Spin-glass behavior and magnetic studies of nickel-iron multi-metal Prussian blue complexes $Ni_{0.75}Cu_{0.75}[Fe(CN)_6] \cdot 6.3H_2O$

Qing Lin[1,2], Zhimin Ji[1], Haifu Huang[1,3], Yun He[1,*], Jianmei Xu[2]

[1]*College of Physics and Technology, Guangxi Normal University, 541004,Guilin,China*
[2] *Department of Information Technology, Hainan Medical College, 571199,Haikou,China*
[3]*Department of Physics, Nanjing University, Nanjing 210093, China*

A multi-metal Prussian blue compound $Ni_{0.75}Cu_{0.75}[Fe(CN)_6] \cdot 6.3H_2O$ was prepared by co-precipitation method. The temperature-dependent magnetic susceptibilities of the compound were measured. The curie-weiss constants are $C = 1.79$ cm$^3 \cdot$K$\cdot$ mol^{-1}, $\Theta = 21.53$ K. These results indicate that there exists a ferromagnetic exchange interaction in the complexes. It undergoes a paramagnetic to ferromagnetic transition at 20 K. The observed value of coercive field (H_c) and remanent magnetization (M_r) for the compound are 1.12 KOe and 0.92 μ_β. This value of H_c is much higher than that for reported most Prussian blue analogues. In addition, there exist a spin-glass behaviour in the compound.This behaviour of χ'' and χ'' is typical of a spin glass state, both the in-phase and outof-phase signals, χ' and χ'', go through a maximum with strong frequency dependence.

Key words: Prussian blue analogue, molecular alloys magnet,magnetic transition, ferromagnetic, spin glass
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INTRODUCTION

In recent years, design and synthesis of molecule-based magnets, involving many fields such as chemistry, physics, materials and life sciences, has become one of the hot research projects on the physics and chemistry nowadays [1-5]. The Ni-Fe cyanides, whose chemical formula is $A_x Ni[Fe(CN)_6]_y \cdot zH_2O$ (A=K,Mn,Cs,Cu), have been attracting renewed interest of the material scientists. Prussian Blue analogues are very promising in terms of multi-functionality [6-9]. Prussian Blue analogues $C_n A_P[B(CN)_6]_q \cdot xH_2O$(Molecular structure of Prussian blue analogue compound as show in figure 1) are molecular-based materials with a 3-D network structure which are strongly bridged by cyano groups and exhibit interesting properties like electric field-induced conductance switching, photo-induced magnetization, etc. Hashimoto [3] have prepared a series of molecular alloy magnet $[A^{II}_x B^{II}_{1-x}]_y[Cr^{III}(CN)_6] \cdot nH_2O$, which magnetic parameters like saturation magnetization(M_s), magnetization(M), coercive field (H_c), transition temperature (T_c), compensation temperature (T_{comp}), etc., can be controlled through changing the value of x or metal cations.Ni-Cu-ferro-cyanides have been getting much interest in the contemporary research.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. So this 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 this context, we have prepared a multi-metal Prussisa blue compound $Ni_{0.75}Cu_{0.75}[Fe(CN)_6] \cdot 6.3H_2O$ by co-precipitation method and the magnetic properties of this compound have been studied.
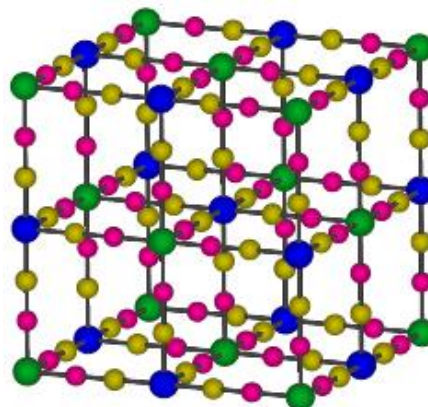

Fig. 1. Structure of Prussian Blue analogs

EXPERIMENTAL

Materials and physical measurements

Material. $NiCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 6H_2O$ and $K_3Fe(CN)_6$ are reagent grade, and without further purification. Elemental analysis (Perkin Elmer Corporation PE2400 II), Fourier transform infrared spectroscopy (Perkin Elmer Corporation PE Spectrum One FT-IR spectrometer, KBr pellet) with the radiation spectrum of the 400–4000 cm^{-1}.

