

Paramagnetism in the kagome compounds $(\text{Zn,Mg,Cd})\text{Cu}_3(\text{OH})_6\text{Cl}_2$

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Frustrated magnetism on the kagome lattice has been a fertile ground for rich and fascinating physics, ranging from experimental evidence of a spin liquid to theoretical predictions of exotic superconductivity. Among experimentally realized spin- $\frac{1}{2}$ kagome magnets, herbertsmithite, kapellasite, and haydeeite $[(\text{Zn,Mg})\text{Cu}_3(\text{OH})_6\text{Cl}_2]$ are all well described by a three-parameter Heisenberg model, but they exhibit distinctly different physics. We address the problem using a pseudofermion functional renormalization-group approach and analyze the low-energy physics in the experimentally accessible parameter range. Our analysis places kapellasite and haydeeite near the boundaries between magnetically ordered and disordered phases, implying that slight modifications could dramatically affect their magnetic properties. Inspired by this, we perform *ab initio* density functional theory calculations of $(\text{Zn,Mg,Cd})\text{Cu}_3(\text{OH})_6\text{Cl}_2$ at various pressures. Our results suggest that by varying pressure and composition one can traverse a paramagnetic regime between different magnetically ordered phases.

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Introduction. Quantum magnetism in low-dimensional systems with parametric or geometrical frustration has been a highly inspiring field of research ever since the seminal paper of Pomeranchuk [1]. A Holy Grail of the field has been the spin- $\frac{1}{2}$ antiferromagnet on the kagome lattice (Fig. 1), where the geometrical frustration inherent in the individual triangles is only marginally alleviated through a corner sharing lattice pattern [2]. It is widely conjectured to host a spin liquid phase, albeit the nature and the topological classification of this phase are still controversial [3–15]. It may host exotic superconducting phases [16, 17].

Recently, significant progress has been achieved regarding experimental realizations of kagome magnets. The couplings in the actual materials, however, differ significantly from idealized models. The most prominent materials are herbertsmithite $[\text{ZnCu}_3(\text{OH})_6\text{Cl}_2]$ [18, 19] and its polymorphs, kapellasite $[\text{ZnCu}_3(\text{OH})_6\text{Cl}_2]$ [20, 21] and haydeeite $[\text{MgCu}_3(\text{OH})_6\text{Cl}_2]$ [22–26], with ground states ranging from potentially paramagnetic (PM) to weakly ferromagnetic (FM) phases. This variety

of ground states in structurally similar systems calls for a thorough theoretical investigation of the experimentally relevant couplings and their implications. In this Rapid Communication, we focus on the following aspects: (1) Which phases—ordered or PM—are realized, depending on Heisenberg couplings J_1 , J_2 , and J_d (Fig. 1)? (2) What determines the nature of magnetic interactions, and why are they so different in these compounds? (3) Can we deliberately manipulate these materials to probe different parts of the phase diagram, and, in particular, the PM (possibly spin-liquid) phase indicated in Fig. 2?

To begin with, we map out the zero-temperature phase diagram of the J_1 - J_2 - J_d kagome model. Specifically, we employ the pseudofermion functional renormalization group (PF-FRG) [27–29] method to compute magnetic fluctuations. We find that the experimentally estimated parameters place kapellasite near the borderline between the PM and the antiferromagnetically ordered cuboc-2 phase and haydeeite near the PM/FM border. Using *ab initio* density functional theory (DFT) calculations, we then discuss the reliability of these parameters and possible microscopic origins for their variations. We proceed with suggestions on how one can modify these compounds to shift them away from their current positions and explore other parts of the phase diagram. Among other aspects, our results provide an independent assessment of the initial placement of the materials in the phase diagram.

