

## Microscopic Understanding of Negative Magnetization in Cu, Mn, and Fe Based Prussian Blue Analogues

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A crossover of the field-cooled magnetization from positive to negative has been observed below the magnetic ordering temperature (17.9 K) in a multimetal Prussian Blue analogue (PBA),  $\text{Cu}_{0.73}\text{Mn}_{0.77}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ . The reverse Monte Carlo (RMC) modeling (using the program RMCPOW) has been used to derive the various scattering contributions (e.g., nuclear diffuse, nuclear Bragg, magnetic diffuse, and magnetic Bragg) from the observed neutron diffraction patterns. The RMC analysis combined with the Rietveld refinement technique show an antiferromagnetic ordering of Mn moments with respect to the Cu as well as the Fe moments. Our study gives the first neutron magnetic structure evidence towards the microscopic understanding of the negative magnetization in the PBAs. This information can be effectively utilized to design suitable PBAs for making multifunctional devices.

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In the last two decades, molecular magnetism [1–3] has emerged as a fast growing field for research and development activities. The molecular magnetic compounds are often predicted to be the smart magnets of the future. The ambient temperature synthesis of these materials using organic, organo-metallic, and/or coordination metal chemistry methods enables easy incorporation of additional molecular functionalities, e.g., photo-activity, conductivity, polarizability, transparency, etc., into these magnetic compounds. In particular, Prussian Blue analogues (PBAs) [1–8], the derivatives of the first coordination compound Prussian Blue  $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot 14\text{--}16\text{H}_2\text{O}$  [1], have shown very interesting multifunctional properties upon application of external stimuli, e.g., temperature, magnetic field, light, pressure, humidity, etc. These compounds may be represented by the general formula  $A_m[B(\text{CN})_6]_n \cdot z\text{H}_2\text{O}$  where  $A$  and  $B$  are  $3d$  or  $4d$  magnetic ions. The phenomena like photoinduced magnetic ordering [9], pressure induced magnetization and linkage isomerism [10], electric field induced conductance switching [11], etc., are some of the examples showing the multifunctional character of these materials. These functionalities are promising for practical applications of these molecular materials. In the present study, we have observed a crossover of the field-cooled magnetization from positive to negative for the compounds of the  $\{\text{Cu}_x\text{Mn}_{1-x}\}_{1.5}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  series, below their magnetic ordering temperatures. Though, the reversal of magnetization in case of molecular magnets [12,13] including the PBAs [14–17] has been studied in many reports, the microscopic experimental evidence towards the understanding of the phenomenon is lacking so far. A microscopic understanding of this phenomenon would facilitate design of various multifunctional devices from the PBAs [4]. In this regard, neutron diffraction technique

plays an important role. However, due to the relatively smaller concentration of magnetic ions in the PBAs, the magnetic contribution is often masked by the larger diffuse scattering contribution in the neutron diffraction patterns of these compounds. The large diffuse scattering arises from the presence of various structural defects in these compounds and these defects can affect their magnetic properties significantly [8]. Under such situations the Rietveld refinement [18] of neutron diffraction patterns alone cannot determine the magnetic structure of these compounds satisfactorily. We have employed a reverse Monte Carlo (RMC) simulation based program RMCPOW [19] alongwith the Rietveld refinement technique on the neutron scattering data to explain the microscopic origin of the negative magnetization for one of the representative of PBAs, namely  $\text{Cu}_{0.73}\text{Mn}_{0.77}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  ( $x = 0.486$ ) of the above-mentioned series. The RMCPOW is particularly suited for the above-said situation as it can separate out the nuclear Bragg, magnetic Bragg, nuclear diffuse and magnetic diffuse scattering contributions from the total scattering in a neutron diffraction pattern. The present study gives the first experimental microscopic understanding of the theoretical design of a mixed ferroferrimagnet PBA involving various magnetic sublattices [14–16].