Magnetization measurements were measured on a Quantum Design MPMS-7 magnetometer in the scope of 2–300 K.

Synthesis of $Ni_{0.75}Cu_{0.75}[Fe(CN)_6]\cdot 6.3H_2O$

Polycrystalline compound $Ni_{0.75}Cu_{0.75}$ [Fe (CN)$_6$]·6.3H$_2$O was prepared by co-precipitation method. To a solution of NiCl$_2$·6H$_2$O (1.5mmol, 0.3565g) in water (150 ml) was mixed 150ml CuSO$_4$·6H$_2$O (1.5mmol, 0.5456g) solution. Then a solution of K$_3$Fe(CN)$_6$ (2mmol，0.6585g) in water (100 ml) was slowly added to the mixed solution of NiCl$_2$·6H$_2$O and CuSO$_4$·6H$_2$O, and a solid was precipitated immediately. After sitting for 48 h, the precipitates were filtered, washed repeatedly with water and dried at 45°C. Elemental analysis to measure C, H, N mass ratio: Found: C, 16.94%; H, 3.14%; N, 20.53%; Calc: C, 17.27%; H, 3.04%; N, 20.15%.

IR SPECTRUM ANALYSIS

The IR spectrum of the compound has been recorded over the 400-4000cm^{-1} range, and shown in Fig. 2. It shows two bands at 2105.66 and 2163.73 cm^{-1} indicating the existence of two types of cyanide groups in the crystal lattice of the compound. Compared to the compound K$_3$Fe(CN)$_6$ ($\nu_{(CN)}$=2121.29cm^{-1}), Ni$_{0.75}$Cu$_{0.75}$ [Fe (CN)$_6$]·6.3H$_2$O shows two bands (2105.66 and 2163.73 cm^{-1}) in 2200–2000 cm^{-1} range, which are consistent with the formation of bridging cyanide groups and there are two different coordination environment, which may due to the change in the spin states and valence states of metal ions. The broad peak at 3413.61cm^{-1} and 1607.46 cm^{-1} are assigned to the ν(O-H) of the crystal water stretching vibrations.
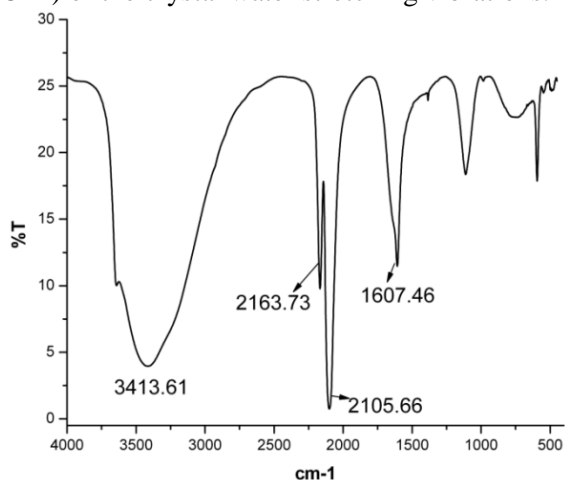

Fig. 2. FT-IR spectrum of the compound

MAGNETIC MEASUREMENT

DC magnetic susceptibility

Figure 3 depicts the field-cooled magnetization (*M*) versus temperature (*T*) curve at 1 kOe magnetic field (*H*) in the temperature range 2 – 300 K. A sharp rise in *M* is observed around 20 K. Magnetic transition temperature (=20 K) of the compound was estimated from minima of dM/dT vs. T curve, which corresponds to the steepest rise of magnetization with decreasing temperature (as shown in Figure 4). The compound undergoes a paramagnetic to ferro/ferrimagnetic type phase transition at 20 K which is lower than that for the parent compound, Ni$_{1.5}$[Fe(CN)$_6$]·xH$_2$O (T$_C$= 23.6K) [18].
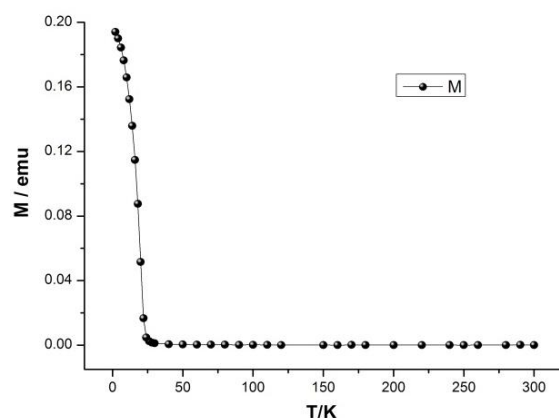

