Coupled frustrated quantum spin-1/2 chains with orbital order in volborthite

Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O

O. Janson, J. Richter, P. Sindzingre, and H. Rosner

1Max-Planck-Institut für Chemische Physik fester Stoffe, D-01187 Dresden, Germany
2Institut für Theoretische Physik, Universität Magdeburg, D-39016 Magdeburg, Germany
3Laboratoire de Physique Théorique de la Matière Condensée, Univ. P. & M. Curie, Paris, France

(Dated: October 4, 2010)

We present a microscopic magnetic model for the spin-liquid candidate volborthite Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O. The essentials of this DFT-based model are (i) the orbital ordering of Cu(1) 3d$_{x^2−y^2}$ and Cu(2) 3d$_{z^2}$ (ii) three relevant couplings $J_{ic}$, $J_1$ and $J_2$ (iii) the ferromagnetic nature of $J_1$ and (iv) frustration governed by the next-nearest-neighbor exchange interaction $J_2$. Our model implies magnetism of frustrated coupled chains in contrast to the previously proposed anisotropic kagome model. Exact diagonalization studies reveal agreement with experiments.

PACS numbers: 71.20.Ps, 75.10.Jm, 75.25.Dk, 91.60.Pn

I. INTRODUCTION

The search for new magnetic ground states (GS) is a major subject in solid state physics. Magnetic monopoles in the spin ice system Dy$_2$Ti$_2$O$_7$ (Ref. 1–3), the metal-insulator transition in the spin-Peierls compound TiOCl$_2$4 and the quantum critical behavior in Li$_2$ZrCuO$_4$5,6 are among recent discoveries that demonstrate the power of combining precise experimental techniques with modern theory. However, for a rather large number of problems experiment and theory don’t keep abreast, since it is often tricky to find a real material realization for a well studied theoretical model. The most remarkable example is the concept of a “resonating valence bond”7 — a magnetic GS formed by pairs of coupled spin-singlets lacking the long range magnetic order (LRO). Subsequent studies revealed a fascinating variety of disordered GS8,9 commonly called “spin liquids” in order to emphasize their dynamic nature, and even raised the discussion of their possible applications.

Following the common belief that the spin liquid GS may emerge from the interplay of low-dimensionality, quantum fluctuations and magnetic frustration, considerable effort has been spent on the search for spin-1/2 Heisenberg magnets with kagome geometry. The synthesis of herbertsmithite Cu$_3$Zn(OH)$_6$Cl$_2$10, the first inorganic spin-1/2 system with ideal kagome geometry, and subsequent studies revealed besides the desired absence of magnetic LRO a (i) intrinsic Cu/Zn structural disorder and (ii) the presence of anisotropic interactions complicating the spin physics.11 The recently synthesized kapellasite12 was predicted to imply modified kagome physics due to an additional relevant coupling13.

Since the search for a system representing the pure kagome model is far from being completed, it is natural to consider systems with lower symmetry where the distortion is small enough to keep the essential physics.14 This way, the attention has been drawn to the mineral volborthite Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O, where the Cu sites form a slightly distorted kagome network.15 However, the local environment of two independent Cu sites is essentially different: Cu(1) forms dumbbells of two short Cu–O bonds and four long Cu–O bonds; “2+4”, while Cu(2) resides in a plaquette formed by four short bonds (Fig. 1 top). Recently, DFT studies of CuSb$_2$O$_6$, implying the “2+4” local environment of Cu atoms, revealed that orbital ordering (OO) drastically changes the nature of the magnetic coupling from three-dimensional (3D) to one-dimensional (1D).16 The crucial impact of OO onto mag-
The experimental data.

croscopic model evidence an improved agreement with
strong similarities to the physics of frustrated coupled
ing away from the kagome model. Moreover, we reveal
expected microscopic magnetic model for volborthite, mov-
Here, we show that DFT calculations yield an unex-
provide a reliable microscopically based model.

