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β-$Cu_3V_2O_8$: magnetic ordering in a spin-$\frac{1}{2}$ Kagomé-staircase lattice

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Abstract

The spin-$\frac{1}{2}$ Cu^{2+} ions in β-$Cu_3V_2O_8$ occupy the sites of a Kagomé-staircase lattice, an anisotropic variant of the Kagomé net: buckled layers and imbedded plaquettes of three edge-shared CuO_4 squares break the ideal Kagomé symmetry. Susceptibility and heat capacity measurements show the onset of short-range ordering at approximately 75 K, and a magnetic phase transition with the characteristics of antiferromagnetism at ∼29 K. Comparison to the Curie–Weiss theta ($\theta_{CW} = -135$ K) indicates that the geometric frustration is largely relieved by the anisotropy.

1. Introduction

Geometrically frustrated spin systems are based on the placement of antiferromagnetically interacting spins at the corners of a triangular lattice [1]. Such systems often remain magnetically disordered even when cooled well below the ordering temperature expected in a mean-field picture. For the two-dimensional (2D) triangular lattice of Heisenberg spins, the magnetic energy of an antiferromagnetic (AFM) system is reduced by adopting the 120° spin state. For the Kagomé geometry, a 2D lattice consisting of corner-sharing equilateral triangles, propagation of the 120° spin state throughout the lattice results in a large ground state degeneracy and frustration of long-range order [2]. The 2D Kagomé net is realized in many spin-1, spin-$\frac{3}{2}$, and spin-$\frac{5}{2}$ compounds exhibiting geometric magnetic frustration, including $SrCr_8Ga_4O_{19}$ [3, 4], $Ba_2Sn_2Ga_3ZnCr_7O_{22}$ [5], and the jarosites $KM_3(OH)_6(SO_4)_2$ [6–8] with M = V, Cr, or Fe.

Theoretical studies have shown that magnetic order is not expected in the spin-$\frac{1}{2}$ Heisenberg antiferromagnet on the Kagomé lattice [9–11]. Recently Volborthite, $Cu_3V_2O_7(OH)_2{\cdot}2H_2O$ [12], a $S = \frac{1}{2}$ Kagomé-like material, was reported. This compound

consists of isosceles spin triangles instead of the ideal equilateral triangles, but magnetic measurements showed neither long-range ordering nor a spin gap down to 1.8 K in spite of strong AFM interactions ($J/k_B = -84$ K and $\theta_{CW} \sim -100$ K). Here we report the magnetic characterization of β-$Cu_3V_2O_8$, an $S = \frac{1}{2}$ magnetic material based on a novel anisotropic variation of the Kagomé net: the Kagomé-staircase lattice. The Kagomé staircase is found in $M_3V_2O_8$ compounds with M = Ni^{2+} ($S = 1$) [13], Co^{2+} ($S = \frac{3}{2}$) [14], Zn^{2+} ($S = 0$) [15], and Cu^{2+} ($S = \frac{1}{2}$) [16]. These materials consist of buckled Kagomé layers of edge-sharing transition metal (II) oxide octahedra separated by nonmagnetic $V^{5+}O_4$ tetrahedra. The lower symmetry of the 'staircase' magnetic layers and the resulting anisotropic intralayer superexchange interactions result in the reduction of geometric frustration and magnetic ordering in the Ni and Co variants [17]. Long-range magnetic ordering in Kagomé antiferromagnets that have been doped with nonmagnetic impurities has been attributed to 'order by disorder' that selectively pins down a particular spin configuration among the many possible ground states [18]. In contrast, magnetic ordering in the Kagomé-staircase materials is a consequence of breaking the ideal Kagomé symmetry in a periodic way through buckling of the magnetic layers. Spins with a smaller quantum number have a stronger tendency toward quantum disorder. Thus, the spin-$\frac{1}{2}$ Kagomé-staircase compound β-$Cu_3V_2O_8$ presents a unique opportunity to observe the competition between the frustrating influence of quantum effects and geometry versus the tendency toward magnetic ordering due to strong anisotropy.