Herbertsmithite, kapellasite (KL), and haydeeite (HD) feature geometrically perfect Cu^{2+} $S = \frac{1}{2}$ kagome planes

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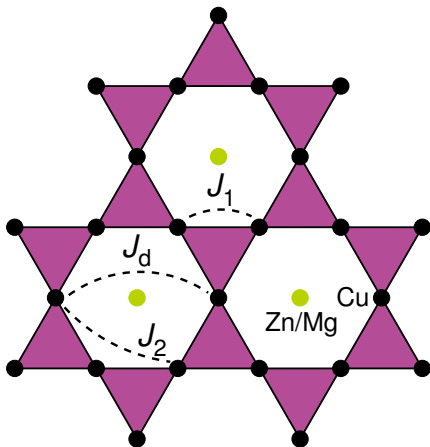


FIG. 1. For all kagome magnets considered, the lattice is formed by Cu^{2+} $S=\frac{1}{2}$ spins (black), and the Heisenberg exchange couplings are given by nearest neighbor J_1 , second nearest neighbor J_2 , and diagonal J_d across the hexagons. Kapellasite and haydeeite feature in-plane Zn^{2+} and Mg^{2+} ions (green), respectively, at the center of the hexagons, triggering appreciable values for J_d .

with the nearest-neighbor (NN) superexchange J_1 mediated by OH^- and Cl^- . The minimal model also includes subdominant interactions J_2 and J_3 and significant J_d (Fig. 1). Experiment [30] and calculations [31, 32] suggest that in herbertsmithite, where only Cu is present in the kagome planes, both J_3 and J_d are negligible, and thus the material is well described by a NN antiferromagnetic model with $J_1 \approx 180$ K, with a small but non-negligible J_2 [29, 33]. The quantum paramagnetic ground state of such an antiferromagnet has been intensively studied theoretically (see, e.g., Refs. [3–9, 11–15, 34]), and there is experimental evidence of a spin liquid state in herbertsmithite [19, 35, 36].

On the other hand, in KL and HD, the Zn and Mg ions, respectively, occupy the centers of the Cu hexagons [21], thus spanning the Cu pairs connected by J_d . This seems to explain why the J_d interaction is sizable, and differs considerably between the two compounds. However, the nature of this interaction is probably more complex than that, as discussed in detail in the Supplemental Material [37]. Bernu *et al.* [38] extracted J 's in KL from the temperature dependencies of magnetic susceptibility and specific heat, while Boldrin *et al.* [26] did the same for HD, using spin-wave dispersion. With the caveat that these are distinctly different experimental procedures, the estimated exchange coupling constants are $(J_1, J_2, J_d) = (-12, -4, 15.6)$ K for KL [38] and $(J_1, J_d) = (-38, 11)$ K, with $J_2/J_1 \ll 0.1$ for HD [26]. The small and negative values of J_1 signal a large cancellation of the anti- and ferromagnetic contributions to the NN superexchange, which, as we discuss in the Supplemental Material [37], is quite unexpected, but that they are close in both compounds is consistent with their similar geometries. Further investigations using electron spin

resonance estimated the symmetric exchange anisotropy D to be only $|D/J_1| \sim 3\%$ [39], thus justifying the use of the (J_1, J_2, J_d) isotropic Heisenberg model as a good starting point for both KL and HD.

Model and Methods. The Heisenberg Hamiltonian reads

$$\hat{\mathcal{H}} = J_1 \sum_{\langle ij \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + J_d \sum_{\langle\langle\langle ij \rangle\rangle\rangle_d} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \quad (1)$$

where $\hat{\mathbf{S}}_i$ is the spin- $\frac{1}{2}$ operator at site i . Here, $J_1, J_2 \leq 0$ (ferromagnetic) and $J_d \geq 0$ (antiferromagnetic), normalized so that $|J_1| + |J_2| + J_d = 1$. The indices $\langle ij \rangle$, $\langle\langle ij \rangle\rangle$, and $\langle\langle\langle ij \rangle\rangle\rangle_d$ denote sums over NN and next-NN bonds, and the diagonals of hexagons, respectively (Fig. 1).

