Magnetic structure of molecular magnet Fe[Fe(CN)$_6$]·4H$_2$O

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Abstract. We have studied the magnetic structure of Fe[Fe(CN)$_6$]·4H$_2$O, prepared by precipitation method, using neutron diffraction technique. Temperature dependent DC magnetization study down to 4.2 K shows that the compound undergoes from a high temperature disordered (paramagnetic) to an ordered magnetic phase transition at 22.6 K. Rietveld analysis of neutron diffraction pattern at 60 K (in its paramagnetic phase) revealed a face centred cubic structure with space group Fm3m. The structure contains three-dimensional network of straight Fe^{3+}–C≡N–Fe^{3+} chains along the edges of the unit cell cube. Fe^{3+} ions occupy 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2) positions. Fe^{3+}(0, 0, 0) is surrounded octahedrally by six nitrogen atoms and Fe^{3+} (1/2, 1/2, 1/2) is surrounded octahedrally by six carbon atoms. Magnetic Rietveld refinement of neutron diffraction data at 11 K shows a ferromagnetic coupling between the two inequivalent Fe^{3+} sites. Refinement yielded an ordered moment of 4.4(6) and 0.8(6) $\mu_{\rm B}$ per Fe ion located at (0, 0, 0) and (1/2, 1/2, 1/2), respectively. Ordered moments are found to align along the face diagonal. The observed net moment from low temperature neutron diffraction study is consistent with DC magnetization results.

Keywords. Molecular magnet; neutron diffraction; DC magnetization; ferromagnet.

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1. Introduction

Molecular magnetic materials [1] are the subject of an active research in recent years because of their possible applications in future information processing and storing devices. Prussian Blue [2] analogues represented by the general formula, A$_n$[B(CN)$_6$]$_m$·xH$_2$O [3–8] where A and B are transition metals, are one of the most promising candidates in this regard [9–11]. One of the salient features of these materials is the easy route for their synthesis. These materials can be prepared by mild chemistry methods at room temperature e.g. co-precipitation method. An easy control of their magnetic properties like transition temperature, saturation magnetization, coercive field etc., is possible simply by changing the concentration of magnetic ions [11] or by replacing a magnetic ion by another magnetic ion [4–8].

Amit Kumar and S M Yusuf

Ferri-ferricyanide, $Fe[Fe(CN)_6] \cdot xH_2O$, is one of the basic compounds in the Prussian Blue family. Bozorth *et al* [12] reported the results of DC magnetization study on the ferri-ferricyanide (T_C = 22 K, saturation magnetization = 3.8 μ_B per $(CN)_6$). But their evidences suggested that the sample had contained some impure phase and the correct composition of 'ferri-ferricyanide' was not known. However, ferri-ferricyanide being one of the important basic compounds in the Prussian Blue family, it is very much essential to know the chemical structure and the true nature of magnetic ordering in this compound. With this motivation, we have prepared single-phase ferri-ferricyanide and studied by DC magnetization and neutron diffraction techniques. Neutron diffraction, being a microscopic technique, can measure the magnitude and direction of site moments in ordered ferri-ferricyanide molecular magnet and hence unveils its microscopic magnetic structure. In this paper we report the chemical and magnetic structure of ferri-ferricyanide, $Fe[Fe(CN)_6] \cdot xH_2O$. Here, for the first time by using neutron diffraction technique, we have shown the existence of low-spin and high-spin Fe^{3+} ions in $Fe[Fe(CN)_6] \cdot xH_2O$.

2. Experimental

Ferri-ferricyanide was prepared by the co-precipitation method. In this method 100 ml 0.1 M $K_3Fe(CN)_6$ aqueous solution was slowly added to 200 ml 0.1 M $FeCl_3$ aqueous solution and the resulting solution was heated up to 53°C. Hot solution was allowed to cool at room temperature and diluted to double of its initial volume after cooling. Dark green precipitate, so obtained, was filtered, washed many times with demineralized water and acetone and finally allowed to dry in air. The sample was ground to very fine powder. Neutron diffraction pattern of the prepared polycrystalline sample was recorded using a 1-D position sensitive detector based neutron powder diffractometer (λ = 1.249 Å) at Dhruva reactor, Trombay. For low temperature measurements the sample was mounted in a closed cycle helium refrigerator with lowest possible temperature of 11 K. DC magnetization measurements were carried out using a vibrating sample magnetometer (Oxford Instruments model) as a function of temperature and magnetic field.