A standard tool to treat such peculiarities properly is
density functional theory (DFT) calculations that can
structural peculiarities of volborthite were not considered.

AKM which was based on geometry only, while the struc-
tural peculiarities of volborthite were not considered.

The GS was recently investigated by $^{51}$V nuclear magnetic
resonance (NMR) following earlier NMR and muon spin relaxation
studies. The GS is characterized by the absence of mag-
etic LRO, high density of low energy excitations and
and two distinct scales of spin fluctuations. At 4.5 Tesla,
vollborthite undergoes a transition to another magnetic
phase. The fingerprint of this transition is a step-like feature in the magnetization curve. Similar features are
observed at 25 and 46 Tesla, hinting at a series of succes-

sive transitions. Between 60 and 70 Tesla, the slope of magnetization diminishes indicating a possible on-
set of a magnetization plateau. Magnetic susceptibility
measurements yield a broad maximum at temperatures
much smaller than the Curie-Weiss temperature, indicat-
ing strong frustration.

Extensive experimental information stimulated theo-
retical studies aiming to find a consistent description for
magnetism of volborthite. Since the pure kagome model
doesn’t account for the experimental data, the studies
were focused on the GS and thermodynamical prop-
erties of the anisotropic kagome model (AKM). However,

ttempts to reach consistency by varying the degree of
anisotropy were not satisfying so far. The most strik-
ing disagreement is the deviation of the theoretical mag-
etic susceptibility $\chi$ even at rather high temperatures
($T \sim J$).

This disagreement originates from the choice of the
AKM which was based on geometry only, while the struc-
tural peculiarities of volborthite were not considered.

A standard tool to treat such peculiarities properly is
density functional theory (DFT) calculations that can
provide a reliable microscopically based model. Here, we show that DFT calculations yield an unex-
pected microscopic magnetic model for volborthite, mov-
ing away from the kagome model. Moreover, we reveal
strong similarities to the physics of frustrated coupled
chains due to OO. Our subsequent simulations of the mi-
 microscopic model evidence an improved agreement with
the experimental data.

II. DFT CALCULATIONS

The DFT calculations have been performed in the local
density approximation (LDA) using the full potential code fplo8.65–32. For the scalar relativistic calcula-
tions, the Perdew and Wang parametrization of the ex-
change-correlation potential has been used. All calcu-
lations have been performed on well-converged k-
meshes.

The reliability of DFT calculations depends crucially
on the accuracy of the experimental structural data used
as input. The chemical composition of volborthite ham-
pers structural studies due to the considerable content
of V and H atoms, which are poor scatterers of neu-
trons and x-rays, respectively. Therefore, prior to inves-
tigations of subtle electronic effects, the structural data
should be addressed. Among several structural data sets
available we have chosen a structural model (exp) based
on joint x-ray and neutron diffraction studies. Although
such combination improves the reliability of the result-
ing data, the statistics (number of reflections) is not suf-
ficient for fully conclusive results. Therefore, we have
carried out a structural optimization relaxing the atomic
coordinates and minimizing the forces, since LDA calcula-
tions for cuprates usually yield accurate and consistent
results. Moreover, to evaluate the influence of the differ-
et structural models, we perform calculations for the
experimental as well as for the optimized structure.

The LDA-optimized crystal structure (opt) yields con-
siderably lower total energy and atomic forces. Although
individual bond lengths and angles change up to several
percents (O–H distance increased by $\sim$10%), the overall
structural motive and the different local environment of
Cu(1) and Cu(2) are inherited from the original model.

LDA yields a valence band width of 7 eV (Fig. 2) typ-
ical for cuprates, and a metallic GS in contrast to the
green, transparent samples. This well-known problem of
the LDA originates from the underestimation of strong
on-site correlations for a Cu $3d^9$ configuration. Never-
theless, LDA is a reliable tool to evaluate the relevant
orbitals and couplings. For most cuprates, an effective
one-band model is well justified by a band complex at
Fermi level ($\varepsilon_F$) formed by $N$ antibonding bands, where
$N$ is the number of Cu atoms per cell. In contrast, in
volborthite ($N = 3$), six bands in vicinity of $\varepsilon_F$ (Fig. 2)
evidence a sizable hybridization of two different $3d$
orbitals at each Cu site that need to be included into the
modeling.