In the PF-FRG approach [27–29, 40, 41], we first rewrite Eq. (1) in terms of pseudofermions as $\hat{\mathbf{S}}_i = \frac{1}{2} \sum_{\alpha\beta} \hat{c}_{i,\alpha}^\dagger \boldsymbol{\sigma}_{\alpha\beta} \hat{c}_{i,\beta}$, ($\alpha, \beta = \uparrow, \downarrow$), where $\hat{c}_{i,\alpha}$ are the pseudofermion operators, and $\boldsymbol{\sigma}$ are Pauli matrices. This enables us to apply Wick's theorem and develop a diagrammatic technique. To this end, an infrared frequency cutoff Λ is introduced in the fermion propagator. The FRG ansatz (for recent reviews, see, e.g., Refs. [42, 43]) then formulates an infinite hierarchy of coupled integrodifferential equations for the evolution of all m -particle vertex functions under the flow of Λ . Within PF-FRG, the truncation of this system of equations to a closed set is accomplished by the inclusion of only two-particle reducible two-loop contributions, which ensures sufficient backfeeding of the self-energy corrections to the two-particle vertex evolution [44]. A crucial advantage of the PF-FRG is that the diagrammatic summation incorporates vertex corrections between all interaction channels, i.e., treats magnetic ordering and disordering tendencies on equal footing. The PF-FRG equations are solved numerically by discretizing the frequency dependencies of the vertex functions and limiting the spatial dependencies to a finite cluster. We used 64 discretized frequencies and a cluster of 432 sites. In the PF-FRG approach, the onset of magnetic long-range order is signaled by a breakdown of the smooth RG flow, whereas a smooth evolution down to $\Lambda \rightarrow 0$ (where Λ is the infrared frequency cutoff) indicates PM behavior [27] (Fig. 3). From the effective low-energy two-particle vertex, we obtain the spin-spin correlation function in real space, which we then convert into the momentum-resolved spin susceptibility (see Fig. 4).

Previous applications of the PF-FRG method to frustrated magnets have been extremely successful. In particular, (i) the determined magnetic and nonmagnetic phases of the spin- $\frac{1}{2}$ Heisenberg J_1 - J_2 antiferromagnet on the square lattice and the locations of the phase transitions quantitatively agree with DMRG, exact diagonalization, and other methods [27], (ii) the phase diagram of the J_1 - J_2 - J_3 Heisenberg model on the honeycomb lattice agrees perfectly with exact diagonalization [40, 45], (iii) the phase diagram of the Kitaev-Heisenberg model is also correctly determined within the PF-FRG [41, 46],

