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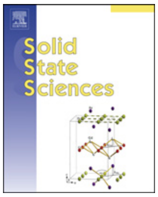

Field-induced spin-flop-like metamagnetism in α-CoB_4O_7

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ABSTRACT

We successfully obtained pure α-CoB_4O_7 powder sample by a two-step synthesis method. First, a new cobalt polyborate with unknown crystal structure was synthesized by boric acid flux method in a sealed system. Subsequently, α-CoB_4O_7 powder was obtained by the thermal decomposition of this new phase at 800 °C. The purity was carefully checked by Le Bail fitting of its powder XRD with good convergence. The magnetic susceptibilities in paramagnetic region agree well with Curie–Weiss law with $\theta = -17.7$ K, $C = 3.13$ cm^3 K mol^{-1}. *Ac* magnetic measurements confirm its long-range AFM ordering at ~5 K. The field-dependent magnetization curve at 1.85 K indicates a spin-flop-like phase transition, with $H_c = 35$ kOe. Considering the relatively weak magnetic super-exchange, we believe this transition is due to the large magnetic anisotropy of Co^{2+}.

1. Introduction

Transition metal borates may display important properties, such as catalytic activities [1], interesting magnetic behaviors [2], and reversible Li-ion uptake [3,4]. The first published Co–B–O phase diagram contains only two ternary compounds, $Co_3B_2O_6$ and $Co_2B_2O_5$ [5,6]. CoB_4O_7 and Co_3BO_5 were thereafter observed, which possess MgB_4O_7 and ludwigite-type structures, respectively [7,8]. Recently, high-pressure (HP) technique has been widely used to obtain unusual structures for borate materials. In the cobalt anhydrous borate system, a typical case of HP-CoB_2O_4 with interestingly edge-shared BO_4 tetrahedra was observed at 6.5 GPa and 950 °C [9]. In 2003, Nazar prepared the polycrystalline CoB_4O_7 by high-temperature solid state reaction at 880 °C, using a non-stoichiometric ratio ($5H_3BO_3$:$1CoCO_3$). Moreover, they also obtained single crystals using flux methods, but accompanied by other two impurity phases [10]. So far, no magnetic data was reported for CoB_4O_7, we suspect that the low purity of the sample is the possible reason. Herein our study, a two-step synthesis method is applied to ensure the high purity of polycrystalline CoB_4O_7. It is worth noting that Huppertz identified an HP-polymorph of CoB_4O_7, defined as β-phase, using stoichiometric Co_2O_3 and B_2O_3 as raw materials at 7.5 GPa and 1250 °C [11]. We attempted to prepare β-CoB_4O_7 using as-synthesized α-CoB_4O_7 compressed at 5.5 GPa and 950 °C, which is the strongest condition currently we can achieve. The resultant solid, characterized by powder XRD (shown in Fig. S1), is neither the starting phase nor β-CoB_4O_7. Probably the current HP condition is not strong enough to induce such α- to β-phase transition. Therefore we only performed the *dc* and *ac* magnetic measurements on α-CoB_4O_7. The major characteristic of the magnetic coupling between Co^{2+} cations is antiferromagnetic (AFM), and a long-range (AFM) ordering was observed below ~5 K. A filed induced spin-flop-like metamagnetic transition is detected at 1.85 K.

2. Experimental section

Boric acid flux method at sealed system was applied as the first step. Typically, 1 mmol $Co(CH_3COO)_2 \cdot 4H_2O$ and 10 mmol H_3BO_3 were ground, and this mixture was loaded into a 25 mL Teflon autoclave, which is further sealed in a steel vessel. After heating at 220 °C for 5 days, the system was cooled naturally. The resultant solid was extensively washed by warm water (50 °C) to remove all the residual H_3BO_3. The first-step product is purple needle-like single crystals, which is a precursor for the next annealing process.

