

論文の内容の要旨

Photo-induced magnetization of a two-dimensional cobalt–octacyanidotungstate bimetal assembly

(二次元コバルト–オクタシアノタングステン錯体の光磁性現象)

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Introduction

Photo-induced phase transitions have been intensively studied as one of the attractive issues of non-equilibrium phenomena. Several types of materials exhibiting photo-induced phase transition have been reported up to date, for example, chalcogenides, metal oxides, spin-crossover complexes, and cyanide-bridged bimetal assemblies. Cobalt–octacyanidotungstate bimetal assemblies have been reported to show photo-induced magnetization with a high Curie temperature (T_C) and a large coercive field (H_C). This phenomenon is known to be caused by an optically charge-transfer-induced spin transition (CTIST) from $\text{Co}^{\text{III}}_{\text{low-spin}(ls)}(S = 0) - \text{W}^{\text{IV}}(S = 0)$ to $\text{Co}^{\text{II}}_{\text{high-spin}(hs)}(S = 3/2) - \text{W}^{\text{V}}(S = 1/2)$ phases. That is, light irradiation induces the charge transfer from $\text{W}^{\text{IV}}(S = 0)$ to $\text{Co}^{\text{III}}_{ls}(S = 0)$ to produce $\text{Co}^{\text{II}}_{ls}(S = 1/2) - \text{W}^{\text{V}}(S = 1/2)$, and then a spin transition occurs from $\text{Co}^{\text{II}}_{ls}(S = 1/2)$ to $\text{Co}^{\text{II}}_{hs}(S = 3/2)$, which results in the electronic state of $\text{Co}^{\text{II}}_{hs}(S = 3/2) - \text{W}^{\text{V}}(S = 1/2)$. However, the electronic structure to discuss the optical transitions and the mechanism of photomagnetic effects has not been clarified yet. In the present work, a cobalt–octacyanidotungstate bimetal assembly, $(\text{H}_5\text{O}_2^+)[\text{Co}^{\text{III}}(4\text{-bromopyridine})_2\{\text{W}^{\text{IV}}(\text{CN})_8\}]$ is reported. Interestingly, this compound exhibits the $\text{Co}^{\text{III}}_{ls} - \text{W}^{\text{IV}}$ phase over a wide temperature range from 2 K to 390 K, even though other reported cobalt–octacyanidotungstate bimetal assemblies take the $\text{Co}^{\text{II}}_{hs} - \text{W}^{\text{V}}$ phase at room temperature. A light irradiation to this compound causes photo-induced magnetization. First-principles calculations show the electronic structure of this compound to reveal the mechanism of the charge-transfer process.

Results and discussions

Synthesis, crystal structure, and characterization

The single crystal and the powder-form sample of $(\text{H}_5\text{O}_2^+)[\text{Co}^{\text{III}}(4\text{-bromopyridine})_2\{\text{W}^{\text{IV}}(\text{CN})_8\}]$ were synthesized by mixing $\text{Na}_3[\text{W}^{\text{V}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$, $\text{Co}^{\text{II}}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, and 4-bromopyridine·HCl in an acidic condition

at room temperature. Elemental analyses confirm that the formula of this compound is $(\text{H}_5\text{O}_2)[\text{Co}(4\text{-bromopyridine})_2\{\text{W}(\text{CN})_8\}]$.

Since the single crystals are in a very thin hexagonal plate-form (e.g., *ca.* $100 \times 50 \times 4 \mu\text{m}$), a synchrotron radiation X-ray single-crystal measurement at KEK was carried out to determine the crystal structure. This compound has a monoclinic crystal structure in the $P2_1/c$ space group ($a = 13.0471(10) \text{ \AA}$, $b = 13.5910(10) \text{ \AA}$, $c = 14.6790(10) \text{ \AA}$, and $\beta = 106.3410(10)^\circ$) (Figure 1). The asymmetric unit consists of a Co^{3+} ion, a $[\text{W}(\text{CN})_8]^{4-}$ ion, two 4-bromopyridine ligands, and two water molecules. The coordination geometry of the Co site is a six-coordinate pseudo octahedron, in which the two axial positions of Co are occupied by the N atoms of 4-bromopyridine, and the four equatorial positions are occupied by the cyanide N atoms of $[\text{W}(\text{CN})_8]^{4-}$. The average distance of Co–N is 1.92 \AA , indicating that the Co ion takes a trivalent state. The coordination geometry of the W site is an eight-coordinate square antiprism, where the four CN groups of $[\text{W}(\text{CN})_8]^{4-}$ are bridged to Co. The other four CN groups are not bridged to Co, but connected to H_5O_2^+ by hydrogen bonds. The cyanide-bridged Co and W ions form two-dimensional layers in the bc -plane, and the oxonium cations H_5O_2^+ are intercalated between the layers. The $\{\text{Co}^{\text{III}}[\text{W}^{\text{IV}}(\text{CN})_8]\}^-$ layers take negative charge, and the positive charge of H_5O_2^+ keeps the whole charge of this compound neutral.

