Rb_xBa_yMn_{[3-(x+2y)]/2}[Fe(CN)₆]_z·zH₂O prussian blue analogues: Controlling magnetic ordering by alkaline earth metal cation substitution and magnetic field

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We have controlled the nature of magnetic ordering in Rb_xBa_yMn_{[3-(x+2y)]/2}[Fe(CN)₆]_z·zH₂O prussian blue analogues by alkaline earth metal cation (Ba²⁺) substitution and application of an external magnetic field. Structural analysis, by employing Rietveld refinement of X-ray and neutron diffraction patterns, reveals a tetragonal crystal structure for all these compounds. The presence of Fe³⁺-C ≡ N-Mn²⁺ chains in the structure, and absence of both cyanide flipping (Mn²⁺-C ≡ N-Fe³⁺) and charge transfer from Mn²⁺ to Fe³⁺ (Fe²⁺-C ≡ N-Mn³⁺) have been confirmed by infrared and Mössbauer studies. The analysis of the low temperature neutron powder diffraction data reveals a long-range antiferromagnetic ordering in these compounds. The magnetic structure is layered, consisting of an antiparallel stacking of ferromagnetic sheets along the crystallographic *c*-direction. Within each sheet in the *ab* plane, the ordered moments of Mn²⁺ [5.04(1) μ_B for (x = 0.84, y = 0) and 4.99(7) μ_B for (x = 0.19, y = 0.3) sample at 1.5 K] and Fe³⁺ [0.98(3) μ_B for (x = 0.84, y = 0) and 0.99(3) μ_B for (x = 0.19, y = 0.3) sample at 1.5 K] are aligned ferromagnetically along the *c*-axis. Interestingly, dc magnetization study indicates that on application of an external magnetic field, an antiferromagnetic to ferrimagnetic-like phase transition occurs below ~5 K. This phase transition becomes more and more prominent with increasing magnetic field as well as for higher Ba substitution. The role of a number of factors (such as ionic radius of Ba²⁺ ion and change in net ligand strength around Mn due to chemical insertion of Ba²⁺ ions) on the affecting nature of magnetic ordering has been discussed. The observed magnetism in these compounds is seen in light of the orbital model of superexchange interaction between magnetic ions (Mn²⁺ and Fe³⁺) mediated by cyanide ligands. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3695453>]

I. INTRODUCTION

Technological demands for improved materials require designing new classes of magnetic materials. In this domain, designing molecular magnets^{1–4} by using molecular approaches (i.e., by appropriately changing the spin centers and the connecting organic/inorganic ligands using organic, organo-metallic, and/or coordination metal chemistry methods) is an emerging field of research. Molecular magnets show very interesting multifunctional behavior upon application of external stimuli, e.g., temperature, magnetic field, light, pressure, humidity, etc. Therefore, molecular magnets have an immense potential for their use in next generation smart sensors and devices. In molecular magnets, the prussian blue analogues (PBAs),^{5–27} with general formula A_nM_x{M'(CN)₆}_y·zH₂O (*M*, *M'* = transition metal ions, *A* = alkali/alkaline metal ions), form one of the most attractive classes. The PBAs exhibit a versatile behavior and have many important unique aspects such as (i) there is no change in their basic crystal structure on substitution of different transition metal ions at *M* and *M'* positions; (ii) the cyanide

ligand has a remarkable ability to transmit an effective magnetic exchange interaction between magnetic centers and the exchange interaction can be easily tuned by simple orbital symmetry rules; (iii) a wide range of physical properties can be accessed by varying the stoichiometry and composition (by changing the spin centers *M* and *M'*); and (iv) they show interesting properties, such as photo-induced magnetization,²³ pressure induced magnetization,²⁸ humidity induced magnetization,²¹ spin crossover,²⁹ etc. Such flexibilities make PBAs suitable for various important applications, such as waste recovery,³⁰ hydrogen storage,³¹ heterogeneous catalysis,^{32,33} molecular electronics,³⁴ etc.

For M_m[M'(CN)₆]_n·zH₂O PBA compounds with *m* > *n*, the charge neutrality demands that (1-(*n*/*m*)) [M'(CN)₆] sites are vacant and these are occupied by oxygen atoms of coordinated water molecules at the empty N sites. An insertion of interstitial alkali/alkaline metal cations in such PBAs brings about a reduction in the number of [M'(CN)₆] vacancies, i.e., reduction in coordinated water molecules, which in turn strengthens the ligand field around *M*. Thus by the judicious selection of alkali/alkaline metal ions, one can control the basic factors governing the interesting physical behavior of PBAs. Until now, most of the PBAs have been studied with *A* = Na⁺, K⁺, Cs⁺, and Rb⁺. The Na_nCo_x[Fe(CN)₆]_y·zH₂O, K_nCo_x[Fe(CN)₆]_y·zH₂O,