2. Experiment

β-$Cu_3V_2O_8$ [16] was synthesized by heating α-$Cu_3V_2O_8$ [19] in a cubic anvil press at 900 °C under a pressure of approximately 40 kbar for 2 h. α-$Cu_3V_2O_8$ was made from stoichiometric mixtures of CuO and V_2O_5 heated at 700 °C overnight in air. Nonmagnetic, isostructural $Zn_3V_2O_8$ was synthesized by heating ZnO, V_2O_5, and $ZnCl_2$ mixed in a 3:1:2 ratio at 600 °C for 4 h in air. The product was washed with distilled water to remove the $ZnCl_2$ flux. Measurements on $Zn_3V_2O_8$ provide an estimate of the nonmagnetic contribution to the low-temperature heat capacity of β-$Cu_3V_2O_8$.

3. Results and discussion

All of the samples were determined to be single phase by means of powder x-ray diffraction. β-$Cu_3V_2O_8$ was found to be monoclinic with $a = 6.253(1)$ Å, $b = 8.002(1)$ Å, $c = 6.377(1)$ Å, and $\beta = 111.45(2)°$, in close agreement with previously reported data [16]. Unlike in the Ni and Co variants, the $Cu^{2+}O_6$ octahedra in β-$Cu_3V_2O_8$ are distorted significantly, with two longer apical Cu–O bonds, and four shorter in-plane bonds. The arrangement of the long and short bonds leads to the presence of plaquettes made of three edge-shared CuO_4 squares running nearly parallel to the *b*-direction within the basic Kagomé net (figure 1(a)). The edge-sharing within the plaquettes leads to Cu–O–Cu angles between 85° and 95°. The plaquettes are coupled through the apical oxygens, in a stretched edge-sharing geometry, with substantially longer Cu–O–Cu distances and near-90° Cu–O–Cu angles (figure 1(b)). The Cu site in the middle of the plaquette (Cu1) is crystallographically inequivalent to the other two (Cu2). The significant differences in the Cu^{2+}–O–Cu^{2+} bond angles, and their divergence from the ideal edge-shared 90° angle, are all indicative of an anisotropic superexchange interaction. Magnetic coupling between the Kagomé layers is expected to be small on the basis of the relatively large interlayer distance (∼6.2 Å). Thus, β-$Cu_3V_2O_8$ is a 2D magnetic system dominated by anisotropic coupling interactions between the $S = \frac{1}{2}$ spins on a Kagomé-based lattice.

