Construction of cyanide-bridged Co-W assemblies exhibiting a thermal phase transition near room temperature

([1]*Graduate School of Science, University of Tokyo*)
○Kazuki Nakamura,[1] Koji Nakabayashi,[1] Kenta Imoto,[1] Shin-ichi Ohkoshi,[1]

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Phase transitions in solids are important for the development of functionalities and the control of magnetic, electric, and optical properties. Cyanido-bridged metal assemblies are good candidates for phase transition materials, because they exhibit various phase transitions related to spin crossover, ferromagnetic ordering, and charge transfer.[1] We have reported cyanido-bridged Co-W assemblies exhibit a large thermal hysteresis based on the charge transfer between $Co^{II/III}$ and $W^{V/IV}$ sites.[2] Bistability at room temperature is an important factor developing functionalities. Thus, we synthesized a cyanide-bridged Co-W assembly with bistable phases at room temperature, $Cs^{+}_{0.1}(H_5O_2^{+})_{0.9}[Co(4\text{-bromopyridine})_{2.3}\{W(CN)_8\}]$ (**CsCoW**), which is a Cs^{+}-substituted compound of $(H_5O_2^{+})[Co(4\text{-bromopyridine})_2\{W(CN)_8\}]$ showing a Co^{III}-W^{IV} phase over a wide temperature range of 2-390 K.[3]

The red powder of **CsCoW** was prepared by mixing an aqueous solution of $Co^{II}Cl_3{\cdot}6H_2O$, 4-bromopyridine hydrochloride, and CsCl, with an aqueous solution of $Cs_3[W(CN)_8]{\cdot}2H_2O$ and CsCl. The crystal structure of **CsCoW** has a-two-dimensional cyanido-bridged Co-W layers with oxonium ions and Cs^{+} ions between the layers (Figure1). Figure 2 shows the product of the molar magnetic susceptibility (χ_M) and temperature (T) vs. T plot of **CsCoW**. The thermal hysteresis loop with ΔT = 53 K shows bistability at room temperature. The magnetic study, variable-temperature UV-vis and IR absorption spectroscopies revealed a charge transfer-induced phase transition between a Co^{II}-W^{V} high temperature phase and a Co^{III}-W^{IV} low temperature phase.

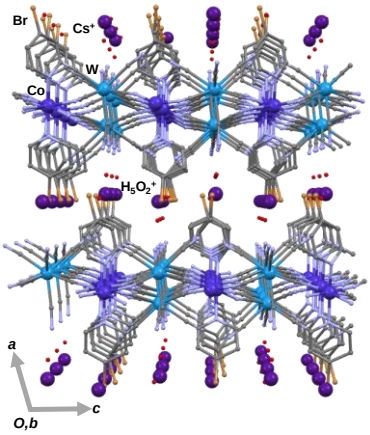

Fig. 1. Crystal structure of **CsCoW** viewed along the *b* axis.

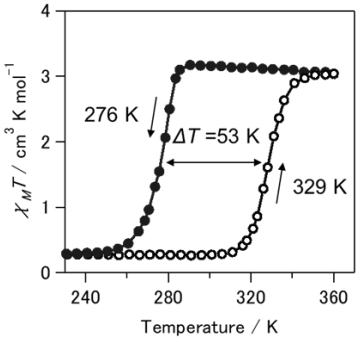

Fig. 2. $\chi_M T$-T plot of **CsCoW** at 1000 Oe.

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