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Pressure effects on a dimetallic ferrimagnet $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$

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Abstract

We have investigated pressure effects on a dimetallic ferrimagnet $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ (en; ethylenediamine) through the magnetic measurements using a diamond anvil cell in the pressure region up to $P = 4.7$ GPa. This ferrimagnetic compound has an eminent high transition temperature (Tc) of 69 K at ambient pressure in the structurally characterized molecule-based magnet system. Under hydrostatic pressure, Tc linearly increases against pressure, and exceeds 130 K at $P = 4.7$ GPa. The amount of the saturated moment hardly changes in the considered pressure region. This pressure experiment might become a prototype of artificial material control for the high-Tc molecule-based magnet.

Keywords: Pressure effects; Dimetallic ferrimagnet; Molecule-based magnet; Diamond anvil cell; Transition temperature

1. Introduction

One of the fascinating targets in the area of molecule-based magnet is to create ferromagnets and/or ferrimagnets exhibiting high transition temperature (Tc). There have been two scientific approaches in its study. One is a molecular design based on organic radicals or C_{60} from the side of organic chemistry. The other is one using metal–complex units and organic ligands from the inorganic chemistry side [1].

As for organic magnets, syntheses of many ferromagnets have been succeeded since the discovery of β-phase *p*-NPNN ($T\mathrm{c} = 0.61$ K) in 1991 [2] and, in some compounds, its Tc exceeds ten times as large as that for β-phase *p*-NPNN: γ-phase: BBDTA $GaCl_4$ (organic radical ferromagnet; $T\mathrm{c} = 7.0$ K) [3], *p*-NC · C_6F_4 · CNSSN (organic radical week-ferromagnet; $T\mathrm{c} = 35.5$ K at ambient pressure, $T\mathrm{c} = 71$ K at $P = 16$ kbar) [4–6], and TDAE–C_{60} (C_{60} system; $T\mathrm{c} = 16$ K) [7,8]. The spin density per one molecule in the organic system, however, is quite small comparing to that of metal–complex system, and the organic system might not be appropriate for creating a strong magnet. From the view point of quantum magnetism, the magnetic property of the organic material is very interesting, and furthermore varies sensitively against external stress like pressure due to the softness and lightness. It has been experimentally confirmed that the ferromagnetic structure is generally unstable under pressure, and in some organic compounds, the ferromagnetic state disappears under small hydrostatic pressure of less than 10 kbar (β-phase *p*-NPNN [9–11], *p*-Cl-TEMPO [12], Dupeyredioxyl [13], TDAE–C_{60} [14,15]).

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Metal–complex compounds are constructed with metal ions and organic ligands, and various high-*T*c ferromagnets and ferrimagnets have been reported in Prussian Blue type of system as follows: $CsMn^{II}[Cr^{III}(CN)_6]$ (ferrimagnet, *T*c = 90 K) [16], $CsNi^{II}[Cr^{III}(CN)_6]$ (ferromagnet, *T*c = 90 K) [17], $Cs_2Mn^{II}[V^{II}(CN)_6]$ (ferrimagnet, *T*c = 125 K) [18], $Cs_{0.75}Cr_{1.125}{}^{II}[Cr^{III}(CN)_6]$ (ferrimagnet, *T*c = 190 K) [19], $Cr_3{}^{II}[Cr^{III}(CN)_6]_2 \cdot 10H_2O$ (ferrimagnet, *T*c = 240 K) [19], and $V[Cr(CN)_6]_{0.86} \cdot 2.8H_2O$ (ferrimagnet, *T*c = 315 K) [20]. They possess large spontaneous magnetization due to the high spin state. However, their crystal structures have not been solved yet, and the correlation between magnetic property and crystal structure has been unknown.

Dimetallic ferrimagnet $[Mn(L)]_3[Cr(CN)_6]_2 \cdot n_2O$ [21,22] series have an eminent transition temperature of about 70 K in the structurally characterized molecule-based magnets; (1) L = en (ethylenediamine), n = 4, *T*c = 69 K, (2) L = glya (glycine amide), n = 2.5, *T*c = 71 K, (3) no L, n = 12, *T*c = 63 K. This dimetallic system has an ideal three-dimensional network, extended by Cr^{III}–CN–Mn^{II} linkage, and the antiferromagnetic interaction between Cr^{III} ion and Mn^{II} one results in the appearance of huge spontaneous moment for $S = 9/2$. The crystal structure with the antiferromagnetic molecule stacking is assumed to be generally stable under external stress. Thus, we have focused our attention on this series as a target of material control for high *T*c by using pressure, and have investigated the pressure effects on $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ firstly.

