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Water-induced ferromagnetism in cobalt acetylide CoC_2 nanoparticles

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Abstract

Transition metal acetylide CoC_2 is highly absorbent of water due to its ionic character. In the anhydrous phase, CoC_2 forms NaCl-like cubic structure where the orientation of C_2^{2-} dianions are disordered. Once the material is exposed to air or water, the lattice of CoC_2 is expanded anisotropically by the absorbed water, which restricts the orientation of C_2^{2-} dianions. The magnetism of CoC_2 also changes drastically by air/water exposure owing to the orientation ordering of C_2^{2-} dianions. The anhydrous CoC_2 behaves as superparamagnet down to 1.8 K because the magnetic domains of CoC_2 are cut into pieces by orientation disorder of C_2^{2-} dianions, while the hydrous CoC_2 shows the ferromagnetism thanks to the large ferromagnetic domains caused by the orientation ordering of C_2^{2-} dianions.

Keywords: Ferromagnetism; Molecule-based magnet; Transition metal acetylide; Structural change; Water absorption; Water-induced ferromagnetism

1. Introduction

Although molecule-based magnets are promising for various applications due to the design ability of the component molecules and magnetic ions, Curie temperatures of the almost all molecule-based magnets are far below room temperature except few materials [1,2]. We have been investigating transition-metal complexes to find a new molecule-based room temperature magnet, resulting in finding that the well-ordered cobalt acetylide CoC_2 shows ferromagnetism even in room temperature [3,4]. The important feature of CoC_2 besides the ferromagnetism is its air and water stability, which is an advantage for applications. By the way, though CoC_2 is a water stable material, CoC_2 absorbs about 1–2 H_2O molecule per Co^{2+} when the material is exposed to air or water. Considering the fact that the molecular volume of CoC_2 is small, absorption of such a large amount of water should affect the crystal structure and the magnetism of CoC_2, while the exact role of the absorbed water have been unclear. In the present paper, we report the water-induced structural change, and reveal that the absorbed water plays an important role in ferromagnetism.

2. Experimental

Anhydrous CoC_2 were prepared as follows: 675 mg (5.2 mmol) of anhydrous $CoCl_2$ and 320.5 mg (5 mmol) of anhydrous CaC_2 were milled and suspended in 300 ml

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of acetonitrile (dehydrated) under argon atmosphere in a water- and oxygen-free grove-box. The suspension was heated to 80 °C for 130 h in an airtight glass container. Then the suspension was filtrated, and washing the residual with 100 ml of acetonitrile (dehydrated), 100 ml of ethanol (dehydrated) and 100 ml of dichloromethane gave anhydrous CoC_2 as beige powder. It is noted that, according to the ICP analysis, anhydrous CoC_2 contains ca. 35% of CaC_2 as raw material. Consequently, the results of the magnetism shown later are obtained by dividing the measured value by 0.65. Hydrous CoC_2 for magnetic measurement was obtained by exposing anhydrous CoC_2 to air (25 °C, humidity 70%). Though hydrous CoC_2 can also be formed by water-exposure in short time, slow water absorption in air atmosphere allow us to measure the magnetism of the intermediate state between hydrous and anhydrous. For the powder X-ray diffraction (XRD) measurement, hydrous CoC_2 was prepared by washing the air-exposed (2 days) sample with water to remove $Ca(OH)_2$. We confirmed that the peak position and width of CoC_2 are not changed by water exposure, while the peaks of CaC_2 and $Ca(OH)_2$ disappear after washing with water.

XRD pattern of hydrous CoC_2 was measured with *Mac science* MXP^{3}VA Powder X-ray Diffractometer at 293 K, using Cu Kα radiation (λ = 1.5418 Å). That of anhydrous CoC_2 encapsulated in glass tube (0.03ϕ) was carried out at the beam line 1A of the Photon Factory in KEK, using synchrotron radiation (λ = 0.9988 Å). Magnetic susceptibilities were measured by using *Quantum-Design* MPMS-XL SQUID magnetometer for powder sample embedded in epoxy resin to keep CoC_2 nanoparticles from rotating.

