Vol 13 No 5, May 2004
1009-1963/2004/13(05)/0746-04

Chinese Physics

© 2004 Chin. Phys. Soc.
and IOP Publishing Ltd

Spin-glass state and ferromagnetic order in Cu(II)–Fe(III) cyanides*

He Yun(何 云)[a)b)], Dai Yao-Dong(戴耀东)[c)], Huang Hong-Bo(黄红波)[a)],
Lin Jun(林 俊)[a)], and Hsia Yuan-Fu(夏元复)[a)†]

[a)] *Department of Physics, Nanjing University, Nanjing* 210093, *China*
[b)] *College Physics and Information Technology, Guangxi Normal University* 541004, *China*
[c)] *College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing* 210016, *China*

(Received 24 July 2003; revised manuscript received 18 November 2003)

The static and dynamic magnetic properties of a Prussian blue analogue, molecular magnet $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot 3NH_3 \cdot 6H_2O$ were investigated in detail. The H dependence of the linear AC susceptibility, the irreversibility in the field-cooled (FC) / zero-field-cooled (ZFC) magnetization (M_{FC}/M_{ZFC}) and the relaxation of M_{ZFC} suggest that the magnetic system can be visualized as containing a ferromagnetic cluster of spin below T_C, mixed with small spin-glass clusters formed below temperature T_g less than T_C. The observed magnetic properties are explained with a ferromagnetic-spin-glass phase model. The magnetic ordering of the sample occurs below 19.8K.

Keywords: spin glass, exchange interaction, ferromagnetic interaction, magnetic Prussian blues
PACC: 7550B, 7550C, 7550L

1. Introduction

The advantages of molecule-based magnets compared to traditional ones are that the magnets can be obtained through a selection of proper spin sources (e.g., transition metal ions, organic radicals) and coordinating ligands.[1] As one of the best examples of a bimetallic and mixed-valence cyanometallate, the Prussian blue family has received much attention due to its large spontaneous magnetization, high critical temperature and large coercivity.[2] Recently, photoinduced magnetization changes were observed to be due to charge transfer between magnetic coupling ions in a Prussian blue analogue and indicated their potential application in photo-magnetic devices.[3] Thus, the Prussian blue and its analogues have been investigated in depth. The magnetic properties of a number of Prussian blue analogues come from the exchange interactions;[4] the nature of the M–CN–M′ interaction is essentially explained by the super-exchange interaction model,[5] due to the large asymmetric CN^- anion and an enhanced molecular spin. The magnetic orbitals on adjacent transition metal centres M and M^- contribute to the super-exchange interactions as follows: e_g-e_g and t_{2g}-t_{2g} give rise to antiferromagnetic contributions; e_g-t_{2g} gives rise to ferromagnetic contributions. In earlier studies, the magnetic properties of a number of Prussian blue and analogues have been shown to exhibit long-range ferromagnetic or antiferromagnetic ordering below critical temperature T_C. However, the compound of $K_xCo[Fe(CN)_6]_y z H_2O$($x \sim 0.16$, $y \sim 0.72$, $z \sim 4.4$) exhibits behaviour characteristic of cluster glass (CG), with no true long-range order being present.[6,7] As already referred to,[8] a novel member of the Prussian blue family, $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot 3NH_3 \cdot 6H_2O$, was synthesized, in which NH_3 ligands are in stochastic distribution. We studied in detail the AC susceptibility and DC magnetization of (Cu–Fe) hexacyanide $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot 3NH_3 \cdot 6H_2O$. Our results show behaviour characteristic of spin-glass and ferromagnetic order.

2. Experimental details

The Prussian blue analogue $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xNH_3 \cdot yH_2O$ was prepared by the following method. An aqueous solution of $[Cu(NH_3)_6](NO_3)_2$ (1.0mmol) was added to an aqueous solution of $K_3[Fe(CN)_6]$ (0.5mmol) at room temperature. The reaction con-