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$\text{Cs}_n\text{Co}_x[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ PBAs exhibit a photomagnetic effect, i.e., photo-induced increase in magnetization and transition temperature.^{23,35} The $\text{RbMn}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ PBA has been studied extensively and it shows a temperature- and photo-induced phase transition.²⁹ This compound displays a drop in the magnetic susceptibility at 225 K and an abrupt increase in the magnetic susceptibility at 300 K in the cooling and warming processes, respectively. This magnetic phase transition is accompanied by a structural change from a face centered cubic to a tetragonal structure. It is reported that a metal-to-metal charge transfer from Mn^{2+} to Fe^{3+} and a Jahn-Teller distortion of the produced Mn^{3+} ion cause the structural and magnetic phase transitions. The high-temperature (HT) crystallographic phase is composed of Mn^{2+} ($S = 5/2$), and Fe^{3+} ($S = 1/2$) ions while the low-temperature (LT) phase is composed of Mn^{3+} ($S = 2$), and Fe^{2+} ($S = 0$) ions. Recently, PBAs with alkaline earth metal cations substitution at A site were investigated by some of us.²⁷ A detailed study on structural disorder for $\text{Ba}_x\text{Mn}[\text{Fe}(\text{CN})_6]_{2(x+1)/3} \cdot z\text{H}_2\text{O}$ ($x = 0$ and 0.3) (Ref. 27) PBAs was carried out by reverse Monte Carlo (RMC) simulations of neutron diffraction data. In that report, we have established a decrease in the amount of structural disorder with Ba substitution. The electron configuration for alkaline earth metals is ns^2 (two valence electrons) while for alkali metals, the configuration is ns^1 (one valence electron). The alkaline earth metals have higher ionization energies as compared to that of alkali metals. Further, in alkaline earth metals, the ionic radius of Ba^{2+} (135 pm) lies between that of Na^+ (102 pm) and Rb^+ (152 pm). The chemical insertion of Ba^{2+} ions in $\text{RbMn}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ PBA may change net ligand strength around Mn and also cause an internal strain in the structure thereby altering structural parameters which in turn affects the nature of magnetic ordering. In the present study, we have, therefore, prepared $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ [$(x = 0.84, y = 0)$, $(x = 0.67, y = 0.08)$, $(x = 0.55, y = 0.19)$, $(x = 0.38, y = 0.28)$, and $(x = 0.19, y = 0.3)$] compounds and their single phase nature is established by X-ray and neutron diffraction studies. Here, we have brought out various aspects of magnetism and magnetic ordering viz. (i) the nature of the magnetic ground state, (ii) its evolution under temperature and applied magnetic field, and (iii) the effect of ionic size on magnetic ordering due to the substitution of Ba^{2+} . Besides, the presence of $\text{Fe}^{3+}\text{-C} \equiv \text{N-Mn}^{2+}$ chains in the crystal structure, and the absence of a cyanide flipping as well as any charge transfer from Mn^{2+} to Fe^{3+} have been established by carrying out infrared (IR) and Mössbauer spectroscopic experiments. Interestingly, a ferrimagnetic-like ordering of Mn^{2+} ($S = 5/2$) spins and Fe^{3+} ($S = 1/2$) spins at temperatures below ~ 5 K is evident from our dc magnetization study. However, an antiferromagnetic (AFM) ground state is confirmed in the low temperature neutron diffraction study under zero applied magnetic field. The present work, therefore, indicates an antiferromagnetic to a ferrimagnetic-like phase transition on application of external magnetic field and provides an understanding as to how the magnetic ordering in PBAs can be altered by using externally applied magnetic field. The outcome of our study is very significant as it can be exploited in the rational design of PBAs molecular magnets, suited for their practical applications.

II. EXPERIMENTAL SECTION

Polycrystalline $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ [$(x = 0.84, y = 0)$, $(x = 0.67, y = 0.08)$, $(x = 0.55, y = 0.19)$, $(x = 0.38, y = 0.28)$, and $(x = 0.19, y = 0.3)$] compounds were synthesized by a co-precipitation method, maintaining the charge neutrality. The required amount of aqueous solutions of 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]$, 0.4 M BaCl_2 , and 0.4 M RbCl were prepared separately. The prepared solutions were mixed thereafter and heated up to 80°C . A required amount of 0.1 M aqueous solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, heated up to about 80°C , was added slowly to the continuously stirred mixture of 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]$, 0.4 M BaCl_2 , and 0.4 M RbCl . The precipitate of the required composition formed at once. The hot solution containing the precipitate was allowed to cool at room temperature. The precipitate was filtered, washed many times with doubly distilled water and ethanol as well, and finally allowed to dry in air. The dried precipitate was ground to a very fine powder.

X-ray diffraction (XRD) measurements were performed on all the samples at room temperature in the scattering angular (2θ) range of 10° – 60° in equal 2θ steps of 0.02° using a Cu-K_α radiation. Low temperature (1.5–13.5 K) neutron diffraction patterns on two selected compounds [$(x = 0.84, y = 0)$, and $(x = 0.19, y = 0.3)$] in the series were recorded at the DMC powder diffractometer ($\lambda = 2.4585 \text{ \AA}$), SINQ, Paul Scherrer Institute, Switzerland. The infrared (IR) spectra were recorded in the range of 1900 – 2350 cm^{-1} by loading the samples in a KBr pellet on a Bruker VERTEX 80v FT-IR spectrometer. The dc magnetization measurements were carried out on all the samples using a commercial (Oxford Instruments) vibrating sample magnetometer (VSM) and a SQUID magnetometer as a function of both temperature and magnetic field. For the zero-field-cooled (ZFC) measurements, the samples were cooled in the absence of a magnetic field down to the lowest temperature of 1.8 K and the measurements were carried out in the warming cycle under an applied magnetic field. For the corresponding field-cooled (FC) measurements, the samples were cooled in the presence of a magnetic field (the same as the measuring field in the ZFC case) and then measurements were carried out in the warming cycle with field on. In our dc magnetization measurements, the sample cooling rate was kept at 10 K/min and the warming rate was kept at 3 K/min. The Mössbauer spectrum has been obtained using a spectrometer operated in a constant acceleration mode (triangular wave) in the transmission geometry. The source employed is Co-57 in Rh matrix of strength 50 mCi. The calibration of the velocity scale is done by using a α -Fe metal foil. The outer linewidth of the calibration spectra is 0.29 mm/s. Mössbauer spectra were fitted by a least square fit program (MOSFIT) assuming Lorentzian line shapes. The observed isomer shift is relative to that of a Fe-metal foil.