The precursor is in fact a new cobalt polyborate, however, the obtained crystals are too small for single crystal X-ray diffraction (XRD). The structure of this phase remains unsolved. The characteristic of its powder XRD pattern can be recognized by the very sharp peak at 9° (Cu Kα radiation). This precursor was step-wise annealed in a muffle furnace at different temperatures. Each step

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stays for 5 h, and the powder XRD was collected after cooling down. As shown in Fig. S2 in the supporting information, α-CoB_4O_7 appeared after 800 °C. The heated sample was further washed by water to remove the possible remaining boron oxide during the thermal decomposition process. Powder XRD of the final product was subjected to a Le Bail refinement using TOPAS [12], which gave a good convergence and indicated the high purity of α-CoB_4O_7 for magnetic measurements (See Fig. S3).

It should be noted that the first-step product would be $CoB_{12}O_{14}(OH)_{10}$ if using 1 mmol $Co(CH_3COO)_2 \cdot 4H_2O$ and 20 mmol H_3BO_3 as the starting ratio. The similar procedure of heating $CoB_{12}O_{14}(OH)_{10}$ will not lead to α-CoB_4O_7.

The *dc* and *ac* magnetic susceptibilities, and field dependence of magnetization were obtained on crystalline samples using a Model MagLab System 2000 magnetometer. Typical field cooling (FC) magnetizations in the temperature range of 2–300 K were performed under external fields of 10 kOe. The isothermal magnetization curve was measured at 1.85 K up to 70 kOe. The *ac* magnetic susceptibilities were measured at a 5 Oe oscillating field and frequency range of 111–1111 Hz. The experimental susceptibilities were corrected for the sample holder and the diamagnetism contributions estimated from Pascal's constants [13]. Powder X-ray diffraction data for α-CoB_4O_7 were collected at room temperature on a Rigaku D/Max-2000 diffractometer (Cu Kα, $\lambda = 1.5406$ Å, 40 kV and 100 mA, graphite monochromator, scintillator detector, step scan 0.02°/2 s).

3. Results and discussion

With a polycrystalline sample, the temperature-dependent magnetic susceptibility of α-CoB_4O_7 was measured in the range of 2–300 K at 10 kOe under field cooling condition (see Fig. 1). The reciprocal susceptibility χ_m^{-1} (T) above 20 K follows the Curie–Weiss law quite well with a result of $\theta = -17.7$ K, $C = 3.13$ cm^3 K mol^{-1} as shown in Fig. 1b. The room temperature effective magnetic moment could be estimated from the Curie constant to be $\mu_{eff} = 5.0\mu_B$, higher than the theoretical value of spin-only Co^{2+} (3.9 μ_B if setting $S = 3/2$ and $g = 2$). It is an indication of the strong spin-orbit coupling in the Co^{2+} system. It is well accepted that g is virtually necessarily above 2.00 for Co^{2+} system. Given $C = 3.13$ cm^3 K mol^{-1}, the calculated g is 2.58. Such a value could be found in various Co^{2+} systems in literature [14–17]. The negative Weiss temperature (−17.7 K) suggests the dominant interactions between Co^{2+} are antiferromagnetic (AFM), which is also confirmed by the monotonous decrease of the $\chi_m T$ products with the temperature decreasing (see Fig. 1b). A cusp of χ_m–T plot at around 6 K and the very sharp decrease below this temperature point to a long-range AFM ordering. The *ac* susceptibilities at different frequencies confirm this ordering and the Neel temperature is about 5 K (see Fig. 2). The $\theta/T_N \sim 3.5$, which is usual for an antiferromagnet. The AFM characteristic is also reflected by the small values of the magnetic susceptibilities, for example, 0.15 cm^3 mol^{-1} at 6 K and 10 kOe. The low signals of the magnetic susceptibilities from the target sample further confirm its high purity.

