Magnetic behavior of mixed spin prussian blue analog cylindrical nanowire

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Abstract
In this work, we implemented Monte Carlo simulations in order to describe the magnetic phase transition properties of a mixed ferro-ferrimagnetic ternary alloy cylindrical nanowire with formula $AB_pC_{1-p}$. The ternary compound, known as Prussian Blue Analog, exhibits two interpenetrating lattices, one containing components with spin $-3/2$ and the other one with a random distribution of spin $-1$ and spin $-5/2$ compounds. The concentration of spin $-3/2$ compounds $p$, and the interaction ratio $R$ were independently modulated to study their influence on the critical temperature, saturation magnetization and compensation temperature. The results show that it is possible to modify the transition temperature and saturation magnetization of the system just by manipulating $p$ and $R$ values, and it was determined, not only the existence of compensation in the sample, but also the fact that it is possible to determine the behavior of the compensation temperature by varying these parameters. In addition, a critical concentration value $p_c$, which is a threshold related to the compensation temperature, was determined from magnetization curves and compared to the one computed through a percolation analysis.

Introduction
Molecule based magnets are materials of high interest since they show multiple properties such as photo-induced magnetization [1], compensation and multicompenation behavior [2–5] and inverted magnetic hysteresis loop [5, 6]. These highlighted properties make these materials with potential applications in nanotechnology, remarkably in the areas of magnetic optical recording [1] and hydrogen storage [7, 8]. In the last decade, Prussian Blue Analogs (PBA), a kind of molecular based magnets, have been widely studied due to the possibility to manipulate their compositional concentration during their synthesis and the affectation that this manipulation has over the magnetic properties of the system.

Theoretically, PBA have been modeled as ternary metallic alloys with formula $AB_pC_{1-p}$ and have been analyzed using effective field theory [9, 10], mean field theory [6], Bethe approximation [11], Monte Carlo simulations [2, 4, 12], Green’s functions [13], among others.

The interest lays now in the PBA (Ni$_{12}$Mn$_{12-p}$)$_{1.5}$[Cr$_{3/2}$](CN)$_6$ · $n$H$_2$O that has been synthesized and studied experimentally before [14]. This material is described by two exchange interactions: $J_{\mathrm{Ni-Cr}}>0$ (ferromagnetic) and $J_{\mathrm{Mn-Cr}}<0$ (antiferromagnetic) and corresponding spin values $S_{\mathrm{Cr}} = \frac{3}{2}$, $S_{\mathrm{Ni}} = 1$, and $S_{\mathrm{Mn}} = \frac{5}{2}$. Even though PBA, in different configurations, has been studied computational, experimental and theoretically, there are just a few magnetic studies concerning nanowire PBA systems. In the last years, those nanowires have been studied both experimentally [15–17] and computationally [12] and there are left many interesting properties of those systems to analyze.

In this work, we study the magnetic properties of a nanowire PBA system, as well as the influence of the concentration value $p$ and the interaction ratio $R$ on the main magnetic features such as compensation and critical temperature. Furthermore, we focused on the behavior around critical point for $R$ ($R_c$) and we also determined and analyzed the critical concentration value for $p$ ($p_c$) and the influence that his value has on the
overall magnetic behavior of the system. Even though PBA can show first-order phase transitions at specific conditions \[18\], their study is not considered for the scope of our work.

**Model and method**

The sample used in our study case, which is depicted in figure 1, is a ternary alloy cylindrical nanowire of radius \(r = 10\) and length \(L = 15\) unit cells (u.c.) on a cubic lattice with periodic boundary conditions in the \(z\)-direction. The generic stoichiometry for a Prussian Blue ternary alloy is \(ABpC_{p-1}\), composed by two interpenetrating sublattices: one sublattice is composed by Type - A (\(A\) for short) magnetic components with spin \(S_A = \pm \frac{3}{2}\); the other one is composed of Type - B (\(B\)) and Type - C (\(C\)) magnetic components with spins \(S_B = \pm 1\) and \(S_C = \pm \frac{1}{2}\), and an occupation probability \(p\) and \(1 - p\), respectively. Every \(A\) has \(B\) or \(C\) neighbors and every \(B\) and \(C\) has just \(A\) neighbors. The Hamiltonian describing the interaction of the system is defined as

\[
\mathcal{H} = - \sum_{(i,j)} J_{ij} S_i S_j
\]

where

\[
S_i = S_A
\]

\[
S_j = \begin{cases} 
S_B & \text{if } j = B \\
S_C & \text{if } j = C 
\end{cases}
\]

\[
J_{ij} = \begin{cases} 
J_{AB} & \text{if } j = B \\
J_{AC} & \text{if } j = C 
\end{cases}
\]

