Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 9253–9256 **9253**
DOI: 10.1021/ic100906s

Finite Magnetization Plateau from a Two-Dimensional Antiferromagnet: Density Functional Analysis of the Magnetic Structure of $Cu_3(P_2O_6OH)_2$

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Received May 7, 2010

We evaluated the intrachain and interchain spin exchanges of $Cu_3(P_2O_6OH)$ consisting of $(Cu2-Cu2-Cu1)_\infty$ chains by density functional calculations to find that the magnetic properties of $Cu_3(P_2O_6OH)_2$ are not governed by the $J_1-J_2-J_2$ trimer chain along the *c*-direction, but by a two-dimensional (2D) antiferromagnetic lattice in which $J_1-J_3-J_3$ trimer chains along the $(a-c/2)$-direction are interconnected by J_6 monomer chains along the *a*-direction. Despite its 2D character, $Cu_3(P_2O_6OH)_2$ shows a 1/3 magnetization plateau because it is a spin-1/2 trimer system with one dominant antiferromagnetic dimer exchange.

1. Introduction

A magnetic system with an energy gap in the magnetic excitation spectrum has a magnetization plateau in the magnetization curve. Spin-gapped systems with spin-singlet ground state such as the Haldane system $Ni(C_2H_8N_2)_2NO_2(ClO_4)$,[1] the spin-Peierls cuprate $CuGeO_3$,[2] and the orthogonal-dimer compound $SrCu_2(BO_3)_2$[3] exhibit a zero-magnetization plateau. A finite-magnetization plateau is observed for a magnetic system possessing an energy gap within the magnetic excited states, as found for NH_4CuCl_3,[4] $Cu_3(OH)_2(CO_3)_2$,[5] and $Cu_3(P_2O_6OH)_2$.[6,7] A finite-magnetization plateau in such magnetic systems has been understood in terms of the Oshikawa–Yamanaka–Affleck theory developed for one-dimensional (1D) magnetic chains,[8] namely, the magnetization curve of a one-dimensional (1D) chain with spin S per site can have a plateau at the magnetization m per site if $n(S - m) =$ integer, where n is the period of the magnetic ground state. $Cu_3(OH)_2(CO_3)_2$ had been considered to be a diamond-chain system, but a recent electronic structure study showed[9] that $Cu_3(OH)_2(CO_3)_2$ is not a 1D but a two-dimensional (2D) magnetic system because it has substantial spin exchanges between adjacent diamond chains through the CO_3 bridges. The spin–lattice needed to interpret the magnetic properties of a given system is often selected by the geometrical pattern of the magnetic ion arrangement. In this qualitative selection process, one includes spin exchanges of superexchange (SE) type (e.g., Cu–O–Cu)[10] but often neglects spin exchanges of supersuperexchange (SSE) type (e.g., Cu–O···O–Cu). Consequently, the properties of numerous magnetic systems[9,11–19] have been explained using incorrect spin–lattices. Electronic structure consideration is crucial in identifying the correct

