Metamagnetic phase transition in a new transition metal polyborate, \( \text{CoB}_{12}\text{O}_{14}\text{(OH)}_{10} \)

J Ju\(^1\), J Sasaki\(^1\), S Kasamatsu\(^1\), G Li\(^2\), J Lin\(^2\), and N Toyota\(^1\)

\(^1\)Physics Department, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.

\(^2\)The State Key Laboratory for Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.

E-mail: jujing@ldp.phys.tohoku.ac.jp

Abstract. New transition metal polyborate, \( \text{CoB}_{12}\text{O}_{14}\text{(OH)}_{10} \) is synthesized by using boric acid as a flux. This material has isomorphic structure with \( \text{MB}_{12}\text{O}_{14}\text{(OH)}_{10} \) (\( M = \text{Mg} \) or \( \text{Ni} \)), consisting of two-dimensional borate layers and quasi-square lattice of \( \text{Co}^{2+} \). The \( \text{Co}^{2+} \) ions locate in the plane of the two-dimensional layer, bridged through \( \text{B}_n\text{O}_{n+1} \) chains in the plane and connected with the three-membered ring borate groups out of the plane. The dc magnetic susceptibility and magnetization measurements show that the material undergo an antiferromagnetic phase transition at \( T_N = 5 \) K. At \( T < T_N \), a metamagnetic phase transition is observed at \( H_c = 2 \) T, associated by a spin-flop. The structural and magnetic properties of the transition metal polyborate represent an example of interesting magnetic interaction in diluent magnetic systems.

Metal borates, usually having complex structures composed of triangular and tetrahedral borate groups,\(^1\) have been the subject of interest in materials sciences because of their pronounced luminescent and nonlinear optical properties.\(^2,3\) In recent years, considerable interest raises for the magnetic and electronic properties of the transition metal borates, such as \( \text{SrCu}_2(\text{BO}_3)\)\(_2\), which exhibits singular quantized magnetization plateaus with a ground state of the \( \text{Cu} \) dimer mediated by planar \( \text{BO}_3 \)\(^4\). In fact transition metal borates are a large family of compounds that have diverse structures ranging from low dimensional to 3-dimensional frameworks. On the other hand, borate anions have been well known to mediate magnetic exchange interactions between bridged magnetic ions.\(^5,6\) The important roles of the borate groups, though being non-magnetic, are not only to fix the metal ions into the desired structure, but also to transmit magnetic interactions between the individual metal ions via the superexchange mechanism. For these reasons, the magnetism of transition metal borates has long been of considerable interest to both chemists and physicists.

In this paper we report on the synthesis and crystal structure of a new transition metal polyborate \( \text{CoB}_{12}\text{O}_{14}\text{(OH)}_{10} \) isostructural to \( \text{MB}_{12}\text{O}_{14}\text{(OH)}_{10} \) (\( M = \text{Mg} \) or \( \text{Ni} \)),\(^9,10\) and discuss the magnetic phase transitions reviewed by means of dc magnetic susceptibility and magnetization measurements.

\(^{1}\)To whom any correspondence should be addressed.
CoB\(_{12}\)O\(_{14}\)(OH)\(_{10}\) is synthesized by direct reaction of metal salt and boric acid in molten boric acid flux at 220°C. As an example, a Teflon autoclave is charged with Co(NO\(_3\))\(_2\)·6H\(_2\)O (99.9% purity, 0.7276 g) and H\(_3\)BO\(_3\) (99.5% purity, 3.0915 g), and the mixture is heated up to 220°C and kept for 10 days. The product, which is isolated by dissolving the excess boric acid in hot water, is lightly pink crystallites. For the magnetic measurement the crystallites are grinded into a fine powder, and then pressed into a troche with a diameter of 6.0 mm and a thickness of 1.5 mm. The troche is fixed in a sample holder of a straw that has negligibly small diamagnetic signal. The dc susceptibilities and magnetizations are measured using a superconducting quantum interference device magnetometer (SQUID, Quantum Design Co.). The magnetic susceptibility (\(\chi\)) is measured in the temperature range from \(T = 2.0\) to 300 K under an applied field \(H\) of 3 kOe. The magnetization measurements are carried out using SQUID up to 7 T.

The powder X-ray diffraction data are recorded on a Rigaku D/Max-2000 diffractometer at 50 kV, 100 mA for Cu K\(\alpha\) radiation. The structural analysis shows that CoB\(_{12}\)O\(_{14}\)(OH)\(_{10}\) is isostructural to MB\(_{12}\)O\(_{14}\)(OH)\(_{10}\) (\(M = Mg\) or Ni) in space group \(P2_1/c\) with the unit cell parameters of \(a = 11.553(2)\) Å, \(b = 8.5601(17)\) Å, \(c = 8.6852(17)\) Å and \(\gamma = 102.83(3)°\). The structure is characterized by two-dimensional (2D) layers consisting of B\(_3\)O\(_8\) and B\(_3\)O\(_7\) groups as fundamental borate units as shown in Fig. 1. The B\(_3\)O\(_8\) and B\(_3\)O\(_7\) groups are both 3-membered rings and can be expressed as \((2T+\Delta)\) and \((T+2\Delta)\) (\(T\) and \(\Delta\) respectively represent tetrahedral and trigonal coordinations of boron) according to the notation of Clark et al.\(^{11}\) The \((2T+\Delta)\) 3-membered rings are connected with each other to form 8-membered ring windows within the basal plane (100) as shown in Fig. 2 (a). The Co\(^{2+}\) ions locate at the centers of the 8-membered ring windows to form a quasi-square sublattice as indicated by the dotted lines. On the