This Hamiltonian is given in the framework of the mixed Ising spin model, i.e. \(S_C = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}\), \(S_A = \pm \frac{3}{2}, \pm \frac{1}{2}\) and \(S_B = \pm 1, 0\). As the exchange interaction between \(A\) and \(B\) magnetic ions is always ferromagnetic \((J_{AB} > 0)\), we assume a static value of \(J_{AB} = 1\) for further normalization. On the other hand, exchange interaction between \(A\) and \(C\) is antiferromagnetic, that is, \(J_{AC} < 0\). Energies were calculated using interactions between nearest neighbors and every sample was randomly generated under the respective probability conditions 15 times for comparison and respective error measurements. With the aim of studying the magnetic properties of the ternary alloy, Monte Carlo simulations were performed using single spin-flip Metropolis algorithm \[19\] implemented in VEGAS simulation package \[20\].

Temperature was slowly cooled down from a normalized temperature \(k_B T / J_{AB} = 10\) to 0 using a step of \(k_B \Delta T / J_{AB} = 5 \times 10^{-2}\), where \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature. We used \(2 \times 10^4\) Monte Carlo steps (MCS) for each temperature and the final configuration for each temperature was.
taken as the first one for the next temperature step. Finally, in order to obtain the thermal averages, the first $10^4$ MCS were discarded to ensure the reaching of equilibrium.

The total magnetization $M_T$ was obtained as

$$M_T = \langle M_T \rangle = \left\langle \frac{1}{N_T} \left( |N_A M_A| + |N_B M_B| + |N_C M_C| \right) \right\rangle$$

where $M_A$, $M_B$ and $M_C$ are the average magnetizations of each type, defined as

$$M_A = \langle m_A \rangle = \left[ \frac{1}{N_A} \left( \sum_i S_{Ai} \right) \right]$$

$$M_B = \langle m_B \rangle = \left[ \frac{1}{N_B} \left( \sum_i S_{Bi} \right) \right]$$

$$M_C = \langle m_C \rangle = \left[ \frac{1}{N_C} \left( \sum_i S_{Ci} \right) \right]$$

being $N_A$, $N_B$ and $N_C$ the total number of $A$, $B$ and $C$ sites respectively, and $N_T$ the total amount of ions $N_T = N_A + N_B + N_C$. In addition, $\langle \rangle$ represents thermal average and $[\ ]$ represents configuration average.

In order to obtain transition temperatures, magnetic susceptibility was computed as

$$\chi = \left[ \frac{N_T \langle (M_T^2) \rangle - \langle M_T \rangle^2}{k_B T} \right]$$

In equation (9), the calculations performed over the magnetization $M_T$ can also be applied to each type of sites $A$, $B$ or $C$ individually by using $M_A$, $M_B$ or $M_C$ respectively; this allows to define a susceptibility per-type.

Values of critical temperature ($T_C$) for different samples were estimated by locating the maximum value of susceptibility in $A$ sites, because this sublattice is comparable between the samples, unlike the sublattices of $B$ and $C$ sites.

Compensation phenomena is exhibited when a certain temperature is reached, such that, sub-lattice magnetizations cancel each other and total magnetization vanishes, this value ($T_{comp}$) was thus calculated as follows: while cooling down the system, every pair of consecutive total magnetization datapoints was considered in order to analyze the temperature for which a sign change occurs in the total magnetization (from positive to negative). The mean value between those two datapoints was taken as the compensation temperature.

Results

In order to study the influence of the nanowire length on the critical properties, we have simulated several nanowires with different values of $L$. As shown in figure 2, the length value of $L = 15$ u.c. shows a stable value of critical temperature, and it is possible to recreate the overall nanowire behavior with this sample length. In this way, $L$ was fixed at 15 u.c. for making the further simulations.