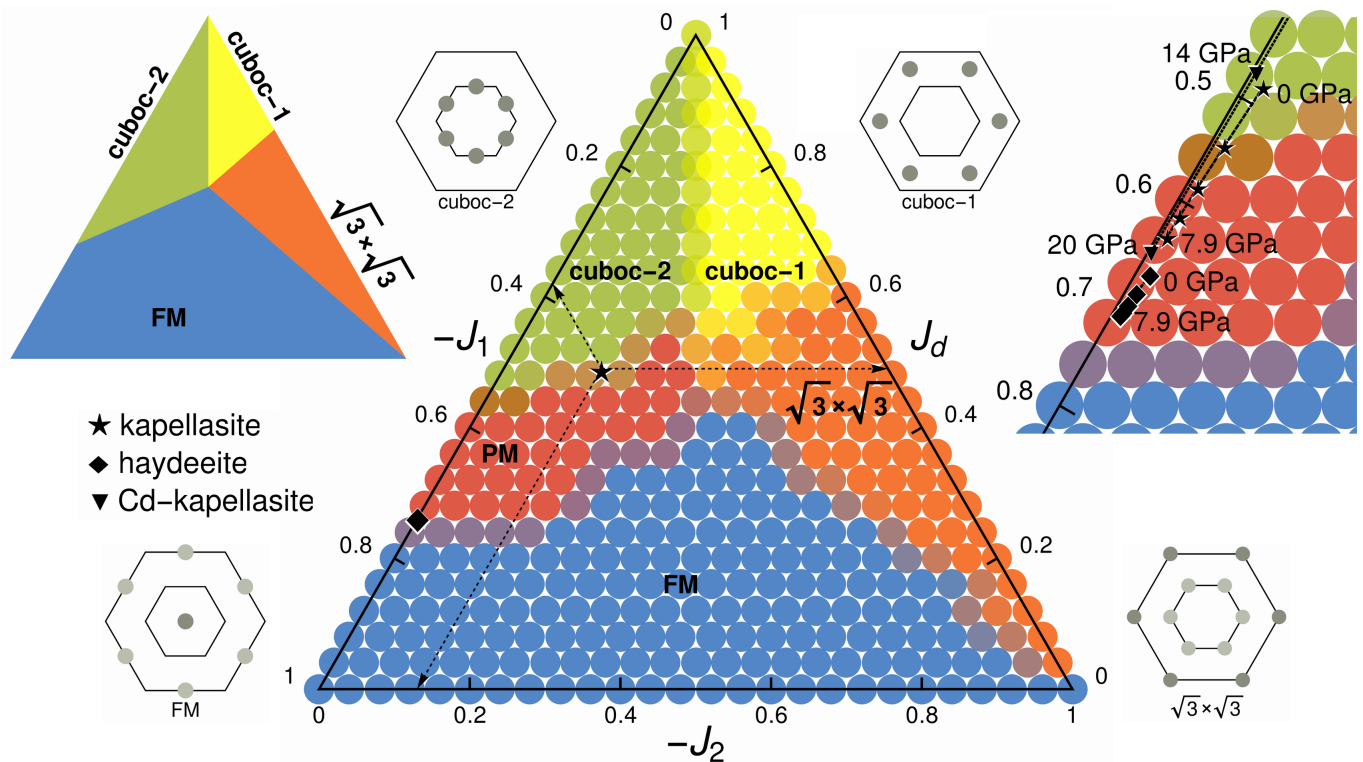


FIG. 2. Quantum phase diagram of the J_1 - J_2 - J_d Heisenberg model as defined in Eq. (1). It features a large paramagnetic (PM) domain for intermediate J_d . The exchange couplings estimated from fitting experimental data for kapellasite and haydeeite are marked [26, 38]. The static spin structure factors in the extended Brillouin zone are shown next to each phase. The corresponding classical phase diagram is shown in the upper left. The evolution of the couplings in the different materials under application of pressure, as calculated by *ab initio* methods, is shown in the enlarged region on the right.

in particular, the short range nature of the spin correlations in the Kitaev limit is correctly reproduced, and (iv) the spin structure factor of the NN Heisenberg antiferromagnet on the Kagome lattice in PF-FRG is in very good quantitative agreement with DMRG [9, 29], which is of particular relevance to the problem at hand.

For *ab initio* DFT calculations we used the generalized gradient approximation (GGA) functional [47]. Structure optimizations were performed with the projector augmented wave method within the VASP code [48, 49], and accurate total energies were calculated using the all-electron FPLO code [50].

Results. The PF-FRG quantum phase diagram of the J_1 - J_2 - J_d model of Eq. (1) is depicted in Fig. 2. Individual data points are labeled according to which type of phase they belong to in the PF-FRG. For small J_d , FM dominates. For intermediate J_d and large J_2 , a $\sqrt{3} \times \sqrt{3}$ order is found which changes into the cuboc-1 order for increasing J_d . The cuboc orders describe 12-sublattice noncoplanar orders in which the spins orient towards the corners of a cuboctahedron [51, 52] (that is, along the 12 possible [110] directions). For the domains discussed so far, the quantum phase diagram approximately matches the classical phase diagram of Eq. (1) (Fig. 2). Quantum corrections start to become visible closer to the cuboc-1/cuboc-2 boundary, as J_2 becomes smaller than J_1 (for

large J_d). The classical first order transition line between the cuboc-1 and cuboc-2 phases is then replaced by a narrow vertical strip ($J_1 \approx J_2$) in the quantum case, depicted by a merging gradient in Fig. 2, where an effectively 1D paramagnetic chain regime is found. As the most important modification to the classical picture, however, an extended PM regime emerges for $J_2/J_1 < 1$ separating the cuboc-2 from the FM domain. Its spin susceptibility profile has a well-defined wave-vector dependence featuring dominant short-distance correlations with soft maxima at cuboc-2 ordering wave vectors and subdominant FM correlations. This type of magnetic fluctuation profile is rather peculiar for a PM phase and fundamentally different from what is found for herbertsmithite [29, 30]. As we enter the PM regime from the cuboc-2 phase by lowering J_d , the magnetic correlations change quantitatively but not qualitatively, as is manifest from a comparison of their spin susceptibility profiles in Fig. 4(c) and Fig. 4(d). The only notable difference is more spectral weight smearing in the PM regime. Within the PM regime, the spin correlations are found to be short-ranged, and calculations of the dimer response function rule out any kind of valence-bond crystal order up to a 36-site cell. Note that the J_1 - J_2 - J_d model has been recently analyzed by variational Monte Carlo (VMC) [53]. There, in the large J_d regime, noncoplanar