Fig. 3. Temperature dependence of magnet for the compound
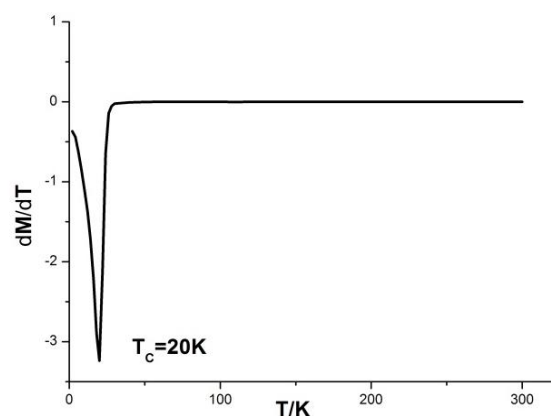

Fig. 4. dM/dT vs T for the compound

The inverse susceptibility as a function of temperature in the paramagnetic state is shown in Fig. 5.The curve rises slowly till the temperature is lowered from 25 to 300K .The in-phase susceptibility χ_m of Ni$_{0.75}$Cu$_{0.75}$[Fe(CN)$_6$]·6.3H$_2$O shows a sharp maximum at 2 K. This kind of behaviour is a characteristic of a ferromagnet
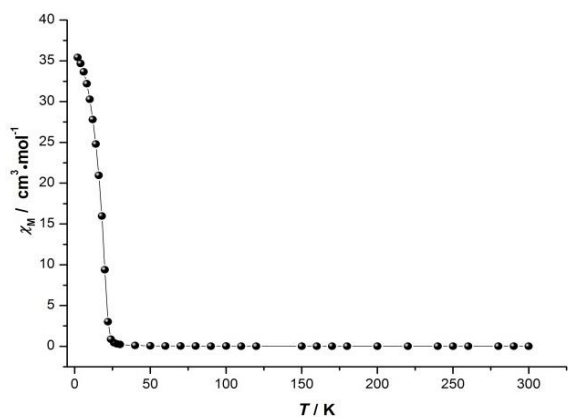
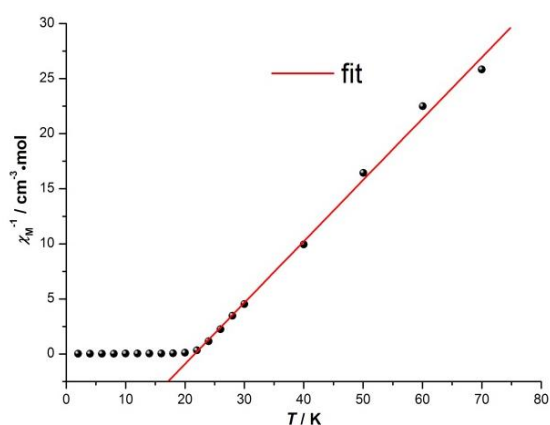**Fig. 5.** Temperature dependence of χ_m for the compound.

Fig. 6. χ_m^{-1} vs T for the compound.