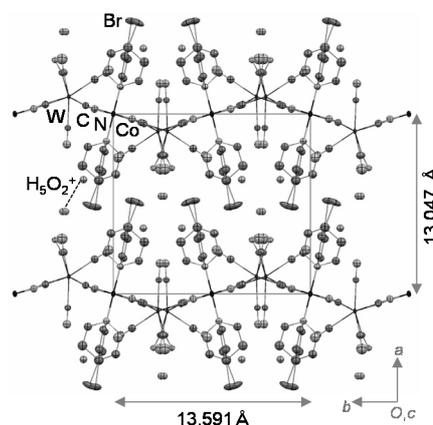


Figure 1. Crystal structure.

In the microscopic ultraviolet–visible measurement, the absorption peak for the transmission mode along the direction of the out-of bc -plane is observed around 700 nm (1.8 eV). The magnetic susceptibility was measured by superconducting quantum interference device (SQUID) using the assembled single crystals (*c.a.* 8×10^5 pieces of crystals). The $\chi_{\text{M}}T$ value is almost zero from 2 K to 390 K , which indicates that this compound takes the electronic state of $\text{Co}^{\text{III}}(S = 0) - \text{W}^{\text{IV}}(S = 0)$ over the wide temperature range of $2 - 390 \text{ K}$. Such a stabilization of the $\text{Co}^{\text{III}} - \text{W}^{\text{IV}}$ phase over the wide temperature range has not been reported so far.

Periodic structure calculations of the electronic structure

The periodic structure calculation of $(\text{H}_5\text{O}_2^+)[\text{Co}^{\text{III}}(4\text{-bromopyridine})_2\{\text{W}^{\text{IV}}(\text{CN})_8\}]$ was performed by Vienna *ab initio* simulation package (VASP) to reveal the optical transitions of this compound, where the crystal structure determined by the single-crystal X-ray analysis was used. The band structure and the density of states (DOS) show that the band gap is composed of a W 5d valence band and a Co 3d conduction band (Figure 2a). The calculated optical absorption spectrum reproduced well the experimental spectrum (Figure 2b). The lowest-energy transition was a transition from the valence band mainly composed of d_{z^2} orbitals of W and p orbitals of N to the conduction band mainly contributed from d_{z^2} orbitals of Co and sp orbitals of N (Figure 2c). This indicates that the lowest-energy transition of this compound is the charge transfer from W^{IV} to Co^{III} through the orbitals of the bridging CN ligands. Since the valence band from d orbitals of Co is below -3.5 eV , the absorption of d-d transition in Co is not observed in the visible region. Thus, visible light irradiation does not cause the spin transition in Co^{III} .

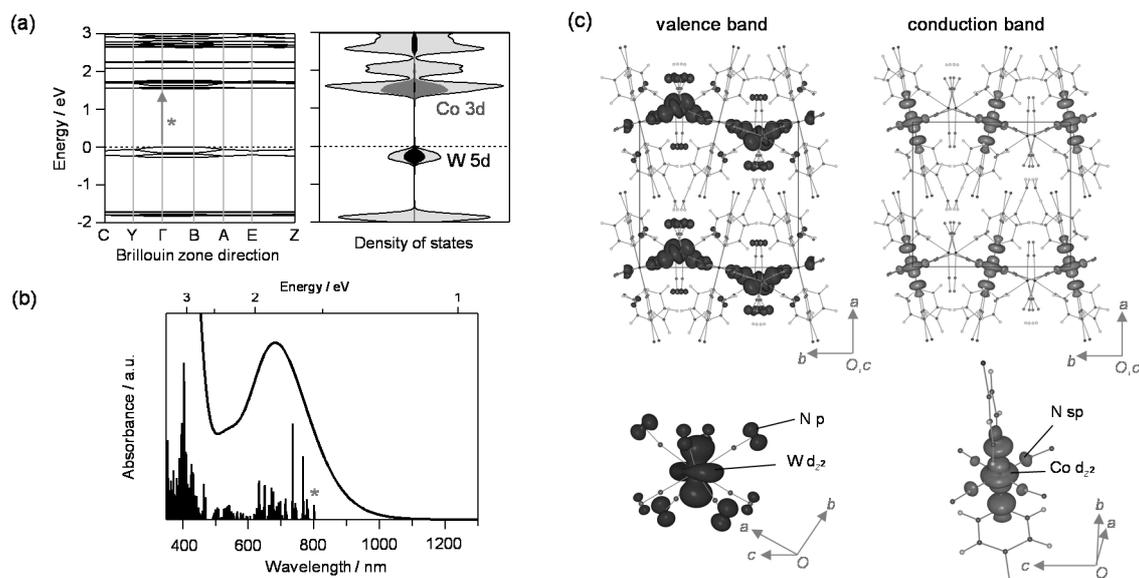


Figure 2. (a) Band structure and DOS. (b) Calculated optical absorption spectrum. (c) Charge density maps.

