
Proceedings of the CSMAG'07 Conference, Košice, July 9–12, 2007

Effect of Pressure on Magnetic Properties of $\text{TM}_3[\text{Cr}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ Nanoparticles

A. ZENTKO, M. ZENTKOVÁ, V. KAVEČANSKÝ, M. MIHALIK,
Z. MITRÓOVÁ

Institute of Experimental Physics, Slovak Academy of Sciences
040 01 Košice, Slovak Republic

Z. ARNOLD, J. KAMARÁD

Institute of Physics of the AS CR, v.v.i.
Na Slovance 2, 182 21 Prague 8, Czech Republic

M. CIESLAR

Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

AND V. ZELENĚÁK

P.J. Šafárik University, Moyzesova 11, 04154 Košice, Slovakia

Effect of pressure on magnetic properties of magnetic nanoparticles, based on Prussian blue analogues, were studied in pressures up to 1.2 GPa. The $\text{Mn}_3[\text{Cr}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ and $\text{Ni}_3[\text{Cr}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ nanoparticles were prepared by reverse micelle technique. Transmission electron microscopy images show nanoparticles with average diameter of about 3.5 nm embedded in an organic matrix. The characteristic X-ray peaks of nanoparticles are more diffused and broader. Systems of nanoparticles behave as systems of interacting magnetic particles. The Curie temperature T_C is reduced from $T_C = 56$ K for Ni-Prussian blue analogues to $T_C = 21$ K for Ni-nanoparticles system and from $T_C = 65$ K for Mn-Prussian blue analogues to $T_C = 38$ K for Mn-nanoparticles system. One can explain this reduction of the Curie temperature and of the saturated magnetization μ_s by dispersion of nanoparticles in an organic matrix i.e. by a dilution effect. Applied pressure leads to a remarkable increase in T_C for system of Mn-nanoparticles ($\Delta T_C/\Delta p = +13$ K/GPa) and to only slight decrease in T_C for system of Ni-nanoparticles ($\Delta T_C/\Delta p = -3$ K/GPa). The pressure effect follows behavior of the mother Prussian blue analogues under pressure. The increase in saturated magnetization, attributed to compression of the organic matrix, is very small.

PACS numbers: 75.30.Cr, 75.50.Ee, 75.50.Gg, 75.50.Xx

1. Introduction

In the last few years, there has been considerable interest in preparation and investigation of magnetic nanoparticles (NAP) because of their potential applications in high density recording media, but also for the reasons as macroscopic tunneling [1] and quantum computing [2]. After discovery of single-molecule magnet behavior in Mn_{12} -acetate with highest spin ground state $S = 51/2$ [3] one of the important issue of magnetism is the study of objects with magnetic moments intermediate between this value and the value of metallic NAP with $S \geq 1000$ [4]. NAP based on Prussian blue analogues (PBA) prepared by reverse micelle technique with $S < 1000$ are promising candidates. The first report on application of this technique for preparation of NAP based on PBA has been made by Vaucher et al. in [3]. Later in paper [5] authors referred about preparation of cyanide bridged $\text{Cr}^{\text{III}}\text{-Ni}^{2+}$ nanoparticles. Magnetic properties of Ni-NAP are interpreted as behavior of superparamagnetic particles. Magnetic properties of the mother PBA with stoichiometry is $\text{A}_3^{2+}[\text{B}^{\text{III}}(\text{CN})_6]_2^{3-} \cdot n\text{H}_2\text{O}$ are quite well understood assuming (i) only the super-exchange interaction between the nearest-neighbour metal A^{2+} and B^{III} ($\text{A}^{2+}\text{-N} \equiv \text{C-B}^{\text{III}}$) ions have to be considered; (ii) if the magnetic orbital symmetries of the metal ions are the same, the super-exchange interaction is antiferromagnetic (J_{AF}); conversely, when their magnetic orbital symmetries are different, the super-exchange interaction is ferromagnetic (J_{F}). The cluster glass behaviour is frequently observed in this system [6, 7]. The results of the pressure effect on magnetic properties of the mother PBA were recently published in [8]. In our paper we study the pressure effect on magnetic properties of $\text{Mn}^{2+}\text{-Cr}^{\text{III}}\text{-NAP}$ and $\text{Ni}^{2+}\text{-Cr}^{\text{III}}\text{-NAP}$ embedded in an organic matrix.