![Fig. 1 Two fundamental borate units in CoB\(_{12}\)O\(_{14}\)(OH)\(_{10}\).](image)

![Fig. 2 Schematic views of the CoB\(_{12}\)O\(_{14}\)(OH)\(_{10}\) structure for the 2D layer along [100] (a) and the interlayer pathways along \(a\) axis (b).](image)
other hand, as shown in Fig. 2 (b), the other 3-membered ring borate units (T+2 ) are connected to the basal plane from both sides to provide a long-range bridge via hydrogen bonds for the Co$^{2+}$ ions from two neighboring layers. The structural descriptions of NiB$_{12}$O$_{14}$(OH)$_{10}$ were reported previously.$^{10}$

Figure 3 shows the temperature dependence of the magnetic susceptibility marked by open circles. Above $T = 5$ K, $\chi$ follows a Curie-Weiss law with the Weiss temperature, $\theta = -11.5$ K, and the Curie constant, $C = 1.98$ cm$^3$·mol$^{-1}$·K. The negative $\theta$ indicates an antiferromagnetic interaction between Co$^{2+}$ ions. The $C$ value corresponds to an effective magnetic moment, $M_{\text{eff}} = 3.95 \mu_B$ per Co$^{2+}$ ion, which is slightly larger than the spin-only value ($3.87 \mu_B$). Co$^{3+}$ is in the high-spin state ($S = 3/2$) and the $g$ factor deduced is about 2.04, indicating of a negligible orbital contribution. The susceptibility decreases sharply from $T = 5$ K, indicating an antiferromagnetic phase transition happens at $T_N = 5$ K. The nonzero $\chi$ at $T = 2$ K might be caused by the powder sample used in the experiment.

The isothermal magnetization curve at $T = 2$ K is exhibited in Fig. 4. The magnetic moment increases slowly at low applied field. At the critical field $H_c = 2$ T, a remarkable kink anomaly appears, followed by a rapid increase in the magnetization, which almost saturates at 7 T. The saturation moment is $3.15 \mu_B$/Co, very close to the expected value $g\mu_B S = 3.06 \mu_B$ for Co$^{3+}$ ($S = 3/2$, $g = 2.04$). These magnetization behaviors totally indicate that the ground state below $T_N$ is an antiferromagnetic ordering. The kink anomaly can be considered to be a metamagnetic phase transition associated by a spin-flop.

Similar to NiB$_{12}$O$_{14}$(OH)$_{10}$, CoB$_{12}$O$_{14}$(OH)$_{10}$ exhibits antiferromagnetic ordering at $T_N = 5$ K and spin-flop at $H_c = 2$ T. The critical field is considerably smaller than $H_c = 5.5$ T in NiB$_{12}$O$_{14}$(OH)$_{10}$. Furthermore, the magnetization reaches saturation at the applied field less than 7 T, whereas which is about 24 T for the nickel isomorph.$^{10}$ The spin state of Co$^{2+}$ in CoB$_{12}$O$_{14}$(OH)$_{10}$ is $S = 3/2$. The stronger magnetic interaction is expected in CoB$_{12}$O$_{14}$(OH)$_{10}$ due to the high spin state, which might lead to the smaller critical field and easier saturation.

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References
[1] Heller G 1986 *Topics in current chemistry* **131** 39
[2] Becker P 1998 *Adv. Mater.* **10** 979
[3] Keszler D A 1999 *Curr. Opin. Solid State Mater. Sci.* **4** 155
[4] Kageyama H, Yoshimura K, Stern R, Mushnikov N V, Onizuka K, Kato M, Kosuge K, Slichter C P, Goto T and Ueda Y 1999 *Phys. Rev. Lett.* **82** 3168
[5] Grishachev V V, Kolotov O S, Krasnojon A P and Pogozhev V A 2002 *J. Magn. Magn. Mater.* **241** 81
[6] Attfield J P, Bell A M T, Rodriguez-Martinez L M, Greneche J M, Cernik R J, Clarke J F and Perkins D A 1998 *Nature* **396** 655
[7] Fernandes J C, Guimarães R B and Continentino M A 2004 *Phys. Rev. B* **69** 054418
[8] Fernandes J C, Sarrat F S, Guimarães R B, Freitas R S and Continentino M A 2003 *Phys. Rev. B* **67** 104413
[9] Razmanova Z P, Rumanova I M and Belov N V 1979 *Sov. Phys. Dokl.* **24** 34
[10] Ju J, Sasaki J, Yang T, Kasamatsu S, Negishi E, Li G, Lin J, Nojiri H, Rachi T, Tanigaki K and Toyota N 2006 *Dalton Trans.* 1597
[11] Christ C L and Clark J R 1977 *Phys. Chem. Minerals* **2** 59