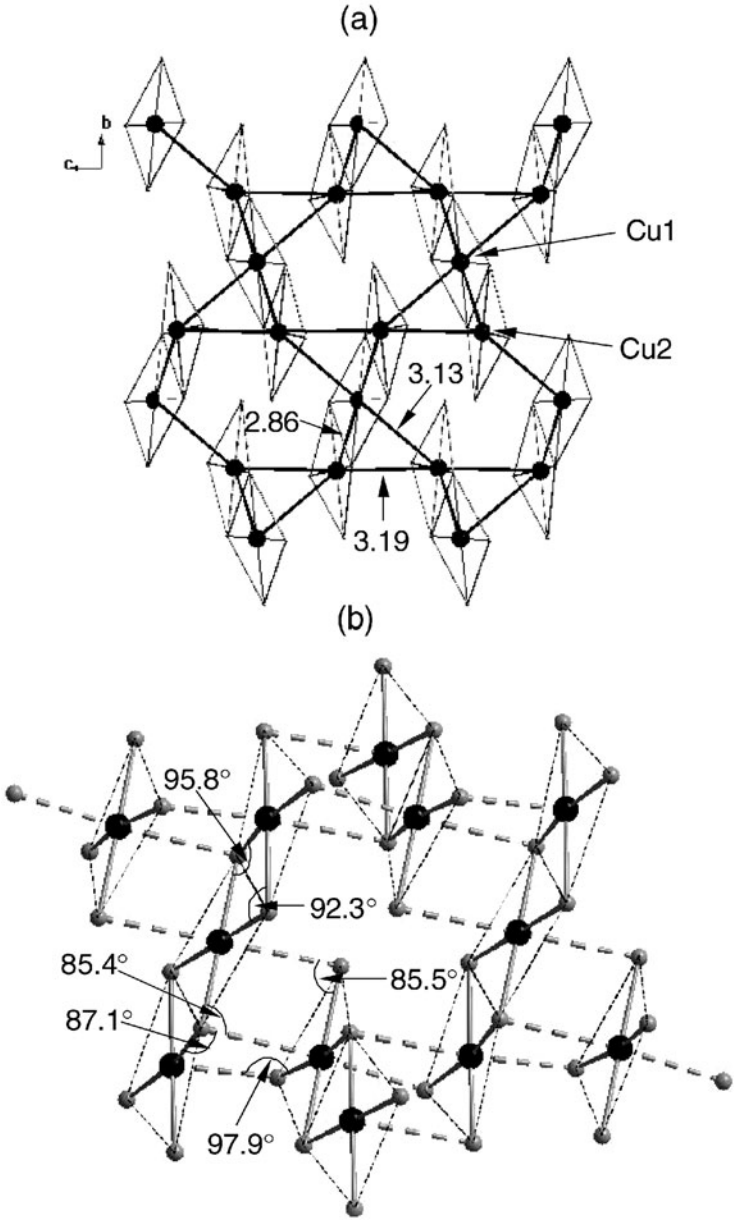

Figure 1. (a) The 'Kagomé-staircase' lattice in β-$Cu_3V_2O_8$. The basic Kagomé net is emphasized with bold black lines. Plaquettes of three edge-shared $Cu^{2+}O_4$ squares are shown. The inequivalent Cu sites are labelled, as are the Cu–Cu distances (in Å). (b) Detail of the local geometry around the Cu atoms, showing the Cu–O–Cu bond angles and the triple CuO_4 plaquettes. Black circles: Cu; grey circles: O. Solid grey lines are Cu–O bonds $\leqslant$2 Å; broken grey lines are long Cu–O bonds ($\geqslant$2.3 Å).

Magnetic susceptibility data were obtained for β-$Cu_3V_2O_8$ between 2 and 300 K using a Quantum Design PPMS magnetometer. The field cooled (FC) magnetic susceptibility $\chi(T)$ of β-$Cu_3V_2O_8$ at an applied field of 1 T is shown in figure 2, with its inverse susceptibility, $1/\chi$, as an inset. The high-temperature $1/\chi$ data, above 200 K, were fitted to the

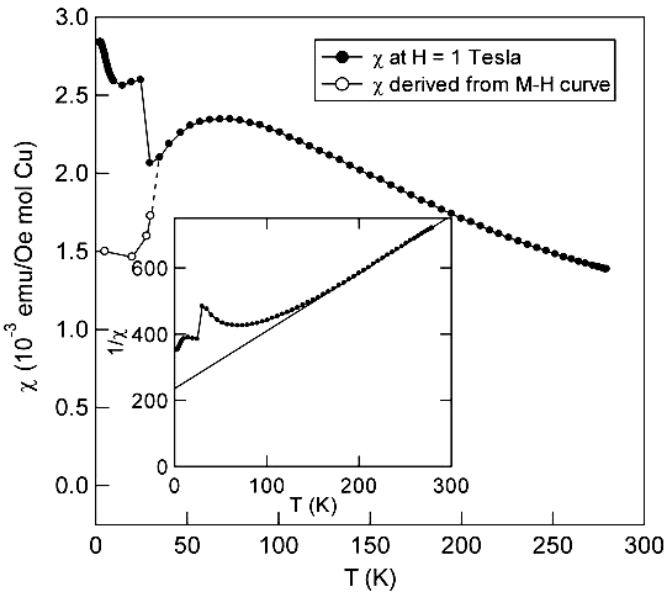

Figure 2. The FC magnetic susceptibility of β-$Cu_3V_2O_8$ taken at $H = 1$ T (solid circles) and the paramagnetic contribution to the susceptibility derived from M–H curves taken between 5 and 30 K (open circles). The inset shows the inverse susceptibility, $1/\chi$. The solid line is the Curie–Weiss fit.