The magnetic order results from combined ferromagnetic and neighbouring anti-ferromagnetic interactions. High temperature dc susceptibility ($\chi_m=M/H$) is found to obey the Curie-Weiss law.Fig. 6 shows temperature dependence of χ_m^{-1} in the temperature range 2–80 K.The Curie constant, C, and the Curie–Weiss temperature, θ,are determined from a linear fitting of $1/\chi = (T-\theta)/C$ (Curie–Weiss law) to the linear region[10-14]. Fitting yielded that the Curie constant C=1.79 cm³· K· mol⁻¹, paramagnetic curie temperature θ = 21.53K .The positive value of θ indicates the existence of a predominant ferromagnetic interaction.The positive value of θ indicates the existence of a predominant ferromagnetic interaction. The values of T_c, Θ and C in 100 Oe are different from those values for ferrimagnet $Ni_{1.5}[Fe(CN)_6]\cdot xH_2O$ [18] and $Cu_3[Fe(CN)_6]_2$ $11.6H_2O$ (T_c=18.1K) [10].

A curve of $\chi_m T$ vs T is shown in Figure.7, the μ_{eff} value at room temperature is 2.82 cm³·K·mol⁻¹·T.Upon lowering the temperature, and then
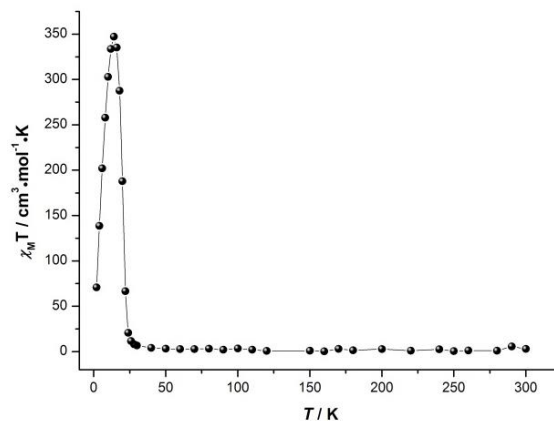

Fig. 7. $\chi_m T$ versus T plot of the compound.

sharply increase after 25 K with a further decrease of the temperature. The $\chi_m T$ of $Ni_{0.75}Cu_{0.75}[Fe(CN)_6]\cdot6.3H_2O$ shows a sharp maximum value of 350 cm³·K·mol⁻¹·T at 14 K, and then finally decreases more rapidly on further cooling.For a ferrimagnetic compound $\chi_m T$ vs. T curve undergoes to a minima before rising around magnetic ordering temperature [15-18].As shown in Fig. 8, it goes up in a mild way in the temperature range of 2–300 K, followed by a sharp increase at 25 K. With further lowering of the temperature,μ_{eff} drops down sharply, reaching the minimum values at 2 K, which could be attributed to an intermolecular antiferromagnetic interaction and/or a zero-field splitting (ZFS) effect. This kind of behaviour is a characteristic of a ferrimagnet[18-19].
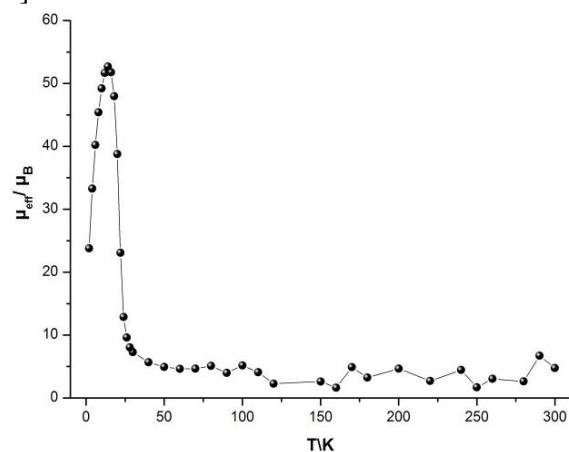

Fig. 8. μ_{eff} versus T plot of for the compound

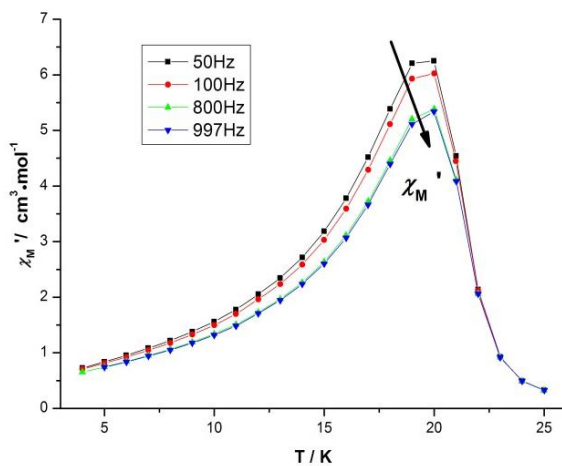### 4.2. Ac magnetic susceptibility

At a fixed temperature and a zero dc field or a certain applied field, the χ' and χ'' values were also measured as a function of the ac frequency, *f*, ranging from 50 to 997 Hz (as shown in Figure 9). It is also confirmed that there exist a spin-glass behave in the compound through ac magnetization curves. The temperature dependence of zero-static