The polycrystalline samples of the  $\{\text{Cu}_x\text{Mn}_{1-x}\}_{1.5} \times [\text{Fe}(\text{CN})_6]z\text{H}_2\text{O}$  series were prepared by mixing 0.1 M aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Mn}(\text{NO}_3)_2$ , in the appropriate proportions, to rapidly stirred aqueous solution of 0.1 M  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . The precipitates, so obtained, were filtered, washed many times with distilled water and finally dried at room temperature. The relative percentages of the Cu, Mn, and Fe metal atoms as per the formula unit were confirmed by the x-ray fluorescence spectroscopy. The room temperature neutron diffraction patterns for some

of the compounds were recorded using the powder diffractometer-II ( $\lambda = 1.249 \text{ \AA}$ ) at Dhruva Reactor, Trombay, Mumbai, India. The low temperature (80 and 1.7 K) neutron diffraction patterns for the  $\text{Cu}_{0.73}\text{Mn}_{0.77}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  compound were recorded at the DMC cold powder diffractometer ( $\lambda = 4.20014 \text{ \AA}$ ), SINQ at Paul Scherrer Institute, Switzerland. DC magnetization measurements were carried out using a commercial (Oxford Instruments) vibrating sample magnetometer as a function of temperature down to 1.5 K and magnetic field up to 70 kOe.

Figure 1(a) shows the Rietveld refined neutron diffraction pattern for the  $x = 0.486$  compound at room temperature over a  $Q$  range of 0.35 to  $3.95 \text{ \AA}^{-1}$ . The diffraction pattern is well fitted over the  $Q$  range of 0.9 to  $3.95 \text{ \AA}^{-1}$  using the Rietveld refinement technique, with a face centered cubic (fcc) space group ( $Fm\bar{3}m$ ), confirming a single phase formation for the present compound. The chemical structure of the compound consists of linear chains of

$\text{Fe-CN-Cu/Mn-NC-Fe}$  along the cube edges. Owing to the 3:2 ( $m : n$ ) stoichiometry, the charge neutrality [6,8] necessitates that  $1/3$  of the  $\text{Fe}(\text{CN})_6$  sites are vacant and they are filled by the water molecules where the O atoms of the water molecules (at the empty N site of  $\text{Fe}(\text{CN})_6$ ) are bonded to the Cu/Mn ions. There are, also, a lot of non-coordinated water molecules (depending up on the preparation condition) occupying the interstitial  $8c$  and  $32f$  crystallographic sites. The diffraction pattern shows a lot of diffuse scattering in the form of small modulations in the background. However, in the Rietveld refinement method, these modulations are often absorbed in the background as the technique mainly deals with the Bragg scattering. The origin of the observed diffuse scattering in the PBAs lies in the inherent structural defects [7,8,20–22]. Here, the partial occupancies of the Fe, C, N and noncoordinated water molecules sites and the substitution of the nearly 50% of the Mn ions at the (0, 0, 0) site by the Cu ions are the main structural defects. The diffraction pattern in Fig. 1(a) also shows a distinct broad peak at the (100) Bragg position which is forbidden under the fcc ( $Fm\bar{3}m$ ) space group. In fact, the broad peak is observed at all temperatures down to 1.7 K. Thus, the observation of the broad peak at low- $Q$  value ( $\sim 0.6 \text{ \AA}^{-1}$ ) indicates the presence of short range chemical (nonmagnetic) correlations for this compound. Here, we use the RMCPOW program to study the nature of short range correlations. The details of the application of the RMCPOW program in studying such chemical correlations have been described in our earlier papers [7,8]. The output of the RMCPOW analysis for the 80 K neutron diffraction data (collected at PSI, Switzerland) is plotted in Fig. 1(b). The analysis of the oxygen pair-correlation functions reveals that the clustering of the O atoms of the coordinated as well as noncoordinated water molecules at and around the empty  $\text{Fe}(\text{CN})_6$  sites is responsible for the unindexed peak at the (100) Bragg position [7,8,23]. The RMC analysis also rules out any chemical superlattice ordering of the Cu and Mn ions at the (0, 0, 0) site.