3. Results and discussion

Figure 1 shows the neutron diffraction pattern of the prepared polycrystalline sample at 60 K. The diffraction pattern was analysed by Rietveld refinement technique using FULLPROF program [13]. The pattern could be indexed with the Fm3m space group. Starting values for the positions of carbon, nitrogen and water molecules were taken from ref. [2]. Owing to the high background and limitations of powder diffraction, we treated water molecules as pseudoatoms {H_2O} with an average scattering length $b(H_2O) = b(O) + 2b(H) = -1.68$ fm. In our refinement the best fitting was achieved by taking four water molecules per formula unit. Results of the analysis are listed in table 1. The distances between various atoms obtained from the analysis are Fe_1–N = 2.003(6) Å, Fe_2–C = 1.941(6) Å, C–N =
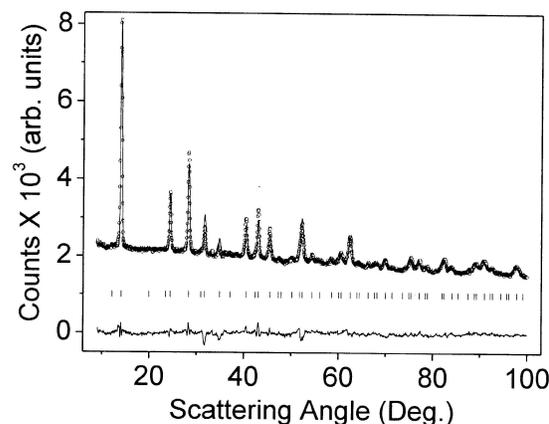
Figure 1. Observed and fitted neutron diffraction patterns and their difference at 60 K. Open circles: observed data; solid line: Rietveld fitted curve; short vertical lines: position of Bragg peaks.

1.16(2) Å, Fe$_1$–Fe$_2$ = $a/2$ = 5.1095(5) Å and Fe$_1$–Fe$_1$ = Fe$_2$–Fe$_2$ = a = 10.219(1) Å, where Fe$_1$ and Fe$_2$ are Fe^{3+} ions at (0, 0, 0) and (1/2, 1/2, 1/2), respectively (see table 1). The calculated values of interatomic distances are close to the values reported for the parent Prussian Blue compound, Fe$_4$[Fe(CN)$_6$]$_3$·14H$_2$O [2].

Structure of the ferri-ferricyanide contains three-dimensional network of Fe$_1$–N≡C–Fe$_2$ chains along the edges of the unit cell cube. The four water molecules present in the formula unit are uncoordinated and may be considered as zeolitic water. Fe$_1$ and Fe$_2$ are surrounded octahedrally by N and C atoms, respectively. Octahedral crystalline field splits the 3d orbitals of Fe^{3+}(d^5) ion into low energy t_{2g} (d$_{xy}$, d$_{yz}$, d$_{zx}$) and high energy e_g (d$_{z2}$, d$_{(x2-y2)}$) orbitals. It is evident from the interatomic distances that nitrogen octahedra is slightly bigger (3%) than the carbon octahedra. It is, therefore, expected that Fe$_2$ should be affected by a stronger ligand field than Fe$_1$. The ligand field influences the spin configuration of the Fe^{3+} ions directly.

Table 1. Structural parameters of Fe[Fe(CN)$_6$]·4H$_2$O at 60 K.

Space group = Fm3m, a = 10.219(1) Å, Z = 4					
Atoms	x	y	z	p	B (Å^2)
Fe$_1$	0	0	0	1	0.5(1)
Fe$_2$	1/2	1/2	1/2	1	0.5(1)
C	0.310(1)	0	0	6	1.6(2)
N	0.196(1)	0	0	6	1.6(2)
{H$_2$O}	1/4	1/4	1/4	2	18(1)
{H$_2$O}	0.331(9)	0.331(9)	0.331(9)	2	18(1)
R_p = 1.82%, R_{wp} = 2.46%, R_{exp} = 2.27%					
p = occupancy, B = temperature factor					

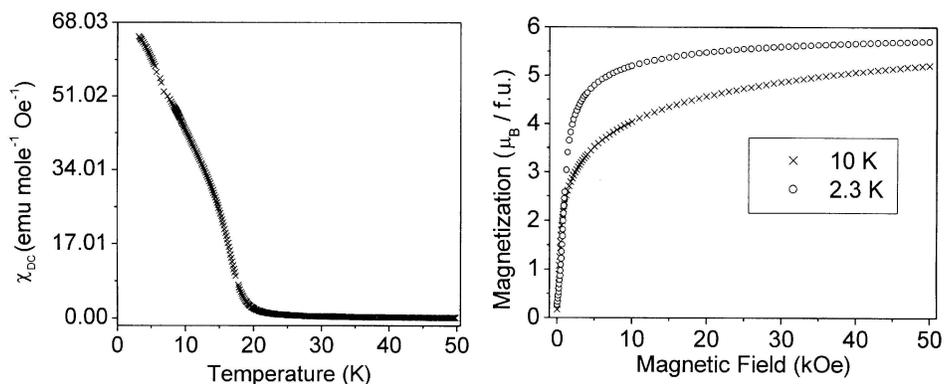**Figure 2.** χ_{DC} vs. T curve at 200 Oe field and virgin DC magnetization curves at 10 and 2.3 K.
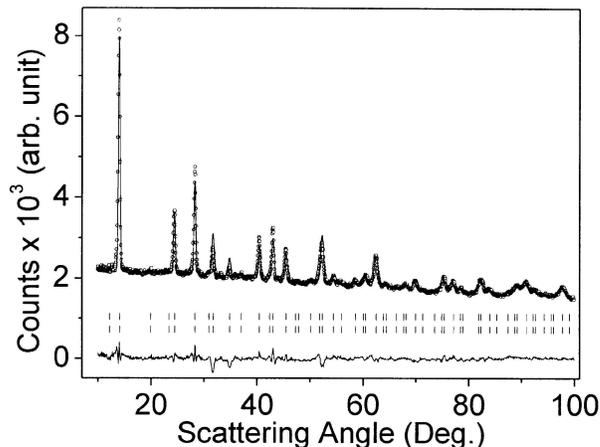