III. RESULTS

A. Characterization of the samples by XRD, IR, and Mössbauer spectroscopy

Figure 1 shows the observed and Rietveld refined X-ray diffraction patterns for $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$

FIG. 1. (Color online) Observed (open circles) and calculated (solid lines) X-ray diffraction patterns for $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ at room temperature. Solid line at the bottom of each curve is the difference between observed and calculated patterns. Vertical lines at the bottom of each panel show the position of allowed Bragg peaks. The (hkl) values corresponding to the Bragg peaks are also given.

[($x = 0.84$, $y = 0$), ($x = 0.67$, $y = 0.08$), ($x = 0.55$, $y = 0.19$), ($x = 0.38$, $y = 0.28$), and ($x = 0.19$, $y = 0.3$)] samples at room temperature. The structural refinement was performed with the Rietveld refinement technique using the Fullprof Program³⁶ in the WINPLOTR suite of programs. Refinement shows the single phase nature of all samples with tetragonal structure (space group: $I-4m2$). The important structural parameters (atomic coordinates, and site occupancies), derived from the analysis, are given in Table I. The crystal structure of these compounds consists of a three-dimensional network of $\text{Mn-N} \equiv \text{C-Fe}$ chains along (001) and (110) directions of unit cell (Fig. 2(a)). Due to stoichiometry of these compounds, some of the Fe ($2a$), C ($8g$), and N ($8g$) sites are vacant and the O atoms of the coordinated water molecules occupy the empty N sites. The lattice constants (a and c) show a small decrement with increase in Ba concentration (Fig. 2(b)).

The presence of $\text{Mn-N} \equiv \text{C-Fe}$ chains in the structure of these compounds was confirmed by carrying out the IR spectral study (Fig. 3). In the case of a non-bridging $\text{Fe}^{3+}\text{-CN}$ (i.e., nitrogen end of the CN ligand is uncoordinated), the CN stretching frequency is 2128 cm^{-1} . In the literature it is reported that the CN stretching frequency increases by approximately $30\text{--}70\text{ cm}^{-1}$ when the nitrogen end of the CN ligand is coordinated to the other metal ion.³⁷ In Fig. 3, the frequency f_1 centered at 2151 cm^{-1} corresponds to the CN stretching mode Mn-NC-Fe .²⁹ Another absorption band on the low wave number side at 2130 cm^{-1} (f_2) is also present for all the compounds. The origin of f_2 will be explained while discussing the results of Mössbauer spectroscopy.

TABLE I. Results of the Rietveld refinement for $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ samples (x' , y' , and z' denote the fractional coordinates).

Composition (x , y)	Atom	Wyckoff site	x'	y'	z'	Occupancy
0.84, 0	Fe	$2a$	0	0	0	1.0
	Mn	$2b$	0	0	0.5	1.08
	Rb1	$2c$	0	0.5	0.25	0.38
	Rb2	$2d$	0	0.5	0.75	0.46
	C	$8g$	0.184	0.184	0	6.0
	N	$8g$	0.281	0.281	0	6.0
	O	$8g$	0.281	0.281	0	0.44
0.67, 0.08	Fe	$2a$	0	0	0	1.0
	Mn	$2b$	0	0	0.5	1.08
	Rb1	$2c$	0	0.5	0.25	0.31
	Rb2	$2d$	0	0.5	0.75	0.36
	Ba1	$2c$	0	0.5	0.25	0.06
	Ba2	$2d$	0	0.5	0.75	0.02
	C	$8g$	0.185	0.185	0	6.0
	N	$8g$	0.291	0.291	0	6.0
	O	$8g$	0.291	0.291	0	0.28
0.55, 0.19	Fe	$2a$	0	0	0	1.0
	Mn	$2b$	0	0	0.5	1.03
	Rb1	$2c$	0	0.5	0.25	0.27
	Rb2	$2d$	0	0.5	0.75	0.28
	Ba1	$2c$	0	0.5	0.25	0.09
	Ba2	$2d$	0	0.5	0.75	0.1
	C	$8g$	0.183	0.183	0	6.0
	N	$8g$	0.291	0.291	0	6.0
	O	$8g$	0.291	0.291	0	0.47
0.38, 0.28	Fe	$2a$	0	0	0	1.0
	Mn	$2b$	0	0	0.5	1.03
	Rb1	$2c$	0	0.5	0.25	0.14
	Rb2	$2d$	0	0.5	0.75	0.24
	Ba1	$2c$	0	0.5	0.25	0.12
	Ba2	$2d$	0	0.5	0.75	0.16
	C	$8g$	0.195	0.195	0	6.0
	N	$8g$	0.289	0.289	0	6.0
	O	$8g$	0.289	0.289	0	0.54
0.19, 0.3	Fe	$2a$	0	0	0	1.0
	Mn	$2b$	0	0	0.5	1.1
	Rb1	$2c$	0	0.5	0.25	0.11
	Rb2	$2d$	0	0.5	0.75	0.08
	Ba1	$2c$	0	0.5	0.25	0.11
	Ba2	$2d$	0	0.5	0.75	0.19
	C	$8g$	0.205	0.205	0	6.0
	N	$8g$	0.281	0.281	0	6.0
	O	$8g$	0.281	0.281	0	0.48

To bring forth a clear quantitative picture regarding the valence and spin states of the Fe ions in these compounds, Mössbauer spectral study (Fig. 4) was carried out at room temperature on one of these samples ($x = 0.84$, $y = 0$). The observed spectrum is fitted with two components having isomer shifts (δ) of -0.18 and -0.0232 mm/s and quadrupole splittings (ΔE_q) of 0.3688 and 0.3020 mm/s , respectively. The linewidths for these two components are 0.2864 and 0.2221 mm/s , respectively. The majority of the Fe ions ($81.04 (\pm 0.02)\%$), having $\delta = -0.18\text{ mm/s}$ and $\Delta E_q = 0.3688\text{ mm/s}$ values and shown by a bigger doublet in the fitted spectra, correspond to the low-spin state of Fe^{3+} ions

FIG. 2. (Color online) (a) Crystal structure of $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ compounds. Water molecules are omitted for clarity. (b) Variation of lattice constants (a and c) with Ba concentration at room temperature. The data points are shown along with error bars.