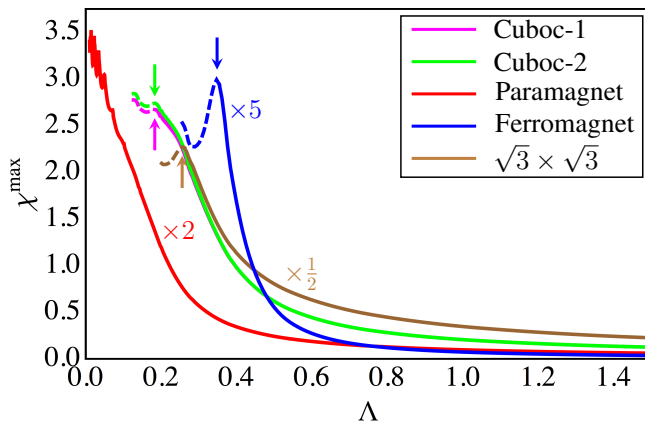


FIG. 3. Representative RG flows of the magnetic susceptibilities at the ordering wave vectors of the four ordered regimes of Fig. 2 and the paramagnetic regime. The points at which the solid lines become dashed (marked by arrows) indicate an instability in the flow and express the onset of order. In the smooth flow (red curve) indicating paramagnetism, no such instability is found. The small oscillations below $\Lambda \approx 0.1$ in this flow are due to frequency discretization.

cuboc-1 order is absent, and cuboc-2 order is reduced to a small part of the parameter space. Instead, for a significant range of J_d and depending on J_2/J_1 , two distinct gapless $U(1)$ chiral spin liquids with a spinon Fermi surface are found over an extended region. As opposed to the PF-FRG, which treats magnetic order and disorder tendencies on the same footing, a certain bias of VMC against cuboc-1 and cuboc-2 orders can be argued for on the basis of the variational wave functions employed. The noncoplanar structure of cuboc-1 and cuboc-2 orders implies that the corresponding chosen Jastrow wave functions are inaccurate as the Jastrow factor does not correctly describe the relevant quantum fluctuations on top of the classical state [53]. On the other hand, PF-FRG does not suffer from this deficiency, and, if anything, may slightly *overestimate* the PM domain.

The location of the high-temperature series expansion estimate of exchange couplings for KL [38] is marked within the center triangle by a star at $(0.38, 0.13, 0.49)$ in Fig. 2. This is very close to the boundary between the cuboc-2 and the quantum PM phases. Experimentally, KL shows no spin freezing and persistent fluctuations down to 20 mK (by μ SR), a diffused continuum of excitations (inelastic neutron scattering), and the divergence of the intrinsic local susceptibility for $T \rightarrow 0$ in NMR [54]. The static spin structure factor shows a well-defined wave-vector dependence exhibiting AFM short-range correlations [51, 55], consistent with the cuboc-2 pattern. This whole set of experiments has been interpreted in favor of a gapless quantum spin liquid [54] close to the cuboc-2 AFM order. The delicate location of KL might have important experimental implications, in that only moderate modifications in material synthesis or experimental conditions amounting to strain, pressure,

defects/impurities, and the imminent presence of different type of anisotropies would lead to significant effects. Slight modifications of the Heisenberg coupling constants could drive kapellasite either into a weak cuboc-2 order or towards a quantum PM phase. As tentatively observed in current experiments, this finding is consistent with the compound exhibiting strong magnetic frustration and significant ordering fluctuation tendencies towards cuboc-2 at the same time. Our PF-FRG calculations show that this kapellasite location yields a critical flow, that is, neither shows a robust and smooth RG flow down to $\Lambda = 0$ that would point at quantum PM nor exhibits a clear signature of an order-induced breakdown.

The location of the linear spin-wave estimate of exchange couplings for haydeecite [26] is marked by the diamond at $(0.77, 0.0, 0.23)$ in Fig. 2. Remarkably, it is likewise located at the border with the PM regime, but now on the FM side. Experiments [26] suggest a very weak FM order below 4.2 K. From our PF-FRG analysis, ferromagnetic order is weak but unambiguous, and the magnetic fluctuations clearly show FM signatures: a dominant peak at Γ and subdominant peaks at M_e [see Fig. 4(e)].

