



## Spin-Glass Behaviour and Magnetic Properties of Multi-Metallic Prussian Blue Compound $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6]\cdot 5.9\text{H}_2\text{O}^\ddagger$

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Multi-metal prussian blue compound  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6]\cdot 5.9\text{H}_2\text{O}$  has been synthesized. The temperature-dependent magnetic susceptibilities indicate that there exist a ferrimagnetic interaction in the compound and magnetic transition at 9.5 K. The Curie constant of  $C = 6.59 \text{ cm}^3 \text{ K mol}^{-1}$  and Curie temperature of  $\theta = -11.28 \text{ K}$  were observed in fitting according to Curie-Weiss law. The observed value of coercive field and remanent magnetization at 4 K for the compound are 230 Oe and  $0.072 \mu_B$ . The presence of spin-glass behaviours in the compound is ascribed mainly to domain mobility or domain growth under different cooling conditions. The behaviour of  $\chi'$  and  $\chi''$  is typical of a spin glass state through a maximum with strong frequency dependence. The observed values for the isomer shift, the quadrupole splitting is  $0.41(9) \text{ mm/s}$ , I.S. is  $-0.15(4) \text{ mm/s}$ , values which are characteristic of low-spin Fe(III) ( $S = 1/2$ ) ions. The Mössbauer spectroscopy study revealed the presence of low spin Fe(III) ( $S = 1/2$ ).

**Keywords:** Prussian blue analogue, Magnetic, Spin glass, Magnetic transition, Mössbauer spectroscopy.

### INTRODUCTION

Compared with previous ion or alloy magnet, molecular-based magnetic material is studied, designed and prepared on the bases of the molecular level and may be obtained through the solution method because of its synthetic conditions of mild<sup>1,2</sup>. At the same time, it is likely to bring a breakthrough in the field of magnetic materials, due to the infinity of molecular synthesis and the diversity of selection for the ions and ligand. But for most molecular-based magnet, their magnetic transition temperature ( $T_c$ ) is lower than room temperature so that practical application is limited. Therefore design and preparation of molecular-based magnetic material with a special magnetic properties which can be controlled, particularly with high Curie temperature  $T_c$ , are one of the main challenges in the study of molecular-based ferromagnet. Hashimoto et al. have prepared a series of molecular alloy magnet  $[\text{A}^x\text{B}^{1-x}]_y[\text{Cr}(\text{III})(\text{CN})_6]\cdot n\text{H}_2\text{O}$ , which magnetic parameters like saturation magnetization ( $M_s$ ), Weiss paramagnetic Curie temperature ( $\theta$ ), magnetization ( $M$ ), coercive field ( $H_c$ ), transition temperature ( $T_c$ ), compensation temperature ( $T_{\text{comp}}$ ), etc.<sup>3-5</sup> can be controlled through changing the value of  $x$  or metal cations. Previous workers have synthe-

sized a number of prussian blue analogues  $\text{C}_n\text{A}_p[\text{B}(\text{CN})_6]_q\cdot x\text{H}_2\text{O}$  (Molecular structure of prussian blue analogue compound as shown in Fig. 1). Among these molecular alloy magnet, it exhibits some special magnetic phenomenon, such like the spontaneous magnetization changes its sign twice with changing temperature, one or even two compensation temperatures, photoinduced magnetic-pole inversion, an inverted hysteresis loop, etc. So, the ideas of synthesis for the type of molecule-based magnets can provide a new way to overcome some difficulties on the study of molecular-based magnet. In the paper, we have synthesized multi-metal Prussian blue compound  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6]\cdot 5.9\text{H}_2\text{O}$  by co-precipitation method and have studied the magnetic properties of this compound.

### EXPERIMENTAL

$\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  are reagent grade and without further purification. Elemental analysis (C, N, H) were performed on Perk-Elmer 2400 II analyser. IR spectrum were recorded on a Perkin-Elmer FT-IR spectrophotometer as KBr pellet in the  $4000\text{--}400 \text{ cm}^{-1}$  range. Magnetization measurements were measured on a Quantum Design MPMS-5 magnetometer in the scope of 2-300 K.