($S = 1/2$). Similar values of hyperfine parameters were found for the low-spin Fe^{3+} ions in the $\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 4 \text{H}_2\text{O}$,⁹ $\text{Cu}_{1.5}[\text{Fe}(\text{CN})_6] \cdot 6 \text{H}_2\text{O}$,³⁸ and $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 7 \text{H}_2\text{O}$ (Ref. 39) compounds. The remaining Fe ions ($18.96 (\pm 0.02)$

FIG. 3. (Color online) IR absorption spectra for all the compounds at room temperature. The patterns are shifted relative to each other for better visibility.

FIG. 4. (Color online) Mössbauer spectrum of $(x = 0.84, y = 0)$ compound at room temperature. Open circles show the observed data and the thick solid line is the least square fitted curve. Two thin solid lines represent the components of the least square fitted curve.

%) are having $\delta = -0.0232 \text{ mm/s}$ and $\Delta E_q = 0.3020 \text{ mm/s}$, shown as a smaller doublet in the fitted spectra. These values of $\delta = -0.0232 \text{ mm/s}$ and $\Delta E_q = 0.3020 \text{ mm/s}$ also correspond to the low-spin state of Fe^{3+} ions ($S = 1/2$), however, with a different chemical environment around Fe^{3+} . The derived values of hyperfine parameters manifest the presence of low spin Fe^{3+} ions, occupying $2a$ site, in two different chemical environments created by interstitial Rb^+ ions. From our X-ray diffraction study, it is evident that Rb ions are located at both $2c$ ($0, 1/2, 1/4$) and $2d$ ($0, 1/2, 3/4$) crystallographic positions (see Table I) and it gives rise to two distinct chemical environments around Fe ions. This fact is also confirmed from the neutron diffraction study, presented later. The presence of such two different chemical environments around low spin Fe^{3+} has been previously reported.^{40,41} The increased s -electron charge density at Fe^{3+} nucleus as compared to standard metallic Fe, brings about the observed negative isomer shift in these compounds.

We now discuss further the Mössbauer and the IR results to gain insight in crystal structure. The doublets appearing in the Mössbauer spectrum (Fig. 4) can be assigned to the sequences $\text{Fe}^{3+}\text{-C} \equiv \text{N-Mn}^{2+}$ in the compound (which appear in the IR spectra at $f_1 = 2151 \text{ cm}^{-1}$). The absorption line f_2 (2130 cm^{-1}) in the IR spectra may originate due to the presence of various CN stretching frequencies in the compounds (i) $\text{Mn}^{2+}\text{-C} \equiv \text{N-Fe}^{3+}$ chains may develop due to flipping of CN.^{10,11,37,42,43} If the Fe ion is bonded to N, a higher 3d electron density on Fe^{3+} ion causes a reduced s -electron density at the Fe^{3+} nucleus and gives a positive isomer shift. However, the absence of any positive isomer shift in the Mössbauer spectrum refutes the possibility of cyanide flipping ($\text{Mn}^{2+}\text{-C} \equiv \text{N-Fe}^{3+}$); (ii) $\text{Fe}^{2+}\text{-C} \equiv \text{N-Mn}^{3+}$ chains may develop due to charge transfer from Mn^{2+} to Fe^{3+} .²⁹ In this case, the presence of low spin Fe^{2+} ($S = 0$) ions should be reflected as a singlet with $\Delta E_q = 0$ in the Mössbauer spectrum (due to zero contribution of 3d electrons of Fe^{2+} ($S = 0$) ions toward the electrical field gradient). However, the absence of any component with $\Delta E_q = 0$ refutes the possibility of any charge transfer from

Mn^{2+} to Fe^{3+} ($\text{Fe}^{2+}\text{-C} \equiv \text{N-Mn}^{3+}$); and (iii) the absorption f_2 can be assigned to $\text{Fe}^{3+}\text{-C} \equiv \text{N}$ sequences, which may arise due to an excess of the starting material $\text{K}_3[\text{Fe}(\text{CN})_6]$ during the synthesis of the compounds. This conclusion is also supported by the fact that the value of the observed f_2 band is very close to the CN stretching frequency 2128 cm^{-1} for a non-bridging $\text{Fe}^{3+}\text{-CN}$.