field ac magnetic susceptibilities show that the in-phase component (χ'') has the maximum at about 19 K for frequencies of 50, 100, 800, and 997 Hz and that a significant out-of-phase component (χ'') appears, confirming the long-range ferrimagnetic ordering . The ac susceptibility measurements for the compound also confirm the magnetic phase transition in both complexes, showing a peak in the in-phase (χ'') signal and out-of-phase (χ'') signal that is non-zero below 23 K, defining T_c for this magnet. Surprisingly, both the in-phase and out-of-phase signals, χ' and χ'', go through a maximum with strong frequency dependence.


(a)

(b)
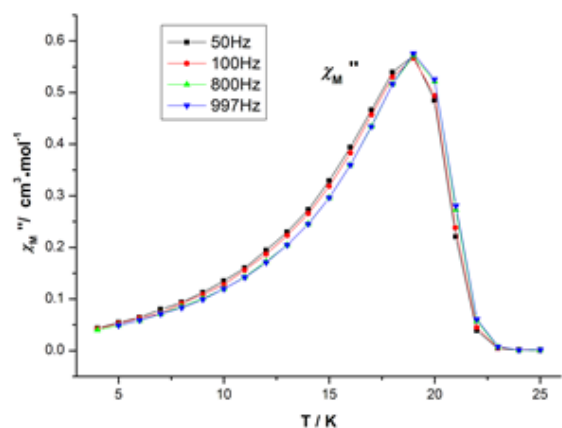
Fig. 9. χ' (T) (Fig. 9b) and χ'' (T) (Fig. 9a) curves of ac magnetic susceptibility of the sample with different frequencies.

On decreasing temperature, the in-phase signals χ' behave: increase abruptly at around 20 K, reach the maximum at about 18 K, and then decrease slowly toward zero. The out-of-phase signals χ'' increase steadily to the maximum around 18-20 K, and then decrease slowly. Although there is no frequency dependence for both the χ'' and χ'', obvious frequency dependence was observed at lower temperatures for both samples (as shown in

Figure 10).The frequency dependence of ac magnetic susceptibilities suggests the presence of a degree of spin-glass behavior.The relative shift of frequency (*c*) is $c = \dfrac{\Delta T_f}{T_f \Delta \log w}$, which fall within the range typical for the conventional spin-glass system (10^{-2}–10^{-3}).
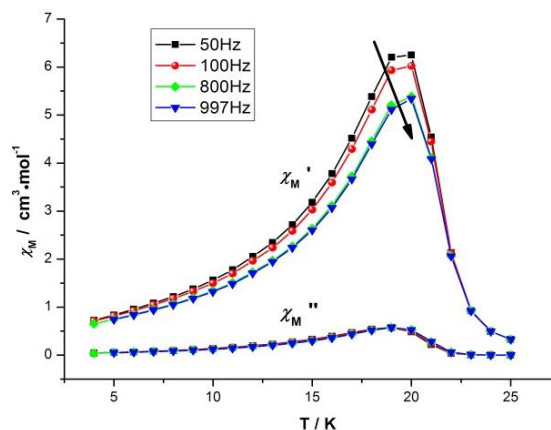
Fig.10. χ(T) curves of the sample.
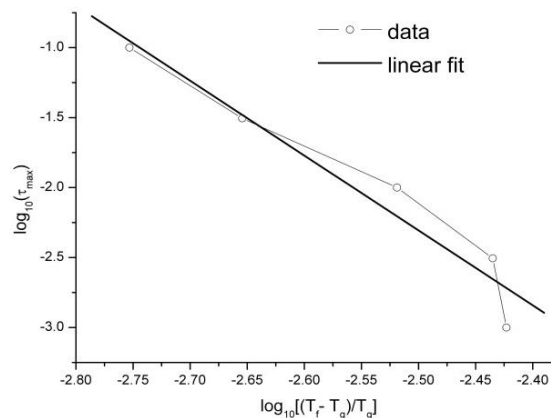
Fig.11. the $\log_{10}((T_f\text{-}T_g)/T_g)$ dependence of the $\log_{10}(\tau)$.