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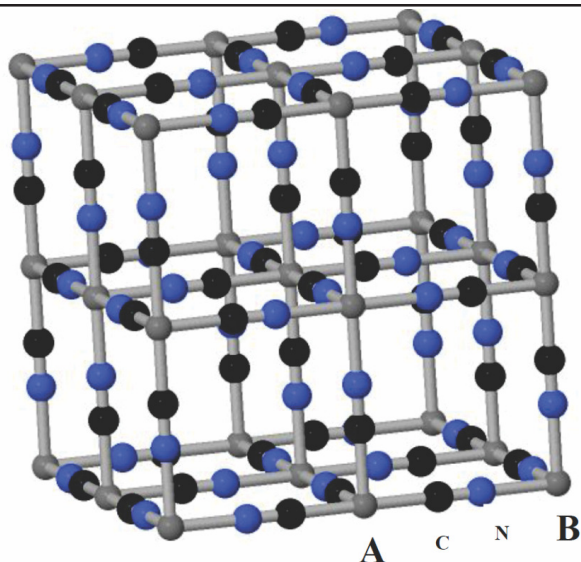


Fig. 1. Structure of Prussian blue compound

**Synthesis of  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6]\cdot 5.9\text{H}_2\text{O}$ :** Polycrystalline compound was prepared by coprecipitation method. To a solution of 25 mL  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (0.25 mmol) was mixed 125 mL  $\text{Mn}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$  (1.25 mmol) solution. Then a solution of 100 mL  $\text{K}_3\text{Fe}(\text{CN})_6$  (1 mmol) was slowly added to the mixed solution of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$  and a solid was precipitated immediately. After 48 h, the precipitates were filtered, washed repeatedly with water and dried at 45 °C. Elemental analysis to measure C, N, H mass ratio: found: C, 17.44; N, 21.35 %; H, 3.06; calcd: C, 17.94; N, 20.92 %; H, 2.96.

**IR spectrum:** The IR spectrum of compound has been recorded over the 4000-400  $\text{cm}^{-1}$  range and shown in Fig. 2. It shows two bands at 2078 and 2151  $\text{cm}^{-1}$  indicating the existence of two types of cyanide groups in the crystal lattice of compound<sup>6,7</sup>. Compounds are easily identified by their stretching frequencies in 2200-2000  $\text{cm}^{-1}$  range, which are consistent with the formation of bridging cyanide groups and there are two different coordination environment. The broad peak at 3404 and 1611.5  $\text{cm}^{-1}$  are assigned to the  $\nu(\text{O-H})$  of the crystal water stretching vibrations.