FIG. 2: (Color online) Density of states (upper panel), the
band structure (lower panel, center) and the orbital-resolved
density of states for Cu(1) (left) and Cu(2) (right) of the
optimized structure (3d$_{x^2-y^2}$ is shown with a dashed line).
The relevant Cu 3d orbitals are revealed by projecting the density of states (DOS) onto local orbitals. The resulting orbital-resolved DOS is shown in Fig. 4. For both Cu(1) and Cu(2), the 3d_{x^2-y^2} and 3d_{z^2-r^2} states are relevant and hybridized with each other. To evaluate the relevant couplings, we consider two orbitals (3d_{x^2-y^2} and 3d_{z^2-r^2}) per Cu atom and fit the six bands using the Wannier functions (WFs) technique.\textsuperscript{31,33}

Prior to evaluation of the relevant couplings, the correct orbital GS should be found. LDA yields an essentially different filling of the orbitals: for Cu(1) the 3d_{x^2-y^2} is close to half-filling and the 3d_{z^2-r^2} is almost filled (Fig. 2 left), while for Cu(2) it is the other way round (Fig. 2 right). However, the closer proximity to half-filling in the LDA picture does not necessarily provide the correct answer, as revealed for the related system CuSbO\textsubscript{6}.\textsuperscript{18} Thus, we cross-check the LDA result by LSDA+U calculations. In agreement with the LDA, the latter yield the magnetically active Cu(1) 3d_{x^2-y^2} and Cu(2) 3d_{z^2-r^2} (see details below).

The relevant transfer integrals can be extracted from the WFs considering the hoppings between the GS orbitals (Cu(1) 3d_{x^2-y^2} and Cu(2) 3d_{z^2-r^2}). The leading terms are \( t_1 \) and \( t_{ic} \), which coincide with two NN couplings in the AKM (Fig. 1 bottom). Surprisingly, the next-nearest-neighbor (NNT) coupling \( t_{2c} \) is also sizable, while other couplings are considerably smaller. A small value of the inter-layer coupling supports the 2D nature of magnetism.

The correct description of the orbital GS requires an appropriate description of correlations in the Cu 3d shell, which can be treated in a mean-field way using the LSDA+U scheme. By stabilizing solutions comprising different orbital occupations and a subsequent comparison of their total energies, we evaluate the orbital GS. The separation between the orbital GS and the lowest lying excited orbital state (3d_{x^2-y^2} for Cu(1) and Cu(2)) exceeds 500 meV (\( \sim 6000 \) K), almost two orders of magnitude larger than the magnetic exchange (\( \sim 100 \) K). Therefore, orbital and spin degrees of freedom are mostly decoupled and can be analyzed separately.

The leading exchange integrals \( J_1, J_2 \) and \( J_{ic} \) are obtained mapping the results of LSDA+U total energy calculations onto a Heisenberg model.\textsuperscript{34} A careful analysis of the results shows that the individual values of exchange integrals are sensitive to (i) the structural model, (ii) the Coulomb repulsion \( U_d \) and (iii) the double-counting correction (DCC) scheme.\textsuperscript{35} The crucial influence of these parameters is visualized in Fig. 3 where the results for the experimental and optimized structures are shown. For each structural model, we use the limiting cases for the DCC — around-the-mean-field (AMF) and the fully localized limit (FLL)\textsuperscript{36} and vary \( U_d \) within a reasonable range\textsuperscript{36} Depending on these parameters, we obtain \( J_1 = -80 \pm 10 \) K, \( J_2 = 35 \pm 15 \) K and \( J_{ic} = 100 \pm 60 \) K for the experimental and \( J_1 = -65 \pm 15 \) K, \( J_2 = 45 \pm 15 \) K and \( J_{ic} = 100 \pm 60 \) K for the optimized lattice.

