Pressure Response of Cyanide-Bridged Molecule-Based Magnets

A reversible crystalline-to-amorphous phase change was observed in a cyanide-bridged Mn-Cr bimetallic ferrimagnet. The reversible amorphization occurred in a pressure range where the magnetic ordering temperature (T_C) continued to increase and the saturation magnetization (M_s) kept a constant value against pressurization. When pressure was reduced after the complete disappearance of M_s, the reversible phase change did not occur. In a Ni-Cr ferromagnet, both T_C and M_s approached zero prior to transformation into an amorphous phase. The variation in these pressure responses is due to the degree of orthogonality in orbital overlap, and to whether the cubane unit has structural defects or not.

In molecule-based magnets, applying hydrostatic pressure enables us to manipulate magneto-structural correlations. However, the available pressure range has been limited to less than 1.5 GPa until recent days. We have investigated magneto-structural correlations for typical high-T_C molecule based magnets through magnetization measurements and X-ray powder diffraction (XRPD) experiments under pressures of over 10 GPa by using a diamond anvil cell (DAC) [1, 2]. We have used a unique technique for magnetic measurements using a miniature DAC for a commercial SQUID magnetometer [3]. Here we describe results for two target materials, (1) $[Mn(en)]_3[Cr(CN)_6]_2\cdot 4H_2O$ ($T_C = 69$ K) and (2) $[Ni(dipn)]_3[Cr(CN)_6]_2\cdot 3H_2O$ ($T_C = 42$ K), which have the highest T_C reported to date for a structurally characterized 3d-metal molecule-based ferrimagnet and a ferromagnet, respectively. In both materials, the three-dimensional (3-D) magnetic network between the metallic magnetic ions is constructed via the cyanide ligand, and the network frame is more flexible and stronger than that in organic radical systems. In order to study the magneto-structural correlation in cyanide-bridged magnets, pressures higher than 10 GPa are required, and we have been successful in obtaining new experimental knowledge on the magneto-structural correlation. Figure 1 gives an overview of the pressure responses for materials (1) and (2) from both structural and magnetic viewpoints.

Figure 2 shows the pressure dependences of the magnetic ordering temperature (T_C) and saturation magnetization (M_s) for materials (1) and (2), estimated from magnetization measurements at 0.5 Tesla as a function of temperature. In both materials, the magnetization sufficiently below T_C saturates at 0.5 Tesla, and the value of M_s was acquired experimentally from the value of magnetization at 5 K. In (1), T_C increases linearly with pressure for $P < 5$ GPa, and begins to decrease at around 7 GPa. On the other hand, M_s is constant for pressures below 7 GPa, above which it decreases. The pressure response of T_C was reversible for $P < 5$ GPa. However, after releasing pressure at 19.5 GPa, the temperature dependence of the magnetization did not recover. For material (2), T_C has a maximum at around 1 GPa, above which it decreases. At around 5 GPa, the ferromagnetic signal could not be observed. On the other hand, M_s is constant for $P < 1.5$ GPa, with a rapid decrease for higher pressures.

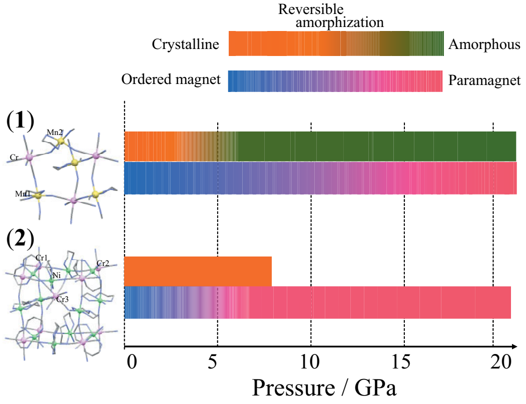

Figure 1
Overview of the pressure responses of two cyanide-bridged bimetallic magnets, (1) $[Mn(en)]_3[Cr(CN)_6]_2\cdot 4H_2O$ and (2) $[Ni(dipn)]_3[Cr(CN)_6]_2\cdot 3H_2O$.