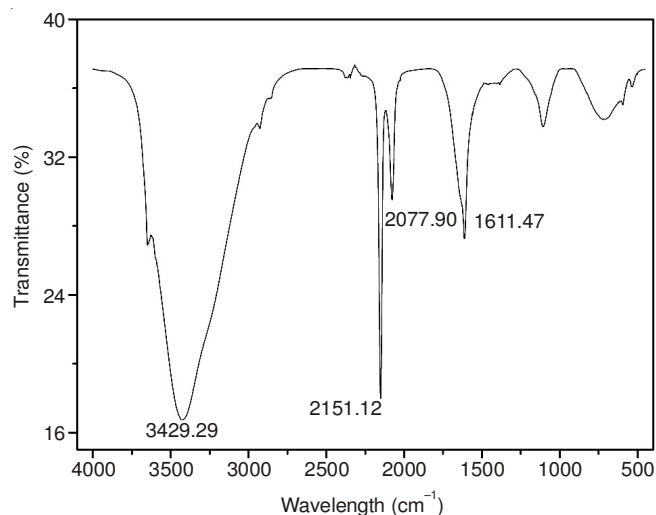


Fig. 2. FT-IR spectrum of the Prussian blue

## RESULTS AND DISCUSSION

**DC magnetic susceptibility:** The magnetic susceptibility of the compound  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6]\cdot 5.9\text{H}_2\text{O}$  was measured from 2-300 K (Fig. 3), which corresponds to the steepest rise of magnetization with decreasing temperature. A magnetic transition temperature ( $T_c$ ) of 9.5 K is estimated by minima of  $dM/dT$  vs T curve. According to  $\chi_m^{-1}$  versus T curve (Fig. 4), in 300-20 K range, the values of  $\chi_m$  gradually increase and then sharply increase after 20 K with a further decrease of the temperature. The curves of  $\chi_m^{-1}$  vs T above 30 K obey the Curie-Weiss law with a Curie constant of  $C = 6.59 \text{ cm}^3 \text{ K mol}^{-1}$  and Weiss paramagnetic Curie temperature of  $\theta = -11.28 \text{ K}$ . The values of  $T_c$ ,  $\theta$  and C in 0.5 KOe are different from those values for ferrimagnet  $\text{Co}_{1.5}[\text{Fe}(\text{CN})_6]\cdot 6\text{H}_2\text{O}$  ( $T_c = 16 \text{ K}$ ,  $C = 5.4 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $\theta = -15 \text{ K}$ )<sup>8</sup>.

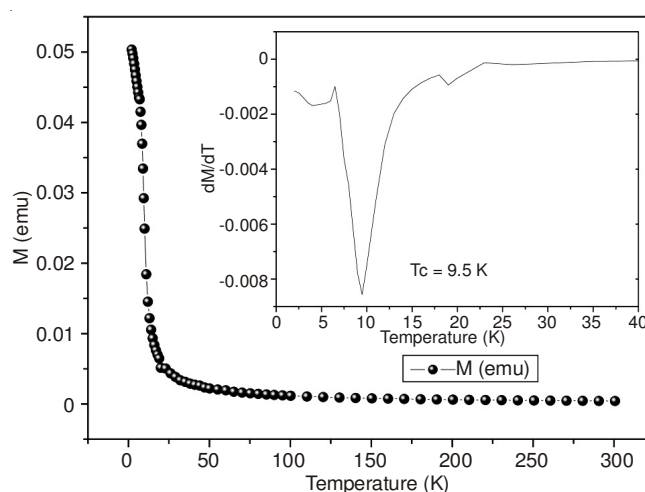


Fig. 3.  $M$  vs.  $T$  for the compound (Inset: plot of  $dM/dT$  vs.  $T$ )

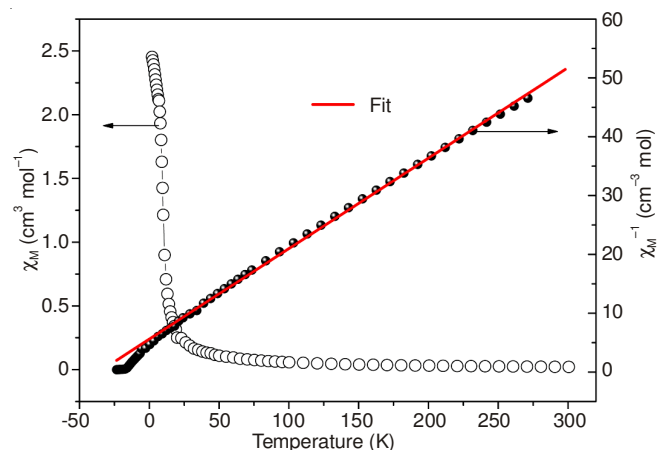
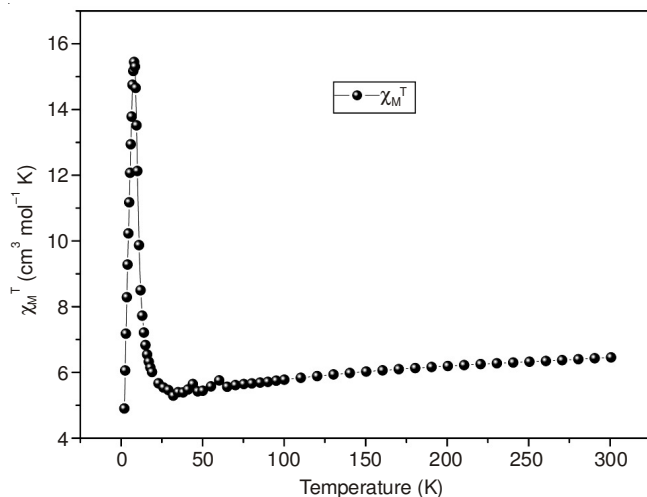
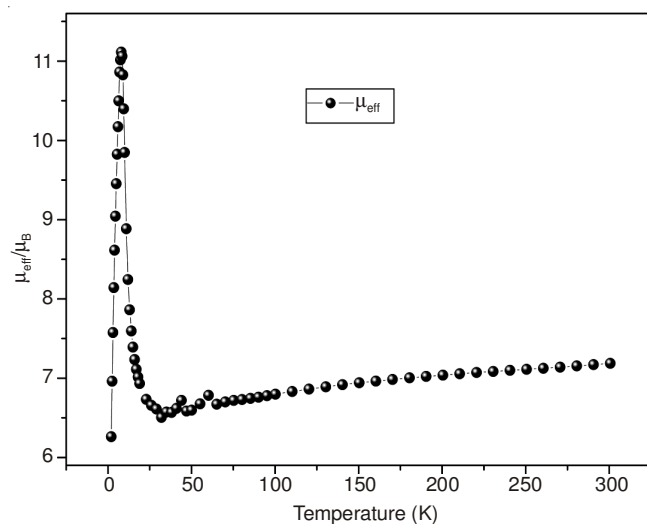