2. Experimental

The reverse micelles technique described in [5] was used for preparation of $\text{Mn}^{2+}\text{-Cr}^{\text{III}}$ and $\text{Ni}^{2+}\text{-Cr}^{\text{III}}$ cyano-bridged nanoparticles dispersed in an organic matrix. The content of organic surfactants in the samples was estimated to about 22 wt.% (Ni-NAP) and 28 wt.% (Mn-NAP) by thermogravimetric analysis (TGA) (SETARAM 9L). The compounds were characterized by IR spectroscopy (Avatar 330) confirming the presence of Mn- and Ni-based PBA. Transmission electron microscopy (TEM) observations were performed on JEOL JEM 200FX transmission electron microscope operated at 200 kV. X-ray diffraction (XRD) powder diagrams were recorded using a Philips X-Pert equipment at $\text{Cu } K_{\alpha}$ radiation. Magnetization measurements were carried out with a SQUID magnetometer (MPMS). Pressure was generated by a hydrostatic CuBe pressure cell filled with a mixture of mineral oils serving as the pressure transmitting medium and operating up to 1.2 GPa [9]. Pressure induced changes of the saturated magnetization μ_s and the Curie temperature T_{C} are reversible.

3. Results and discussion

Dark-field (Fig. 1a) and bright-field TEM images show spherical Ni-NAP with average diameter of about 3.5 nm dispersed in an organic matrix. The distribution of the size is quite narrow and can be fit by a Gaussian distribution (Fig. 1b). The characteristic XRD peaks of PBA are more diffused and broader.

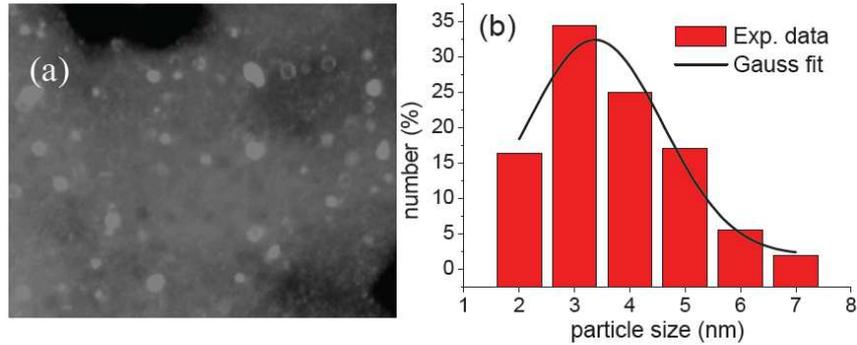


Fig. 1. The Ni-NAP embedded in an organic matrix; (a) dark-field TEM image; (b) distribution of NAP determined from TEM by an analysis of the picture.

The average size of about 4.5 nm determined from X-ray measurements corresponds with TEM results. The system of Mn-NAP was prepared for the first time. Statistically there are at least two kinds of region with different concentration of magnetic NAP than the average concentration. An evidence for our assumption is indirect and comes from magnetization measurements. We expect that both systems Ni-NAP and Mn-NAP behave as systems of strongly interacting magnetic particles. The super-exchange interaction is dominant intra-NAP magnetic interaction. The dipole-dipole interaction is dominant inter-NAP magnetic interaction [5]. The dispersion of NAP into an organic matrix leads to a dilution of the mother PBA and consequently the Curie temperature is reduced from $T_C = 56$ K for Ni-PBA to $T_C = 21$ K for Ni-NAP system and from $T_C = 65$ K for Mn-PBA to $T_C = 38$ K for Mn-NAP system. We define the Curie temperature as a minimum of dM/dT on the sharp increase in $M(T)$ (Fig. 2a and b). In the case of Mn-NAP we found two satellite minima in dM/dT . Each of these minima indicates T_C of Mn-PBA sub-systems and represents two extra regions with different concentration of magnetic NAP.

We expect that pressure affects inter-NAP distance (high compressibility of an organic matrix) and changes magnetic properties of NAP. The applied pressure strengthens magnetic super-exchange interaction of Mn-NAP with dominant J_{AF} and increases T_C with pressure coefficient $\Delta T_C/\Delta p = +13$ K/GPa (Fig. 2a) mainly due to the increased overlapping of magnetic orbitals [8]. As it is shown in Fig. 2b, pressure decreases T_C ($\Delta T_C/\Delta p = -3$ K/GPa) for system of Ni-NAP with dominant J_F which is mainly attributed to less effective magnetic coupling due to