In this section, the magnetic behavior of the ternary alloy nanowire is discussed, following the fact that we used different concentration values $p$ and different values of the exchange ratio $R = |J_{AC}|/|J_{AB}|$. The role of this
exchange ratio as an indicator of the predominant interaction in the system, allows the full qualitative
description of its features in the range of $0 \leq R \leq 1$ as proven by [3] and [21].

Figure 3 shows the magnetic phase diagram, relating reduced critical temperature $k_B T_C / J_{AB}$ and exchange
ratio $R$ for several values of $p$. These simulations give information about the dominant interaction
(ferromagnetic or antiferromagnetic). For $p = 0$, the stoichiometry of the system is reduced to an $AC$ combined
system with spins $3/2$ and $5/2$ and a ferrimagnetic interaction. The critical temperature increases as $R$ increases,
and it can be observed that for this value of concentration $p$, the behavior exhibits the steepest slope. On the
other hand, for a value of $p = 1$, the system becomes a pure ferromagnetic $AB$ combined system with spin $3/2$
and $1$, respectively. In this case, the system is not affected by the values of $R$ as there are not $C$ sites in the system.
It is also evident that there is a specific point where all the curves intersect them. This critical value $R_C$ exposes
the existence of a point where system $T_C$ does not depend on the concentration values of $B$ or $C$; this occurs because
in the Hamiltonian of equation (1), the energy contributions due to ferromagnetic interactions balance the ones
from antiferromagnetic interactions for any value of $p$. This critical value of $R_C \approx 0.47$ has been widely studied
both by simulations and also experimentally over PBA [12].

With a wider look into figure 4, it is possible to explore the whole panorama of the critical temperature
behavior. Figure 4 exhibits the behavior of both $T_C$ (marks) and $T_{comp}$ (dashed) of the alloy as functions of $p$, for
several values of $R$. For values above $R_C$ (figure 4(a)), $T_C$ decreases as $p$ increases, reaching the convergence point
in $p = 1.0$. On the other hand, for values below $R_C$ (figure 4(b)), $T_C$ increases as $p$ increases, reaching again the
convergence point in $p = 1.0$. This behavior can be understood by looking in more detail at the Hamiltonian of
equation (1), which, by replacing $J_{AB} = 1$ and introducing the definition of $R$, can be rewritten as

$$H = - \sum_{\langle i,j \rangle \in B} S_i S_j + R \sum_{\langle i,k \rangle \in C} S_i S_k, \quad i \in A$$

(10)

where an $A$ site (denoted by $i$) could have neighbors of type $B$ (denoted by $j$) and neighbors of type $C$ (denoted
by $k$), so the first sum accounts for the $AB$ interactions, while the second sum takes care of the $AC$ bonds.

Equation (10) makes clear the fact that, when $p$ is close to $0$, the second term of the Hamiltonian prevails, then,
for higher ratio $R$, the whole energy of the system increases and more thermal energy is required to drive the
system to a disordered state, thus $T_C$ increases too. Similarly, when $p \approx 1$, the low concentration of $C$ ions causes
that the contribution of the first term of the Hamiltonian outperform the second one, no matter the value of $R$.
Consequently, the $T_C$ converges to the one of an $AB$ ferromagnetic system, around $4.25[k_B T_{AB}]$.

Moreover, it is also possible to observe that $T_{comp}$ only occurs for certain values of $p$ for each $R$, when the
positive magnetization induced by the $AB$ sublattice equals the magnitude of the negative magnetization
induced by the $C$ sublattice. Therefore, higher values of interaction strength $R$ demand a higher concentration of
$B$ sites (higher $p$) to balance the total magnetization and allow for the existence of $T_{comp}$, as seen in figure 4.

This behavior shows the apparent capability to manipulate $T_C$ and $T_{comp}$ of the material with the
manipulation of $p$ given that, total magnetization values are conditioned by both, $R$ and $p$.

