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# $CoV_2O_6$ Single Crystals Grown in a Closed Crucible: Unusual Magnetic Behaviors with Large Anisotropy and $^1/_3$ Magnetization Plateau

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Transition-metal oxides with a linear chain structure have attracted much attention in solid-state physics and chemistry since the discovery of their various fascinating magnetic phenomena. Major interest in linear-chain systems is currently focused on the investigation of magnetic ground states that depend on magnetic ions with low spin values. For $S = {}^1/_2$ systems, many copper- and vanadium-based oxides such as $CuGeO_3$,[1] $BaCu_2V_2O_8$,[2] $(VO)_2P_2O_7$,[3] and $NaV_2O_5$[4] are found to exhibit a spin-singlet ground state with a finite spin gap due to their strong quantum spin fluctuations. For $S = 1$ systems, nickel oxides including $PbNi_2V_2O_8$,[5] $SrNi_2V_2O_8$,[6] and $Y_2BaNiO_5$[7] are also found to have a nonmagnetic ground state and serve as typical examples of the realization of Haldane's conjecture.[8] For $S = {}^3/_2$ systems, almost all cobalt oxides, such as $BaCo_2Si_2O_7$,[9] $CoNb_2O_6$,[10] and $BaCo_2V_2O_8$,[11] show a three-dimensional (3D) Neel ordering at low temperature. Besides magnetic ground states, field-induced quantum phase transitions are also one of the most promising features of spin-chain systems. For a spin-gap system, field-induced magnetic ordering can occur when a high enough magnetic field is applied. Such a quantum phase transition has been observed in $PbNi_2V_2O_8$.[12] On the other hand, cobalt oxides usually exhibit large magnetic anisotropy and also show interesting field-induced magnetic transitions. For example, an unusual spin-flop transition has been observed in $CoNb_2O_6$,[10] while an order−disorder transition has been realized in $BaCo_2V_2O_8$.[13]

One cobalt oxide, $CoV_2O_6$,[14] crystallizes in the monoclinic structure of space group $C121$ with $a = 9.256$ Å, $b = 3.508$ Å, $c = 6.626$ Å, and $\beta = 111.55°$. As shown in Figure 1a, one of the most remarkable structural features is that magnetic $Co^{2+}$ ions are equivalent to arrays of edge-shared $CoO_6$ octahedra forming linear chains, while nonmagnetic $V^{5+}$ ions in $VO_5$ square pyramids form zigzag chains by sharing their basal edges along the $b$ axis, resulting in a quasi-one-dimensional (1D) structural arrangement. In this communication, we report the growth of $CoV_2O_6$ crystals in a closed crucible and the observation of unusual magnetic behaviors of $CoV_2O_6$ that are clearly different from those in the linear-chain systems mentioned above.

A polycrystalline sample of $CoV_2O_6$ was synthesized by a standard solid-state reaction method using a mixture of high-purity $CoC_2O_4 \cdot 2H_2O$ (2N) and $V_2O_5$ (3N) reagents in a 1:1 molar ratio. The mixture was carefully ground to homogeneity with ethanol (99%) in an agate mortar and then calcined in an alumina crucible at 600 °C for 40 h with several intermediate grindings. Crystal growth of $CoV_2O_6$ was carried out in a commercial electric furnace. Since $CoV_2O_6$ exhibits an incongruent melting feature on the basis of the phase diagram of $CoO-V_2O_5$ systems,[15] the flux method

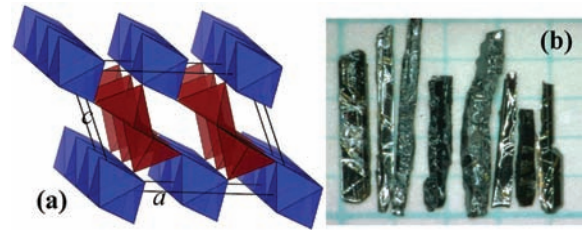


***Figure 1.*** (a) Crystal structure of $CoV_2O_6$. Blue octahedra and red square pyramids represent $CoO_6$ and $VO_5$, respectively. (b) Single crystals of $CoV_2O_6$ grown in a closed crucible using the flux method.

was suitable for the growth of single crystals. To avoid impurities from the flux in the grown crystals, we selected one of starting materials, $V_2O_5$, to be self-fluxed. A mixture of polycrystalline $CoV_2O_6$ and $V_2O_5$ in a ratio of 3:2, which corresponds to a 3:5 $CoO/V_2O_5$ ratio, was melted in an alumina crucible ($\Phi$ 42 × 50 mm$^3$), and then the crucible was capped with a cover using $Al_2O_3$ cement (C-989, Cotronics Corp.). The closed crucible was placed into the furnace, which was then heated to 780 °C and kept at that temperature for 20 h to ensure that the solution would melt completely and homogeneously. The furnace was slowly cooled to 600 °C at a rate of 1 °C/h and then cooled to room temperature at a rate of 100 °C/h. With this procedure, $CoV_2O_6$ crystals with needle morphology (Figure 1b) were obtained by mechanical separation from the crucible.

Recently, we successfully grew some vanadium oxides by the flux method.[16−18] To grow large $CoV_2O_6$ single crystals with high quality, the following important points of the growth process should be noted: To allow slow, spontaneous nucleation in the melt, a very slow cooling rate is suitable for the growth. Further, to avoid the inclusion of the melt into the crystal by overcooling of the melt, the furnace must be kept at a constant temperature several times in the cooling process. In addition, to carefully avoid the evaporation of $V_2O_5$ at high temperature, which would result in an unsteady solution system during the growth, the alumina crucible must be capped with a cover using $Al_2O_3$ cement to form a closed system.