Curie–Weiss law. The fit yielded a Curie constant $C = 0.57$ emu K^{-1}/mol Cu and a Curie–Weiss temperature $\theta_{CW} = -135$ K. The effective magnetic moment (μ_{eff}) for Cu was found to be 2.1 μ_B, close to the expected moment for Cu^{2+}. The negative θ_{CW} value implies that AFM near-neighbour interactions dominate. From the mean field theory, with $\theta_{CW} = zJS(S+1)/(3k_B)$, the superexchange interaction J between z nearest-neighbour Cu^{2+} ($S = \frac{1}{2}$) ions on a Kagomé lattice is approximated by θ_{CW} [20]. The experimentally obtained value of J/k_B of -135 K is comparable to those found for other low-dimensional copper oxide compounds characterized by edge-sharing Cu–O–Cu bonds, such as $CuGeO_3$ [21]. Another estimate of the superexchange constant obtained by fitting the $\chi(T)$ data above 200 K to the high-temperature series expansion for a spin-$\frac{1}{2}$ Heisenberg antiferromagnet on an ideal Kagomé lattice [22] yielded $J/k_B = -90.3$ K. The distortion of the Kagomé layers in β-$Cu_3V_2O_8$, however, limits the usefulness of this fit.

$\chi(T)$ shows a broad maximum at ~75 K, characteristic of the onset of short-range or low-dimensional ordering. This may be attributed to the low-dimensional AFM ordering within the Kagomé layers, or correlations within the embedded plaquettes of edge-shared Cu–O squares. A sharp feature appears at ~29 K, suggesting a three-dimensional magnetic phase transition. The increase in $\chi(T)$ below this temperature is due to the contribution of a small amount of ferromagnetism accompanying the magnetic ordering.

Figure 3 shows the field dependence of the magnetization of β-$Cu_3V_2O_8$ at 5 K. Magnetic hysteresis is seen at lower fields. The loop at 5 K indicates a remnant magnetization of ~0.1 μ_B, a small moment compared to the magnetization expected for a fully ferromagnetic (FM) spin-$\frac{1}{2}$ system. This FM contribution is observed to vary in different preparations of β-$Cu_3V_2O_8$, and is assumed to be an extrinsic effect. It is attributed to uncompensated AFM spins at grain boundaries, defects, or surfaces in the polycrystalline sample, as has been observed in thin films of layered antiferromagnets [23]. The intrinsic paramagnetic contribution to the susceptibility

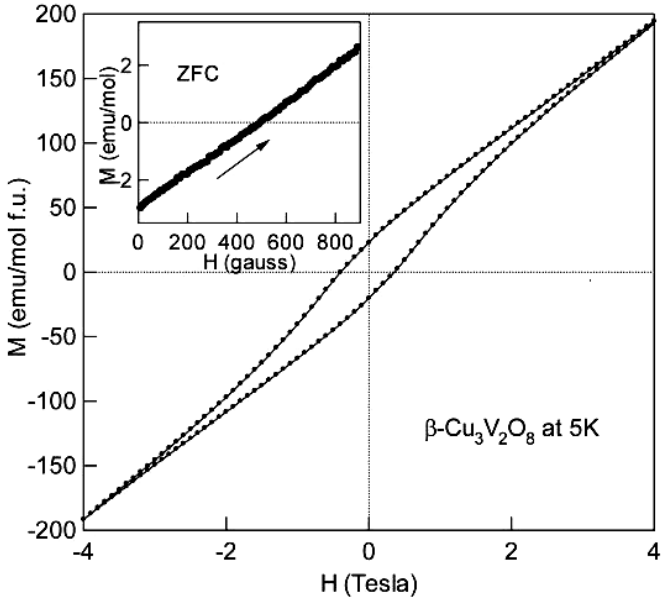

Figure 3. Magnetization versus applied field at 5 K for β-$Cu_3V_2O_8$. The inset shows the M/H plot at low fields.

of β-$Cu_3V_2O_8$ below 29 K was obtained by measurement of M versus H curves at different temperatures and deriving $\Delta M/\Delta H$ from the reversible region of the hysteresis loop. These data, which show that $\chi(T)$ drops significantly below 29 K, are shown in figure 2, confirming that the magnetic transition is due to AFM ordering.