B. Ground state magnetic structure by neutron diffraction study

To determine the ground state magnetic structure of these compounds, neutron diffraction patterns were recorded under zero magnetic field at various temperatures for $(x = 0.84, y = 0)$ and $(x = 0.19, y = 0.3)$ compounds in the paramagnetic state as well as in the magnetically ordered state. A simultaneous nuclear and magnetic structure refinement was carried out by the Rietveld refinement technique using the Fullprof Program.³⁶ Neutron data analysis demonstrated that the crystal structure could be well refined using $I-4m2$ space group similar to the X-ray diffraction case, and the derived structural parameters are consistent with those obtained from the X-ray diffraction data analysis (see Table I). The Rietveld refined neutron diffraction patterns for the compound with $x = 0.84$, and $y = 0$ at 1.5 and 13.5 K and for the compound with $x = 0.19$, and $y = 0.3$ at 1.5 and 10.6 K are shown in Fig. 5. The appearance of extra Bragg peaks at 1.5 K in Fig. 5 at scattering vector magnitudes, $Q \sim 0.84\text{ \AA}^{-1}$, $1.33\text{ \AA}^{-1}$, and $1.79\text{ \AA}^{-1}$, where any nuclear Bragg reflection is forbidden for the space group $I-4m2$, confirms a 3 D long-range antiferromagnetic ordering for both samples. The extra

FIG. 5. (Color online) Rietveld refined neutron-diffraction patterns of (a) $(x = 0.84, y = 0)$ at 1.5 K, (b) $(x = 0.84, y = 0)$ at 13.5 K, (c) $(x = 0.19, y = 0.3)$ at 1.5 K, and (d) $(x = 0.19, y = 0.3)$ at 10.6 K. The observed and calculated diffraction patterns are indicated by circles and solid line, respectively. Solid line at the bottom shows the difference between observed and calculated patterns. Vertical lines at the bottom show the positions of magnetic Bragg peaks (space group: $P-1$) at 1.5 K only and nuclear Bragg peaks (space group $I-4m2$). The magnetic peaks observed at 1.5 K are labeled with asterisks.

(magnetic) Bragg peaks were indexed as (100), (111), and (201) with respect to the chemical unit cell. The size of the magnetic unit cell is found to be same as the chemical unit cell. The values of the Mn^{2+} and Fe^{3+} ordered magnetic moments for the $(x = 0.84, y = 0)$ and $(x = 0.19, y = 0.3)$ compounds have been plotted as a function of temperature in Figs. 6(a) and 6(b). The Néel temperatures (T_N) of 13.5 K for $(x = 0.84, y = 0)$ compound and 10.6 K for $(x = 0.19, y = 0.3)$ compound are evident from Figs. 6(a) and 6(b). For the $(x = 0.84, y = 0)$ sample, the ordered moments of $5.04(1)\text{ }\mu_B$ per Mn ion and $0.98(3)\text{ }\mu_B$ per Fe ion at 1.5 K are found to align along the crystallographic c -direction. For the $(x = 0.19, y = 0.3)$ sample, the ordered moments of $4.99(7)\text{ }\mu_B$ per Mn ion and $0.99(3)\text{ }\mu_B$ per Fe ion at 1.5 K are found to align along the crystallographic c -directions. The observed ordered moment values are consistent with the theoretically estimated ordered moment of $5\mu_B$ for $\text{Mn}^{2+}(t_{2g}^3e_g^2, S = 5/2)$ ion and $1\text{ }\mu_B$ for $\text{Fe}^{3+}(t_{2g}^5e_g^0, S = 1/2)$ ion. The analysis of the neutron diffraction patterns reveals that both compounds

FIG. 6. (Color online) Temperature evolution of the Mn^{2+} and Fe^{3+} ordered magnetic moments in (a) $(x = 0.84, y = 0)$ and (b) $(x = 0.19, y = 0.3)$ compounds. (c) Magnetic structure (ground state) at 1.5 K (one unit cell is shown). Large (red) arrows and small (blue) arrows correspond to the ordered Mn^{2+} and Fe^{3+} magnetic moments, respectively, along the crystallographic c -axis. Layer 1 and 2 denote the layers of magnetic ions in ab plane. Magnetic orbitals are also shown along z (c) axis and in xy (ab) plane to view the superexchange pathways between Mn^{2+} and Fe^{3+} ions via the CN ligand.

have a layered antiferromagnetic structure in which the magnetic coupling between layers (e.g., between layers 1 and 2) is antiferromagnetic (Fig. 6(c)). Within a layer, Mn ($S = 5/2$) and Fe ($S = 1/2$) spins are aligned in the parallel direction. In Fig. 6(c), magnetic orbitals are also shown along the z (c) axis and in the xy (ab) plane to view the superexchange pathways between Mn^{2+} and Fe^{3+} ions via the CN ligand. This discussion will be given later. The spin values of Mn and Fe obtained from our neutron diffraction study also confirm the absence of (i) cyanide flipping, (ii) Fe^{2+} ions, and (iii) Mn^{3+} ions in these compounds, as manifested from our Mössbauer study.

C. Low field dc magnetization study

The nature of magnetic ordering in the compounds has been further determined by carrying out dc magnetization study at low magnetic field. The temperature dependence of the ZFC and FC dc magnetization M for all the samples under 100 Oe is shown in Fig. 7. There is an onset of magnetic ordering below ~ 20 K for all the compounds. It can be seen that as Ba concentration (y) increases, a hump appears over the temperature range of 5–17 K. As temperature is further decreased below ~ 5 K, there is a sharp increase in magnetization indicating a long-range magnetic ordering. The appearance of hump indicates that either a short-range magnetic ordering is present over 5–17 K in the Ba substituted samples or some kind of magnetic transition is taking place over 5–17 K. Figure 8(a) shows the χT versus T curves for all compounds in the 5–50 K temperature range, where χ is

FIG. 7. (Color online) dc magnetization vs temperature curves under FC and ZFC modes at 100 Oe field. Arrows indicate the appearance of the hump over 5–17 K with Ba substitution.

