Collinear order in a frustrated three-dimensional spin-$\frac{1}{2}$ antiferromagnet Li$_2$CuW$_2$O$_8$

K. M. Ranjith, R. Nath, M. Skoulatos, L. Keller, D. Kasinathan, Y. Skourski, and A. A. Tsirlin

1School of Physics, Indian Institute of Science Education and Research Thiruvananthapuram-695016, India
2Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
3Department of Physics, Technical University Munich, 85748 Garching, Germany
4Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany
5Dresden High Magnetic Field Laboratory, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany
6National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia

Strong magnetic frustration in three dimensions (3D) manifests itself in the spin-$\frac{1}{2}$ insulator Li$_2$CuW$_2$O$_8$. Density-functional band-structure calculations reveal a peculiar spin lattice built of triangular planes with frustrated interplane couplings. The saturation field of 29 T contrasts with the susceptibility maximum at 8.5 K and a relatively low Néel temperature $T_N \approx 3.9$ K. Magnetic order below $T_N$ is collinear with the propagation vector $(0, \frac{1}{2}, 0)$ and an ordered moment of 0.65(4) $\mu_B$ according to neutron diffraction data. This reduced ordered moment together with the low maximum of the magnetic specific heat ($C_{\text{max}}/R \approx 0.35$) pinpoint strong frustration in 3D. Collinear magnetic order reveals crucial role of quantum fluctuations even on a 3D frustrated lattice of spin-$\frac{1}{2}$, where a non-collinear spiral state would be stabilized classically.

PACS numbers: 75.10.Jm, 75.30.Et, 75.50.Ee, 71.20.Ps

Magnetic frustration, the competition of exchange couplings between localized spins, has broad implications for ground states, excitation spectra, and low-temperature properties. Prominent manifestations of the frustration include peculiar behaviors of spin ice [1], the formation of quantum spin liquids [2], and non-collinear magnetic structures that give rise to spin chirality and strong magnetoelectric coupling [3]. The properties of frustrated magnets change drastically depending on the dimensionality of the spin lattice. Rigorous mapping between theory and experiment requires that magnetic models or real materials are relatively simple. In this context, the case of isotropic (Heisenberg) exchange on a three-dimensional (3D) lattice of quantum spin-$\frac{1}{2}$ ions is perhaps least studied, given the lack of model materials and the complexity of the numerical treatment of purely quantum spins in 3D. On the materials side, 3D spin-$\frac{1}{2}$ frustrated magnetism has been proposed for the hyperkagomé lattice [4] in Na$_4$Ir$_3$O$_8$ [5], but the involvement of the 5$d$ Ir$^{4+}$ ion with its inherently strong spin-orbit coupling may lead to deviations from the isotropic Heisenberg regime [6,7]. A similar hyperkagomé-like exchange network was recently reported in PbCuTe$_2$O$_6$ [8].

Here, we report a long-sought 3D frustrated magnet built of spin-$\frac{1}{2}$ Cu$^{2+}$ (3d) ions that feature nearly isotropic Heisenberg exchange with a strong frustration along all three crystallographic directions. The strong frustration manifests itself in thermodynamic properties, whereas neutron diffraction reveals a collinear magnetic ground state, thus granting us valuable insight into the properties of a 3D frustrated spin-$\frac{1}{2}$ Heisenberg antiferromagnet. We conclude that the stabilization of collinear states by quantum fluctuations, broadly known as an order-from-disorder effect [9], should be also operative in 3D where quantum fluctuations are typically weaker than in low-dimensional magnets.

