m_B and m_C take the characteristic forms for the thermal variations. However, one should notice that the characteristic thermal variation of $|M|$ given in figures 3 and 5 has not been predicted in the Néel theory of ferrimagnetism [13].

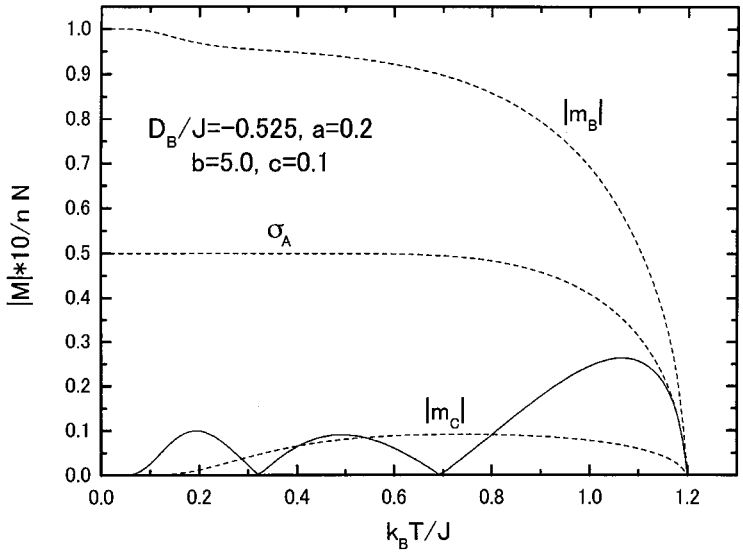

Figure 5. The temperature dependences of the spontaneous magnetization ($|M|/nN$) and the sublattice magnetizations (σ_A, $|m_B|$ and $|m_C|$) in the system with $S = 2$ and $S' = 2$, when the five parameters are fixed at $a = 0.2$, $b = 5.0$, $c = 0.1$, $d = -0.525$ and $\alpha = 2.0$.

In this work, we have used the Zernike approximation [12] for the evaluation of magnetization in a molecular-based ferromagnetic material composed of three magnetic atoms. The approximation is superior to that of the standard mean-field approximation, but the statistical accuracy is less than that of the Bethe–Peierls approximation [9, 10]. Accordingly, when one uses an improved approximation for the evaluation of T_C (or magnetization), the dashed lines in figures 2 and 4 will take values lower than those of figures 2 and 4, while the position of compensation point (points) could not be changed. The main reason that we have used the Zernike approximation in this work is dependent on the intra-chain anisotropy (or the A atom is surrounded by two different (B and C) atoms, such as section 3.1). If the A atom is surrounded only by the same atoms (such as two B atoms with a spin S ($S > \frac{1}{2}$) in section 3.2), one can solve analytically the magnetic properties of the quasi-chainlike system within the Bethe–Peierls approximation. This work will be discussed in future. However, one could not find the possibility of two compensation points in such a system with a spin S less than $S = 2$. In fact, we have examined in detail the possibility of two compensation points in the ferrimagnetically ordered chainlike system composed of spin-$\frac{1}{2}$ A atoms, spin-1 B atoms and spin-1 C atoms within the same framework as the present one. However, we could not find the possibility, even when various sets of parameters are selected.

Finally, as discussed in this work, the study of finding two compensation points in a ferrimagnetically ordered chainlike system may be interesting experimentally and theoretically. Furthermore, the magnetization in such a system is changed in sign (or aligned parallel to the easy axis) above the T_κ and antiparallel below. This situation gives rise to the memory effect that is widely used for magnetic data storage. Especially, the study of a molecular-based ferrimagnetic system with two compensation points may open the new possibility, as proposed in a ferrimagnetic multiplayer system with two compensation points [14]. The recent experimental results in some molecular-based ferromagnetic materials have revealed a very appealing field-thermal-dependent magnetization with two compensation points [15].

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