To summarize, the reported exchange parameters [26, 38] place KL and HD on opposite sides of the (arguably most interesting) paramagnetic region. Moreover, it seems like these two compounds, accidentally, are both at or very close to a borderline between two phases. While making them especially intriguing, it also considerably complicates their study. It is therefore highly desirable to be able to modify the same compounds continuously, in order to “traverse” the phase diagram. In principle, there are several ways to do so.

One option is alloying Mg and Zn by creating a mixed compound $\text{Mg}_x\text{Zn}_{1-x}\text{Cu}_3(\text{OH})_6\text{Cl}_2$ as suggested in Ref. [26]. However, while this proposal creates a system with *average* exchange couplings intermediate between those in KL and HD, in reality it will have random bonds with exchange constants similar to those either in KL or HD and is more likely to freeze into a spin glass state rather than to develop a spin-liquid phase. Besides, chemical substitution of Zn by Mg naturally affects J_d , but the effect on J_1 is harder to predict.

These considerations lead us to propose alternative options without introducing additional disorder. For that, we need first to exercise some caution when using the experimental numbers. Indeed, Refs. [26, 38] are complementary in terms of methodology used to extract the exchange coupling constants; Ref. [38] relies on magnetometry/calorimetry while Ref. [26] does a spin-wave analysis. In both cases, and especially in HD, actual samples have considerable excess of Zn or Mg, substituting for Cu. Each missing Cu creates four incompletely frustrated spins, which may alter the results compared to the stoichiometric compound. While the reported parameters for HD are consistent with a FM ground state, the experimental data [26] looks more complicated than that. Indeed, the ordered moment from neutron scat-

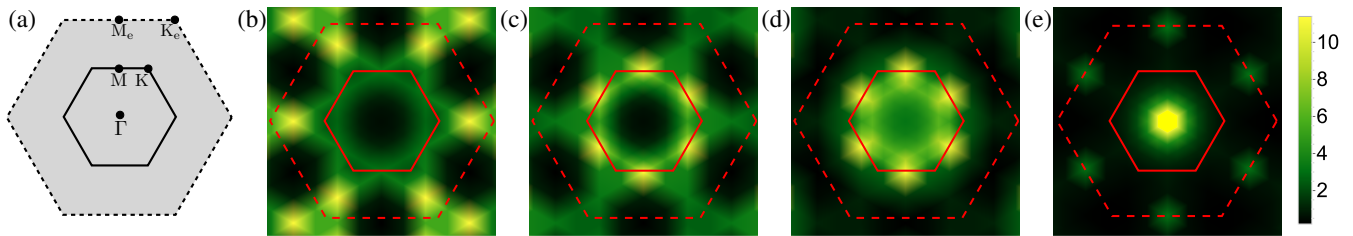


FIG. 4. (a) The first (solid line) and extended (dashed line) Brillouin zones of the kagome lattice. (b)–(e) Representative spin susceptibility profiles obtained in PF-FRG for different regimes of the quantum phase diagram in Fig. 2: (b) cuboc-1, (c) cuboc-2, (d) paramagnetic (PM), (e) ferromagnetic (FM).

tering was estimated to be $\lesssim 0.2\mu_B$ [26], while the saturation moment from magnetization was 0.83 [26] or $1.0\mu_B$ [25], and the spontaneous ordered moment is $0.02\mu_B$ [24] or less [25]. The Curie-Weiss effective moment is $1.83\mu_B$ [24], consistent with an ordered moment greater than $1\mu_B$. A 40 times difference between the saturation and spontaneous magnetization is highly unusual, and so is the discrepancy between spontaneous and neutron-measured moments. While this has been vaguely ascribed to frustration [26], the “frustration parameter”, usually defined as the ratio of the mean field T_{CW} and frustration-suppressed T_N is in fact less than one here. The magnetic susceptibility starts growing with cooling below 5 K, but does not diverge at the putative $T_C = 4.2$ K, and instead starts flattening out below 4 K. Overall, the magnetic behavior described in Ref. [26] is more typical for canted antiferromagnets than for ferromagnets. On the other hand, an independent study [25] found much larger magnetic moment and stronger ferromagnetic behavior.