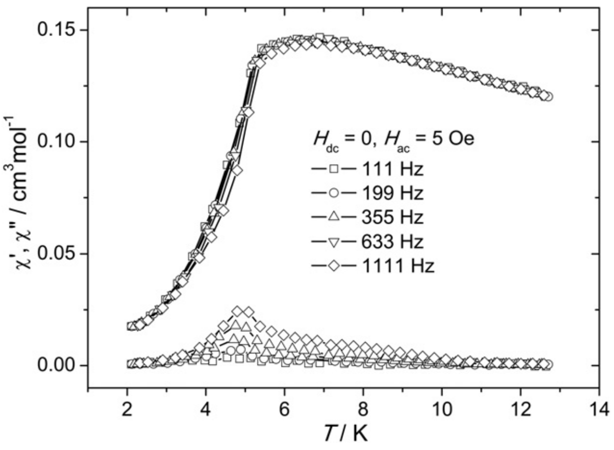

Fig. 2. Temperature-dependent *ac* susceptibilities (χ′, in-phase signals; χ″, out-of-phase signals) at frequencies from 111 to 1111 Hz.

Interestingly, the isothermal magnetization curve at 1.85 K shows a sigmoidal shape, which is a typical characteristic of metamagnet (see Fig. 3). The slow magnetization verse external field is a sign of AFM nature of α-CoB_4O_7. Additionally, the magnetization loop at low field (<1 kOe) was measured carefully, which shows zero magnetic remanence and zero coercive field (see the right inset of Fig. 3). These behaviors prove the ground magnetic state of α-CoB_4O_7 at 1.85 K is AFM. While, with the enhancement of the external field, it transforms to an excited state. The critical field is estimated by the dM/dH curve to be 35 kOe (see the left inset of Fig. 3). The metamagnetism is also confirmed by the FC curves under different magnetic fields (see the insert of Fig. 1a), where the maximum at 6 K is suppressed and moves to low temperatures with field increasing.

According to all the magnetic observations, one can conclude the filed-induced metamagnetism in α-CoB_4O_7 at 1.85 K. The ground state is AFM, and a magnetic phase transition is induced with a critical filed ~35 kOe. Fig. 4 shows its crystal structure at room temperature, where the spacial distances between Co^{2+} are highlighted. Although there is only one crystallographically independent Co^{2+} in the unit cell, the Co^{2+} network is relatively complicated. When considering the distances less than 5 Å, each Co^{2+} are connected to 3 neighbor Co^{2+} with one distance of 4.24 Å and two distances of 4.87 Å as shown in Fig. 4. The metal cations are separated by borate anionic groups, consisted of corner-shared BO_3 and BO_4. In fact, the Co^{2+} network is close related to the black

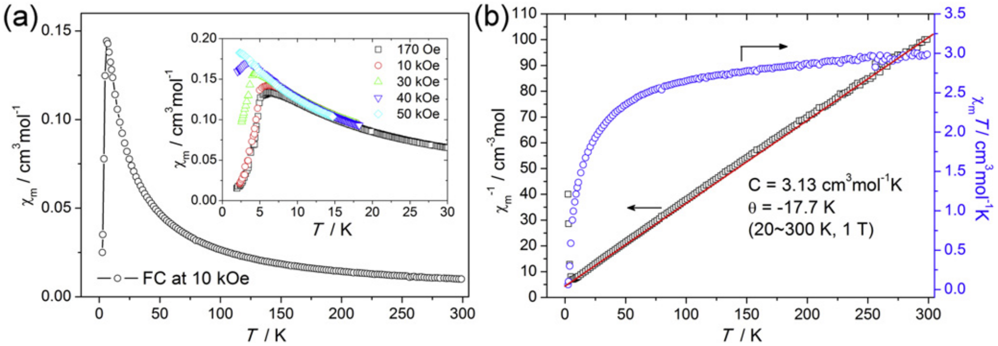

Fig. 1. (a) Molar magnetic susceptibilities $\chi_m(T)$ at 10 kOe field in FC condition for α-CoB_4O_7. The insert is low-temperature susceptibilities at various fields. (b) the Curie–Weiss fitting of the reciprocal susceptibility χ_m^{-1} v.s. T and the products of $\chi_m T$–T curve at 10 kOe at FC condition.