Our work is focused on Li$_2$CuW$_2$O$_8$ featuring magnetic spin-$\frac{1}{2}$ Cu$^{2+}$ ions and non-magnetic W$^{6+}$. The crystal structure of Li$_2$CuW$_2$O$_8$ [10] depicted in the top part of Fig. 1 entails planar CuO$_4$ plaquette units (green) that are held together by WO$_6$ octahedra (gray). Despite the triclinic symmetry of the crystal structure (space group $P\overline{1}$), we expect a relatively simple topology of magnetic interactions, because the unit cell contains only one Cu atom located at the inversion center. Moreover, the presence of inversion centers in the middle of
each Cu–Cu bond implies that the Dzyaloshinsky-Moriya (DM) anisotropy, which is the leading anisotropy term in Cu$^{2+}$ compounds [11], vanishes by symmetry in contrast to PbCuTe$_2$O$_6$ [8], where a twisted arrangement of the CuO$_4$ plaquettes favors the antisymmetric DM exchange. This ensures reliable mapping between experimental results and theory, which is typically developed for the Heisenberg Hamiltonians with isotropic exchange.

Individual magnetic couplings were quantified by DFT calculations performed using the FPLO code [12] within the local-density approximation (LDA) for the exchange-correlation potential [13]. Antiferromagnetic (AFM) contributions to the exchange integrals are obtained as $J_{\text{AFM}}^i = 4t_i^2/U_{\text{eff}}$, where $t_i$ are electron hoppings extracted from the LDA band structure, and $U_{\text{eff}} = 4.5$ eV is an effective on-site Coulomb repulsion [14]. Alternatively, we evaluate total exchange integrals $J_i$, as energy differences between collinear spin states in LSDA+$U$, where a mean-field correction for on-site correlation effects is added to the LDA functional. The local correlation parameters are $U_d = 7.5$ eV and $J_d = 1$ eV for the Coulomb repulsion and Hund’s exchange, respectively [15]. The change in the $U_d$ parameter and/or double-counting correction scheme had no qualitative effect on the model, although quantitative agreement with the experiment became less satisfactory.

Exchange couplings in Li$_2$CuW$_2$O$_8$ are listed in Table I. Taking advantage of the single Cu$^{2+}$ ion in the unit cell, we label all $J$’s according to their relevant crystallographic directions, see Fig. 1. Triclinic symmetry of the crystal structure implies that only $r$ and $-r$ are equivalent, whereas none of the face or body diagonals of the unit cell are related by symmetry.

Sizable exchange couplings on the order of several K are found for Cu–Cu distances up to 10 Å. The leading coupling is along the $b$ direction ($J_{100}$) through a single WO$_6$ octahedron. However, several couplings mediated by two contiguous WO$_6$ octahedra ($J_{011}$, $J_{011}$, $J_{111}$) are only 2-3 times weaker than $J_{100}$. These long-range couplings originate from the contributions of second-neighbor oxygen atoms to Wannier functions centered on Cu sites. For example, the sizable contribution of the $p$-orbitals of O3 are responsible for the coupling $J_{011}$ between those Cu atoms that are more than 9 Å apart (Fig. 1, top right).

The couplings $J_{010}$, $J_{100}$, and $J_{110}$ form a frustrated triangular lattice in the $ab$ plane (Fig. 1, bottom). $J_{011}$ is the leading interaction along $c$, but several other interactions are present as well, and two of them, $J_{001}$ and $J_{101}$, are not compatible with $J_{011}$. They form triangular loops and generate additional frustration. Reduction to the purely one-dimensional (1D) model by retaining only the leading coupling $J_{010}$ could be envisaged, but the 1D behavior is not observed experimentally as we show below. On the other hand, Li$_2$CuW$_2$O$_8$ can not be viewed as a pure triangular-lattice system because the leading interplane coupling $J_{011}$ is as strong as the couplings $J_{100}$ and $J_{110}$ within the plane.