The substantially ferromagnetic nature of \( J_1 \), in accord with Goodenough-Kanamori-Anderson rules, and the relatively small uncertainties of its strength disregarding the parameters used give strong evidence that the pure kagome model is inappropriate for volborthite. The AKM can be ruled out since \( J_1 \) and \( J_{ic} \) support each other and do not give rise to frustration. Our microscopic insight evidences that an essentially different model with frustration governed by NNN exchange \( J_2 \) (competing with both \( J_1 \) and \( J_{ic} \) should be used for volborthite. Despite sizable scattering of the \( J \) values, important general trends can be established. First, the optimized structure has an enhanced \( J_2/|J_1| \) ratio compared to the experimental structure. Second, FLL yields considerably smaller \( J_{ic} \) and somewhat larger values for \( J_2 \) than AMF.

Based on DFT calculations, we obtain a microscopic magnetic model and determine the parameters \( J_1, J_2 \) and \( J_{ic} \). Although we find the relevant region in the phase space, the complexity of volborthite impedes a more accurate estimate of individual exchange integrals, especially \( J_{ic} \). In this case, refining the parameters by numerical simulations of measured physical properties and subsequent comparison to experimental data is an appropriate way towards a deeper understanding.

III. EXACT DIAGONALIZATION

To realize a guided search for a consistent set of exchange integrals, the GS of the \( J_1-J_2-J_{ic} \) model should be investigated. We explore the phase space by considering a Heisenberg model with \( J_1 < 0, J_2 > 0, J_{ic} > 0 \). On a classical level, we find two GS: a ferrimagnetic (FM) phase with magnetization \( m = 1/3 \) and an incommensurate \( m = 0 \) helical (H) phase with spiral correlations along \( J_1-J_2 \) frustrated chains, similar to those of edge...
shared quasi 1D cuprates (see e.g. Ref. [3]). The transition from the fM-phase to the H-phase is driven by the frustrating NNN in-chain coupling $J_2$ and occurs at $J_{2}^{\text{lass}} = |J_1|/4 + J_{ic}/8$. To discuss the GS of the quantum model we use Lanczos exact diagonalization of finite lattices up to $N = 36$ sites. For the quantum model, the fM state competes with a singlet GS with $m = 0$, and the transition is given by $J_{2}^{\text{quant}} = 0.304|J_1| + 0.200J_{ic}$. The transition line together with the DFT-derived exchange integrals are plotted in Fig. 3 (left). Since the experiments evidence zero magnetization of the GS, the fM solutions can be ruled out and the analysis can be restricted to the singlet GS.

To understand the nature of the GS, we consider spin correlations as a sensitive probe for magnetic ordering. While the correlations between the chains are similar to the standard kagome Heisenberg antiferromagnet, they are completely different along the $J_1$-$J_2$ frustrated chains (Fig. 3 right). These in-chain correlations fit to a spiral state with a pitch angle very close to the classical model. Hence, our data suggest well pronounced in-chain spiral correlations together with weaker inter-chain correlations. We mention, however, that these statements are restricted to short-range correlations.

Since the magnetic correlations along the chains are strongest, one could argue that the model exhibits an effectively 1D low-temperature physics as has been discussed previously for other 2D models such as the crossed-chain model, anisotropic triangular lattice, as well as for modified kagome compounds. However, this issue as well as a conclusive answer to the question of helical LRO need further investigation.