The quality of the grown crystal was analyzed by powder X-ray diffraction (XRD) and electron probe microanalysis (EPMA) techniques. XRD data for the crushed grown crystal was collected at room temperature using an MXP18AHF X-ray diffractometer with graphite-monochromatized Cu K$\alpha$ radiation. It was found that all of the peaks in the XRD pattern obtained using the crushed crystals could be indexed with the monoclinic system and identified with the diffraction peaks of $CoV_2O_6$ (ICSD code 46003). The lattice constants of $a = 9.220(7)$ Å, $b = 3.494(3)$ Å, $c = 6.601(5)$ Å, and $\beta = 111.71(3)°$ determined by using a high-purity Si powder as an internal standard are in good agreement with those reported previously.[14] Chemical analysis via energy-dispersive spectroscopy

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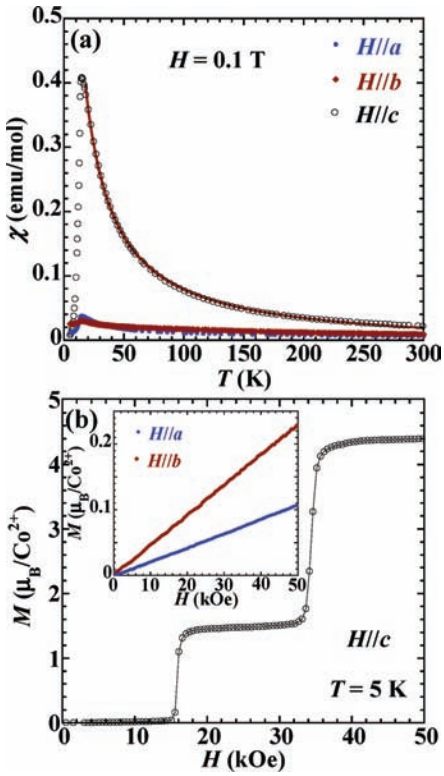


***Figure 2.*** (a) Temperature dependence of the magnetic susceptibilities of $CoV_2O_6$ along the crystallographic *a*, *b*, and *c* axes. The solid line is a fit using an Ising spin chain model for $Co^{2+}$ magnetic systems.[19] (b) Magnetization measured as a function of the applied field *H* along the *c* and (inset) *a* and *b* axes at 5 K.

performed using an EPMA system indicated no other metal elements except for Co and V in these crystals. The results clearly show that the grown crystals have high quality.

The crystallographic axes of the grown crystals were determined using a Bruker SMART three-circle diffractometer equipped with a CCD area detector. The magnetic susceptibility was measured with an applied field of 0.1 T from 5 to 300 K, and the magnetization was measured at 5 K under applied fields from 0 to 5 T using a superconducting quantum interference device magnetometer (MPMS5S, Quantum Design). Figure 2a demonstrates the temperature dependence of the magnetic susceptibilities along the crystallographic *a*, *b*, and *c* axes. The susceptibilities increased with decreasing temperature, while a sharp peak was observed at ~14 K, indicating the onset of antiferromagnetic (AF) ordering. We note that the decrease in susceptibility below 14 K for $H \parallel c$ is more rapid than that for $H \parallel a$ or $H \parallel b$, showing that the *c* axis is the magnetic easy axis. We also note the large difference between the susceptibilities along the *a* or *b* axis and the *c* axis, which persists even up to room temperature, indicative of a large magnetic anisotropy in the system. In addition, the susceptibility above 14 K along the *c* axis can be fit well using an Ising spin chain model for $Co^{2+}$ ($d^7$) magnetic systems,[19] giving $J/k_B = -4.86(6)$ K and $g = 10.1(1)$, the value of which also indicates an unusual magnetic anisotropy.

The anisotropic AF feature of $CoV_2O_6$ was also confirmed through field-dependent magnetization measurements below 14 K. A linear increase in the magnetization was observed at 5 K along the *a* and *b* axes (Figure 2b inset), agreeing with an AF ordering below 14 K. However, a staircase magnetization curve was clearly observed when the field was applied along the *c* axis (Figure 2b), with the first jump in the magnetization observed at ~1.6 T and the second one at ~3.3 T. With increasing magnetic field, the magnetization saturated completely at 4 T, and the ferromagnetic moment was roughly estimated to be ~4.4 $\mu_B/Co^{2+}$, which is much larger than the spin-only value of 3.0 $\mu_B/Co^{2+}$ for the full moments of $Co^{2+}$ ions. This indicates that the $Co^{2+}$ ions in $CoV_2O_6$ are in a high-spin state and exhibit a large orbital moment contribution in the oxygen octahedral environment. We note that the spin moment of ~1.47 $\mu_B/Co^{2+}$, which corresponds to a $^1/_3$ saturation moment of ~4.4 $\mu_B/Co^{2+}$, is observed in the applied fields between 1.6 and 3.3 T. This shows the occurrence of a plateau at $^1/_3$ magnetization. Further, the applied field for the second jump in magnetization was ~2 times as large as that for the first one, also indicating an interesting quantum phase transition in the system.

Ising spin systems have been studied intensively in past decades.[20] It is well-known that a field-induced $^1/_3$ magnetization plateau can occur in frustrated Ising spin systems with a triangular lattice. Such magnetic behavior has been observed in some hexagonal systems, such as $Ca_3Co_2O_6$[21] and $SrCo_6O_{11}$.[22] However, we note that monoclinic $CoV_2O_6$ does not exhibit a triangular lattice as a structural feature.[14] Therefore, we suggest that the $^1/_3$ magnetization plateau observed in $CoV_2O_6$ may arise from the unusual competition between interchain antiferromagnetic and ferromagnetic interactions, which is similar to that in a triangular structural lattice.

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