In order to study the critical temperature for spin glass nature in this system, we utilized the conventional critical slowing-down law [21-23]. This dependence of $T_f(w)$ on frequency (f) is well described by the conventional critical ''slowing down'' of the spin dynamics as described by

$$\frac{\tau}{\tau_0} \propto \left(\frac{T_f - T_g}{T_g}\right)^{-zv} \qquad (1)$$

where $\tau \propto 1/\omega$, T_g is the critical temperature for spin glass ordering which is equivalent to the $T_f(w)$ ($w \to 0$), zv is a constant component, which fall within the range typical value for different spin-glass materials[21-22], τ is the average relaxation time corresponding to the frequency of the ac measurement and τ_0 is the relaxation times for the spin dynamics.

The agreement with Eq.(1) is shown in Fig. 11, where $\log_{10} f$ is plotted as a function of $\log_{10}((T_f - T_g)/T_g)$. The best fit to the form shown in Eq.(1) is obtained by choosing the value of critical temperature for spin glass ordering $T_g =$ 19K, which minimized the least square deviation from a straight line fit.

In fact, the temperature value of the maximum of χ at a given frequency (n) corresponds to the blocking temperature $(T_N = T_{max})$, whereby it is assumed that the switching of the oscillating AC field matches the relaxation rate of the magnetization . Both in the real and in the imaginary components the peaks shift to lower temperatures with decreasing frequencies.However the intensities of the peaks behave differently;While for the real component the intensity of the peaks increase with decreasing frequencies, in the imaginary component the peaks decreases with decreasing frequencies.This behaviour of χ'' and χ'' is typical of a spin glass state.

4.3. Field-dependent of magnetization and hysteresis behavior

In order to understand further regarding the nature of magnetic ordering,the ferrimagnetic behavior is characterized by the measurements of field-dependent magnetization and hysteresis behavior, as shown in Fig. 12 .The observed M_s value is 2.82 μ_β, at 50 kOe, but the compound does not reach full saturation.
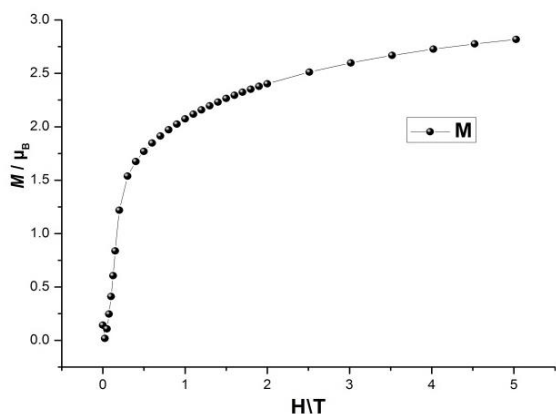

Fig.12. Field-dependent magnetization curves.

The hysteresis curves is measured at 4K, shown in the Fig. 13. The coercive field (H_c) value of 1.12 kOe and remanent magnetization (M_r) value of 0.92 μ_β for the compound.The observed value of H_c is an order of magnitude higher than that for many other hexacyano analogues [7].For example, the observed value of H_C for CsNi[Cr(CN)$_6$]·2H$_2$O [6]
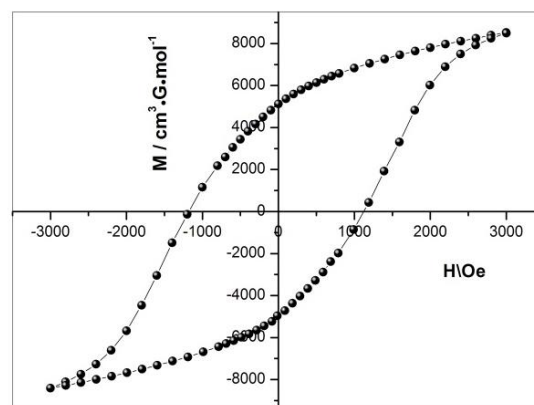
Fig.13. The hystersis loop for the compound.

