Bipolar magnetization switching and its control in a Prussian blue type molecular magnetic compound

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Abstract. Prussian blue analogue (PBA) molecular magnetic materials have opened up the possibility of combining the molecular functionalities with their magnetic properties. A tremendous effort is on for finding appropriate PBAs that are suitable for memory and sensor applications. We have observed the magnetic pole reversal in multi-metal Prussian blue type compounds \( \{\text{Cu}_x\text{Mn}_{1-x}\}_{1.5}\left[\text{Fe(CN)}_6\right]_z\text{H}_2\text{O} \). Our molecular field theory calculations agree very well with the observed temperature dependent magnetization reversal behaviour. As the applied magnetic field is increased, the negative magnetization keeps changing its character and finally becomes positive with typical ferrimagnetic/ferromagnetic type behaviour. A highly reversible-bipolar switching of magnetization using low applied magnetic fields is demonstrated. Possible applications of the observed magnetic pole reversal phenomenon in novel magneto-electronic devices such as volatile magnetic memory and thermo-magnetic switches have been revealed.

1. Introduction

The Prussian blue [1] is the very first coordination compound discovered in 1704. This compound belongs to a general category of 3d metal hexacyanide based molecular magnetic compounds [2] that show interesting magnetic properties. Prussian blue \( \text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_6]_3\cdot14-16\text{H}_2\text{O} \) [1] is a ferromagnet with the Curie temperature \( T_C \) of 5.6 K. The derivatives of Prussian blue with other 3d/4d metal ions, so called Prussian blue analogues (PBAs) [3-6], show higher magnetic ordering temperature up to 376 K [7]. The rational design of these PBA compounds might enable one to tailor the magnetic properties for specific applications. A tremendous effort is on for finding appropriate PBAs that are suitable for memory [8] and sensor applications. We observed a peculiar phenomenon of magnetic pole reversal in one of the compounds of the \( \{\text{Cu}_x\text{Mn}_{1-x}\}_{1.5}\left[\text{Fe(CN)}_6\right]_z\text{H}_2\text{O} \) series [3]. A microscopic understanding of the phenomenon, by using a neutron diffraction study and a reverse Monte Carlo calculation, was also reported by us in Ref. 3. In the present paper, an explanation of the observed magnetic pole reversal phenomenon based on molecular field theory calculation has been given. The effect of an external magnetic field on the observed magnetic pole inversion is also demonstrated here. Possible applications of the observed phenomenon in magnetic memory and sensor are also outlined.
2. Experimental

Polycrystalline samples of \( \{\text{Cu}_{x}\text{Mn}_{1-x}\}_{1.5}\text{[Fe(CN)6]}_z\text{H}_2\text{O} \) were prepared by mixing 0.1 M aqueous solutions of \( \text{Cu(NO}_3\text{)}_2 \) and \( \text{Mn(NO}_3\text{)}_2 \), in stoichiometric amounts, to rapidly stirred solution of 0.1 M \( \text{K}_3\text{[Fe(CN)6]} \). The dark brown precipitates obtained were filtered, washed many times with distilled water and finally dried at room temperature. All the samples were characterized thoroughly by the neutron diffraction, x-ray fluorescence, and Mössbauer spectroscopic techniques as described earlier [3]. DC magnetization measurements were carried out using a commercial (Oxford Instruments) vibrating sample magnetometer as a function of temperature and magnetic field.

3. Results and discussion

Field cooled (FC) dc magnetization curve for the \( \text{Cu}_{0.73}\text{Mn}_{0.77}\text{[Fe(CN)6]}_z\text{H}_2\text{O} \) \((x = 0.486)\) compound at 100 Oe is shown in figure 1. The FC magnetization curve increases sharply below 20 K, followed by a peak at 12.8 K and becomes negative below 9.6 K. The estimated magnetic ordering temperature is 17.9 K. The solid line, in figure 1, is the calculated magnetization curve based on molecular field theory (MFT). In this theory, the local magnetic field at a particular site is the sum of the internal molecular field and the external magnetic field. For the present compound, the local fields at the Cu, Mn and Fe ionic sites are given by

\[
\begin{align*}
H_{\text{Cu}} &= H + \gamma_{\text{CuFe}} M_{\text{Fe}} \\
H_{\text{Mn}} &= H + \gamma_{\text{MnFe}} M_{\text{Fe}} \\
H_{\text{Fe}} &= H + \gamma_{\text{FeCu}} M_{\text{Cu}} + \gamma_{\text{FeMn}} M_{\text{Mn}}
\end{align*}
\]

Figure 1. Open circles represent the field cooled dc magnetization data at 100 Oe field. The solid line is the molecular field theory (MFT) calculated curve.