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(1) (a) Katsumata, K.; Hori, H.; Takeuchi, T.; Date, M.; Yamagishi, A.; Renard, J. P. *Phys. Rev. Lett.* **1989**, *63*, 86. (b) Ajiro, Y.; Goto, T.; Kikuchi, H.; Sakakibara, T.; Inami, T. *Phys. Rev. Lett.* **1989**, *63*, 1424.
(2) Hase, M.; Terasaki, I.; Uchinokura, K.; Tokunaga, M.; Miura, N.; Obara, H. *Phys. Rev. B* **1993**, *48*, 9616.
(3) Kageyama, H.; Yoshimura, K.; Stern, R.; Mushnikov, N. V.; Onizuka, K.; Kato, M.; Kosuge, K.; Slichter, C. P.; Goto, T.; Ueda, Y. *Phys. Rev. Lett.* **1999**, *82*, 3168.
(4) Kurniawan, B.; Tanaka, H.; Takatsu, K.; Shiramura, W.; Fukuda, T.; Nojiri, H.; Motokawa, M. *Phys. Rev. Lett.* **1999**, *82*, 1281.
(5) Ohta, H.; Okubo, S.; Kamikawa, T.; Kunimoto, T.; Inagaki, Y.; Kikuchi, H.; Saito, T.; Azuma, M.; Takano, M. *J. Phys. Soc. Jpn.* **2003**, *72*, 2464.
(6) Hase, M.; Kohno, M.; Kitazawa, H.; Tsujii, N.; Suzuki, O.; Ozawa, K.; Kido, G.; Imai, M.; Hu, X. *Phys. Rev. B* **2006**, *73*, 104419.
(7) Hase, M.; Matsuda, M.; Kakurai, K.; Ozawa, K.; Kitazawa, H.; Tsujii, N.; Dönni, A.; Kohno, M.; Hu, X. *Phys. Rev. B* **2007**, *76*, 064431.
(8) Oshikawa, M.; Yamanaka, M.; Affleck, I. *Phys. Rev. Lett.* **1997**, *78*, 1984.
(9) Kang, J.; Lee, C.; Kremer, R. K.; Whangbo, M.-H. *J. Phys.:Condens. Matter* **2009**, *21*, 392201, and the references cited therein.
(10) (a) Goodenough, J. B. *Magnetism and Chemical Bond*; Wiley: Cambridge, MA, 1963. (b) Anderson, P. W. *Solid State Physics*; Seitz, F.; Turnbull, D., Eds.; Academic Press: New York, 1963; Vol. *14*.
(11) Whangbo, M.-H.; Koo, H.-J.; Dai, D. *J. Solid State Chem.* **2003**, *417*, 176.
(12) Koo, H.-J.; Whangbo, M.-H.; VerNooy, P. D.; Torardi, C. C.; Marshall, W. J. *Inorg. Chem.* **2002**, *41*, 4664.
(13) Koo, H.-J.; Dai, D.; Whangbo, M.-H. *Inorg. Chem.* **2005**, *44*, 4359.
(14) Garret, A. W.; Nagler, S. E.; Tennant, D. A.; Sales, B. C.; Barnes, T. *Phys. Rev. Lett.* **1997**, *79*, 745.
(15) Derakhshan, S.; Cuthbert, H. L.; Greedan, J. E.; Rahman, B.; Saha-Dasgupta, T. *Phy. Rev. B* **2007**, *76*, 104403.
(16) Koo, H.-J.; Whangbo, M.-H. *Inorg. Chem.* **2008**, *47*, 128.
(17) Miura, Y.; Yasui, Y.; Moyoshi, T.; Sato, M.; Kakurai, K. *J. Phys. Soc. Jpn.* **2008**, *77*, 104789.
(18) Sakurai, H.; Yoshimura, K.; Kosuge, K.; Tsujii, N.; Abe, H.; Kitazawa, H.; Kido, G.; Michor, H.; Hilscher, G. *J. Phys. Soc. Jpn.* **2002**, *71*, 1161.
(19) Koo, H.-J.; Whangbo, M.-H. *Inorg. Chem.* **2008**, *47*, 4779.

