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Unusually Large Magnetic Anisotropy in a CuO-Based Semiconductor $Cu_5V_2O_{10}$

Zhangzhen He,*,[†] Chensheng Lin,[†] Wendan Cheng,*,[†] Atsushi Okazawa,[‡] Norimichi Kojima,[‡] Jun-ichi Yamaura,[§] and Yutaka Ueda[§]

[†] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[‡] Graduate School of Arts and Sciences, University of Tokyo, Komaba 3-8-1, Meguro, Tokyo 153-8902, Japan

[§] Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

S Supporting Information

ABSTRACT: A CuO-based material $Cu_5V_2O_{10}$ was successfully grown in a closed crucible using $Sr(OH)_2 \cdot 8H_2O$ as flux. The structure of $Cu_5V_2O_{10}$ can be viewed as being composed of two types of zigzag Cu−O chains running along the *b*- and *c*-axes, which shows a two-dimensional crosslike framework with 12-column square tunnels along the *a*-axis. Magnetic measurements show that $Cu_5V_2O_{10}$ exhibits unexpected large magnetic anisotropy, which is the first time magnetic anisotropy energy of $\sim 10^7$ erg/cm^3 in the CuO-based materials has been observed. The origins of large anisotropy are suggested to arise from strong anisotropic exchanges due to the particular bonding geometry and the Jahn−Teller distortion of Cu^{2+} ions. Further, the band structure investigated by the GGA+U method suggests that $Cu_5V_2O_{10}$ is a semiconductor.

CuO-based materials have attracted great scientific attention, since the discovery of high-T_c superconductivity in cuprates. Current interest is focused on the structural diversity of CuO-based materials which are considered as a typical model system for fundamental studies of low-dimensional magnetism. The magnetic superexchange interactions between nominally divalent copper ions are mainly determined by the microscopic spatial coordination of Cu^{2+} and O^{2-} ions with corner-sharing ($\angle$Cu−O−Cu = 180°) or edge-sharing ($\angle$Cu−O−Cu = 90°) configurations. In most cases, the appearance of unique magnetic phenomena originates from the particular topologies of spin networks built by Cu^{2+} ions in CuO-based materials. For example, the spin-Peierls transition is found in one-dimensional (1D) linear chain system $CuGeO_3$,[1] while a spin-singlet ground state is found in the isolated dimer system $CaCuGe_2O_6$.[2] The Bose−Einstein condensation of magnons is observed in two-dimensional (2D) bilayer system $BaCuSi_2O_6$,[3] while the Wigner crystallization of magnons is realized in 2D orthogonal dimer system $SrCu_2(BO_3)_2$.[4] The correlation of magnetic properties and structural features has given an exciting issue in chemistry and physics.

On the other hand, many low-dimensional CuO-based materials such as $LiCu_2O_2$[5] and $LiCuVO_4$[6] are also found to exhibit multiferroic properties at low temperature, showing the induction of magnetization by means of an electric field or induction of polarization by means of a magnetic field. This makes such materials potential as the realization of magnetoeletric devices. In this respect, CuO is very interesting because it is confirmed recently as an induced-multiferroic material with high-T_c of 230 K, due to the peculiar structure built up from two types of zigzag Cu−O chains with strong superexchange interactions.[7] This finding accelerates greatly the search for CuO-based materials with new physical properties.

$Cu_5V_2O_{10}$, one of CuO-based materials, crystallizes in the monoclinic structure of space group $P2_1/c$ with a = 8.393 Å, b = 6.065 Å, c = 16.156 Å, and β = 108.09°.[8] As shown in Figure 1a, Cu ions of $Cu_5V_2O_{10}$ have five different Wyckoff sites, which form distorted octahedra or trigonal bipyramids in oxygen ligand environment, respectively. One of the most remarkable features is that the structure of $Cu_5V_2O_{10}$ can be viewed as being composed of two types of zigzag Cu−O chains running along the *b*- and *c*-axes, which shows a 2D cross-like framework with 12-column square tunnels along the *a*-axis. In this communication, we report on exotic magnetic behaviors with strong spin frustration and unusually large magnetic anisotropy in the single crystals of semiconducting $Cu_5V_2O_{10}$. To the best of our knowledge, this is the first time that large magnetic anisotropy energy up to 10^7 erg/cm^3 at 5 K is found for a CuO-based material.