where, \( M_i \) is the magnetization of the \( i^{\text{th}} \) sub-lattice, \( \gamma_i \) are molecular field coefficients, and \( H \) is the externally applied field. In above expressions, we have considered only the magnetic interactions between nearest neighbour magnetic sublattices as the next nearest neighbour interactions can be neglected because of larger distance (~ 10.3 Å) between them. The sub-lattice magnetizations for Cu, Mn and Fe ionic-sites follow the Brillouin function \( B_0(x) \) dependence and are given by

\[
M_{\text{Cu}} = y_{\text{Cu}} N g \mu_{\text{B}} S_{\text{Cu}} B_{\text{Cu}} \left( \frac{g \mu_{\text{B}} S_{\text{Cu}} H_{\text{Cu}}}{k_B T} \right)
\]
where $S_{\text{Cu}}$, $S_{\text{Mn}}$ and $S_{\text{Fe}}$ are the spin for the Cu, Mn and Fe ions, respectively; $y_i$ is the molar fraction of the $i^{th}$ ionic site; $N$ is the total number of magnetic ions per unit volume and $g$ is the Lande g-factor ($\approx 2$). The above equations (1 to 6) have been solved numerically to get the sublattice magnetization as a function of temperature. The values of various parameters used are as follows: $y_{\text{Cu}} = 0.73$, $y_{\text{Mn}} = 0.77$, $y_{\text{Fe}} = 1$, $S_{\text{Cu}} = 1/2$, $S_{\text{Mn}} = 5/2$, $S_{\text{Fe}} = 1/2$, $Z_{\text{MnFe}} = Z_{\text{CuFe}} = 4$, and $Z_{\text{FeCu}} = Z_{\text{FeMn}} = 6$. The molecular field coefficients are derived from the exchange field coefficients $J_{\text{CuFe}}$ and $J_{\text{MnFe}}$, which are obtained from the magnetic ordering temperatures ($T_C$) of the two end-compounds viz. Cu$_{1.5}$[Fe(CN)$_6$]·zH$_2$O ($T_C = 22.5$ K) and Mn$_{1.5}$[Fe(CN)$_6$]·zH$_2$O ($T_C = 13.5$ K) using the relation $T_C = 2 |J_{ij}| \sqrt{\frac{Z_i Z_j S_i (S_i + 1) S_j (S_j + 1)}{3k_B}}$ where $i = \text{Cu or Mn}$ and $j = \text{Fe}$. The MFT calculations are successful in reproducing the observed magnetization reversal for the present compound. A small deviation, near the ordering temperature is expected as MFT does not hold well near the magnetic ordering temperature. In the MFT calculations, we have considered the negative exchange interactions between Mn and Fe/Cu ions. The results of the MFT calculation are, therefore, consistent with the microscopic understanding of the magnetic pole reversal phenomenon, reported earlier by us using a neutron diffraction technique [3].

\[ M_{\text{Mn}} = y_{\text{Mn}} N g \mu_B S_{\text{Mn}} B_T S_{\text{Mn}} \left( \frac{g \mu_B S_{\text{Mn}} H_{\text{Mn}}}{k_B T} \right) \]  \hspace{1cm} (5)

\[ M_{\text{Fe}} = y_{\text{Fe}} N g \mu_B S_{\text{Fe}} B_T S_{\text{Fe}} \left( \frac{g \mu_B S_{\text{Fe}} H_{\text{Fe}}}{k_B T} \right) \]  \hspace{1cm} (6)

Figure 2. Effect of applied magnetic field on the magnetic pole reversal.

The effect of an external magnetic field on the magnetization reversal behavior of the compound is depicted in figure 2. It is quite evident that the magnitude of negative magnetization changes with applied magnetic field and it is no more negative at any temperature for fields above 1.5 kOe. The reversal of Mn ion spins in the direction of applied field could be a possible reason for the observed magnetization behavior. However, the observed field dependent polarity-reversal of magnetization from a negative to a positive value is not sharp. Various structural defects [4] arising from the partial sites occupancies of the Fe, C, N, the non-coordinated water molecules and the substitution of the nearly 50% of the Mn ions at the (0, 0, 0) site by the Cu ions [3] could be a possible explanation for the observed gradual change in the magnetization of this compound.
Figure 3. Switching of magnetization between positive and negative values under the application of low applied fields in a cyclic manner.

Figure 3 shows the magnetization switching behaviour for the Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_2$H$_2$O compound under two (100 and 1200 Oe) different magnetic fields applied in a cyclic manner. The magnetization of the compound can be switched between negative and positive values without any noticeable decay in its magnitude. The observed field-actuated reproducible magnetization reversal can lead to new device applications such as magnetic data storage (memory) and switches. The basic requirement of a data storage material is the presence of two noticeably different values (bistable states) of a physical property e.g. electrical resistance, magnetization, electrical polarization, reflectivity, etc. These two states of the material should be accessible with the help of an external actuator like heat, light, electric and magnetic fields, etc. In our experiment (figure 3), the realization of the two (positive and negative) magnetization states has been achieved by externally applied magnetic fields (1200 and 100 Oe, respectively). However, once the magnetic field is switched off, the corresponding magnetization-state ceases to exist indicating that this kind of material may be suitable for volatile magnetic memories. On the other hand, the temperature dependent magnetic polarity reversal (figure 1) can be exploited for thermomagnetic switches.

4. Conclusions

The observed magnetic pole reversal phenomenon in the multi metal PBA Cu$_{0.73}$Mn$_{0.77}$[Fe(CN)$_6$]$_2$H$_2$O compound is explained by molecular field theory calculations. The pole reversal disappears as the applied field is increased above 1.5 kOe, possibly due to a spin reversal transition at the Mn site. A highly reversible-bipolar switching of magnetization using low applied magnetic fields is demonstrated and its possible applications in volatile magnetic memory and thermo-magnetic switches have been revealed.

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