is 71 Oe (at 3 K), for V[Cr(CN)$_6$]$_{0.86}$·2.8H$_2$O [8] is 25 Oe (at 10 K) and for Cu$_{1.5}$[Fe(CN)$_6$]·6H$_2$O is 240 Oe, (at 4K) [17]. Magnetic parameters like saturation magnetization(M$_s$), coercive field(Hc), Curie constant (C), Weiss paramagnetic Curie temperature(Θ), transition temperature (T$_c$), are different from the those of the bimetallic cyanide-bridged compounds Ni$_{1.5}$[Fe(CN)$_6$]·xH$_2$O [18] and Cu$_3$[Fe(CN)$_6$]$_2$·11.6H$_2$O [10]. Therefore, 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 [15,17,19].

5. CONCLUSIONS

In the present work we have reported a detailed investigation of magnetic properties of multi-metallic compound Ni$_{0.75}$Cu$_{0.75}$ [Fe (CN)$_6$]·6.3H$_2$O in which local ferromagnet order coexists with spin-glass behavior.The temperature-dependent magnetic susceptibilities of the compound were measured. The curie-weiss constants are C=1.79 cm^3·K· mol^{-1}, Θ=21.53K. These results indicate that there exist a ferromagnetic exchange interaction in the complexes. It undergoes a paramagnetic to ferromagnetic transition at 20K. The observed value of coercive field (H$_c$) and remanent magnetization (M$_r$) for the compound are 1.12 KOe and 0.92 μ_β.This value of Hc is much higher than that for reported most Prussian blue analogues. In addition, there exist a spin-glass behaviour in the compound.This behaviour of χ'' and χ'' is typical of a spin glass state, both the in-phase and outof-phase signals, χ' and χ'', go through a maximum with strong frequency dependence.We thus believe that the Ni-Fe Prussian blue analogue is one of the best examples

of molecule-based magnets for the rational design of the magnetic properties.

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SPIN-GLASS ПОВЕДЕНИЕ И ИЗСЛЕДВАНЕ НА МАГНИТНИТЕ СВОЙСТВА НА МНОГОМЕТАЛНИ (НИКЕЛ-ЖЕЛЯЗО) КОМПЛЕКСИ С ФЕРОЦИАНИД
$Ni_{0.75}Cu_{0.75}[Fe(CN)_6]•6.3H_2O$

Кинг Лин[1,2], Джимин Джи[1], Хайфу Хуанг[1,3], Юн Хе[1,*], Джианмей Ксу[2]

[1]*Колеж по физика и технология, Университет Гуанкси, Гуилин,Китай*
[2] *Департамент по информационни технологии, Медицински колеж в Хайнан, Найкоу, Китай*
[2] *Департамент по физика, Университет в Нанджинг, Нанджинг, Китай*

(Резюме)

Многометалното съединение $Ni_{0.75}Cu_{0.75}[Fe(CN)_6]·6.3H_2O$ е приготвено чрез съутаяване. Измерен е неговия температурно-зависим магнитен сусцептибилитет. Константите на Currie-Weiss са съответно C= 1.79cm³·K· mol⁻¹, Θ = 21.53K. Тези резултати показват, че в тези комплекси е налице феромагнитно-обменно взаимодействие. Преходът от парамагнитни към феромагнитни свойства става при 20 K. Наблюдаваната коерцетивна сила (H_c) и остатъчното намагнетизиране (M_r) за съединението са съответно 1.12 KOe и 0.92 μ_β. Стойността на Нс е много по-висока от съобщаваната за повечето анализи на фери-фероцианида. Освен това налице е spin-glass поведение на това съединение. Това поведение за χ'' и χ'' е типично за spin glass-състоянието, минавайки през максимум със силна честотна зависимост.