To comprise the experimental magnetization curve, we add the magnetic field term to the Heisenberg Hamiltonian and simulate the $m(h)$ dependence. For the boundary of the fM and singlet GS, we find a wide 1/3 magnetization plateau starting at $h_{c1} = 0$. However, the modification of the exchange parameters, in particular increasing of $J_2$ and decreasing of $|J_1|$ and $J_{ic}$, according to the limits set by DFT calculations leads to a significant increase of $h_{c1}$ and to a drastic diminishing of the plateau width. Close to the DFT-boundary ($J_{ic}/|J_1| = 2$, $J_2/|J_1| = 1.1$, $J_{ic} = 100$ K), we obtain $h_{c1} = 22$ T, which is still smaller than the experimentally observed value. We should note that this deviation originates from the minimalistic character of the model and considerable finite size effects. Nevertheless, a slightly modified ratio $J_2/|J_1| = 1.6$ yields $h_{c1} = 55$ T (Fig. 4 bottom) in excellent agreement with the experiment. It should be mentioned that the nature of spin correlations in the 1/3-plateau phase is substantially different compared to the kagome model. Small magnetization jumps seen experimentally cannot be resolved with present lattice sizes and might be related to anisotropic exchange.

We also calculate the temperature dependence of magnetic susceptibility $\chi(T)$ using two different lattices up to $N = 24$ sites. For the proposed model, the orbital order of Cu(1) $3d_{3z^2-r^2}$ and Cu(2) $3d_{x^2-y^2}$ orbitals is crucial. We suggest new experiments to challenge our model: resonant x-ray scattering measurements to study orbital effects and measurements in high magnetic fields (>70 Tesla) to get an access to the magnetization plateau.

ACKNOWLEDGEMENTS

We thank Z. Hiroi for providing us with $\chi(T)$ data. We acknowledge fruitful discussions and valuable comments from Z. Hiroi, F. Mila, G. Nilsen and A. Tsirlin.
1 R. H. Colman, C. Ritter, and A. S. Wills, Chem. Mater. 22, 205111 (2009), arXiv:0911.0307

2 F. Bert, D. Bono, P. Mendels, J.-C. Trombe, P. Millet, A. Amato, C. Baines, and A. Hillier, J. Phys.: Condens. Matter 20, 043704 (2008), arXiv:0804.3107

3 P. W. Anderson, Mater. Res. Bull. 8, 153 (1973).

4 J. P. Perdew and Y. Wang, Phys. Rev. B 45, 136406 (2008), arXiv:0809.0145.

5 D. Kasinathan, K. Koepernik, and H. Rosner, Phys. Rev. B 79, 127101 (2009).

6 A. A. Tsirlin and H. Rosner, Phys. Rev. Lett. 103, 266401 (2009), arXiv:0907.4874.

7 H. Eschrig and K. Koepernik, Phys. Rev. B 80, 104503 (2009), arXiv:0905.4844

8 Only spin degrees of freedom are varied, keeping the orbital GS preserved.

9 The situation is even more complicated because the choice of $U_d$ depends on the relevant orbitals, and thus different values of $U_d$ should be used for Cu(1) and Cu(2).

10 M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B 49, 14211 (1994).

11 According to extensive studies of related Cu$^{2+}$ materials, $U_d=10\pm1.5$ eV for Cu(1) and $U_d=7\pm1.5$ eV for Cu(2) were chosen as typical values with sizable error bars for the resulting exchange integrals to account for the uncertainties in $U_d$. An extensive study of the details including the DCC will be published elsewhere.

12 A. Honecker, J. Schulenburg, and J. Richter, J. Phys.: Condens. Matter 16, S749 (2004), arXiv:cond-mat/03090425

13 Z. Hiroi, M. Hanawa, N. Kobayashi, M. Nohara, H. Takagi, Y. Kato, and M. Takigawa, J. Phys. Soc. Jpn. 70, 3377 (2001), arXiv:cond-mat/0111227.