*Project supported by the National Natural Science Foundation of China (Grant No 19835050).
†Corresponding author. Tel: 0086-25-3594234; Fax: 0086-25-3594234. E-mail: hsia@netra.nju.edu.cn

tinued for more than one week and then the brown–black prismatic crystallites were collected by filtration with a yield of 89%. The inductively coupling plasma (ICP) result of the compound reveals that the weight percentage of Cu, 23.07% and Fe, 13.69% are approximately in agreement with the ratio Cu:Fe=3:2. The infrared (IR) spectrum (KBr pellet, cm^{-1}) shows vibration bands at 2100cm^{-1}, 2171cm^{-1} from [ν(CN)]; 3629cm^{-1}, 3666 cm^{-1} from [$\nu(NH_3)$] and 3176cm^{-1}, 3270cm^{-1}, 3477cm^{-1} from [ν(OH)]. It is observed that the compound is not very stable. The ammonia and water molecules would be liberated slowly, and the crystal structure determines the spatial changes during the phase transition associated with magnetic transition. Therefore, the formula of the compound might be expressed by $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xNH_3 \cdot yH_2O$. The x-ray diffraction pattern recorded by a CCD x-ray diffractometer within a few hours for a fresh single crystal indicates that the lattice parameter is 1.092nm. Magnetization measurements on the sample were performed with a Quantum Design PPMS model-6000 magnetometer (SQUID).

3. Results and discussions

For the infinite-range model in the mean-field theory,[9] the independent random interactions J_{ij} are distributed according to the following law:

$$P(J_{ij}) = \left(\frac{N}{2\pi}\right)^{1/2} \exp\left[-\frac{N}{2}\left(J_{ij} - \frac{J_0}{N}\right)^2\right],$$

where $< J_{ij} >_b = J_o/N$ and $< J_{ij}^2 >_b = 1/N$. In the presence of an external magnetic field H applied along the μ=1 direction, the Hamiltonian of the model can be written as

$$\hat{H} = -\sum_{i,j} J_{ij} \sum_{\mu} S_{i\mu} S_{j\mu} - H \sum_i S_{i1}.$$

In the limit of large and positive J_o, the interactions are mainly ferromagnetic and the system exhibits a ferromagnetic phase. For J_o=0, the interactions are random in sign and the ordering is of the spin-glass type. The border region between ferromagnetic and spin-glass phases occurs for $J_o \approx 1$.

The DC magnetization data were collected in the temperature range from 5K to 30K. Prior to each temperature scanning, the sample was warmed to 80K and then cooled to 5K in zero applied field; a field was then applied and a waiting time of 2h was used before warming. The temperature dependence of the DC magnetization for the sample measured in three different magnetic fields is shown in Fig.1. The magnetic studies of the compound confirm a paramagnetic to ferromagnetic transition occurring around the temperature of 20K, and the compound exhibits ferromagnetic domain structure at low temperature. For the three different magnetic fields, three distinct states are observed in the temperature region studied. For $T >$ 20K the sample is paramagnetic and shows reversible magnetic behaviour. Below 20K the magnetization rises rapidly with decreasing temperature, and exhibits irreversible magnetic behaviour, which is implied by the bifurcation of the field-cooled (M_{FC}) and zero-field-cooled (M_{ZFC}) magnetization curves. The bifurcation point shifts to lower temperature when the applied magnetic field (H) increases. This behaviour is attributed to the formation of clusters and their freezing at $T \sim$ 20K, which has been described by the spin-glass (SG) theory.[10,11] It is evident that the strong irreversibility and shift of bifurcation point to lower T with increasing H are indications of glassy behaviour.[12] The rapid rise in M at $T \sim$20K may be associated with the occurrence of finite range ferromagnetic ordering, forming spin clusters near the critical temperature T_C. Therefore, the clusters become randomly frozen as T is further decreased, indicated by the ZFC magnetization rapidly rising at around 20K and then undergoing a less rapid drop to 14K for H=0.0004T. The absence of true long-range order are apparent from the large difference between M_{ZFC} and M_{FC} below $T_C \sim$ 20K. And the difference between M_{ZFC} and M_{FC} is in the spin-glass phase at low temperature, indicating the presence of short range ferromagnetic ordering within a cluster. This may be a typical reentrant spin-glass (RSG) phenomenon.[9,13,14]