In order to probe the magnetism of Li$_2$CuW$_2$O$_8$ experimentally, we prepared polycrystalline samples by firing stoichiometric mixtures of Li$_2$CO$_3$, CuO, and WO$_3$ at 650°C for 24 h and subsequently at 750°C for 48 h. Thermodynamic properties were measured as a function of temperature ($T$) and field ($H$) using the Quantum Design MPMS SQUID and PPMS devices. High-field magnetization measurements were performed at the Dresden High Magnetic Field Laboratory in pulsed fields.

| $d_{\text{Cu-Cu}}$ | $t_i$ | $J_{\text{AFM}}^i$ | $J_i$ |
|-------------------|------|----------------|------|
| $J_{100}$         | 4.967 | $-21$         | 5    |
| $J_{010}$         | 5.497 | $-38$         | 15   |
| $J_{110}$         | 5.719 | 20            | 4    |
| $J_{001}$         | 5.888 | 16            | 3    |
| $J_{101}$         | 7.433 | $-16$         | 3    |
| $J_{011}$         | 9.288 | 28            | 8    |
| $J_{111}$         | 9.288 | $-27$         | 8    |
Magnetic susceptibility ($\chi$) of Li$_2$CuW$_2$O$_8$ reveals a broad maximum around 8.5 K (Fig. 2 top). A weak kink around 4 K and a bifurcation of the susceptibility curves measured in different fields indicate the long-range AFM ordering around $T_N \simeq 3.9$ K. This behavior resembles quasi-1D magnets, where the broad maximum of the susceptibility above $T_N$ is due to the short-range order in 1D. However, attempts to fit the experimental susceptibility curve with the standard expression for the uniform spin-$\frac{1}{2}$ chain [10] ultimately failed, and even the position of the susceptibility maximum could not be adequately reproduced (Fig. 2 top). This indicates strong magnetic frustration by interchain couplings that impede short-range order, thus shifting the susceptibility maximum to lower temperatures [17].

Magnetization ($M$) of Li$_2$CuW$_2$O$_8$ saturates around $H_s \simeq 29$ T (Fig. 2 bottom). Taking $J_{1D} \simeq 17$ K from the susceptibility fit, we are able to reproduce the saturation field but not the magnetization isotherm itself [13]. Its curvature is much smaller than expected for the 1D model. The nearly linear magnetization curve indicates the 3D nature of Li$_2$CuW$_2$O$_8$, since the curvature of $M(H)$ is reduced when the dimensionality of the spin lattice is increased [19].

Both $\chi(T)$ and $M(H)$ data show that the purely 1D model does not account for the physics of Li$_2$CuW$_2$O$_8$ even well above $T_N$, and this compound cannot be considered as a quasi-1D magnet. Unfortunately, thermodynamics of the full 3D quantum spin model of Li$_2$CuW$_2$O$_8$ is beyond the reach of present-day numerical techniques because of the strong frustration. However, several experimental quantities can be derived on the mean-field level and thus compared to the microscopic exchange parameters.

At high temperatures, $1/\chi(T)$ is linear and follows the Curie-Weiss law with an effective moment of 1.88 $\mu_B$ and Curie-Weiss temperature $\theta \simeq 12$ K [20]. The $\theta$ value is a sum of individual exchange couplings. For a spin-$\frac{1}{2}$ system, $\theta = \frac{1}{4} \sum z_i J_i$, where $z_i = 2$ is the number of couplings per site. Using $J_i$’s from Table 1 we arrive at $\theta \simeq 14$ K in good agreement with the experiment. The saturation field is proportional to the couplings on the bonds, where spins have to be flipped in order to transform the AFM zero-field ground state into a fully polarized (ferromagnetic) state. Considering the experimental magnetic structure of Li$_2$CuW$_2$O$_8$ (Fig. 1 bottom right), we expect $H_s = 2k_B/(g\mu_B)\times(J_{010}+J_{110}+J_{011}+J_{111}) \simeq 29$ T, (1) which is in excellent agreement with the high-field magnetization experiment. Here, we used an effective $g$-factor $g = 2.17$ extracted from the paramagnetic effective moment $\mu_{\text{eff}} = g\sqrt{S(S+1)}$ $\simeq 1.88\mu_B$.