FIG. 8. (Color online) (a) χT vs T curves (obtained from FC dc magnetization curves) for all compounds over the temperature range 5–50 K, and (b) variation of θ_p with Ba concentration (y).

the dc magnetic susceptibility. It may be noted that χT versus T curves first start increasing below ~ 20 K, increase to a maximum at ~ 10 K, then decrease to a minimum ~ 4 K, before rising again. For a ferrimagnet, the χT versus T curve shows a minimum before rising to a maximum with decreasing temperature around the paramagnetic to ferrimagnetic transition temperature. Thus, the present compounds show a ferrimagnetic-like character below ~ 4 K. In the paramagnetic region, the χ^{-1} versus T curves (not shown) for all compounds follow the Curie-Weiss law $\chi = C/(T - \theta_p)$, where C is the Curie constant and θ_p is the paramagnetic Curie temperature. The effective paramagnetic moment (μ_{eff}) per formula unit is derived by putting the value of C (found from the Curie-Weiss fit of the experimental data) in the formula $\mu_{eff} = (3Ck_B/N_A)^{1/2} \mu_B \sim (8C)^{1/2} \mu_B$, where N_A is the Avogadro's number and k_B is the Boltzmann constant. The theoretically expected (spin only) μ_{eff} is calculated by using the formula $\mu_{eff}^2 = \Sigma(g^2 \{n \cdot S(S+1)\}) \mu_B^2$, where g is gyromagnetic ratio (~ 2), n is the number of magnetic ions with spin S in the formula unit, and summation (Σ) runs overall magnetic ions in the formula unit. We found that with the spin values $S = 5/2$ for Mn^{2+} and $S = 1/2$ for Fe^{3+} , the experimental values of μ_{eff} [6.38, 6.44, 6.38, 6.27, 6.39 $\mu_B/\text{f.u.}$ for the samples with increasing y] are close to the theoretically calculated values of μ_{eff} [6.39, 6.41, 6.28, 6.25, 6.44 $\mu_B/\text{f.u.}$ for samples with increasing y]. The derived negative values of θ_p [Fig. 8(b)] for all compounds suggest the presence of dominant negative (antiferromagnetic) exchange interactions for all compounds. The observed spin states of Mn^{2+} and Fe^{3+} ions can be viewed under the framework of ligand field theory. The CN ligand field induces a high spin configuration $t_{2g}^3 e_g^2$ with spin $S = 5/2$ for Mn^{2+} ions and low spin configuration $t_{2g}^5 e_g^0$ with spin $S = 1/2$ for Fe^{3+} ions.^{9,44}

D. High field dc magnetization study

Neutron diffraction measurements (under zero magnetic field) revealed an antiferromagnetic ground state while a

ferrimagnetic-like ordering (under the influence of external magnetic field) was evident from the dc magnetization measurements (Figs. 7 and 8). Therefore, high field dc magnetization measurements have also been carried out to ascertain the nature of magnetic ordering in these compounds under magnetic field. Figure 9(a) shows dc magnetization versus temperature plots in ZFC mode for all the samples at 5 kOe magnetic field. It can be seen that the hump over 5–17 K temperature range is much more prominent at 5 kOe as compared to that at 100 Oe (Fig. 7). Figure 9(b) shows the M versus magnetic field (H) curves for all the compounds at 1.8 K. Theoretically expected (spin only) values of ordered magnetic moment per formula unit are calculated by using the formula $M_s = \sum(gnS) \mu_B$, where g is the gyromagnetic ratio (~ 2), n is the number of magnetic ions with spin S in the formula unit, and summation ($\sum$) runs overall magnetic ions in the formula unit. Theoretical M_s is calculated by considering a ferrimagnetic ordering of $\text{Mn}^{2+}(t_{2g}^3 e_g^2, S = 5/2)$ spins and the low spin $\text{Fe}^{3+}(t_{2g}^5 e_g^0, S = 1/2)$ spins; consistent with the experimental and theoretical μ_{eff} . We found that for all Ba concentrations (y), the experimental values of M_s [3.96, 3.90, 4.11, 4.08, and 4.22 $\mu_B/\text{f.u.}$ for the samples with increasing y] are lower than the theoretically calculated values of M_s [4.40, 4.42, 4.20, 4.15, 4.50 $\mu_B/\text{f.u.}$ for samples with increasing y]. It can be seen from Fig. 9(b) that magnetization is not saturated at 1.8 K even under an applied magnetic field of 60 kOe, which explains the discrepancy between experimentally observed and theoretically calculated values of M_s .

FIG. 9. (Color online) (a) dc magnetization vs temperature curves under the ZFC mode at 5 kOe field. Inset shows an enlarged view of 1.8–20 K temperature regions, and (b) M vs H curves for all compounds at 1.8 K.

IV. DISCUSSION

The above discussed results of dc magnetization and neutron diffraction studies led us to conclude the following points: (i) the compounds have an antiferromagnetic ground state; (ii) the nature of the antiferromagnetic ordering is always long-range, and (iii) in the presence of an external magnetic field, the compounds undergo an antiferromagnetic to a ferrimagnetic-like transition. The possible exchange pathways between Mn^{2+} and Fe^{3+} ions are shown in Figs. 10(a) and 10(b). In accordance with the Goodenough-Kanamori-Anderson (GKA) rules,^{45,46} the superexchange interaction between Mn^{2+} and Fe^{3+} ions via the $2p_\pi$ orbital of CN is antiferromagnetic. On the other hand, the superexchange interaction between Mn^{2+} and Fe^{3+} ions via the $2p_\sigma$ orbital of CN is ferromagnetic. In the cases when both t_{2g} and e_g magnetic orbitals are simultaneously present on transition metal ion M , ferromagnetic and antiferromagnetic interactions with the t_{2g} magnetic orbitals on $[M'(\text{CN})_6]$ coexist and compete.⁴⁷ In our case, we have seen that both ferromagnetic (between e_g and t_{2g} via $2p_\sigma$) as well as antiferromagnetic (between t_{2g} and t_{2g} via $2p_\pi$) exchange interactions are possible [Figs. 10(a) and 10(b)] between $\text{Mn}^{2+}(t_{2g}^3 e_g^2, S = 5/2)$ and $\text{Fe}^{3+}(t_{2g}^5 e_g^0, S = 1/2)$ spins. To further explain the exchange interactions, a schematic illustration of the coupling of magnetic orbitals of Mn^{2+} and Fe^{3+} ions via CN orbitals along z (c) axis and in xy (ab) plane, shown in Fig. 6 (c), can be considered. An antiferromagnetic interaction prevails between Mn^{2+} and Fe^{3+} spins along the crystallographic z (c) axis, while a ferromagnetic interaction prevails between Mn^{2+} and Fe^{3+} spins in the xy (ab) plane. Consequently, the ground state of these compounds is of layered antiferromagnetic type, as shown in Fig. 6(c). On the other hand, our dc magnetization measurements indicate a ferrimagnetic-like ordering under the influence of external magnetic field. The spin configuration under external field is, therefore, different from the observed magnetic ground state