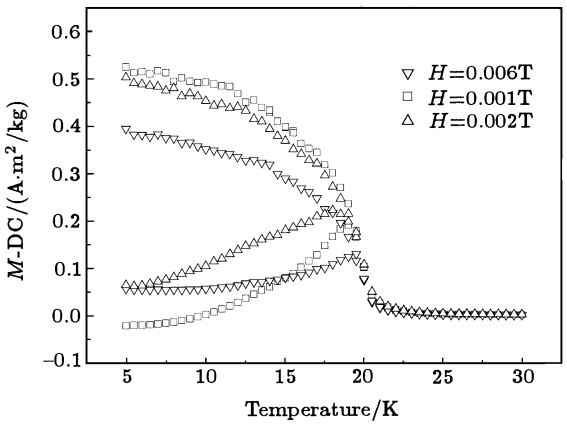


Fig.1. Irreversible curves of M_{ZFC} and M_{FC} measured in 0.0006, 0.001 and 0.002T below 30K for $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot 3NH_3 \cdot 6H_2O$.

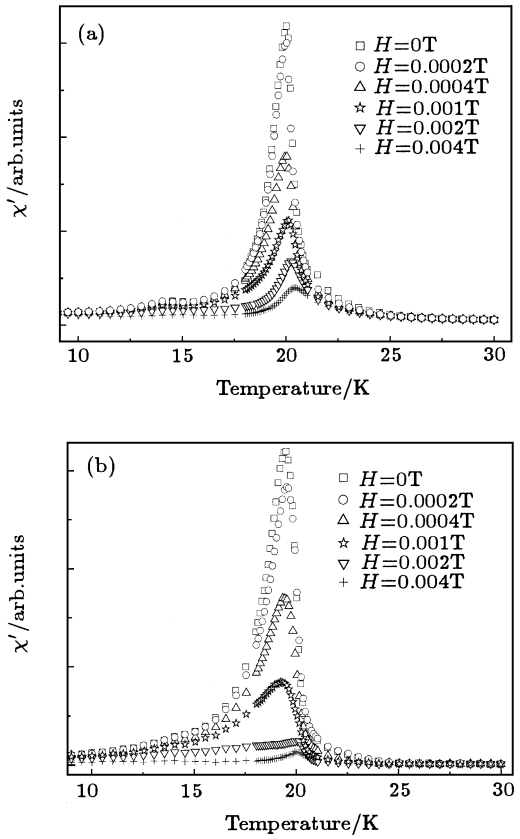


Fig.2. Temperature dependence of the in-phase χ' (a) and out-phase χ'' (b) of the compound measured in alternating field H_{AC}=10^{-6}T, f=2400Hz with a biasing DC field (selected at 0, 0.0002, 0.0004, 0.001, 0.002, 0.004T).

The AC linear susceptibility for frequency f=2400 Hz, H_{AC}=10^{-6}T, with a biasing DC field of 0∼0.004T, is displayed in Fig.2. In order to get magnetization equilibrium, each scan begins at 5K after cooling from 80K and waits for 9999 seconds in related DC fields. The measurement or AC susceptibility gives a detailed insight into the dynamics of freezing. Figure 2 shows the temperature dependence of the real part χ' and imaginary part χ'' under the ZFC condition at a fundamental frequency f=2400Hz. The peak in $\chi'(T)$, accompanied by a peak in $\chi''(T)$ at a temperature around T_C ∼20K, can be associated with the appearance of short range FM ordering. The peaks systematically shift slightly to higher T and sharply decrease in height with increasing DC field H. In the paramagnetic phase ($T > T_C$), the susceptibility exhibits a maximum indicating the presence phase competition in the vicinity of Curie temperature.[15] We assume the reduction of intensity for χ' and χ'' in the presence of DC biasing fields to follow the spin glass model.[12] In this spin-glass phase that moments are frozen into equilibrium orientations but there is no long-range order. The magnetic phase may occur in spatially random systems with competing exchange interactions or super-exchange interactions. In the nature of two mixed phases, both spin-glass and ferromagnetic characters may help to explain a bifurcation between M_{ZFC} and M_{FC}. The in-phase susceptibility χ' exhibits another peak with biasing DC fields-dependence at lower temperature, and the intensity peak of χ' decreases with increasing biasing DC field. The peak disappeared with biasing DC field of 0.002T, indicating the freezing of clusters as T is decreased below T_C.

