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Paramagnetic anisotropy and spin-flop transition in single crystals of the quasi-one-dimensional system β-$Cu_2V_2O_7$

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Magnetic behaviors of β-$Cu_2V_2O_7$ single crystals are investigated by means of magnetic susceptibility, magnetization, and heat capacity measurements. Our experimental results show that β-$Cu_2V_2O_7$ is a quasi-one-dimensional antiferromagnet with Néel temperature of ~26 K. The intrachain and interchain exchanges are estimated to be $J_{\parallel}=39$ K and $J_{\perp}=13.8$ K, respectively. Also, paramagnetic anisotropy is observed in the system, while a typical spin-flop transition is observed with magnetic field applied along the c axis. Magnetic anisotropy energy at 5 K is estimated to be $K=6.05(5)\times10^5$ ergs/cm^3. Spins of Cu^{2+} ions are suggested to arrange parallel to the c axis and perpendicular to the chains.

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One-dimensional (1D) spin systems have been one of the most active fields in condensed matter physics due to the discovery of their various interesting magnetic behaviors. Compounds with a linear chain structure have attracted much attention, however, current interests on 1D spin systems are mainly focused on copper- and vanadium-based oxides containing Cu^{2+} ions ($3d^9$) or V^{4+} ions ($3d^1$). For example, many copper oxides, such as $CuGeO_3$,[1] $BaCuSi_2O_6$,[2] $SrCu_2O_3$,[3] and $BaCu_2V_2O_8$,[4] and vanadium oxides, such as $(VO)_2P_2O_7$ (Ref. 5) and NaV_2O_5 (Ref. 6), are characterized to be a spin singlet ground state with a finite spin gap due to their strong quantum spin fluctuation, while $LiCuVO_4$,[7] $BaCu_2Si_2O_7$,[8] $CuSiO_3$,[9] and $Sr_2V_3O_9$ (Ref. 10) are found to undergo a three-dimensional magnetic ordering at low temperature due to weak interchain interactions. Such different magnetic ground states related to spin and charge correlations in copper- or vanadium-based oxides provide a rich physics.

$Cu_2V_2O_7$, one of the copper-vanadium-based oxides, is composed of magnetic Cu^{2+} ($3d^9, S=1/2$) ions and nonmagnetic tetrahedral VO_4 ($3d^0, S=0$). As shown in Fig. 1(a), one of the most remarkable structural features is that all Cu^{2+} ions are equivalent with the arrays of edge-shared CuO_5 polyhedra forming linear chains, and the linear chains are not parallel to the same direction but extend in two approximately perpendicular directions, showing a cross-linking chain framework.[11,12] $Cu_2V_2O_7$ was found to have two different phases of high-temperature form (β form) and low-temperature form (α form): β form[11] crystallizes in monoclinic system of space group $C2/c$ with $a=7.685(5)$ Å, $b=8.007(3)$ Å, $c=10.29(2)$ Å, and $\beta=110.27(5)°$, while α form[12] crystallizes in orthorhombic system of space group $Fdd2$ with $a=20.645(2)$ Å, $b=8.383(7)$ Å, and $c=6.442(1)$ Å.

Due to their peculiar linear chain structures, magnetic behaviors of α- and β-$Cu_2V_2O_7$ have been investigated by many researchers on polycrystalline samples.[13–15] Ponomarenko *et al.*[13] reported that α-$Cu_2V_2O_7$ is an antiferromagnet with weak ferromagnetism. A spontaneous magnetization was observed below $T_C=35$ K with a small saturation magnetization of $0.04\mu_B$, which was suggested to arise from the canting of spins due to the Dzyaloshinsky-Moriya (DM) interaction. Pommer *et al.*[14] investigated the structural and magnetic properties of $Cu_{2-y}Zn_yV_2O_7$ and suggested that the substitution of Zn for Cu in $Cu_2V_2O_7$ can induce a structural transition from the α form with $y<0.15$ to the β form with $y\geqslant0.15$, leading to a change in magnetic properties from a canted antiferromagnet to an antiferromagnet, due to absence of intrachain DM interaction. The results show that β-$Cu_2V_2O_7$ is likely an antiferromagnet with Néel temperature (T_N) of ~26 K. However, Touaiher *et al.*[15] recently pointed out that the fit for the experimental magnetic susceptibility of β-$Cu_2V_2O_7$ by the dimeric model is more suitable than that by the Bonner-Fisher model. Further, no λ-like feature was observed in heat capacity data at the temperature range of 1.6–40 K. These results indicate that β-$Cu_2V_2O_7$ is likely a Heisenberg antiferromagnet with a spin singlet ground state.

