Magnetic Properties of a Two-Dimensional Mixed-Spin System

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Abstract

Using a Langmuir-Blodgett (LB) synthesis method, novel two-dimensional (2D) mixed-spin magnetic systems, in which each magnetic layer is both structurally and magnetically isolated, have been generated. Specifically, a 2D Fe-Ni cyanide-bridged network with a face-centered square grid structure has been magnetically and structurally characterized. The results indicate the presence of ferromagnetic exchange interactions between the Fe$^{3+}$ ($S = 1/2$) and Ni$^{2+}$ ($S = 1$) centers.

Key words: two-dimensional magnetism; mixed-spin; Langmuir-Blodgett film

1. Introduction

Part of the interest in molecule-based magnets arises from the potential for forming low-dimensional structures with anisotropic physical properties. In this paper, we report on the magnetic behavior of quasi-two-dimensional (2D) Fe-CN-Ni grid networks, in which each magnetic layer is both structurally and magnetically isolated. Culp et al. have developed a unique Langmuir-Blodgett (LB) synthesis method to transfer monolayers of a 2D Fe-CN-Ni grid network, formed at the air-water interface, as thin films onto various substrates [1]. This technique generates a new low-dimensional network which cannot be formed from homogeneous reaction conditions.

The structure of the resulting assemblies of mixed-spin Fe-CN-Ni bilayers transferred as thin films onto Mylar is shown schematically in Fig. 1. Each deposition cycle produces a bilayer of the inorganic grid network sandwiched between an organic layer. The LB films have been structurally characterized by x-ray photoelectron spectroscopy (XPS), FT-IR spectroscopy, x-ray absorption fine structure (XAFS), and grazing incidence synchrotron x-ray diffraction (GIXD). These probes have allowed for the identification of a face-centered square grid structure with an Fe$^{3+}-$Ni$^{2+}$ separation of 5.1 Å, and an average structural domain size of 3600 Å$^2$ [1]. Adjacent bilayers are separated by ≈ 50 Å, and are effectively isolated from each other.

The existence of ferromagnetic exchange between the low spin Fe$^{3+}$ ($S = 1/2$) and Ni$^{2+}$ ($S = 1$) ions is expected after consideration of the exchange interaction in other cyanide bridged Fe$^{3+}-$Ni$^{2+}$ systems [2,3]. The ferromagnetic behavior in these and other metal cyanides has been rationalized by considering the
d-orbital symmetries for the unpaired electrons in the respective metal centers. The magnetic orbital on the Fe$^{3+}$ center is of $t_{2g}$ symmetry while the two Ni$^{2+}$ spins are in orbitals of $e_g$ symmetry. The different symmetry orbitals do not overlap via the cyanide ligand, thereby resulting in the parallel alignment of the spins according to Hund’s rule [4].

2. Magnetic Measurements

The magnetic properties of a sample containing 150 bilayers of the Fe-CN-Ni network on each side of a Mylar film (10 cm$^2$) were investigated using SQUID magnetometry. Measurements were performed with the applied magnetic field oriented either parallel or perpendicular to the plane of the film. The field cooled (FC) magnetization versus temperature for both orientations, measured in a field of 2 mT, are shown in Fig. 2. Both orientations show a break at a $T_c$ of 10 K, and the saturated behavior below 5 K indicates the presence of magneto ordered domains. The presence of long-range magnetic order at 2 K was verified by the measurements shown in Fig. 3. The material shows clear hysteresis loops with coercive fields of 14 mT (parallel orientation) and 11 mT (perpendicular orientation).

The assignment of a ferromagnetic state was made based on high field magnetization studies performed at the National High Magnetic Field Laboratory, Tallahassee (NHMFL). The magnetization of the film was measured up to 30 T using a vibrating sample magnetometer (VSM). As shown in Fig. 2 (inset), the magnetization of the sample saturates around 20 T without evidence for a spin-flop transition. The increased noise above 15 T is due to the addition of a second dc power supply generating the magnetic field. The absence of a spin flop discriminates against antiferromagnetic coupling and the presence of a ferrimagnetic state.

3. Discussion and Summary

A stronger magnetization measured in the parallel orientation in the $M$ vs. $T$ plot in Fig. 2 indicates that the magnetic easy axis is within the XY directions parallel to the film planes. Consistently, in the low field limit ($B \ll B_S$, where $B_S$ is the applied field at which $M$ saturates, $M_S$), the magnetization in the parallel orientation changes more rapidly than in the perpendicular orientation with respect to changes in the external field. This behavior is most likely due to a combination of the single ion anisotropies of the metal centers and the reduced symmetry of the low-dimensional material. In summary, a 2D Fe-Ni cyanide-bridged network with a face-centered square grid structure has been generated using a Langmuir-Blodgett (LB) synthesis method, and the magnetic study on this film shows the presence of ferromagnetism.

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