Specific heat ($C_p$) of Li$_2$CuW$_2$O$_8$ reveals a broad maximum related to the magnetic contribution below 10 K. The phonon part of the specific heat was estimated by fitting $C_p(T)$ above 40 K with a linear combination of Debye functions. The magnetic part $C_{\text{mag}}(T)$ is obtained by subtracting the phonon part from the total heat capacity and verified by integrating $C_{\text{mag}}(T)/T$ to produce the magnetic entropy $S_{\text{mag}} \simeq 5.2$ J/mol K at 30 K in reasonable agreement with $S_{\text{mag}} = R\ln 2 = 5.76$ J/mol K expected for spin-$\frac{1}{2}$.

Magnetic specific heat ($C_{\text{mag}}$) of Li$_2$CuW$_2$O$_8$ features a broad maximum at 6 K with the maximum value of $C_{\text{mag}}/R \simeq 0.35$ (Fig. 3). At first glance, this would be again indicative of a quasi-1D scenario, but the spin-$\frac{1}{2}$ chain with $J_{1D}$ determined from the susceptibility fit should feature the maximum of $C_{\text{mag}}$ at a much higher temperature. The value at the maximum, $C_{\text{max}}$, is very sensitive to the effects of dimensionality and frustration [21]. Our data are in between those for the frustrated (triangular lattice, $C_{\text{max}}/R \simeq 0.22$) and non-frustrated (square lattice $C_{\text{max}}/R \simeq 0.44$) cases in 2D. Given the 3D nature of Li$_2$CuW$_2$O$_8$, this implies very strong frustration that triggers quantum fluctuations, comparable to those in the 1D case of a spin chain ($C_{\text{max}}/R \simeq 0.35$).

The $\Delta$-type anomaly in the specific heat confirms the magnetic ordering transition at $T_N \simeq 3.9$ K in zero field. Remarkably, the ordering temperature does not depend on magnetic field and remains at 3.90±0.05 K for fields up to 9 T. This contrasts with the typical behavior of both quasi-1D [22] and quasi-2D antiferromagnets [23], where $T_N$ reveals non-monotonic field dependence. Weak fields suppress fluctuations related to the low-dimensionality, thus facilitating the formation of the long-range order, whereas stronger fields suppress the antiferromagnetic long-range order itself. The fact that in Li$_2$CuW$_2$O$_8$ we do not observe any change in $T_N$ up to 9 T points against low-dimensional magnetic behavior and confirms the 3D
nature of our system.

Having established that Li$_2$CuW$_2$O$_8$ is a 3D frustrated magnet, we explore its ground state by neutron diffraction. The diffraction data were collected on the DMC instrument at SINQ (PSI, Villigen) using the wavelength of 2.45 Å (Fig. 4). The nuclear scattering above $T_N$ is consistent with the triclinic room-temperature crystal structure reported in the literature [10]. Below $T_N$, two additional magnetic reflections reveal a commensurate magnetic order with the propagation vector $\mathbf{k} = (0, \frac{1}{2}, 0)$. For an antiferromagnet, this implies antiparallel spins along $b$ and parallel spins along $a$ and $c$ (Fig. 1 right). Magnetic moments lie in the $ac$ plane, and the size of the ordered moment is $\mu = 0.65(4) \mu_B$ at 1.5 K.

The value of the ordered moment reflects the magnitude of quantum fluctuations. In a non-frustrated 3D magnet with spin-$\frac{1}{2}$, the ordered moment is about $0.83 \mu_B$ (cubic lattice) [24]. The ordered moment of $0.65 \mu_B$ in Li$_2$CuW$_2$O$_8$ is reminiscent of a 2D case with $\mu = 0.61 \mu_B$ [23], but the spin lattice of Li$_2$CuW$_2$O$_8$ has no apparent 2D features, and the reduced ordered moment should be ascribed to the effect of frustration in 3D.