The field-cooled (FC) dc magnetization curves for the  $x = 0, 0.486$  and 1 compounds of the series, at 200 Oe field, are depicted in Fig. 2. The FC magnetization curve for the  $x = 0.486$  composition increases sharply below 20 K (onset temperature), followed by a peak at 13.5 K and becomes negative below 8.8 K. The magnetic ordering temperature was estimated to be 17.9 K. It is also interesting to note that the crossover of the magnetization is highly reversible; i.e., if we increase the temperature of the sample above 8.8 K, the magnetization becomes positive again. This phenomenon (with the possibility of usage in the future memory applications) is fascinating. There are theoretical calculations [14–16] based on molecular-field theory that predict the negative magnetization in the PBAs. However, no microscopic experimental technique, such as neutron diffraction, is applied so far to understand the origin of the negative magnetization at the atomic level. Neutron diffraction, indeed, can deduce the magnitude and

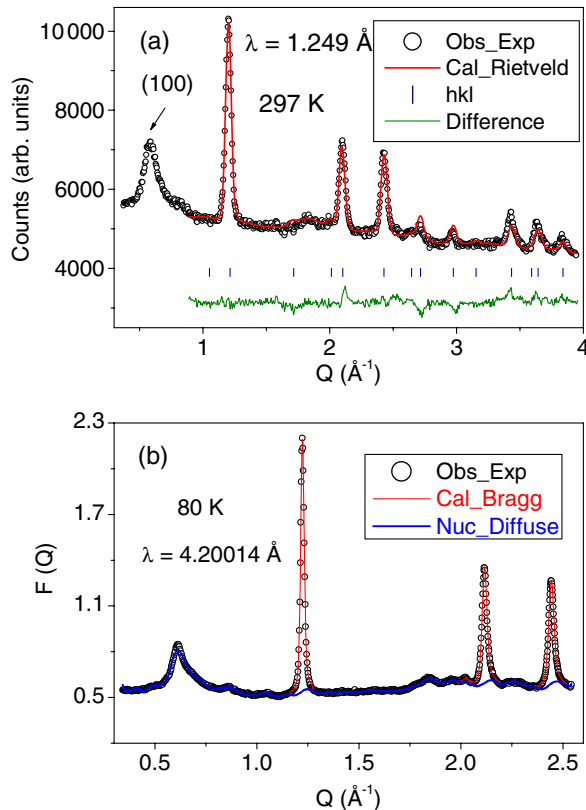


FIG. 1 (color online). (a) Rietveld refined neutron diffraction pattern for the  $x = 0.486$  compound at room temperature. The open circle shows the observed data, and the Rietveld calculated pattern is shown by the solid line. The solid line at the bottom is the difference curve between the observed and the Rietveld calculated curves. The short vertical lines show the position of nuclear Bragg peaks. (b) The observed (open circle) and derived (using RMCPOW) structure factors  $F(Q)$  for the 80 K pattern. The thin (red) and thick (blue) solid lines show the calculated nuclear Bragg and nuclear diffuse scattering contributions, respectively.

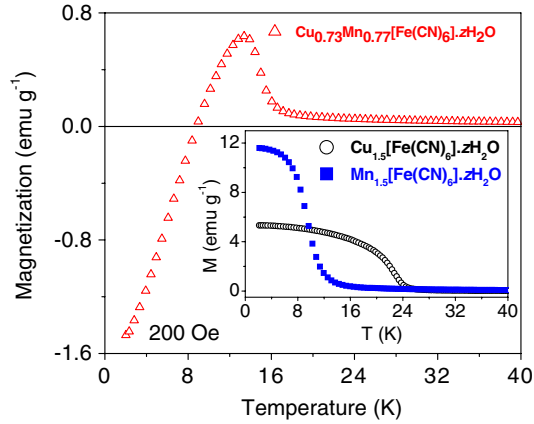


FIG. 2 (color online). FC magnetization curves at 200 Oe for the two end compounds (inset) and the  $x = 0.486$  compound of the  $\{\text{Cu}_x\text{Mn}_{1-x}\}_{1.5}\text{Fe}(\text{CN})_6 \cdot z\text{H}_2\text{O}$  series.