3. Results and discussion

Before analyzing the crystal structure, it is necessary to guess the rough structural model of CoC_2. According to the crystal structures of the related materials CaC_2 [5] and MgC_2 [6], it is suggested that Co^{2+} dications and C_2^{2-} dianions are stacked alternately like as NaCl-type structure. In addition, XRD pattern of CoC_2 approximately depends only on the arrangement of Co^{2+} dication due to its larger scattering factor than that of C_2^{2-}. The observed XRD pattern of anhydrous CoC_2 contaminated with CaC_2 is shown in Fig. 1. The observed pattern is well fitted by the two calculated patterns; one is CaC_2 based on the reported structure [5], and the other is the fcc-arrangement of Co^{2+} sublattices with the lattice constants $a = b = c = 4.82$ Å. The isotropic structure of Co^{2+} dications indicates the static or dynamic orientation disorder of C_2^{2-} like as CaC_2 IV [5], or else the lattice is distorted and the symmetry becomes low such as tetragonal or orthorhombic where the diffraction peaks split. The structural model of anhydrous

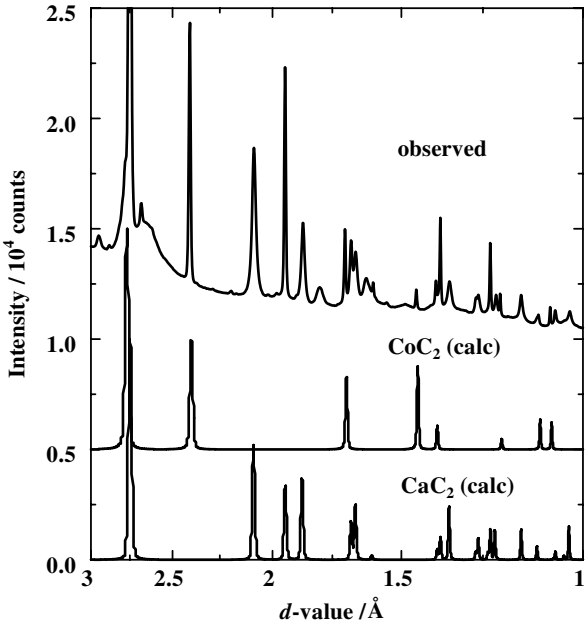

Fig. 1. The observed XRD patterns of anhydrous CoC_2 measured with synchrotron radiation (λ = 0.9988 Å) and the calculated patterns of anhydrous CoC_2 and CaC_2 (raw material). The observed pattern and calculated pattern of anhydrous CoC_2 are vertically shifted by 0.75 and 0.5×10^4, respectively, for clarify. In the calculation of the pattern of anhydrous CoC_2, the body-centered lattice of Co^{2+} sublattice was assumed and the lattice parameters are decided as the calculated pattern reproduces the observed one.

CoC_2 is shown in Fig. 2(b), where only a part of the unit cell is shown to compare with the structure of the hydrous CoC_2 discussed later. Incidentally, the peaks of CoC_2 are fairly sharp, from which the crystallite size D of CoC_2 is estimated as $D > 45$ nm by using Scherrer formula [7].

The air-exposure changes the peak position and width drastically as shown in Fig. 2(a). The observed XRD pattern of hydrous CoC_2 shows good agreement with that expected from the EXAFS result suggesting the MgC_2-type structure.[2] Contrary to anhydrous CoC_2, C_2^{2-} dianions are ordered in hydrous CoC_2 and the Co^{2+} dications forms body-centered tetragonal lattice as shown in Fig. 2(c). In the structure, Co^{2+} dications and C_2^{2-} dianions form alternate chains elongated parallel to the c-axis, which shrinks through air-exposure, while the a- and b-axes related to the inter-chain directions are expanded by the absorbed water. Judging from the crystal structures, intra-chain Co^{2+}–C_2^{2-}–Co^{2+} exchange interaction becomes stronger in hydrous phase due to the shorter Co^{2+}–C_2^{2-} distance and orientation ordering of C_2^{2-}, while the inter-chain interaction becomes weaker due to the longer inter-chain distances. The structural change cut the CoC_2

[2] The structural analysis based on the EXAFS results will be submitted to another journal by K. Kosugi.