The magnetic structure in the $ab$ plane is stabilized by the two stronger interactions $J_{010}$ and $J_{110}$, whereas the weaker interaction $J_{100}$ is overwhelmed. Same applies to the (effective) ferromagnetic order along the $c$ direction, where the experimental magnetic structure is stabilized by $J_{011}$ and $J_{111}$, while the effect of the two other couplings ($J_{001}, J_{101}$) is fully suppressed. Remarkably, this order is quantum in nature. When the spin Hamiltonian of Li$_2$CuW$_2$O$_8$:

$$\hat{H} = \sum_{i,r} J_r \mathbf{S}_i \mathbf{S}_{i+r}$$

with all seven couplings $J_r$ from Table I is considered on the classical level (i.e., with effect of quantum fluctuations not taken into account), the ground state should be incommensurate with non-collinear order along all three directions and the energy of $-8.3$ K compared to $-7.3$ K for the collinear state observed experimentally. The stabilization of the collinear state by quantum fluctuations has been predicted for the spatially anisotropic spin-$\frac{1}{2}$ triangular lattice [20,30], but, to the best of our knowledge, never observed experimentally in a spin-$\frac{1}{2}$ triangular-lattice system. Our work demonstrates that a similar effect may occur in 3D and puts forward the crucial role of quantum fluctuations even in those spin-$\frac{1}{2}$ systems that are not low-dimensional.

In conclusion, we explored frustrated 3D magnetism of Li$_2$CuW$_2$O$_8$. The small curvature of the magnetization isotherm and the field-independent Neél temperature evidence magnetic three-dimensionality, whereas the shift of the susceptibility and specific heat maxima toward low temperatures as well as the reduced ordered moment of 0.65 $\mu_B$ are indicative of strong magnetic frustration. Microscopically, this behavior is rationalized by the complex spin lattice built by triangular planes with frustrated interlayer couplings. Quantum stabilization of the collinear magnetic order is envisaged similar to triangular magnets. Strong frustration and isotropic nature of the magnetic exchange render Li$_2$CuW$_2$O$_8$ an excellent model system for quantitative theoretical analysis of frustrated quantum magnets in 3D.

Financial support of DST India (RN and KMR), Mobilitas MTT77 and IUT23-3 (AAT) as well as FP7 under grant agreement 290605 (MS) is appreciated. We thank PSI for granting the DMC beamtime and acknowledge the support of the HLD at HZDR, member of EMFL. Fruitful discussions with Michael Baenitz, Ioannis Rousochatzakis and Johannes Richter are kindly acknowledged.