the direction of the individual atomic magnetic moments in the magnetically ordered state. However, low number density of magnetic ions ( $\sim 7.4\%$  for the  $x = 0.486$  compound) results in a relatively low magnetic Bragg contribution to the total scattering, which gets overshadowed by the large diffuse scattering [7,8] arising due to various structural defects. In this Letter, this peculiar situation in the PBAs is handled by using the RMCPOW program to separate out the magnetic Bragg scattering contribution. For this purpose, the RMCPOW analysis is first performed on the diffraction pattern at 80 K in the paramagnetic state where the observed intensity was corrected as per the standard data reduction method and also for the paramagnetic form factor. The output of the RMCPOW analysis, consisting of the nuclear diffuse and nuclear Bragg scattering contributions, is used as an input for analyzing the magnetic Bragg and magnetic diffuse scattering for the 1.7 K neutron diffraction data. A small lattice-constant contraction as a function of temperature is taken into account. For this, the lattice constants at 1.7 K were derived using the profile matching option of the Rietveld refinement of 1.7 K data where only the Bragg peak positions were considered. Figures 3(a)–3(c) show the total scattering, nuclear diffuse, magnetic diffuse and magnetic Bragg scattering contributions, respectively, at 1.7 K. The derived magnetic Bragg contribution [Fig. 3(d)] is then analyzed by the Rietveld refinement technique to obtain the magnetic structure. The refinement gave  $0.93(9)$ ,  $-4.90(4)$  and  $2.33(5)\mu_B$  as the values for the ordered magnetic moments per Cu, Mn and Fe ions, respectively. These magnetic moments are found to align along the crystallographic axes. The neutron diffraction experiments, therefore, underline that Mn ionic moment is antiparallel to the Fe as well as to the Cu ionic moments. The arrangement of the ordered moments is depicted in Fig. 4. The derived moments for the Cu and Mn ions are very close to the theoretically expected spin-only moments for the  $\text{Cu}^{2+}$

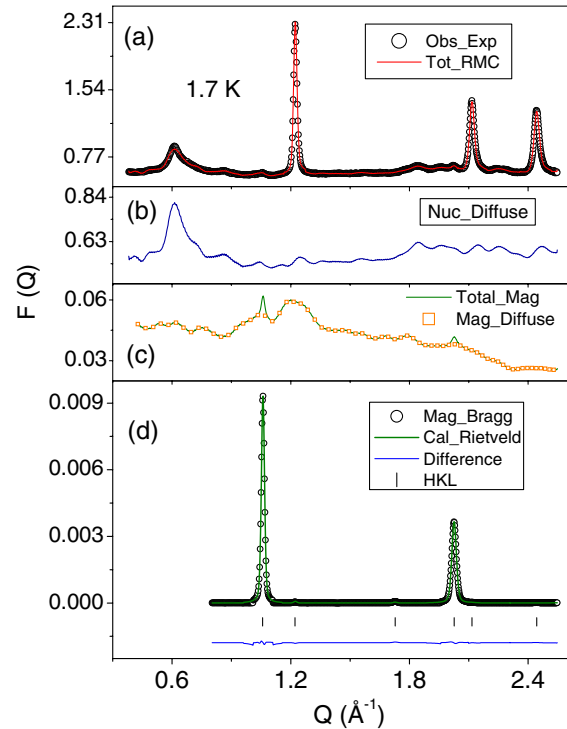


FIG. 3 (color online). The  $Q$  dependence of various intensities at 1.7 K: (a) Observed diffraction pattern (open circle) and the total calculated intensity (solid line) using the RMCPOW, (b) derived nuclear diffuse, (c) derived magnetic diffuse (open square) and total magnetic scattering, i.e., sum of magnetic diffuse and magnetic Bragg (solid line), and (d) the derived magnetic Bragg scattering pattern (open circle), calculated magnetic Bragg (solid line) with the Rietveld refinement. The difference pattern between the derived and calculated magnetic Bragg patterns is shown by a solid line at the bottom.