Fig. 4.  $\chi_m$  and  $\chi_m^{-1}$  vs.  $T$  for the compound

A curve of  $\chi_m T$  vs.  $T$  is shown in Fig. 5. The effective moment  $\chi_m T$  sharply increase to reach maximum of  $15.61 \text{ cm}^3 \text{ K mol}^{-1}$  at 8 K and final decrease at lower temperature, indicating antiferromagnetic interaction<sup>8,9</sup>. A curve of  $\mu_{\text{eff}}$  vs.  $T$  is shown in Fig. 6. The effective moment  $\mu_{\text{eff}}$  first slowly decrease to reach a minima of  $6.48 \mu_B$  at 31 K, then sharply increase to reach maximum of  $11.11 \mu_B$  at 8 K and final decrease at lower temperature, indicating antiferromagnetic interaction between paramagnetic centers. This kind of behaviour is a characteristic of a ferrimagnet<sup>8,9</sup>.

Fig. 5.  $\chi_m T$  versus T plot of the compoundFig. 6.  $\mu_{\text{eff}}$  versus T plot of for the compound

#### Zero-field-cooled and field-cooled magnetization:

Fig. 7 shows the curves of Zero-field-cooled and field-cooled magnetization of compound at different field  $H = 20, 150, 250, 500$  Oe. The values of  $M$  increase and exhibit weak irreversibility in the field-cooled (FC) magnetization curves below  $T_c = 9.5$  K. There are a clear bifurcation phenomenon in the compound  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6] \cdot 5.9\text{H}_2\text{O}$  by the field-cooled ( $M_{\text{FC}}$ ) and zero-field-cooled ( $M_{\text{ZFC}}$ ) magnetization curves.  $T_{\text{irr}}$  is a bifurcation temperature point of which field-cooled and zero field-cooled magnetization curves separates out. In addition, the behaviour that  $M_{\text{ZFC}}$  exhibits a maximum below  $T_{\text{irr}}$  is attributed to the cooperative freezing of spin glass. The irreversible behaviour of  $M$  and shift of bifurcation point to lower temperature with increasing  $H$  are characteristic for spin glasses<sup>10,11</sup>.