Photomagnetism

The photomagnetic effect was investigated using SQUID. The 785-nm light irradiation (220 mW cm^{-2}) at 3 K induced spontaneous magnetization. Magnetization (M) versus temperature (T) curve shows that a value of T_C is 27 K (Figure 3a). M versus external magnetic field (H) curve exhibits an H_c value of 2000 Oe at 2 K. Considering the ground Kramers doublet of an octahedral Co^{II} , an expected saturation magnetization (M_s) value is $3.2 \mu_B$ due to ferromagnetic coupling between $\text{W}^{\text{V}}(S = 1/2, g = 2)$ and $\text{Co}^{\text{II}}(S = 1/2, g = 13/3)$, which is close to the observed M_s value of $3.0 \mu_B$. The photo-induced phase returns to the initial phase upon annealing up to 80 K. These photo irradiation and heating treatment provide reversible phase changes.

To determine the crystal structure of photo-induced phase, the powder XRD pattern was measured after 785-nm light irradiation (250 mW cm^{-2}) at 13 K. Rietveld analysis of the XRD pattern after light irradiation shows that the photo-induced phase has a monoclinic structure in the $P2_1/c$ space group with lattice constants of $a = 13.193(10) \text{ \AA}$, $b = 113.949(11) \text{ \AA}$, $c = 15.040(12) \text{ \AA}$, and $\beta = 107.35(9)^\circ$, which are larger in the two-dimensional layer (bc -plane) by 3% compared to the original phase (Figure 3b). The average Co–N distance of photo-induced phase (2.05 \AA) is larger than that of original phase (1.91 \AA). Such an elongation

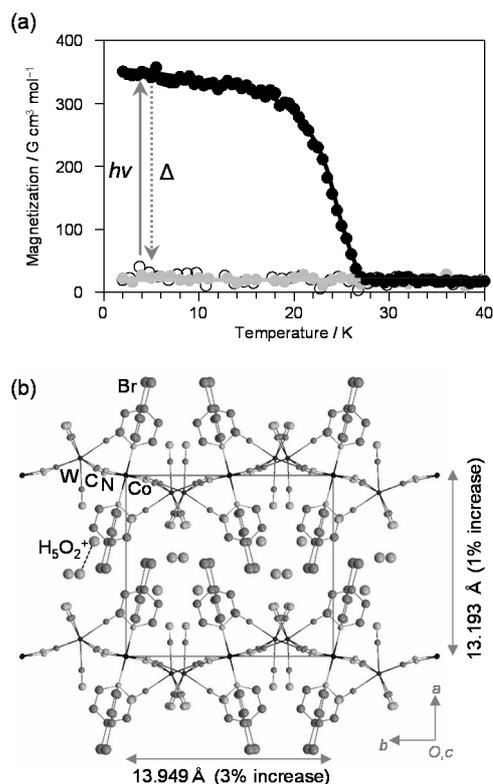


Figure 3. (a) M vs. T curves before (open circles), after irradiation (black circles), and after annealing (gray circles). (b) Crystal structure of the photo-induced phase.

indicates that the valence state of Co changes from +3 to +2 by light irradiation. After annealing up to 60 K, the crystal structure of photo-induced phase returned to that of the original phase.

The photo-induced magnetization can be explained by the optical CTIST effect from $\text{Co}^{\text{III}}_{ls}(S = 0)\text{-W}^{\text{IV}}(S = 0)$ to $\text{Co}^{\text{II}}_{hs}(S = 3/2)\text{-W}^{\text{V}}(S = 1/2)$ phases. When the temperature is under T_C , spontaneous magnetization is observed due to superexchange coupling between $\text{Co}^{\text{II}}_{hs}(S = 3/2)$ and $\text{W}^{\text{V}}(S = 1/2)$ through CN groups.

Conclusions

In my thesis, a two-dimensional cyanide-bridged Co–W bimetal assembly, $(\text{H}_5\text{O}_2^+)[\text{Co}^{\text{III}}(4\text{-bromopyridine})_2\{\text{W}^{\text{IV}}(\text{CN})_8\}]$ was synthesized. This compound shows a stable $\text{Co}^{\text{III}}_{ls}\text{-W}^{\text{IV}}$ phase in the 2–390 K range. Such a wide temperature range $\text{Co}^{\text{III}}_{ls}\text{-W}^{\text{IV}}$ phase has not been reported up to date. Light irradiation to this compound causes the photo-induced phase with a T_C value of 27 K and an H_c value of 2000 Oe. The crystal structures before and after light irradiation were determined by X-ray structural analyses. Additionally, first-principles calculations revealed that the photo-induced phase transition is due to the charge transfer from W 5d valence band to Co 3d conduction band.