( $S = 1/2$ ) and high spin  $\text{Mn}^{2+}$  ( $S = 5/2$ ) ions. However, the magnetic moment for the Fe ion is higher than that expected for the low spin  $\text{Fe}^{3+}$  value ( $1\mu_B$  with  $S = 1/2$ ) [6,8]. In fact, the Mössbauer study unambiguously indicates the presence of the high spin  $\text{Fe}^{3+}$  ( $S = 5/2$ ) component in addition to the low spin  $\text{Fe}^{3+}$  ( $S = 1/2$ ) component in this compound (not shown). This phenomenon is called cyanide flipping or linkage isomerism and is found in many other PBAs [7,8,10,24]. The main reasons for the occurrence of the cyanide flipping are the bidentate nature of the CN ligand and the minimal energy difference between the low and high spin configurations.

In order to understand the magnetization behavior for the  $\text{Cu}_{0.73}\text{Mn}_{0.77}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  compound, the dc magnetization measurements for the two end-compounds of the series are carried out and shown in the inset of Fig. 2. It is observed that the  $\text{Cu}_{1.5}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  compound magnetically gets ordered at 22.5 K. We infer a ferromagnetic ordering of the Cu and Fe moments from our neutron diffraction results for the  $\text{Cu}_{0.73}\text{Mn}_{0.77}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  compound. It is seen from the inset of Fig. 2 that the



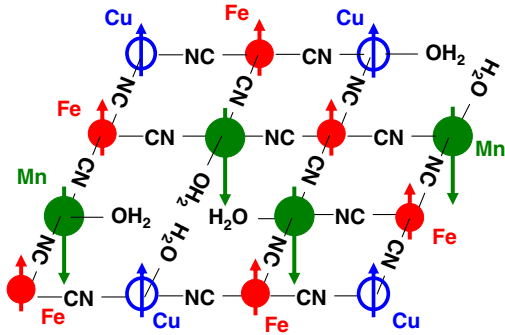


FIG. 4 (color online). Schematic representation of the magnetic structure for the  $\text{Cu}_{0.73}\text{Mn}_{0.77}\text{Fe}(\text{CN})_6 \cdot z\text{H}_2\text{O}$  compound at 1.7 K where 4a Wyckoff site is randomly occupied (maintaining the stoichiometry) by the Cu and Mn ions.

$\text{Mn}_{1.5}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  compound gets ordered at a lower temperature of 13.5 K as compared to the  $\text{Cu}_{1.5}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  compound. Our neutron diffraction study confirms the antiferromagnetic ordering of Mn moments with respect to the Cu and Fe moments. Thus, the ferromagnetic ordering of the nearest neighbor Cu and Fe moments causes the magnetization for the  $x = 0.486$  compound to rise sharply below 20 K. However, below 13.5 K, Mn moments get ordered antiferromagnetically with respect to the Cu and Fe moments, causing the total magnetization to decrease with temperature. Since the ordered moment due to the Mn  $\{0.77 \times 4.90 = 3.77 \mu_B/\text{f.u.}\}$  is larger than the combined value of the Cu and Fe  $(0.73 \times 0.93 + 1 \times 2.33 = 3.01 \mu_B/\text{f.u.})$ , the total magnetization becomes negative below 8.8 K. Therefore, the different ordering temperatures of the ferromagnetic Cu, Fe and the antiferromagnetic Mn moments explain the observed negative magnetization in the present compound. Interestingly, the magneto-crystalline anisotropy plays an important role in achieving the negative magnetization in the present compound as it prevents the total magnetization to flip along the applied field direction below 8.8 K.

In conclusion, we have explained (experimentally) the microscopic origin of the observed negative magnetization in the PBA,  $\text{Cu}_{0.73}\text{Mn}_{0.77}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$  using the power of RMC simulation in combination with the Rietveld refinement technique. In the present study, the magnetic Bragg scattering contribution has been separated out from the nuclear and magnetic diffuse scattering contributions. The magnetic structure determination has, therefore, been achieved. The present work gives a microscopic experimental proof of the existing phenomenological theoretical understanding on the magnetic pole reversal in molecular magnets. This understanding can be effectively utilized not only to design new molecular magnetic compounds but also to tailor their magnetic properties for various applications. The phenomenon can be utilized to design devices such as volatile magnetic memories, thermomagnetic switches and magnetic cooling/heating devices. The experimental procedure used here to deter-

mine the microscopic magnetic structure using neutron scattering can, in fact, be used in many other situations where the weak magnetic scattering is masked by a strong diffuse scattering.

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