14 D. Kasinathan, K. Koepernik, and H. Rosner, Phys. Rev. B 100, 173201 (2009), arXiv:0805.4080

15 M. Yoshida, M. Takigawa, H. Yoshida, Y. Okamoto, and Z. Hiroi, Phys. Rev. Lett. 103, 077207 (2009), arXiv:0906.2846

16 F. Bert, D. Bono, P. Mendels, F. Ladieu, F. Duc, J.-C. Trombe, and P. Millet, Phys. Rev. Lett. 95, 087203 (2005), arXiv:cond-mat/0507250

17 S. Okubo, H. Ohta, K. Hazuki, T. Sakurai, N. Kobayashi, and Z. Hiroi, Physica B 294-295, 75 (2001).

18 Z. Hiroi, private communication.

19 P. Sindzingre, arXiv:0707.4264 (unpublished).

20 A. A. Tsirlin and H. Rosner, Phys. Rev. B 81, 024424 (2010), arXiv:0909.2051

21 O. Janson, A. A. Tsirlin, M. Schmitt, and H. Rosner, Phys. Rev. B 82, 014424 (2010), arXiv:1004.3765

22 Anisotropic structures require the use of a full-potential code, see H. Rosner, M. Schmitt, D. Kasinathan, A. Ormeci, J. Richter, S.-L. Drechsler, and M. D. Johannes, Phys. Rev. B 79, 127101 (2009).

23 K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).

24 J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).

25 See supplementary material for finite lattices used for exact diagonalization, comparison of different exchange-correlation potentials, WF fits, numerical values of transfer integrals, and the basis set used in the DFT calculations.

26 O. Janson, W. Schnelle, M. Schmidt, Y. Prots, S.-L. Drechsler, S. K. Filatov, and H. Rosner, New J. Phys. 11, 113034 (2009), arXiv:0907.4874.

27 H. Eschrig and K. Koepernik, Phys. Rev. B 80, 104503 (2009), arXiv:0905.4844.

28 Only spin degrees of freedom are varied, keeping the orbital GS preserved.

29 The situation is even more complicated because the choice of $U_d$ depends on the relevant orbitals, and thus different values of $U_d$ should be used for Cu(1) and Cu(2).

30 M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B 49, 14211 (1994).

31 According to extensive studies of related Cu$^{2+}$ materials, $U_d=10\pm1.5$ eV for Cu(1) and $U_d=7\pm1.5$ eV for Cu(2) were chosen as typical values with sizable error bars for the resulting exchange integrals to account for uncertainties in $U_d$. An extensive study of the details including the DCC will be published elsewhere.

32 A. Honecker, J. Schulenburg, and J. Richter, J. Phys.: Condens. Matter 16, S749 (2004), arXiv:cond-mat/03090425

33 J. Richter and J. Schulenburg, Eur. Phys. J. B 73, 117 (2010), arXiv:0909.3723

34 Note that due to boundary effects also for the classical model on that finite lattice the expression given above is modified to $J_{2\text{class}} = 0.340|J_1| + 0.166|J_2|$.

35 O. A. Starykh, R. R. P. Singh, and G. C. Levine, Phys. Rev. Lett. 88, 167203 (2002), arXiv:cond-mat/0106260.

36 R. Coldea, D. A. Tennant, A. M. Tsvelik, and Z. Tylczynski, Phys. Rev. Lett. 86, 1335 (2001), arXiv:cond-mat/0007172.

37 D. C. Cabra, M. D. Grynberg, P. C. W. Holdsworth, A. Honecker, P. Pujol, J. Richter, D. Schmalfuß, and J. Schulenburg, Phys. Rev. B 71, 144420 (2005), arXiv:cond-mat/0404279

38 At low temperatures, finite size effects are strong as evidenced by a sizable deviation between the results for different lattices as well as between $N = 18$ and $N = 24$ curves for the lattice 2.
Supplementary material

FIG. S1: Finite lattices used for exact diagonalization on $N = 18$ and $N = 24$ sites.