The theoretical equation of the saturation magnetization of the base state $M(T = 0)$ can be brought in order
to explore the meaning of $p_C$. Being

$$M(T = 0) = \frac{1}{N} \left[ \frac{N}{2} S_A + \left(\frac{N}{2}\right) p S_B + \left(1 - p\right) \left(\frac{N}{2}\right) S_C \right] = \frac{S_A}{2} + \frac{p S_B}{2} + \left(1 - p\right) \frac{S_C}{2}$$

(11)
which considering the spin values of each type, leads to the linear equation

\[ M(T = 0) = \left| \frac{7}{4}p - \frac{1}{2} \right| \]  \hspace{1cm} (12)

Equation (12) is plotted in figure 5 (dashed line) as well as the simulated saturation magnetizations obtained for different values of \( p \) (diamonds), giving a good accuracy between them. The intersection with the \( x \)-axis,

Figure 4. Critical and compensation temperatures as a function of \( p \) for values (a) above and (b) below \( R_C = 0.47 \).

Figure 5. Saturation magnetization as a function of \( p \).
for which $M(T = 0) = 0$, is in agreement with the convergence value of the compensation temperatures at $p \approx p_c$. In this critical value, all magnetization curves exhibit the same behavior with no evident compensation temperature and same saturation magnetization, as shown in Figure 6. The statistical number of $N_b$ is enough to allow the beginning of the magnetic ordering in the overall system independently of $R$, as opposed to the value qualitatively proposed by [12] of $p_c < 0.25$ and closer to the value proposed by [3] of $p_c < 0.3$.

A percolation analysis was also performed in order to relate this emerging magnetic ordering with the possible formation of a structural cluster that spans all across the sample. The procedure goes as follows: an initial sample is generated with $p = 1.0$ and then, with steps of $\Delta p = 0.001$, the concentration $p$ is slowly reduced to $p = 0.0$. In this way, random $B$ ions are uniformly chosen and replaced by $C$ ions. After each reduction step, a percolation indicator $x_p \in \{0, 1\}$ is computed, where $x_p = 1$ means that there is at least one connected graph, composed of just $A$ and $B$ neighboring sites, that starts at one site at the bottom ($z = 0$) of the sample, spans all its way to the top ($z = L$) and then connects to itself through the $z$-axis periodic boundary conditions (if such percolation path does not exist, then $x_p = 0$). The whole procedure is repeated 100 times to generate the corresponding average $\bar{x}_p$ presented in Figure 7. The shading around the line accounts for the standard deviation $\sigma_p$, which is also given in the inset of the same figure. The dashed line marks the threshold $p_t \approx 0.162$, which is chosen as the point where $\sigma_p$ has its maximum. However, this value is way lower than the $p_t$ estimated previously from the magnetization curves; this reveals that the mechanism through which magnetic

\[ p \approx 0.286, \text{ for which } M(T = 0) = 0, \text{ is in agreement with the convergence value of the compensation temperatures at } p \approx p_c. \]

\[ \text{In this critical value, all magnetization curves exhibit the same behavior with no evident compensation temperature and same saturation magnetization, as shown in Figure 6.} \]

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ordering emerges in the PBA is far more complicated and that clustering formation is not a sufficient condition for it to occur.

Conclusions

We have performed a MC study over a PBA nanowire defined by the generic formula \( AB_2C_3 – p \) with exchange values \( J_{AB} = 1 \) (ferromagnetic) and \( J_{AC} < 0 \) (antiferromagnetic) with an exchange ratio defined as \( R = |J_{AC}|/J_{AB} \). We determined the dependence of critical temperature by modulating \( R \) for different concentration values \( p \). Moreover, we obtained the behavior of compensation temperature for different values of \( R \) by varying the concentration, in order to look for a critical point \( p_c \), where all the compensation temperatures converge. This critical value was effectively determined and we found that this value matches the concentration value for which saturation magnetization vanishes. We also analyzed magnetization curves at this critical concentration point to summarize the results. Finally, a percolation analysis revealed that the formation of a connected cluster in the nanowire is not a sufficient condition for the magnetic ordering to emerge in the sample and thus a more complicated mechanism lies beneath the behavior of \( T_{comp} \).

In general it is possible to modulate the compensation temperature and the critical temperature of the Prussian Blue Analog nanowire by varying both concentration and exchange ratio values and the studies on this matter must continue to be made in order to determine important phase points where properties can lead the research to further applications.

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