As shown in the Supporting Information (Figure S3), the susceptibility increases with decreasing temperature and a broad peak is observed at around 50 K, indicative of characteristic low-dimensional magnetism. A jump is shown at ~35 K, while the rapid decrease is shown at ~20 K, suggesting the onset of a canted antiferromagnetic (AF) ordering. A typical Curie−Weiss behavior is observed above 150 K, giving the Curie constant C = 3.88(2) emu K/mol and Weiss constant $\theta = -263.1(1)$ K. The effective magnetic moment (μ_{eff}) is calculated to be 2.49(2) μ_B, which is quite larger than the value of 1.732 μ_B for $S = 1/2$ with $g = 2$. This indicates unusually large magnetic anisotropy in the system. The negative and large Weiss temperature shows a strong AF coupling between Cu^{2+} ions. Also, heat capacity data (Figure S4) shows a clear sign of λ-like peak around 20 K, giving evidence for a long-range AF ordering. We note no anomaly of heat capacity at around 35 K, suggesting that the jump observed in

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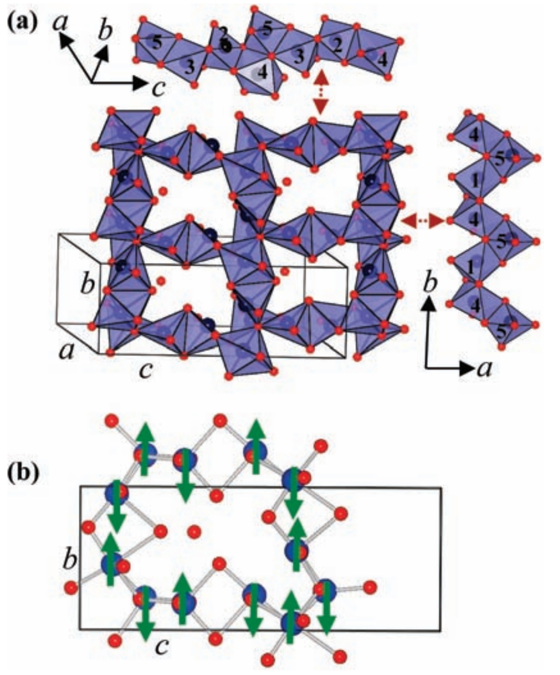

Figure 1. (a) Structural framework of $Cu_5V_2O_{10}$, where polyhedra, large balls, and small balls represent the CuO_n, Cu, and O, respectively. Two types of zigzag CuO_n chains along the *b*- and *c*-axes are seen. The numbers show five different Cu sites. (b) Spin arrangements of Cu^{2+} ions along the *b*-axis of $Cu_5V_2O_{10}$.

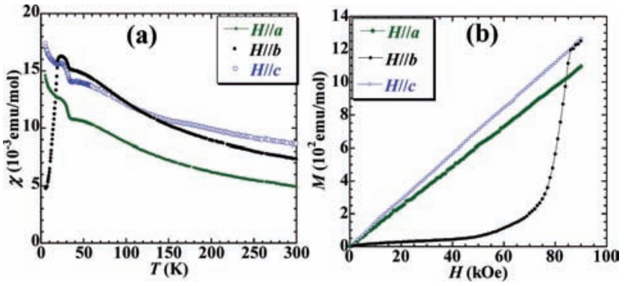

Figure 2. (a) The temperature dependence of the magnetic susceptibilities measured at $H = 0.1$ T along different axes. (b) Magnetization (M) as a function of applied field (H) at $T = 5$ K.

susceptibility at $\sim$35 K seems to be of short-range type. This means that a noncollinear spin arrangement starts at $\sim$35 K and completes at a steady collinear AF phase below $\sim$20 K. In addition, we also note that the ordering temperature (T_c) of $\sim$20 K is rather low compared with Weiss constant (θ_{CW}) of $\sim$263 K, suggesting strong spin frustration in the system. An empirical measure for spin frustration in a magnetic system has been suggested by defining the value of $f = |\theta_{CW}|/T_c$, with the value of $f > 10$ signifying a strong effect.[9] The value of $f = 13$ is obtained in $Cu_5V_2O_{10}$, supporting strong spin frustration inside such 2D square lattice.

Figure 2 shows magnetic measurements along different crystallographic axes of a single crystal sample. We note a large difference between the susceptibilities along the *a* and *b* or *c* axes (Figure 2a), which persists even up to room temperature, confirming unusually large magnetic anisotropy in $Cu_5V_2O_{10}$. In addition, the decrease in susceptibility below 20 K is seen for $H//b$, while the upturn is seen for $H//a$ or $H//c$, showing that the *b* axis is magnetic easy axis. As shown in Figure 2b, a linear increase in magnetization is observed at 5 K along the *a* and *c* axes. Furthermore, magnetization does not saturate even in 9 T and no remanent magnetization near $H = 0$ is observed, agreeing with a collinear AF ordering at low temperature. However, a rapid increase in magnetization is observed at around 8 T along the *b* axis, showing a typical spin-flop transition. This finding also supports magnetic easy *b*-axis and large magnetic anisotropy in the system. Thus, the spin arrangements in $Cu_5V_2O_{10}$ below 20 K can be predicted as of AF type along the *b*-axis (Figure 1b).