Besides the α and β forms, $Cu_2V_2O_7$ was found to have the third phase of γ form,[16] which crystallizes in triclinic system of space group $P\bar{1}$ with $a=5.0873(1)$ Å, $b=5.8233(1)$ Å, $c=9.4020(1)$ Å, $\alpha=99.780(3)°$, $\beta=97.253(3)°$, and $\gamma=97.202(3)°$. It was also found that α form is only stable phase at ambient conditions, whereas both β and γ forms are metastable.[16] Therefore, the quality of $Cu_2V_2O_7$ polycrystalline samples obtained by different synthesis methods should strongly affect their magnetic properties. Different magnetic properties of β-$Cu_2V_2O_7$ in-

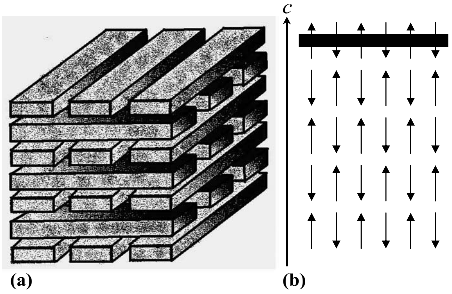

FIG. 1. (a) The cross-linking chain structure of β-$Cu_2V_2O_7$: the chains built by Cu^{2+} ions are parallel to the [110] and [$\bar{1}$10] directions. (b) Spins of Cu^{2+} ions arranged parallel to the c axis and perpendicular to the chains.

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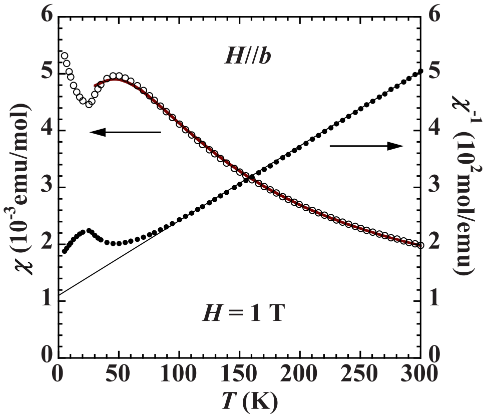

FIG. 2. (Color online) Temperature dependence of magnetic susceptibility and reciprocal one for β-$Cu_2V_2O_7$ measured at an applied field of 1 T along the *b* axis. The thin solid line is a fit to the Curie-Weiss law and the thick one is the Bonner-Fisher fit (Ref. 21).

vestigated by Pommer *et al.*[14] and Touaiher *et al.*[15] lead us to further reinvestigate magnetic ground state of β-$Cu_2V_2O_7$. In this study, we report magnetic behaviors of β-$Cu_2V_2O_7$ single crystals investigated by means of magnetic and heat capacity measurements. Our results suggest that β-$Cu_2V_2O_7$ is a 1D spin-1/2 anisotropic Heisenberg antiferromagnet with $T_N = \sim 26$ K. Also, paramagnetic anisotropy is observed even at room temperature, and spin-flop transition is observed in magnetic field applied along the *c* axis.

β-$Cu_2V_2O_7$ single crystals were grown by flux method in an electric furnace. A mixture of the starting materials with high purity reagents of CuO $(4N, 11g)$, V_2O_5 $(4N, 24.7g)$, and $SrCO_3$ $(4N, 10g)$ was ground carefully and homogenized thoroughly with ethanol (99%) in an agate mortar and then was packed into an alumina crucible capped with a cover using Al_2O_3 cement (C-989, Cotronics Corp.). Such closed crucible was set into the furnace. The furnace was cooled slowly down to 750 °C and then cooled rapidly from 750 to 600 °C. The detailed growth process was described in Ref. 17. Magnetic susceptibility and magnetization were measured using a superconducting quantum interference device (MPMS-5S, Quantum Design) magnetometer, and heat capacity was measured by a relaxation method using a commercial physical property measurement system (Quantum Design).

Figure 2 shows the temperature dependence of magnetic susceptibility and the reciprocal one for β-$Cu_2V_2O_7$ measured along the *b* axis. The susceptibility exhibits a broad maximum at around $T_M = 50$ K, indicative of 1D short-range ordering (SRO). The susceptibility decreases with decreasing temperature, while a Curie-like upturn is seen below ~26 K. Above 100 K, the susceptibility follows well the Curie-Weiss law, giving Curie constant $C = 0.75(3)$ emu K/mol and Weiss temperature $\theta = -81.5(7)$ K. The effective moment is calculated to be $1.73(5)\mu_B$, which is in good agreement with the value of $\mu = 1.73\mu_B$ expected theoretically for free Cu^{2+} ions $(S = 1/2)$ with $g = 2$. The negative Weiss temperature indicates an antiferromagnetic (AF) coupling between Cu^{2+} ions.