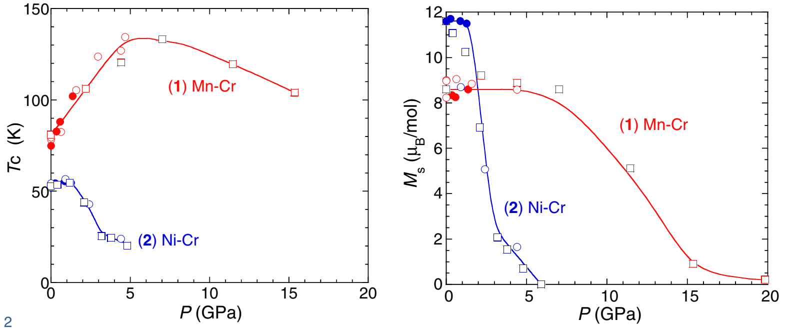

Figure 2
Pressure dependences of T_C and M_s for (1) $[Mn(en)]_3[Cr(CN)_6]_2\cdot 4H_2O$ and (2) $[Ni(dipn)]_3[Cr(CN)_6]_2\cdot 3H_2O$.

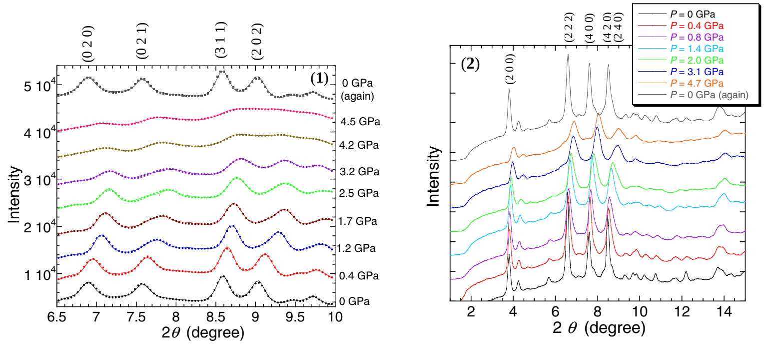

Figure 3
XRPD patterns under applied pressure for (1) $[Mn(en)]_3[Cr(CN)_6]_2\cdot 4H_2O$ and (2) $[Ni(dipn)]_3[Cr(CN)_6]_2\cdot 3H_2O$.

XRPD patterns at room temperature were recorded for both samples at pressures up to 4.5 GPa at BL-1B, using a DAC. For material (1), the XRPD shifts toward higher angles with increasing pressure, whereas the series of diffraction peaks became broader with pressurization. Above 4 GPa, the XRPD pattern suggests that the monoclinic structure has transformed into an amorphous state. Indeed, the variation in lattice volume suggests that the contraction tends to saturate at around 2 GPa. Interestingly, in this pressure region, T_C continued to increase with pressurization. Namely, the structural translation symmetry is lost above 4 GPa. Nevertheless the magnetic network survives, resulting in a continued increase in T_C. The XRPD pattern after releasing at 4.5 GPa is consistent with that at the initial pressure, and we can recognize a reproducibility for the increase and decrease in pressure. The amorphization is considered to originate in the intrinsic existence of defects in the cubane unit. For material (2), even at pressures above 4 GPa, the XRPD pattern remains sharp, and amorphization was not confirmed. Prior to the collapse of structural translation symmetry, the magnetic network is broken, contrary to the results for (1).

The ferrimagnetic material (1) has antiferromagnetic overlapping between the $t_{2g}(Mn^{II})$ and $t_{2g}(Cr^{III})$ orbitals. On the other hand, the ferromagnetic network seen in (2) requires orthogonality between the $e_g(Ni^{II})$ and $t_{2g}(Cr^{III})$ orbitals. Through the present experiments, we have experimentally confirmed that the antiferromagnetic network is more stable than the ferromagnetic network.

REFERENCES

[1] T. Maeda, M. Mito, H. Deguchi, S. Takagi, W. Kaneko, M, Ohba and H. Ōkawa, *Polyhedron*, **24** (2005) 2497.
[2] M. Ohba, W. Kaneko, S. Kitagawa, T. Maeda and M. Mito, *J. Am. Chem. Soc.*, **130** (2008) 4475.
[3] M. Mito, M. Hitaka, T. Kawae, K. Takeda, T. Kitai and N. Toyoshima, *Jpn. J. Appl. Phys.*, **40** (2001) 6641.

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