2. Experimental

The preparation of $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ has been described elsewhere [21]. Fig. 1 shows a cubic picture of the unit cell. The crystal structure belongs to a monoclinic system of space group *C*2/*c* (#15) with lattice parameters $a = 24.505(7)$ Å, $b = 11.323(4)$ Å, $c = 14.810(4)$ Å, $\beta = 120.69(2)°$ and $V = 3533(1)$ Å^3. Three-dimensional network is constructed by the alternative array of $[Cr(CN)_6]^{3-}$ and $[Mn(en)]^{2+}$ ions. The network comprises defective cubes with three Cr atoms, three Mn(1) atoms, and one Mn(2) atom at the seven corners and eight Cr–CN–Mn edges. The Mn–N–C bond angle ranges between 145.7(3)° and 167.4(3)°. The shortest Cr···Mn(1), Cr···Mn(2), and Mn(1)···Mn(2) distances are 5.1553(8), 5.2842(8), and 6.659(1) Å, respectively. The water molecules reside in cavities of the network and form hydrogen bonds with the cyano nitrogen atoms as O–H···N.

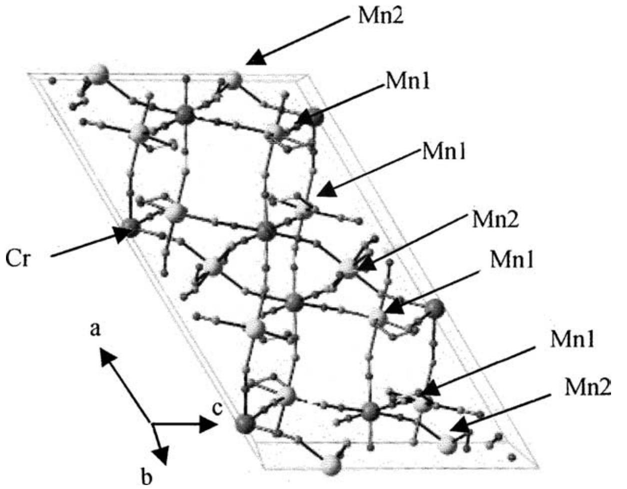

Fig. 1. Projection of the 3D network structure of $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ (en and H_2O are omitted).

The magnetic measurements have been performed in the pressure region up to P = 4.7 GPa and the temperature range from 5 to 200 K. Pressure has been attained using a diamond anvil cell (DAC) [23], which can be inserted into a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5S). The tip diameter of diamond anvils was 0.5 mm. In the center of the gaskets made of Cu–Be, the sample space with diameter 0.2 mm was holed. A very small quantity of sample and some pieces of ruby were held with a transmitting medium into the sample space. The value of pressure was determined by the measurement of the shift of R1 ruby fluorescence at room temperature [24]. The pressure-increase by cooling down to liquid-helium temperature has been estimated to be at most about 14% of the pressure value at room temperature [23]. The magnetic measurements have been done under magnetic field H = 0.5 T, which is enough to saturate the magnetic moment in the ordered state of $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$.

3. Experimental results and discussion

Fig. 2 shows temperature dependence of the magnetization for $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ at H = 0.5 T in the pressure region up to 4.7 GPa. The accurate weight of the used sample could not be measured, but it is estimated to be about 4 µg from the value of magnetization at low temperature. Therefore, M in the vertical axis represents the actual measurement value. At ambient pressure, M rapidly increases below 80 K. For the sake of convenience, here we define *T*c as the temperature below which M rapidly starts to increase. Fig. 3 shows pressure dependence of *T*c for $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$. With increasing pressure, the development of magnetization shifts toward higher temperatures. For $P \leqq 3.0$ GPa, *T*c linearly increases against pressure as d*T*c/d*P* = +15.3 K/GPa, which is smaller than d*T*c/d*P* = +21.9 K/GPa of the similar antiferromagnetic system, the genuine organic radial week-ferromagnet, p-$NC \cdot C_6F_4 \cdot CNSSN$