Figure 3 shows magnetic susceptibilities measured along the *a*, *b*, and *c* axes. Similar to $H \| b$, a Curie-like upturn in susceptibility is also seen below ~26 K for $H \| a$, while a rapid drop is seen at ~26 K for $H \| c$, suggesting that the *c* axis is magnetic easy axis and AF ordering occurs likely at ~26 K. Further, a large diversity of susceptibilities between $H \| a$ and $H \| b$ or $H \| c$, which persists up to room temperature, indicates an intriguing paramagnetic anisotropy in the system. This is in good agreement with electron spin resonance (ESR) measurement on β phase of Zn-substituted $Cu_2V_2O_7$ polycrystalline sample, showing a strong ESR signal above T_N.[14] According to structural analysis,[18] a large Jahn-Teller distortion of Cu^{2+} ions in β-$Cu_2V_2O_7$ is found to run along the *a* axis, leading to an elongated square-pyramidal CuO_5. We suggest that such paramagnetic anisotropy in β-$Cu_2V_2O_7$ may be due to different Van-Vleck contributions affected by the Jahn-Teller distortion. Similar paramagnetic anisotropy can also be seen in 1D spin chain system $LiCuVO_4$.[19]

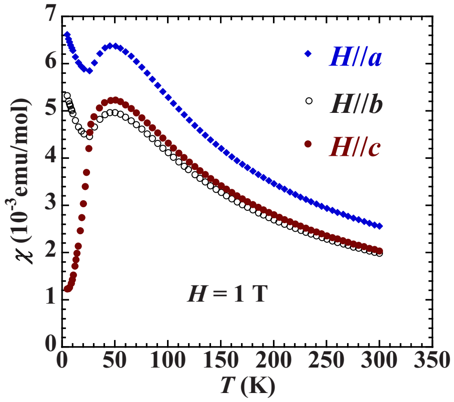

FIG. 3. (Color online) Magnetic susceptibilities measured along the *a*, *b*, and *c* axes.

Figure 4 shows heat capacity data in applied field $H = 0$. Apparently, there is a clear sign of λ-like feature around 26 K with a specific heat jump of $\Delta C = \sim 2.02(4)$ J mol^{-1} K^{-1}, giving clear evidence for a long-range AF ordering. As shown in the inset of Fig. 4, the C/T vs T^2 plot below 25 K decreases linearly toward 0

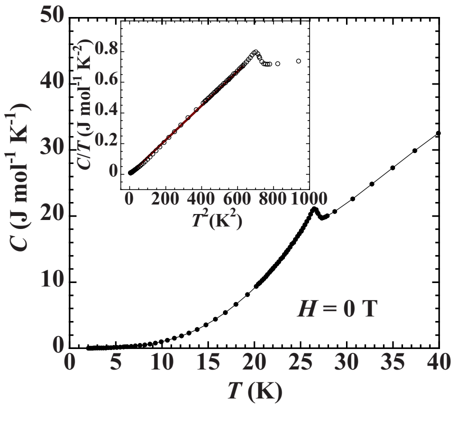

FIG. 4. (Color online) Heat capacity data measured in applied field of $H = 0$. The inset shows C/T vs T^2 plot. The solid line is the fit of βT^3 for heat capacity data below 25 K.

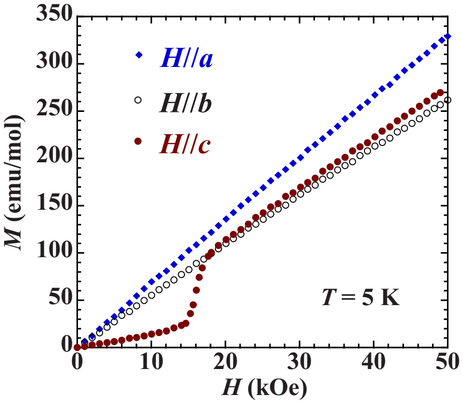

FIG. 5. (Color online) Magnetization as a function of applied field at 5 K.

with decreasing temperature, showing that the heat capacity C follows a T^3 power law with a coefficient β of $\sim 1.1(2)$ mJ mol^{-1} K^{-4}. It is noted that the value of β cannot be used to estimate the Debey temperature since both phonon and magnetic contributions give T^3 terms into total heat capacity at low temperature of $T < T_N$.[20] For a Heisenberg linear chain system at higher temperature of $T > T_N$, the heat capacity from magnetic contribution can be estimated theoretically as $C_m(T) \approx 0.35R$ (~ 2.9 J mol^{-1} K^{-1}) at $T = 0.75 T_M$.[21] We note that the experimental value of the heat capacity at $T = 0.75 T_M$ (~ 37.5 K) for β-$Cu_2V_2O_7$ is ~ 29.8 J mol^{-1} K^{-1}, which is about ten times as large as the theoretical value of ~ 2.9 J mol^{-1} K^{-1}. This suggests that the heat capacity of β-$Cu_2V_2O_7$ is dominated by photon contribution above T_N.