FIG. 10. (Color online) (a) Superexchange interaction between t_{2g} - t_{2g} orbitals of Mn^{2+} and Fe^{3+} ions via $2p_\pi$ orbital of CN ligand. Dotted arrow shows a virtual electron (spin-down) transfer from $2p_\pi$ (of CN) to t_{2g} of the Mn^{2+} ion. The unpaired electron in the t_{2g} state of the Fe^{3+} ion then orients downwards to get coupled antiferromagnetically with the remaining spin up electron in $2p_\pi$ of CN (due to non-orthogonal coupling of $2p_\pi$ - t_{2g} orbitals); (b) Superexchange interaction between e_g - t_{2g} orbitals of Mn^{2+} and Fe^{3+} ions via the $2p_\sigma$ orbital of the CN ligand. Dotted arrow shows a virtual electron (spin-down) transfer from $2p_\sigma$ (of CN) to e_g of the Mn^{2+} ion. The unpaired electron in the t_{2g} state of the Fe^{3+} ion then couples ferromagnetically with the remaining spin up electron in $2p_\sigma$ of CN (due to orthogonal coupling of $2p_\sigma$ - t_{2g} orbitals).

(an antiparallel stacking of ferromagnetic sheets along c -direction) derived from the present neutron diffraction study.

Now we will compare the results of our study on $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ PBA compounds with those reported in literature for various alkali metal ions containing PBAs. The alkali metal ion Rb containing PBA $\text{RbMn}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ (Ref. 29) is reported to show a structural phase transformation from ($F\bar{4}3m$) to tetragonal ($I\bar{4}m2$) upon cooling. However, the present Ba-substituted compounds do not show any structural phase transformation and the crystal structure is tetragonal (space group: $I\bar{4}m2$) at all temperatures. This is due to the small cationic size of Ba^{2+} (135 pm) as compared to Rb^+ (152 pm) as well as different stoichiometric ratio Rb : Mn : Fe. The PBA compound $\text{RbMn}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ is also reported to display a temperature induced change in magnetic susceptibility due to a metal-to-metal charge transfer from Mn^{2+} to Fe^{3+} ions.²⁹ However, under the cooling/warming rates employed in our magnetization measurements, our studied compounds neither show temperature induced change in magnetic susceptibility nor any charge transfer from Mn^{2+} to Fe^{3+} . Tokoro *et al.*⁴⁸ reported that the compound $\text{Rb}_{0.58}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.86}\cdot 2.3 \text{ H}_2\text{O}$ has a tetragonal structure with space group $P4/mmm$. Our studied system $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ shows a tetragonal structure with space group $I\bar{4}m2$. The compound $\text{Rb}_{0.58}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.86}\cdot 2.3 \text{ H}_2\text{O}$ was reported to order magnetically below 11.5 K in an antiferromagnetic state. The magnetic structure of this compound consisted of ferromagnetic stacking of antiferromagnetic sheets along the c -direction. Each sheet consists of Mn^{2+} and Fe^{3+} moments aligning in opposite direction along the c -axis. Our studied compounds also show a long-range antiferromagnetic ordering down to 1.5 K. However, the magnetic structure consists of an antiparallel stacking of ferromagnetic sheets along the c -direction. The nature of the exchange interaction within the ab plane and along the c -axis is different. An antiferromagnetic coupling operates between Mn t_{2g} magnetic orbitals and Fe t_{2g} magnetic orbitals along the z (c) axis and a ferromagnetic coupling operates between the Mn e_g magnetic orbital and Fe t_{2g} magnetic orbital in the ab plane.

A number of PBA compounds, e.g., $\text{Na}_n\text{Co}_x[\text{Fe}(\text{CN})_6]_y\cdot z\text{H}_2\text{O}$, $\text{K}_n\text{Co}_x[\text{Fe}(\text{CN})_6]_y\cdot z\text{H}_2\text{O}$, $\text{Cs}_n\text{Co}_x[\text{Fe}(\text{CN})_6]_y\cdot z\text{H}_2\text{O}$ PBAs, etc. are reported to exhibit a reversible photoinduced magnetization.^{23,35} This photomagnetism is based on the charge transfer-induced spin transition between two phases by photo stimuli: one phase consists of the $\text{Fe}^{2+}(t_{2g}^6e_g^0, \text{LS}, S=0)$ -CN- $\text{Co}^{3+}(t_{2g}^6e_g^0, \text{LS}, S=0)$ sequences and the other consists of the $\text{Fe}^{3+}(t_{2g}^5e_g^0, \text{LS}, S=1/2)$ -CN- $\text{Co}^{2+}(t_{2g}^5e_g^2, \text{HS}, S=3/2)$ sequences. The presence of these two phases was confirmed by Mossbauer and IR spectroscopy in these reports. However, our studied $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ PBA compounds consist of only $\text{Fe}^{3+}(t_{2g}^5e_g^0, \text{LS}, S=1/2)$ -CN- $\text{Mn}^{2+}(t_{2g}^3e_g^2, \text{HS}, S=5/2)$ sequences. There is no signature of any phase consisting of Fe^{2+} ions with $S=0$ and thus our studied compounds are not expected to exhibit photoinduced switching of magnetic states. On the contrary, we have found a magnetic field induced switching of magnetic states from antiferromagnetic to ferrimagnetic-like. The magnetic state of our studied