Measurement of the M–H curve at small applied fields was achieved by setting the field to zero at 100 K, then cooling to 5 K, and then measuring the magnetization with increasing field starting from zero field. For the measurement shown in the inset of figure 3, the sample exhibits a diamagnetic moment below 400 Oe, although the slope of the M–H curve is positive. Although the 5 K M–H curve was measured starting from an apparent zero field, a small negative field (i.e. -1 Oe) might have been applied to the Cu spins upon cooling through the transition as a result of the zero setting of the magnetometer, resulting in the observed diamagnetism. To investigate this further, zero field cooled (ZFC) and FC measurements at 10 and -10 G (figure 4) were made using a SQUID magnetometer (Quantum Design, MPMS) with the field set to zero by two different methods:

(a) using the built-in zero-field setting feature of the magnetometer at 298 K, which leaves a remnant field of $\sim$250 mG; and
(b) applying a DC current through the AC excitation coils to set the magnetometer to read exactly zero field at 310 K.

For both zero-setting methods, a hysteresis below 30 K is evident between the ZFC and FC measurements. The magnetization seen in the FC measurement is greater than that of the ZFC measurement for the data taken at 10 G, and the same is true (with reversed sign) at -10 G. The ZFC magnetizations are very sensitive to how the zero field has been set, in several cases coming out with a sign that is inconsistent with the sign of the measurement field. This implies that the spin ordering in β-$Cu_3V_2O_8$ is quite sensitive to the magnitude and direction of low remnant fields. Sign reversal of the net magnetization in ferromagnets such as spinels

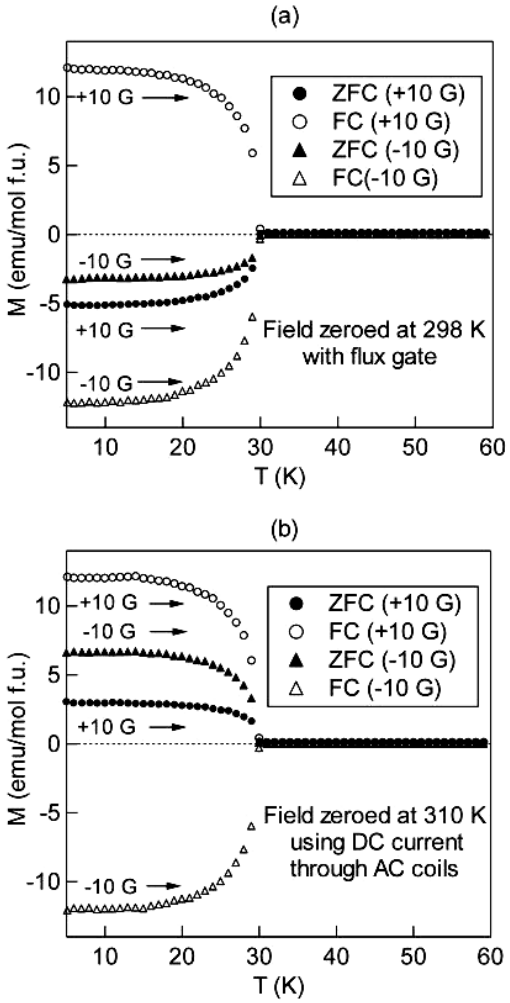

Figure 4. ZFC and FC measurements taken at 10 and −10 G with the zero field set by (a) using the built-in zero-field setting feature of the SQUID magnetometer (Quantum Design, MPMS), and (b) applying a DC current through the AC coils to establish a zero field at 310 K. Arrows indicate the direction in which data were taken.