Figure 5 shows magnetization (M) as a function of applied field (H) at $T = 5$ K. A linear increase in magnetization is observed in $H \| a$ and $H \| b$, agreeing with AF ordering below 26 K, while a rapid increase is observed at $H = \sim 1.5$ T along the c axis, showing a typical spin-flop transition. This is consistent with the susceptibility data, clearly showing that the c axis is magnetic easy axis and β-$Cu_2V_2O_7$ exhibits magnetic anisotropy below T_N. Therefore, the spins of Cu^{2+} ions are suggested to arrange collinearly parallel to the c axis and perpendicular to the chains, as shown in Fig. 1(b). We note that such spin arrangement in β-$Cu_2V_2O_7$ is in agreement with the cross-linking chain structural feature on the a-b plane, showing no canted spins between Cu^{2+} ions in the system.

The combined results from magnetic and heat capacity data clearly show that β-$Cu_2V_2O_7$ is a 1D spin-1/2 anisotropic Heisenberg antiferromagnet with $T_N = \sim 26$ K and the magnetic behaviors are related closely to its peculiar structural features. It is well known that an ideal 1D spin chain system does not show long-range ordering (LRO) above $T = 0$ K due to strong quantum spin fluctuation,[22] however, almost all quasi-one-dimensional spin systems display LRO at their ground states due to interchain interaction ($J_\perp$). We note that the temperature of SRO ($T_M = \sim 50$ K) is about twice as large as that of LRO ($T_N = \sim 26$ K), indicating that the significant interchain interactions and anisotropic spin-spin interactions in β-$Cu_2V_2O_7$ drive the system into AF ordered ground state.

We now estimate the magnitude of interchain interaction and magnetic anisotropy in β-$Cu_2V_2O_7$. For 1D spin-1/2 Heisenberg antiferromagnetic chain system, Bonner and Fisher (BF)[21] have suggested that board maximum of the susceptibility (χ_M) at T_M is related to the intrachain exchange $J_\|$: $\chi_M = 0.0735 N g^2 \mu_B^2 / J_\|$ and $T_M = 1.282 J_\| / k_B$. As shown in Fig. 2, the fitting of experimental susceptibility by BF curve, with temperature-independent $\chi_0 = 2.0(3) \times 10^{-4}$ emu/mol, $g = 2.4(4)$, and $T_M = 50$ K, gives $J_\| = 39$ K. Therefore, the interchain interaction $J_\perp$ can be estimated using the mean-field approximation:[23] $J_\perp = T_N / 1.28[\ln(5.8 J_\| / T_N)]^{1/2}$. With $J_\| = 39$ K and $T_N = 26$ K, we obtain $J_\perp = \sim 13.8$ K. We note that the ratio of $J_\perp / J_\|$ in β-$Cu_2V_2O_7$ (~ 0.354) is much larger than that in $LiCuVO_4$ (~ 0.045) (Ref. 7) or $BaCu_2Si_2O7$ (~ 0.011),[8] indicating a less pronounced 1D character in the system.

On the other hand, the magnitude of magnetic anisotropy in β-$Cu_2V_2O_7$ can also be estimated using a simple uniaxial two-sublattice mean-field model.[24] 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 overcompensates 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 $\chi_\|$ the perpendicular and parallel susceptibilities, respectively.[25] Using the experimental values of $\chi_{\|a} = 6.61(4) \times 10^{-3}$ emu/mol, $\chi_{\|c} = 1.23(1) \times 10^{-3}$ emu/mol, and $H_{SF} = 1.5$ T obtained in Figs. 2 and 4, respectively, we obtain K (5 K) $= 6.05(5) \times 10^5$ ergs/cm^3.

In summary, we have investigated magnetic behaviors of β-$Cu_2V_2O_7$ single crystals by means of magnetic susceptibility, magnetization, and heat capacity measurements. Our results showed that β-$Cu_2V_2O_7$ is a 1D spin-1/2 anisotropic Heisenberg antiferromagnet with Néel temperature of ~ 26 K. Also, paramagnetic anisotropy was observed in the system, while a typical spin-flop transition was observed in a magnetic field of 1.5 T applied along the c axis. The spins of Cu^{2+} ions are suggested to arrange parallel to the c axis and perpendicular to the chains. The intrachain and interchain exchanges are estimated to be 39 and 13.8 K, respectively. Magnetic anisotropy energy at 5 K is estimated to have $6.05(5) \times 10^5$ ergs/cm^3.

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