Published on Web 09/20/2010

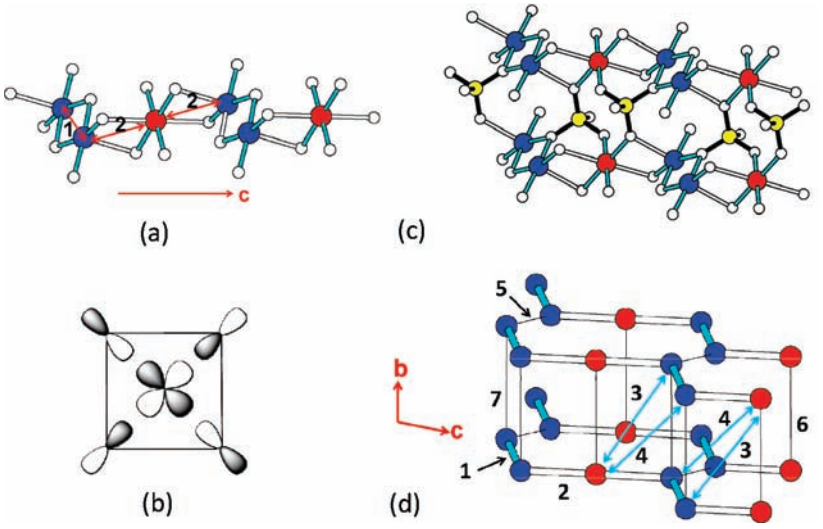

Figure 1. (a) Isolated $(Cu2-Cu2-Cu1)_\infty$ chain of $Cu_3(P_2O_6OH)_2$ made up of edge-sharing $Cu2O_5$ square pyramids and $Cu1O_6$ octahedra. The Cu2 and Cu1 atoms are denoted by blue and red circles, respectively, and the O atoms by small white circles. The Cu−O bonds contained in the magnetic orbitals of the $Cu2O_5$ and $Cu1O_6$ polyhedra are shown as cyan cylinders. The numbers 1 and 2 refer to J_1 and J_2, respectively. (b) The magnetic orbital of a Cu^{2+} ion, in which the Cu $3d_{x^2-y^2}$ orbital makes σ-antibonding interactions with the O 2p orbitals. (c) Two $(Cu2-Cu2-Cu1)_\infty$ chains of $Cu_3(P_2O_6OH)_2$ interconnected by PO_4, where the P atoms are denoted by yellow circles and the P−O bonds by black cylinders. (d) The seven spin exchange paths J_1-J_7 of $Cu_3(P_2O_6OH)_2$, where J_1 and J_2 are the Cu−O−Cu spin exchanges within each $(Cu2-Cu2-Cu1)_\infty$ chain, and J_3-J_7 are the Cu−O···O−Cu spin exchanges between adjacent $(Cu2-Cu2-Cu1)_\infty$ chains. The numbers 1−7 refer to J_1-J_7, respectively.

spin−lattice of a magnetic solid, as will be shown below for $Cu_3(P_2O_6OH)_2$.

Copper hydroxydiphosphate $Cu_3(P_2O_6OH)_2$ has two kinds of copper atoms, Cu1 and Cu2, located respectively at the octahedral and square pyramidal pockets of oxygen atoms created by the $(P_2O_6OH)^{3-}$ ions.[20] The axially elongated $Cu1O_6$ octahedra and the $Cu2O_5$ square pyramids share their edges to form the $(Cu2-Cu2-Cu1)_\infty$ chains along the *c*-direction (Figure. 1a), so the magnetic properties of $Cu_3(P_2O_6OH)_2$ have been interpreted in terms of a spin-1/2 trimer chain model with $J_a-J_b-J_b$ spin exchanges.[6,7] The magnetization curve of $Cu_3(P_2O_6OH)_2$ measured at 1.6 K exhibits a 1/3 magnetization plateau above 12 T,[6] which is consistent with the prediction by the Oshikawa−Yamanaka−Affleck theory for 1D magnetic chains.[8] When analyzed in terms of a $J_a-J_b-J_b$ trimer chain model, the magnetic susceptibility and magnetization data of $Cu_3(P_2O_6OH)_2$ show that J_a and J_b are both antiferromagnetic (i.e., $J_a/k_B = -95$ K and $J_b/k_B = -28$ K),[6] and so do the inelastic neutron scattering data of $Cu_3(P_2O_6OH)_2$ (i.e., $J_a/k_B = -111$ K and $J_b/k_B = -30$ K).[7] In addition, the latter data confirmed that the 1/3 magnetization plateau originates from the energy gap associated with the singlet-to-triplet-like excitations of the antiferromagnetic dimers formed by the dominant J_a interaction. The $J_a-J_b-J_b$ trimer chain model for $Cu_3(P_2O_6OH)_2$ is a consequence of considering only the geometrical pattern of the SE interactions present in the $(Cu2-Cu2-Cu1)_\infty$ chains. Spin exchange interactions between Cu^{2+} ions depend on how their magnetic orbitals overlap.[10,11] In $Cu_3(P_2O_6OH)_2$ the magnetic orbital of a Cu^{2+} ion (Figure 1b), commonly referred to as the "x^2-y^2" orbital, is contained in the basal plane of each $Cu2O_5$ square pyramid and in the equatorial plane of each axially elongated $Cu1O_6$ octahedron. Thus, only those Cu−O bonds contained in the magnetic orbital planes, which are highlighted as cyan cylinders in Figure 1a, can have magnetic orbital character. Thus, the spin exchange of a SE path Cu−O−Cu can be substantial only if both Cu−O bonds of the exchange path possess magnetic orbital character as in J_1, but should be negligible if this is not the case as in J_2. Consequently, the magnetic properties of $Cu_3(P_2O_6OH)_2$, though well-described by the $J_a-J_b-J_b$ chain model with antiferromagnetic J_a and J_b,[6,7] cannot be related to the $J_1-J_2-J_2$ chains running along the *c*-direction. As shown in Figure 1c, the $(Cu2-Cu2-Cu1)_\infty$ chains are interconnected by PO_4 units of the $(P_2O_6OH)^{3-}$ ions. Substantial interchain spin exchange can take place through the SSE paths Cu−O···O−Cu if both Cu−O bonds of these paths possess magnetic orbital character.[11,13] Therefore, to identify the spin−lattice responsible for its magnetic properties, one should evaluate the SE and SSE interactions of $Cu_3(P_2O_6OH)_2$ on the basis of electronic structure calculations.