Figure 3. Observed and Rietveld refined (magnetic) neutron diffraction patterns at 11 K.

Figure 2 shows the DC susceptibility vs. temperature curve and virgin magnetization curves for the ferri-ferricyanide. The compound undergoes a disorder (paramagnetic) to ordered magnetic phase transition at 22.6 K. Magnetization at 2.3 K under 50 kOe field was found to be 5.8 μ_{B} per formula unit. Assuming high spin ($S = 5/2$) for Fe^{3+} at (0, 0, 0) and low spin ($S = 1/2$) for Fe^{3+} at (1/2, 1/2, 1/2), the theoretically expected spin only ordered moment value is 6 μ_{B} per formula unit for parallel ordering between the two Fe^{3+} ions. In order to measure the site moments we carried out the magnetic refinement of low temperature neutron diffraction pattern.

Figure 3 shows the diffraction pattern of ferri-ferricyanide at 11 K. This pattern is similar to pattern at 60 K except some intensity enhancement in low-angle Bragg peaks (table 2) indicating ferro or ferrimagnetic type ordering. Refinement of 60 and 11 K data did not give any evidence of structural phase transition between

Table 2. Observed integrated intensities at 60 and 11 K for the first few Bragg reflections and their differences showing magnetic contributions.

$(h\,k\,l)$	2θ (°)	$I_{60\ \mathrm{K}}$	$I_{11\ \mathrm{K}}$	$I_{11\ \mathrm{K}}-I_{60\ \mathrm{K}}$
1 1 1	12.15	3	92	89
2 0 0	14.04	2648	2789	141
3 1 1	23.38	6	35	29
2 2 2	24.44	711	741	30
4 0 0	28.29	1202	1230	28
3 3 1	30.89	27	51	24

60 and 11 K. From magnetic refinement we obtained 4.4(6) μ_B moment for Fe^{3+} at (0, 0, 0) and 0.8(6) μ_B moment for Fe^{3+} at (1/2, 1/2, 1/2). The theoretically expected values of ordered moments for high-spin and low-spin Fe^{3+} are 5 and 1 μ_B, respectively. The neutron diffraction study, therefore, confirms the existence of high-spin Fe^{3+} at (0, 0, 0) and low-spin Fe^{3+} at (1/2, 1/2, 1/2) which is due to the influence of ligand fields on the splitting of 3d orbitals of Fe^{3+} ions. The net moment derived from the refinement was 5.2 μ_B per formula unit. This is close to the magnetization value 5.24 μ_B at 10 K under 50 kOe field, obtained from DC magnetization data (figure 2). The observed moments are found to align along the face diagonals. The present study also indicates the total quenching of orbital moments.

4. Conclusions

Ferri-ferricyanide, Fe[Fe(CN)$_6$]·4H$_2$O possesses a fcc structure with space group Fm3m. There exists straight chain of atoms containing Fe^{3+}–C≡N–Fe^{3+} along the edges of the unit cell cube. Fe^{3+} ion at (0, 0, 0) is surrounded octahedrally by N atoms and Fe^{3+} at (1/2, 1/2, 1/2) is surrounded by C octahedra. The compound undergoes a paramagnetic to ferromagnetic transition at 22.6 K. Magnetic refinement of 11 K neutron diffraction data yielded 4.4(6) μ_B and 0.8(6) μ_B ordered moments for Fe^{3+} ions at (0, 0, 0) and (1/2, 1/2, 1/2), respectively. The moments are found to align along the face diagonals. The net magnetic moment extracted from the magnetic refinement of 11 K neutron diffraction data agrees well with DC magnetization results. Present study confirms the ferromagnetic ordering between high-spin Fe^{3+} ($S = 5/2$) and low-spin Fe^{3+} ($S = 1/2$) ions.

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