**AC magnetic susceptibility:** It is also confirmed that there exist a spin-glass behaviour in the compound  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6] \cdot 5.9\text{H}_2\text{O}$  through AC magnetization curves. The AC magnetic susceptibility of the compound was measured at 4 Oe AC amplitude with zero-applied DC field in the frequencies 10-1000 Hz range, as shown in Fig. 8. It can be observed that in-phase (real) susceptibility,  $\chi'$  (T) curves

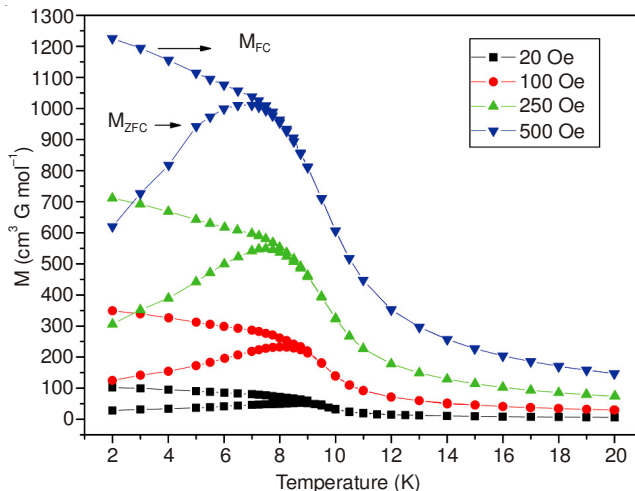
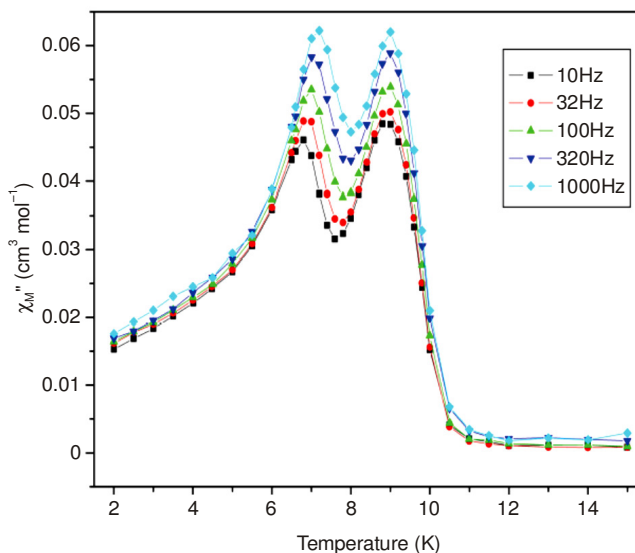
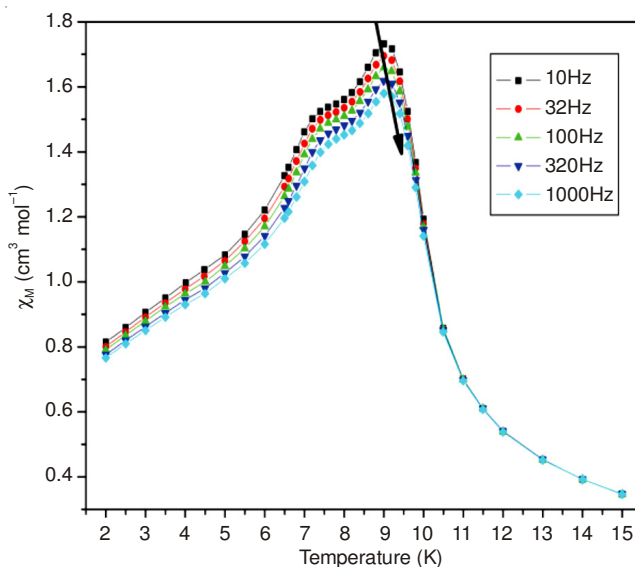


Fig. 7. ZFC and FC magnetization curves with different field

Fig. 8.  $\chi'$  (T) and  $\chi''$  (T) curves of AC magnetic susceptibility of the sample with different frequencies

exhibited a peak at about 9 K and the peak temperature  $T_{\text{f}}(\omega)$  shifts toward higher temperatures with increasing frequency. That the  $\chi$  (T) clearly shows a frequency dependence is typically

assigned to spin glasses<sup>12-14</sup>. The relative shift of frequency ( $c$ ) is  $c = \frac{\Delta T_f}{T_f \Delta \log w} = 0.006$ , which fall within the range typical ( $10^{-2} - 10^{-3}$ ) for the conventional spin-glass system. In addition, the  $\chi'$  show a broad peak at 7 K, but out-of-phase (imaginary) susceptibility<sup>14-16</sup>,  $\chi''$  (T) show two clear peak at 7 and 9 K, as shown in Fig. 8, respectively and the peak temperature shifts toward higher temperatures with increasing frequency.