2. Calculations

We carry out mapping analysis based on first principles density functional (DFT) calculations to determine the values of the seven spin exchange parameters J_1-J_7 of $Cu_3(P_2O_6OH)_2$ defined in Figure 1d, where J_1 and J_2 are intrachain SE's, while J_3-J_7 are interchain SSE's. Our DFT calculations employed the frozen-core projector augmented wave method encoded in the Vienna ab initio simulation packages,[21] and the generalized-gradient approximation (GGA)[22] with the plane-wave-cutoff energy of 400 eV and a set of $6 \times 4 \times 2$ k points for the irreducible Brillouin zone. To describe the strong electron correlation in the Cu 3d states, the GGA plus on-site repulsion method (GGA+U)[23] was used with the effective U values of 4, 5, and 6 eV.

(20) Baies, R.; Caignaert, V.; Pralong, V.; Raveau, B. *Inorg. Chem.* **2005**, *44*, 2376.

(21) (a) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558. (b) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15. (c) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

(22) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(23) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. *Phys. Rev. B* **1998**, *57*, 1505.

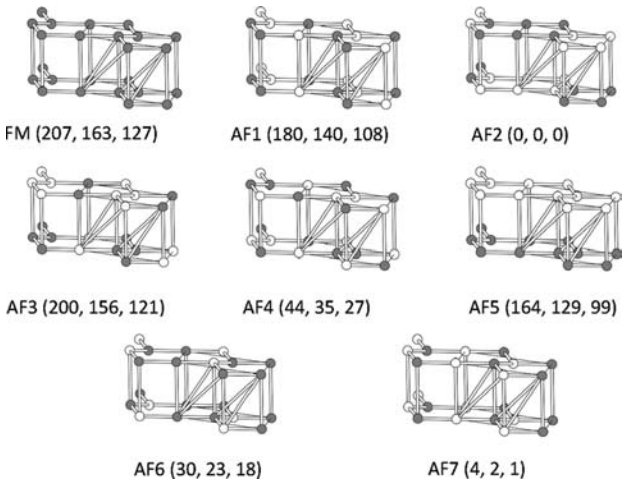

Figure 2. Eight ordered spin states of $Cu_3(P_2O_6OH)_2$ employed to extract the values of the seven exchanges J_1−J_7. The gray and white circles represent the up- and down-spin Cu^{2+} sites, respectively. The three numbers in each parentheses, from left to right, refer to the relative energies in meV per eight formula units obtained from the GGA+U calculations with U = 4, 5, and 6 eV, respectively.