Figure 3 shows the measurement of $M(H)$ under the ZFC condition at several temperatures using the vibrating sample magnetometer in the field range 0–0.7T. Magnetization does not fully saturate even in fields as high as 0.7T at T=5K. The very saturation field of the magnetization is correlated with the spin frustration. At 5 and 13K, ZFC magnetization curves show an S-shaped behaviour (inset of Fig.3). This S-shaped behaviour occurs for temperature below the freezing temperature only, and is observed both in metallic spin glasses (for measurements of $Cu_{1-x}Mn_x$[16,17]) and in nonmetallic spin glasses (such as $Eu_xSr_{1-x}S$[18]).

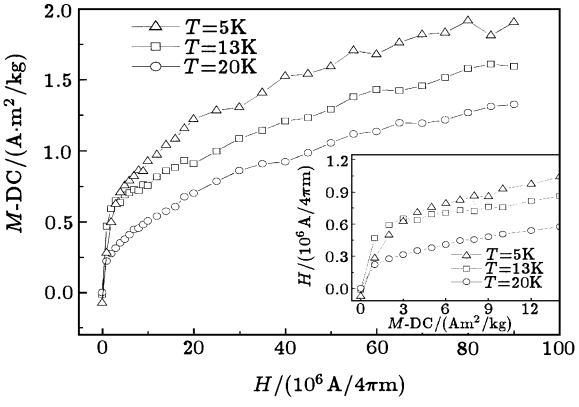


Fig.3. Curves of initial magnetization, measured after zero-field-cooling, for temperatures 5, 13 and 20K. Inset: enlargement of the low-field region, for temperatures 5, 13 and 20K.

4. Conclusions

Our result suggests that molecular magnet $Cu_3^{II}[Fe^{III}(CN)_6]_2{\cdot}3NH_3{\cdot}6H_2O$ exhibits mixed phases in which ferromagnetic order and spin-glass order coexist. The magnetic ordering of the sample occurs below 19.8K.

Acknowledgements

The authors thank Dr. H. P. Kunkel and Dr. X. Zhou, Manitoba University, Canada, for carrying out the magnetization measurements, and Professor G. Williams of Manitoba University for helpful discussions.

References

[1] Kahn O 1993 *Molecular Magnetism* (New York: VCH) ch 12

[2] Verdaguer M, Bleuzen A, Marvaud V, Vaissermann J, Seuleiman M, Desplanches C, Scuiller A, Train C, Garde R, Gelly G, Lomenech C, Rosenman I, Veillet P, Cartier C and Villain F 1999 *Coordination Chem. Rev.* **190–192** 1023

[3] Sato O, Iyoda T, Fujishima A and Hashimoto K 1996 *Science* **272** 704

[4] Mallah T, Thiebaut S, Verdaguer M and Veillet P 1993 *Science* **262** 1554

[5] Ohkoshi S, Iyoda T, Fujishima A and Hashimoto K 1997 *Phys. Rev.* B **56** 11642

[6] Pejakovic D A, Manson J L, Miller J S and Epstein A J 2000 *J. Appl. Phys.* **87** 6028

[7] Pejakovic D A, Manson J L, Miller J S and Epstein A J 2000 *Phys. Rev. Lett.* **85** 1994

[8] Hsia Y, Yu Z, Song Y, Huang H, You X, Zhou X Z, Li Z W, Kunkel H P and Williams G 2002 *Chin. Phys. Lett.* **19** 595

[9] Sherrington D and Kirkpatrick S 1975 *Phys. Rev. Lett.* **35** 1792

[10] Edwards S F and Anderson P W 1975 *J. Phys.* F: *Metal Phys.* **5** 965

[11] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801

[12] Mydosh C M, Levin K and Grest G S 1982 *Phys. Rev. Lett.* **48** 1756

[13] Campbell I A and Senoussi S 1992 *Phil. Mag.* B **65** 1267

[14] Gabay M and Toulouse G 1981 *Phys. Rev. Lett.* **47** 201

[15] Berger A, Mitchell J F, Miller D J and Bader S D 2001 *J. Appl. Phys.* **89** 6851

[16] Emmerich K, Felten G and Schwink C 1980 *J. Magn. Magn. Mat.* **15–18** 173

[17] Schwink C and Schulze U 1978 *J. Magn. Magn. Mat.* **9** 31

[18] Maletta H and Felsch W 1979 *Phys. Rev.* B **20** 1245