TABLE S1: Basis set used in fplo8.65-32.

| atom | core      | valence     | second valence | polarization |
|------|-----------|-------------|----------------|--------------|
| Cu   | 1s 2s 2p  | 3s 3p 4s 3d| 5s 4d          | 4p           |
| V    | 1s 2s 2p  | 3s 3p 4s 3d| 5s 4d          | 4p           |
| O    | 1s        | 2s 2p       | 3s 3p          | 3d           |
| H    | 1s        | 2s          | 2p             |              |
FIG. S2: Comparison of the band structures calculated within the local density approximation (LDA) and the general gradient approximation (GGA) for the experimental (“exp”, top panel) and optimized (“opt”, bottom panel) structures.

TABLE S2: Cells used for LDA and GGA (DFT) as well as spin-polarized LSDA+U and GGA+U (DFT+U) calculations. For each cell, the total number (tot.) as well as the number of symmetrically inequivalent (ineq.) Cu atoms are provided. Basis vectors are given in terms of the unit cell vectors \( \vec{a}, \vec{b}, \vec{c} \). PUC — primitive unit cell, SC — supercell.

| cell   | Sp. gr. | functional | Cu atoms | basis vectors | k-mesh |
|--------|---------|------------|----------|---------------|--------|
|        |         |            | tot.     | ineq.         |        |
| PUC    | P2/m    | DFT        | 3        | 2             | \( \frac{1}{4} \) \((\vec{a} + \vec{b})\) \( \frac{1}{2} \)(\vec{a} - \vec{b}) \\vec{c} \) | \( 12 \times 12 \times 12 \) |
| SC1    | \( \bar{P} \bar{1} \) | DFT        | 3        | 3             | \( \frac{1}{4} \) \((\vec{a} + \vec{b})\) \( \frac{1}{2} \)(\vec{a} - \vec{b}) \\vec{c} \) | \( 8 \times 8 \times 8 \) |
|        |         | DFT+U      |          |               | \( \frac{1}{4} \times \frac{1}{4} \times \frac{1}{4} \) | \( 4 \times 4 \times 4 \) |
| SC2    | \( \bar{P} \bar{1} \) | DFT        | 6        | 6             | \( \frac{1}{4} \) \((\vec{a} + \vec{b})\) \( \frac{1}{2} \)(\vec{a} - \vec{b}) \\vec{c} \) | \( 6 \times 3 \times 6 \) |
|        |         | DFT+U      |          |               | \( \frac{1}{4} \times \frac{1}{4} \times \frac{1}{4} \) | \( 3 \times 2 \times 3 \) |
| SC3    | \( \bar{P} \bar{1} \) | DFT        | 6        | 6             | \( \frac{1}{4} \) \((\vec{a} + \vec{b})\) \( \frac{1}{2} \)(\vec{a} - \vec{b}) \\vec{c} \) | \( 4 \times 7 \times 5 \) |
|        |         | DFT+U      |          |               | \( \frac{1}{4} \times \frac{1}{4} \times \frac{1}{4} \) | \( 2 \times 4 \times 3 \) |
FIG. S3: The Wannier functions fit (WF) and the tight-binding fit (TB) together with the LDA band structure for the experimental (“exp”, top panel) and optimized (“opt”, bottom panel) structures.

TABLE S3: Transfer integrals $t$ as a function of the structural model (exp or opt) and the exchange-correlation potential (LDA or GGA), calculated using the Wannier functions technique. The numbers given correspond to hoppings between the magnetically active orbitals (Cu1 3d$_{3z^2-r^2}$ and Cu2 3d$_{x^2-y^2}$).

|       | $t_1$, meV | $t_2$, meV | $t_{ic}$, meV | $t_1$, meV | $t_2$, meV | $t_{ic}$, meV |
|-------|------------|------------|---------------|------------|------------|---------------|
| exp   | LDA        | GGA        | LDA           | opt        | GGA        | GGA           |
|       | 91         | 93         | 117           | 117        | 119        | 119           |
|       | 59         | 57         | 64            | 64         | 62         | 62            |
|       | 156        | 156        | 155           | 155        | 157        | 157           |