3. Results and Discussion

To extract the values of J_1−J_7, we first define eight ordered spin states (Figure 2) using a (2a, 2b, 2c) supercell, which contains eight formula units (FUs), and then determine their relative energies on the basis of GGA+U calculations. The relative energies of these states determined by GGA+U calculations are summarized in Figure 2. (The calculated Cu spin moments in these states are given in Table S1 of the Supporting Information.) In terms of the spin Hamiltonian

$$\hat{H} = -\sum_{i<j} J_{ij}\hat{S}_i\hat{S}_j \qquad (1)$$

defined in terms of the exchanges $J_{ij} = J_1$−J_7 to be determined, the total spin exchange energies of the eight states (per eight FUs) are expressed as in eq 2.[24]

$$\begin{aligned}
&\text{FM}: (-8J_1 - 16J_2 - 16J_3 - 16J_4 - 8J_5 - 8J_6 - 16J_7)/4\\
&\text{AF1}: (-8J_1 + 16J_2 + 16J_3 + 16J_4 + 8J_5 - 8J_6 - 16J_7)/4\\
&\text{AF2}: (+8J_1 - 16J_2 + 16J_3 - 16J_4 + 8J_5 + 8J_6 + 16J_7)/4\\
&\text{AF3}: (-8J_1 + 16J_2 - 16J_3 - 16J_4 - 8J_5 + 8J_6 + 16J_7)/4\\
&\text{AF4}: (+8J_1 + 16J_2 - 16J_3 + 16J_48 - J_5 + 8J_6 + 16J_7)/4\\
&\text{AF5}: (-8J_1 - 16J_2 + 16J_3 + 16J_4 - 8J_5 + 8J_6 + 16J_7)/4\\
&\text{AF6}: (+8J_1 + 16J_3 - 16J_4 + 8J_5 - 8J_6 - 16J_7)/4\\
&\text{AF7}: (+8J_1 + 16J_2 + 16J_3 - 16J_4 + 8J_5 - 8J_6 - 16J_7)/4
\end{aligned} \qquad (2)$$

Table 1. Values of the Spin Exchange Parameters J_1−J_7 in k_BK of $Cu_3(P_2O_6OH_2)$ Obtained from GGA+U Calculations As a Function of U[a,b]

	U = 4 eV	U = 5 eV	U = 6 eV
J_1	−479 (1.00)	−376 (1.00)	−291 (1.00)
J_2	−3 (0.01)	−3 (0.01)	−3 (0.01)
J_3	−69 (0.14)	−56 (0.15)	−45 (0.15)
J_4	15 (−0.03)	12 (−0.03)	10 (−0.03)
J_5	34 (−0.07)	28 (−0.07)	23 (−0.08)
J_6	−90 (0.19)	−71 (0.19)	−55 (0.19)
J_7	36 (−0.08)	29 (−0.08)	23 (−0.08)

[a] The numbers in parentheses are relative values. [b] The Cu···Cu distances of the spin exchange paths are 3.059 Å for J_1, 3.281 Å for J_2, 5.625 Å for J_3, 5.975 Å for J_4, 4.432 Å for J_5, and 4.782 Å for J_6 and J_7.

Thus, by mapping the relative energies of the eight ordered states determined from the GGA+U calculations onto the corresponding energies derived from the total spin exchange energies, we obtain the values of J_1−J_7 listed in Table 1.

J_1 is most strongly antiferromagnetic, and its magnitude decreases with increasing U as has been observed for other magnetic systems.[16,19,25] This comes about because, to a first approximation, an antiferromagnetic spin exchange is inversely proportional to U.[11] The calculated J_1 is identified as J_a found experimentally, so that the calculated exchange values are overestimated by a factor of approximately 3−5, as typically found for GGA+U calculations. However, the relative values of J_1−J_7 are not very much affected by the values of U.