compounds is determined by a competition between possible antiferromagnetic and ferromagnetic superexchange interactions between Mn^{2+} and Fe^{3+} moments (rather than a charge transfer, found for compound $\text{K}_n\text{Co}_x[\text{Fe}(\text{CN})_6]_y\cdot z\text{H}_2\text{O}$). Moreover, in the present study, a magnetic transition occurs at low temperatures, which becomes more and more prominent with increasing Ba concentration. The effect of chemical insertion of Ba^{2+} ions on establishing magnetic ordering may be linked to a number of facts, as discussed in the Introduction, the different electronic configuration, ionization energy, ionic radius of Ba and change in net ligand strength around Mn.

In the area of molecular magnetic compounds, preparation of tunable compounds (i.e., those in which magnetic properties can be controlled by an external stimuli) is an important objective. The present study demonstrates it successfully. Such tunable compounds can be used for future molecular memory and switching devices. Furthermore, in our study, the magnetic properties respond to external perturbations of ionic substitution, temperature and magnetic field in a unique way and it gives us an insight into the intrinsic (structural, electronic, and magnetic) nature of these PBA compounds.

V. SUMMARY AND CONCLUSIONS

In summary, we have shown that the magnetic state in $\text{Rb}_x\text{Ba}_y\text{Mn}_{[3-(x+2y)]/2}[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O}$ PBA compounds can be controlled by an alkaline earth metal cation (Ba^{2+}) substitution and externally applied magnetic field. The structure of the Ba-substituted PBAs is tetragonal with space group $I\bar{4}m2$. The lattice constants show a small decrement with increase in Ba concentration. The location of Rb^+ and Ba^{2+} cations at two different crystallographic sites [$2c$ (0, 1/2, 1/4) and $2d$ (0, 1/2, 3/4)] gives rise to two distinct chemical environments around Fe^{3+} ions, leading to two different values of negative isomer shift in the Mössbauer spectrum. IR study indicates the presence of $\text{Fe}^{3+}\text{-C} \equiv \text{N-Mn}^{2+}$ chains in the structure of these compounds, a fact which is confirmed by the Mössbauer spectroscopic study. Our IR study also hints toward the possibility of presence of $\text{Mn}^{2+}\text{-C} \equiv \text{N-Fe}^{3+}$ and $\text{Fe}^{2+}\text{-C} \equiv \text{N-Mn}^{3+}$ chains in these compounds due to CN flipping and metal-to-metal charge transfer from Mn^{2+} to Fe^{3+} , respectively. However, our Mössbauer and neutron diffraction studies clearly refute such possibilities. Magnetization (M) versus temperature (T) measurements (under 100 Oe field) in both FC and ZFC conditions show that a broad hump appears over a temperature range of T_N [13.5 K for ($x=0.84, y=0$) compound and 10.6 K for ($x=0.19, y=0.3$) compound] to 5 K indicating the presence of a short-range spin-spin correlation or some kind of magnetic transition. The broad hump becomes more prominent with increasing Ba^{2+} concentration. As temperature is further decreased below ~ 5 K, there is a sharp increase in magnetization indicating the appearance of a long-range magnetic ordering at $T < 5$ K. Moreover, as magnetic field is increased to ~ 5 kOe, the hump becomes more prominent. M versus magnetic field measurements at 1.8 K indicate a ferrimagnetic-like ordering between Mn^{2+} ($S=5/2$) spins and Fe^{3+} ($S=1/2$) spins. The

appearance of extra Bragg peaks in the neutron diffraction patterns under zero external magnetic field, where the nuclear Bragg reflections are forbidden, confirms a long-range AFM ground state of these compounds. These compounds have a layered antiferromagnet structure in which the magnetic coupling between layers is antiferromagnetic. The observed ordered moment values of the ($x = 0.84$, $y = 0$) and ($x = 0.19$, $y = 0.3$) compounds are consistent with the theoretically estimated ordered moment of $5\mu_B$ for the $\text{Mn}^{2+}(t_{2g}^3 e_g^2, S = 5/2)$ ion and $1\mu_B$ for the $\text{Fe}^{3+}(t_{2g}^5 e_g^0, S = 1/2)$ ion. It is apparent that the nature of the antiferromagnetic ordering is always long-range. Moreover, an application of external magnetic field induces an antiferromagnetic to ferrimagnetic-like transition. We have seen this phenomenon in the light of the superexchange interaction between Mn^{2+} and Fe^{3+} ions via the CN ligand. We have shown that both ferromagnetic as well as antiferromagnetic exchange pathways are possible between Mn^{2+} and Fe^{3+} spins. The competition between these two exchange interactions brings about the observed behavior of the compounds under different conditions. Neutron diffraction measurements under an external magnetic field would throw more light on the observed transition from antiferromagnetic to ferrimagnetic-like state under magnetic field in these compounds.

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