*rnath@iisertvm.ac.in
†altsirlin@gmail.com

[1] M. J. P. Gingras and P. A. McClarty, Rep. Prog. Phys. 77, 056501 (2014).
[2] L. Balents, Nature 464, 199 (2010).
[3] S.-W. Cheong and M. Mostovoy, Nature Materials 6, 13 (2007).
[4] M. J. Lawler, A. Paramekanti, Y. B. Kim, and L. Balents, Phys. Rev. Lett. 101, 197202 (2008); Y. Zhou, P. A. Lee, T.-K. Ng, and F.-C. Zhang, ibid. 101, 197201 (2008); E. J. Bergholtz, A. M. Läuchli, and R. Moessner, ibid. 105, 237202 (2010).
[5] Y. Okamoto, M. Nohara, H. Aruga-Katori, and H. Talaghi, Phys. Rev. Lett. 99, 137207 (2007).
[6] G. Chen and L. Balents, Phys. Rev. B 78, 094403 (2008).
[7] M. R. Norman and T. Micklitz, Phys. Rev. B 81, 024428 (2010); T. Micklitz and M. R. Norman, ibid. 81, 174417 (2010).
[8] B. Koteswararao, R. Kumar, P. Khuntia, S. Bhowal, S. K. Panda, M. R. Rahman, A. V. Mahajan, I. Dasgupta, M. Baenitz, K. H. Kim, and F. C. Chou, Phys. Rev. B 90, 035141 (2014).
[9] C. L. Henley, Phys. Rev. Lett. 62, 2056 (1989).
[10] M. Álvarez-Vega, J. Rodríguez-Carvajal, J. G. Reyes-Cárdenas, A. F. Fuentes, and U. Amador, Chem. Mater. 13, 3871 (2001).
[11] L. Shekhtman, O. Entin-Wohlman, and A. Aharony, Phys. Rev. Lett. 69, 836 (1992); L. Shekhtman, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B 47, 174 (1993).
[12] K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).
[13] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[14] S. Lebernegg, A. A. Tsirlin, O. Janson, and H. Rosner, Phys. Rev. B 88, 224406 (2013); R. Nath, K. M. Ranjith, J. Sichelschmidt, M. Baenitz, Y. Skourski, F. Alet, I. Rouschatzakis, and A. A. Tsirlin, ibid. 89, 014407 (2014).
[15] We used the around-mean-field double-counting correction, similar to: S. Lebernegg, A. A. Tsirlin, O. Janson, R. Nath, J. Sichelschmidt, Y. Skourski, G. Amthauer, and H. Rosner, Phys. Rev. B 84, 174436 (2011); S. Lebernegg, A. A. Tsirlin, O. Janson, and H. Rosner, ibid. 89, 165127 (2014).
[16] D. C. Johnston, R. K. Kremer, M. Troyer, X. Wang, A. Klümpfer, S. L. Bud’ko, A. F. Panchula, and P. C. Canfield, Phys. Rev. B 61, 9558 (2000).
[17] For example: D. C. Johnston, R. J. McQueeney, B. Lake, A. Honecker, M. E. Zhitomirsky, R. Nath, Y. Furukawa, V. P. Antropov, and Y. Singh, Phys. Rev. B 84, 094445 (2011).
[18] Magnetization curve and specific heat of the uniform spin-\(\frac{1}{2}\) chain were obtained from quantum Monte-Carlo simulations performed in the ALPS package: A. Albuquerque, F. Alet, P. Corboz, P. Dayal, A. Feiguin, S. Fuchs, L. Gamper, E. Gull, S. Gürtler, A. Honecker, R. Igarashi, M. Körner, A. Köhler, S. Manmana, M. Matsumoto, I. McCulloch, F. Michel, R. Noack, G. Pawlowski, L. Pollet, T. Pruschke, U. Schollwöck, S. Tod, S. Trebst, M. Troyer, P. Werner, and S. Wessel, J. Magn. Magn. Mater. 310, 1187 (2007).
[19] See, for example, Fig. 3 in: P. A. Goddard, J. L. Manson, J. Singleton, I. Franke, T. Lancaster, A. J. Steele, S. J. Blundell, C. Baines, F. L. Pratt, R. D. McDonald, O. E. Ayala-Valenzuela, J. F. Corbey, H. I. Southerland, P. Sengupta, and J. A. Schlüter, Phys. Rev. Lett. 108, 077208 (2012).
[20] See Supplemental material for the Curie-Weiss fit of the magnetic susceptibility, Debye fit of the heat capacity as well as LDA band structure and electronic DOS.
[21] B. Bernu and G. Misguich, Phys. Rev. B 63, 134409 (2001).
[22] A. Möller, M. Schmitt, W. Schnelle, T. Förster, and H. Rosner, Phys. Rev. B 80, 125106 (2009); B. Pan, Y. Wang, L. Zhang, and S. Li, Inorg. Chem. 53, 3606 (2014).
[23] P. Sengupta, C. D. Batista, R. D. McDonald, S. Cox, J. Singleton, L. Huang, T. P. Papageorgiou, O. Ignatchik, T. Herrmannsdörfer, J. L. Manson, J. A. Schlüter, K. A. Funk, and J. Wosnitza, Phys. Rev. B 79, 060409(R) (2009); A. A. Tsirlin, R. Nath, A. M. Abakumov, Y. Furukawa, D. C. Johnston, M. Hemmida, H.-A. Krug von Nidda, A. Loidl, C. Geibel, and H. Rosner, ibid. 84, 014429 (2011).
SAMPLE PREPARATION

Polycrystalline samples were prepared by firing stoichiometric mixtures of Li$_2$CO$_3$, CuO, and WO$_3$ at 650°C for 24 h and at 700°C for 48 h with intermediate re-grindings. Sample quality was controlled by powder x-ray diffraction (XRD). The XRD data were collected on the Empyrean diffractometer from PANalytical using the CuK$_\alpha$ radiation ($\lambda$ = 1.54060 Å). No impurity peaks were detected.

MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility was measured on a polycrystalline sample using the MPMS SQUID magnetometer in the temperature range 2 – 380 K. Inverse magnetic susceptibility 1/χ(T) data for Li$_2$CuW$_2$O$_8$ measured at 1 T are shown in Fig. S1. To fit the bulk magnetic susceptibility data at high temperatures, we used the expression

$$\chi(T) = \chi_0 + \frac{C}{T + \theta_{CW}},$$

where $\chi_0$ is the temperature-independent contribution that consists of the diamagnetism of core electron shells ($\chi_{\text{core}}$) and Van-Vleck paramagnetism ($\chi_{VV}$) of the open shells of the Cu$^{2+}$ ions present in the sample. The second term is the Curie-Weiss (CW) law with the Curie-Weiss temperature ($\theta_{CW}$) and Curie constant $C = N_A \mu_B^2 / 3k_B$, where $N_A$ is Avogadro’s number, $k_B$ is the Boltzmann constant, and the effective moment $\mu_{\text{eff}} = g \sqrt{S(S+1)} \mu_B$. Our fit in the temperature range between 100 K and 380 K yields $\chi_0 \simeq -3.825 \times 10^{-5}$ cm$^3$/mol, $C \simeq 0.44$ emu K/mol, and $\theta_{CW} \simeq 12$ K. The effective moment was calculated to be $\mu_{\text{eff}} \simeq 1.88 \mu_B$/Cu which corresponds to a Landé $g$-factor $g \simeq 2.17$.

![Figure S1. Inverse magnetic susceptibility of Li$_2$CuW$_2$O$_8$ as a function of temperature measured at 1 T along with Curie-Weiss fit.](image)

HEAT CAPACITY

Heat capacity was measured on a small pressed pellet using the relaxation technique. The measurement was performed with the Quantum Design PPMS in the temperature range 1.8 – 300 K. The heat capacity $C_p$ as a function of temperature measured at zero field is present in Fig. S2.

In order to estimate the phonon contribution of the specific heat $C_{ph}(T)$, the $C_p(T)$ data above 40 K were fitted by a sum of Debye contributions

$$C_{ph}(T) = 9R \sum_{n=1}^{3} c_n \left(\frac{T}{\theta_{Dn}}\right)^3 \int_0^{\theta_{Dn}} \frac{x^4dx}{(e^{x} - 1)^2},$$

where $\theta_{Dn}$ are characteristic Debye temperatures and $c_n$ are integer coefficients indicating the contributions of different atoms (or group of atoms) to $C_{ph}(T)$. A similar procedure has been adopted in several recent studies of quantum magnets [1, 2]. Figure S2 shows the fit of $C_p(T)$ by Eq. (4) with $c_1 = 10$, $c_2 = 1$, and $c_3 = 2$ where $c_1$ is the total number of light atoms (Li and O), $c_2$ corresponds to one Cu atom per formula unit, and $c_3$ is for two W atoms per formula unit. The sum of $c_n$ is 13, which is the total number of atoms per formula unit. Because of the large differences in the atomic masses, we used three different Debye temperatures: $\theta_{D1}$ for Li$^+$ and O$^{2-}$, $\theta_{D2}$ for Cu$^{2+}$, and $\theta_{D3}$ for W$^{6+}$. One expects that the Debye temperature varies inversely with the atomic mass. Indeed, we obtained $\theta_{D1} \simeq 850$ K, $\theta_{D2} \simeq 340$ K, and $\theta_{D3} \simeq 130$ K.

![Figure S2. Temperature dependence of heat capacity measured at zero field for Li$_2$CuW$_2$O$_8$. The solid spheres are the raw data, the red solid line is the phonon contribution $C_{ph}$ as found from the fit to Eq. (4), and the blue solid line denotes the magnetic contribution $C_{mag}$. The inset shows the magnetic entropy $S_{mag}$ as a function of T. The dashed horizontal line is the value $S_{mag} = R \ln 2$ expected for Cu$^{2+}$ spins.](image)
FIG. S3. LDA density of states for Li$_2$CuW$_2$O$_8$. The Fermi level is at zero energy. Note that the band structure is metallic because strong correlation effects in the Cu 3$d$ shell are nearly absent in LDA.