As anticipated, the intrachain exchange J_2 is negligible and the interchain exchanges J_3 and J_6 are substantially antiferromagnetic ($J_3/J_1 \approx 0.15$, and $J_6/J_1 \approx 0.19$) with nearly comparable strength (For the spin dimer analysis for J_2, J_3, and J_6, see Table S2 and Figures S1 and S2 in the Supporting Information). The remaining exchanges are weak (Table1). Therefore, the magnetic properties of $Cu_3(P_2O_6OH)_2$ are best described by the three antiferromagnetic exchanges J_1, J_3, and J_6, which lead to the 2D spin−lattice shown in Figure 3. The spin exchanges J_1 and J_3 form J_1−J_3−J_3 trimer chains along the ($a - c/2$)-direction, and these chains are interconnected by J_6 monomer chains along the a-direction. Consequently, it is not the J_1−J_2−J_2 trimer chains along the c-direction but the J_1−J_3−J_3 trimer chains along the ($a - c/2$)-direction that are responsible for the J_a−J_b−J_b trimer chain behavior observed for $Cu_3(P_2O_6OH)_2$. Thus, the spin wave dispersions of $Cu_3(P_2O_6OH)_2$ will be flat along the c-direction, but dispersive along the ($a - c/2$)- and a-directions. This prediction can be verified by inelastic neutron scattering experiments.

It should be noted that the 1/3 magnetization plateau of $Cu_3(P_2O_6OH)_2$, though interpreted in terms of a J_a−J_b−J_b trimer chain model and found consistent with the Oshikawa−Yamanaka−Affleck theory for 1D magnetic chains,[8] arises actually from a 2D antiferromagnet. A similar situation has been observed for $Cu_3(OH)_2(CO_3)_2$,[5] in which there occur substantial spin exchanges between diamond chains.[9] $Cu_3(P_2O_6OH)_2$ and $Cu_3(OH)_2(CO_3)_2$ have a common feature in that both are a spin-1/2 trimer system with one dominant antiferromagnetic dimer exchange, which is connected to considerably weaker antiferromagnetic exchanges to form a 2D spin−lattice.

(24) (a) Dai, D.; Whangbo, M.-H. *J. Chem. Phys.* **2001**, *114*, 2887. (b) Dai, D.; Whangbo, M.-H. *J. Chem. Phys.* **2003**, *118*, 29.

(25) Xiang, H. J.; Lee, C.; Whangbo, M.-H. *Phys. Rev. B* **2007**, *76*, 220411(R).

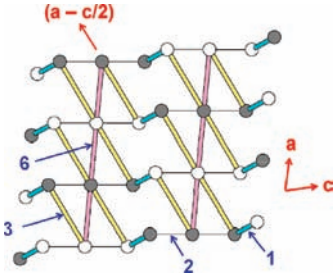

Figure 3. Spin−lattice model for $Cu_3(P_2O_6OH_2)$ predicted by the three antiferromagnetic exchanges J_1, J_3, and J_6 determined from the GGA+U calculations. The numbers 1, 2, 3, and 6 refer to J_1, J_2, J_3, and J_6, respectively. The up-spin and down-spin Cu sites in the lowest-energy spin arrangement AF2 are represented by filled and empty circles, respectively.

4. Concluding Remarks

In summary, the $J_a-J_b-J_b$ chain behavior of $Cu_3(P_2O_6OH)_2$ is not caused by the $J_1-J_2-J_2$ trimer chains along the *c*-direction, but by the $J_1-J_3-J_3$ trimer chains running along the $(a - c/2)$-direction. $Cu_3(P_2O_6OH)_2$ has a 2D spin−lattice in which the $J_1-J_3-J_3$ chains are interconnected by J_6 monomer chains along the a-direction. Despite its 2D character, $Cu_3(P_2O_6OH)_2$ shows a 1/3 magnetization plateau because it is a spin-1/2 trimer system with one dominant antiferromagnetic dimer exchange, which is connected to considerably weaker antiferromagnetic exchanges.

Acknowledgment. Work at KHU was supported by Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (2007-531-C00028), and at NCSU by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG02-86ER45259, and also by the computing resources of the NERSC center and the HPC center of NCSU.

Supporting Information Available: The calculated Cu spin moments in the eight ordered spin states (Table S1), and results of the spin dimer analysis for J_2, J_3, and J_6 (Table S2, Figures S1 and S2) (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.