To estimate the magnitude of magnetic anisotropy of $Cu_5V_2O_{10}$, we use a simple uniaxial two-sublattice mean-field model.[10] In general, when an external field is applied along the magnetic easy axis of an antiferromagnet, the spin moments tend to flip toward directions perpendicular to the field to gain a magnetic energy of $0.5(\chi_\perp - \chi_{||})H^2$. If the magnetic anisotropy is not significant, the spin-flop transition appears at a critical field H_{SF} and the gain of magnetic energy compensates the anisotropy energy loss due to deviation of spin moments from the preferred spin orientation. Therefore, the anisotropy energy K, which is usually used to evaluate the magnitude of magnetic anisotropy, can be estimated by the equation: $K(T) = 0.5(H_{SF})^2[\chi_\perp - \chi_{||}]$, where H_{SF} is the spin flop transition field, and $\chi_\perp$ and $\chi_{||}$ are the perpendicular and parallel susceptibilities, respectively.[11] Using the experimental values of $\chi_b = 4.85(5) \times 10^{-3}$ emu/mol, $\chi_c = 1.73(9) \times 10^{-2}$ emu/mol, and $H_{SF} = 8.38(8)$ T at 5 K, respectively, we obtain $K(5\text{K}) = 4.40(9) \times 10^7$ erg/cm^3, of which this value is greater than 5×10^5 erg/cm^3 in Fe,[12] 8×10^5 erg/cm^3 in Ni,[13] and 4×10^6 erg/cm^3 in hcp Co.[14]

To identify the nature of magnetic anisotropy of $Cu_5V_2O_{10}$, ESR measurements are carried out. Above 25 K, the spectra show a significant deviation from Lorentzian profile and additional line broadening at around 0.2 T (Figure S5). These features are suggested to arise from the spin diffusion in low-dimensional magnets.[15] Below 25 K, a typical Lorentzian line-shape gives a mean *g*-factor of 2.24(3), agreeing with Cu^{2+} ions in tetragonally distorted octahedral environment. It is well-known that the major magnetic anisotropy contributions for a CuO-based material originate from the antisymmetric Dzyaloshinsky-Moriya (DM) interactions as seen in $SrCu_2(BO_3)_2$[16] or the symmetric anisotropic exchanges as seen in $LiCuVO_4$.[17] We note that $Cu_5V_2O_{10}$ exhibits a symmetric crystal structure with a space group of $P2_1/c$, ruling out the DM interactions, while Cu^{2+} ions in the cross-like framework built by Cu−O zigzag chains would give rise to a strongly anisotropic ring exchange.[18] Such anisotropic exchanges arising from a particular bonding geometry reflect the comparable linewidths, which show the line broadening especially for resonance along the *a*-axis of $Cu_5V_2O_{10}$. Also, we note a large Jahn−Teller distortion of Cu^{2+} ($3d^9$) ions in $Cu_5V_2O_{10}$ running along the *b*- or *c*-axis,[8] leading to large paramagnetic anisotropy due to different Van-Vleck contributions affected by the Jahn−Teller distortion. Similar paramagnetic anisotropy is also seen in $LiCuVO_4$.[19]

Electronic structure of $Cu_5V_2O_{10}$ is investigated using GGA+U method. The results (Figures S6 and S7) show that the top of the valence and bottom of conduction bands are composed of V 3d, O 2p, and Cu 3d orbitals, respectively. An indirect band gap of $\sim$1.64 eV is obtained between valence and conduction bands, showing that $Cu_5V_2O_{10}$ is a semiconductor similar to β-$Cu_2V_2O_7$.[20] Although further studies such as neutron scattering and NMR measurements are desirable, the present results indicate clearly that $Cu_5V_2O_{10}$ is an interesting 2D CuO-based magnet.

ASSOCIATED CONTENT

Ⓢ Supporting Information. The detailed growth procedure, characterization, and band calculation of $Cu_5V_2O_{10}$ single crystals; the temperature dependence of magnetic susceptibility measured on the polycrystalline sample; heat capacity data; ESR data; electronic structure. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
hcz1988@hotmail.com; cwd@fjirsm.ac.cn

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