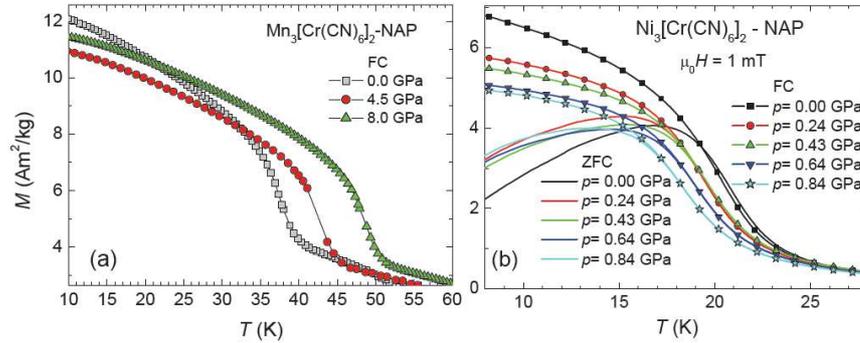


Fig. 2. The temperature dependence of magnetization: (a) Mn-NAP and (b) Ni-NAP.

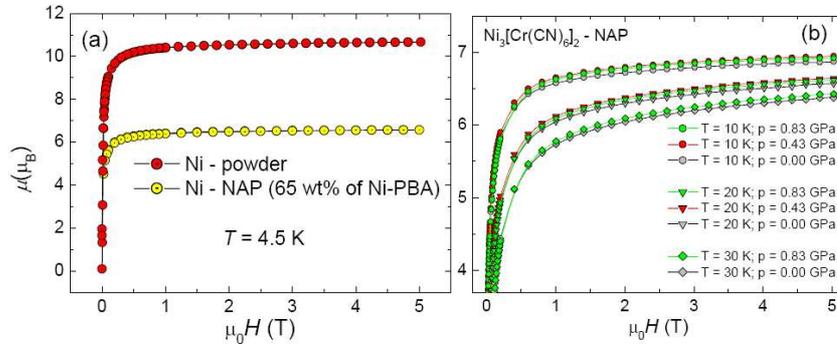


Fig. 3. The field dependence of magnetization: (a) comparison of mother Ni-PBA and Ni-NAP; (b) the pressure effect on magnetization of Ni-NAP system at different temperatures.

the reduction in the bonding angle $\text{Ni}^{2+}-\text{N}\equiv\text{C}-\text{Cr}^{\text{III}}$ from an ideal value of 180° [8]. Figure 3a demonstrates a dilution effect. The shape of the magnetization curve for Ni-NAP is the same as for Ni-PBA and the reduction of the saturated magnetization μ_s is mainly due to reduced ratio of mother PBA (only 65 wt.%) in the system. The applied pressure increases magnetic moment μ_s (Fig. 3b). This behaviour is opposite to the behaviour of the mother Ni-PBA [8] and is attributed to the reduction of inter-NAP distances by compression of the organic matrix.

Acknowledgments

This work was supported by VEGA 2/7184/27, APVT project No. 20-005204, ISTC SK-113/CZ-46 and project number 1001000632 GA ASCR.

References

- [1] L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **383**, 145 (1996).
- [2] M.N. Lerunberger, D. Loss, *Nature* **410**, 789 (2001).
- [3] S. Vaucher, M. Li, S. Mann, *Angew. Chem. Int. Ed.* **39**, 1793 (2000).
- [4] J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H.U. Gudel, S. Decurtins, *Angew. Chem. Int. Ed.* **39**, 1605 (2000).
- [5] L. Catala, T. Gacoin, J.P. Boilot, E. Riviere, C. Paulsen, E. Lhotel, T. Mallah, *Adv. Mater.* **15**, 826 (2003).
- [6] M. Verdaguer, G. Girolami, *Magnetism: Molecules to Materials V*, Eds. J.S. Miller, M. Drilon, Wiley-VCH Verlag, Weinheim 2004, p. 283.
- [7] M. Zentková, M. Mihalik, J. Kovač, A. Zentko, Z. Mitróová, M. Lukáčová, V. Kavčanský, L.F. Kiss, *Phys. Status Solidi B* **243**, 272 (2006).
- [8] M. Zentková, Z. Arnold, J. Kamarád, V. Kavčanský, M. Lukáčová, S. Mat'áš, M. Mihalik, Z. Mitróová, A. Zentko, *J. Phys., Condens. Matter* **19**, 266217 (2007).
- [9] M. Zentkova, Z. Arnold, Matus Mihalik, M. Mihalik, A. Zentko, J. Kamarad, Z. Mitroova, S. Matas, *J. Electr. Eng.* **57**, No. 8/S, 29 (2006).