200 K. Finally, the high-$T$ fit was extrapolated down to 2.1 K and $C_{\text{mag}}(T)$ was estimated by subtracting $C_{\text{ph}}(T)$ from $C_p(T)$ [see Fig. S2].

In order to check the reliability of the fitting procedure, we calculated the total magnetic entropy ($S_{\text{mag}}$) by integrating $C_{\text{mag}}(T)/T$ between 2.1 K and high-temperatures as

$$ S_{\text{mag}}(T) = \int_{2.1}^{T} \frac{C_{\text{mag}}(T')}{T'} dT'. \quad (5) $$

The resulting magnetic entropy is $S_{\text{mag}} \approx 5.2$ J/mol K at 30 K. This value reasonably matches the expected theoretical value [$S_{\text{mag}} = R \ln(2S + 1) \approx 5.76$ J/mol K] for the spin-$\frac{1}{2}$ Cu$^{2+}$ ions in Li$_2$CuW$_2$O$_8$.

**BAND STRUCTURE**

Electronic band structure of Li$_2$CuW$_2$O$_8$ was calculated using the full-potential FPLO code with the basis set of local atomic-like orbitals and local density approximation (LDA) for the exchange-correlation potential. We used 4004 $k$-points in the symmetry-irreducible part of the first Brillouin zone (crystallographic unit cell, LDA calculation) and up to 64 $k$-points for the 8-fold and 9-fold supercells in LSDA+$U$.

LDA density of states (Fig. S3) and band structures (Fig. S4) evidence metallic behavior because strong correlation effects in the Cu 3$d$ shell are largely underestimated in LDA. When LSDA+$U$ is used, the band gap of about 3.0 eV and magnetic moments of about 0.86 $\mu_B$ on Cu atoms are obtained. No experimental information on the electronic structure of Li$_2$CuW$_2$O$_8$ is presently available. The large band gap in LSDA+$U$ is in reasonable agreement with the pale-yellow color of powder samples.

For the evaluation of magnetic exchange couplings, we used two approaches. The so-called model approach rests upon mapping the LDA band structure onto a one-orbital tight-binding model, which is then supplemented by the Hubbard term to produce the Heisenberg model for low-lying excitations, given the limit of strong correlations and the half-filled regime. In our case, the Fermi level is crossed by only one band originating from the Cu orbital that has the $d_{x^2-y^2}$ symmetry, where $x$ and $y$ are directed along short Cu–O bonds within the CuO$_4$ plaquette. Therefore, we fit this single band using Wannier functions and obtain hopping parameters $t_i$. Then AMF contributions to the exchange integrals are calculated as $J_{i}^{\text{AFM}} = 4t_i^2/U_{\text{eff}}$, where $U_{\text{eff}}$ is an effective on-site Coulomb repulsion, which may be different from the $U$ parameter in LSDA+$U$.

The second approach is the supercell method, where energies of several collinear spin configurations are mapped onto the Heisenberg Hamiltonian to produce individual exchange couplings $J_i$. This requires large supercells. In the case of Li$_2$CuW$_2$O$_8$, we could obtain most of the couplings from the 8-fold supercell (2$a \times 2b \times 2c$), whereas the coupling $J_{111}$ along the body diagonal required an even larger, 9-fold supercell (3$a \times 3b \times c$).

*rnath@iisertvm.ac.in
†alttsirlin@gmail.com

[1] R. Nath, A. A. Tsirlin, H. Rosner, and C. Geibel, Phys. Rev. B 78, 064422 (2008).
[2] N. S. Kini, E. E. Kaul, and C. Geibel, J. Phys.: Cond. Mat. 18, 1303 (2006).