**Field-dependent of magnetization and hysteresis behaviour:** The ferrimagnetic behaviour is further characterized by the measurements of hysteresis behaviour and field-dependent magnetization (Fig. 9). Field-dependent magnetization curves measured at 4 K shows that a rapid increase in  $M$  at low magnetic field and then the values of  $M$  gradually increase with a further increase of the magnetic field<sup>17-20</sup>. The observed  $M_s$  value is  $4.31 \mu_B$ , at 50 kOe, but the compound does not reach full saturation. The hysteresis curves is measured at 4 K, shown in the Fig. 10. The coercive field ( $H_c$ ) value of 230 Oe and remanent magnetization ( $M_r$ ) value of  $0.072 \mu_B$  for the compound  $\text{Co}_{1.5}[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$  (5 K,  $M_r = 0.64 \mu_B$ ,  $H_c = 480$  Oe)<sup>8</sup>. Magnetic parameters like saturation magnetization ( $M_s$ ), coercive field ( $H_c$ ), Curie constant ( $C$ ), Weiss paramagnetic Curie temperature ( $\theta$ ), transition temperature ( $T_c$ ), are different from the those of the bimetallic cyanide-bridged compounds  $\text{Mn}_{1.5}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ ,  $\text{Co}_{1.5}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ . Therefore,

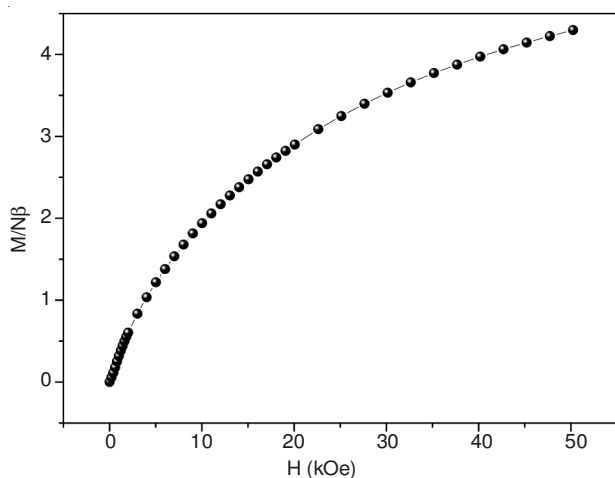


Fig. 9. Field-dependent magnetization curves

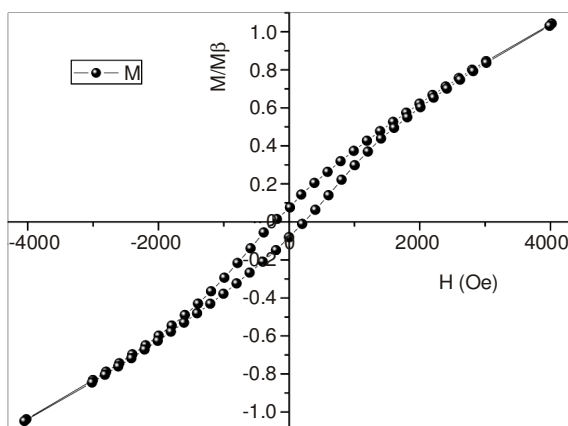


Fig. 10. Hysteresis loop for the compound

synthesis ideas of molecular alloy magnet can be regarded as a synthesis method to expand a new type of magnetic functional materials, which magnetic properties can be tuned and controlled by changing the composition of different transition metal cations<sup>15,17,20</sup>.