has been attributed to the different temperature and field dependences of the magnetization of the individual magnetic sublattices [24, 25]. Although similar behaviour is observed in β-$Cu_3V_2O_8$, the behaviour of this sample is more consistent with uncompensated interfacial ferromagnetically aligned spins oriented by small remnant fields in the magnetometer during 'zero-field cooling' rather than a bulk effect. The measurement of a negative magnetization is then just related to the relative orientations of the oriented spins at the interfaces and the measurement field.

The heat capacity was measured using a standard semi-adiabatic heat pulse technique. The magnetic contribution to the heat capacity (C_m) for β-$Cu_3V_2O_8$ was obtained by subtracting the lattice contribution from the raw data (figure 5). The lattice contribution was estimated from the heat capacity data for $Zn_3V_2O_8$, the nonmagnetic isostructural analogue of the Kagomé-staircase structure. The inset in figure 5 shows the raw data for β-$Cu_3V_2O_8$ and nonmagnetic

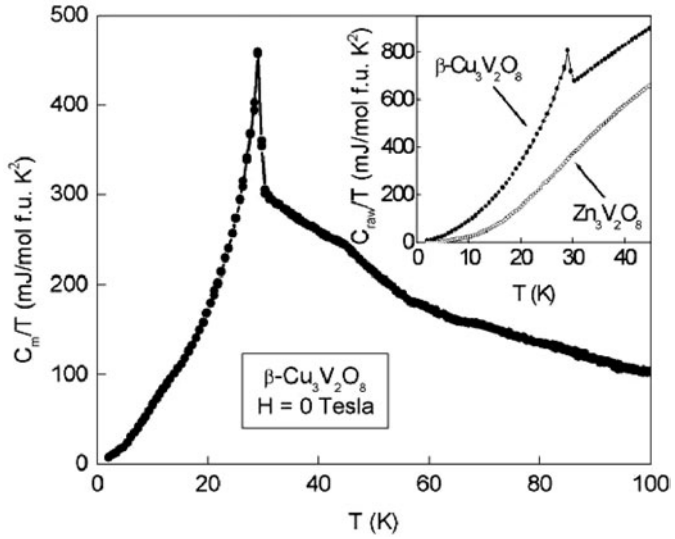

Figure 5. The temperature dependence of the magnetic contribution to the heat capacity of β-$Cu_3V_2O_8$ represented as C_m/T. The inset shows the raw data (C_{raw}/T) for β-$Cu_3V_2O_8$ and nonmagnetic $Zn_3V_2O_8$.

$Zn_3V_2O_8$. C_m for β-$Cu_3V_2O_8$ shows a sharp transition at 29 K, which is preceded by a broad feature at ∼50 K. The observed transitions are consistent with the $\chi(T)$ data—that is, 3D AFM ordering preceded by low-dimensional spin ordering. Integrating C_m/T against T up to 100 K (assuming a smooth curve from 2 to 0 K) gives an entropy of ∼5.6 J K^{-1}/mol Cu, approximately equal to the entropy expected to be needed to fully disorder a mole of a spin-$\frac{1}{2}$ system.

4. Summary and conclusions

On the basis of this preliminary report of its magnetic properties, β-$Cu_3V_2O_8$ is shown to be an interesting magnetic system. A single 3D magnetic ordering transition is seen above 29 K, with indications of short-range or low-dimensional ordering at higher temperatures. In contrast, the spin-1 analogue $Ni_3V_2O_8$ shows *four* magnetic transitions above 2 K and the spin-$\frac{3}{2}$ analogue $Co_3V_2O_8$ shows two magnetic transitions (and an incomplete accounting of the spin entropy in those transitions) [17]. Most theoretical and experimental work has focused on ideal Kagomé lattices. Future studies on the novel Kagomé-staircase structure will clarify the effects of anisotropic magnetic coupling in the frustrated Kagomé net.

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