**Measurement of Mössbauer spectrum:** The room temperature Mössbauer spectroscopy of the compound have been measured (Fig. 11). The value of isomer shift (IS), quadrupole splitting (QS) and line width are listed in Table-1. Presumably the rapid motion of the magnetic iron electronic moments causes the quenching of the magnetic hyperfine structure. The observed values (Table-1) for the isomer shift, line width is  $0.36(0)$  mm/s at 298 K, as shown in Fig. 12. The quadrupole splitting is  $0.41(9)$  mm/s, I.S. is  $-0.15(4)$  mm/s, values which are characteristic of low-spin Fe(III) ( $S = 1/2$ ) ions<sup>19-21</sup>.

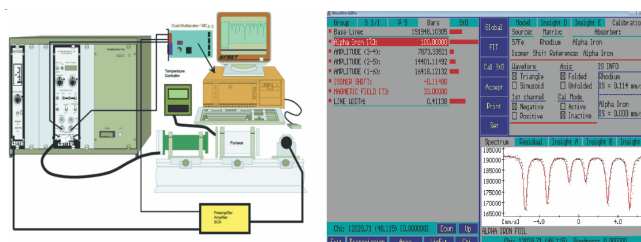


Fig. 11. Mössbauer spectrum measurement

TABLE-1 MÖSSBAUER PARAMETER OF THE SAMPLE $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6] \cdot 5.9\text{H}_2\text{O}$	
Temperature (K)	300 K
IS (mm/s)	-0.15(4)
QS (mm/s)	0.41(9)
Line width (mm/s)	0.36(0)
The isomer shift (IS) values relative to a-Fe at room temperature (with error of $\pm 0.02$ mm/s). QS, quadrupole splitting; T, temperature.	

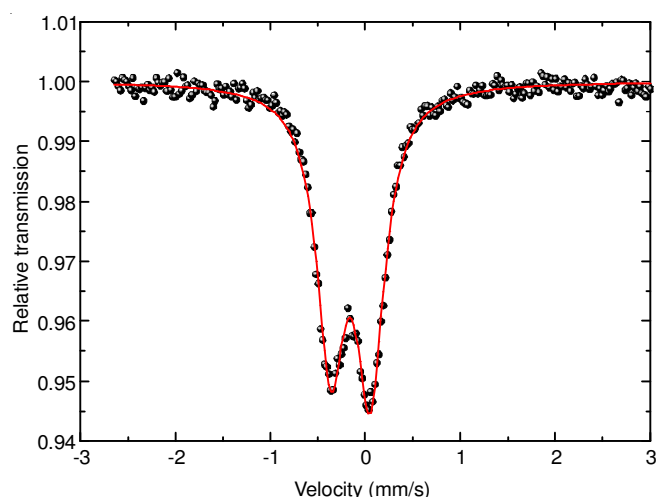


Fig. 12. Mössbauer parameters of  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6] \cdot 5.9\text{H}_2\text{O}$

## Conclusion

An investigation of multi-metal compound  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6] \cdot 5.9\text{H}_2\text{O}$  with spin-glass behaviour and ferromagnet are reported. The compounds exhibits spontaneous magnetic ordering at low temperatures; in the temperature range 30-300 K, the magnetic susceptibilities can be fit

to the Curie-Weiss law with a Curie constant of  $C = 6.59 \text{ cm}^3 \text{ K mol}^{-1}$  and Curie-Weiss temperature of  $\Theta = -11.28 \text{ K}$ . The Mössbauer result of indicate that the isomer shift, line width is  $0.36(0) \text{ mm/s}$  at  $298 \text{ K}$ . The quadrupole splitting is  $0.41(9) \text{ mm/s}$ , I.S. is  $-0.15(4) \text{ mm/s}$ , values which are characteristic of low-spin Fe(III) ( $S = 1/2$ ) ions. Bifurcation phenomenon of ZFC-FC DC magnetization, the maximum of magnetic susceptibility shifts toward higher temperatures with the frequencies (32-1000 Hz) indicate spin-glass state in the Sample  $\text{Co}_{0.25}\text{Mn}_{1.25}[\text{Fe}(\text{CN})_6] \cdot 5.9\text{H}_2\text{O}$ , which mainly due to domain mobility growth under different cooling conditions.

#### ACKNOWLEDGEMENTS

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