Given the experimental situation, we decided to address the question theoretically by performing DFT+ U calculations (see Supplemental Material). We used the FPLO program with $U = 6 - 8$ eV, using the fully-localized double counting scheme, orthogonal projection of $3d$ density, and gradient corrections in the DFT functional, and we found that, in agreement with previous observations [32], this setup gives the closest agreement with the experiment for KL. As discussed in detail in the Supplemental Material, the exchange coupling constants in these materials are not only small, but they also depend on the technical details of the setup (we remind the reader that while DFT is a first principles method, DFT+ U is not), which accounts, for instance, for the difference between Refs. [32] and [55]. On the other hand, the trends in the dependence of the exchange parameters on the geometry and chemistry in these compounds are quite robust, and therefore such calculations can be used as a guidance for modifying existing materials in order to steer them toward one or another magnetic phase.

With this setup, using reported crystal structures (and optimized positions of hydrogen, since these are not known experimentally) we obtained for KL $(J_1, J_2, J_d) = (-12.5, -0.55, 16.1)$ K, corresponding to $(0.43, 0.02, 0.55)$

. This is rather close to $(-12, -4, 15.6)$ K [38], albeit a bit deeper in the cuboc-2 phase. For HD we find $(-21.2, 0.57, 12.8)$ K, or $(0.61, 0.02, 0.37)$, placing it in the PM regime (see inset in Fig. 2). By comparing calculations for the same structure, but substituting Zn for Mg, or for the same composition but different structure, we found, not surprisingly, that J_1 is predominantly (80–90%) controlled by the structure and J_d by the bridging element. The smaller Cu-O-Cu angle in HD of 104.98°

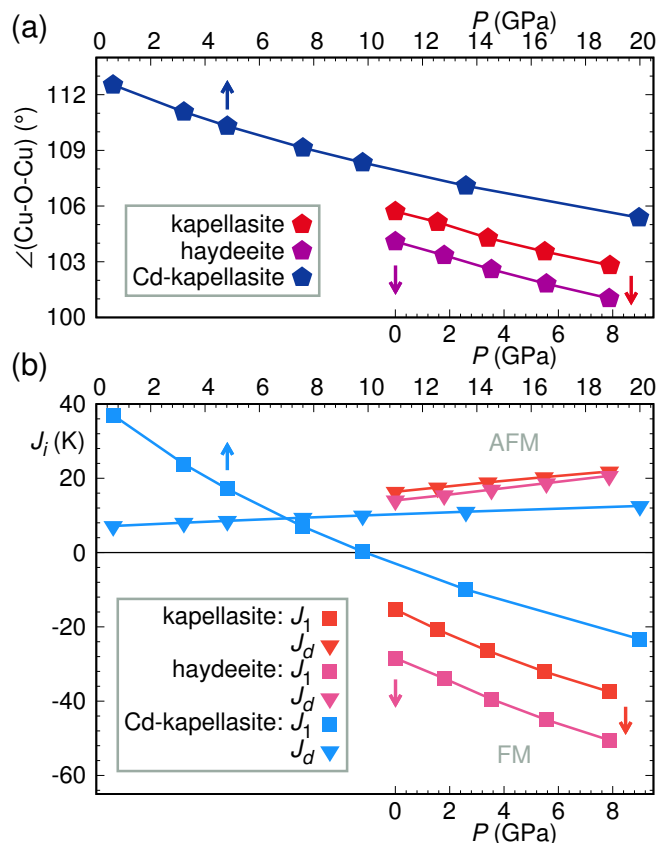


FIG. 5. (a) Predicted evolution of Cu-O-Cu angles as a function of pressure for kapellasite, haydeeite, and the hypothetical Cd-kapellasite. (b) Pressure induced changes in the two dominant exchange coupling parameters J_1 and J_d for the three compounds.

vs 105.84° in KL results in a larger value for J_1 , while the additional hopping path *via* semicore Zn $3d$ states provides a larger J_d . The principal discrepancy with the experimental values appears to be the overestimation of J_d in HD. Regardless of whether this is an experimental problem (*e.g.*, imperfect samples) or theoretical (*e.g.*, overestimation of Mg-O $sp\sigma$ hopping), the trends in the dependence of the exchange parameters with respect to both structural and chemical changes are well reproduced. Having identified the origin of the behavior of J_1 and J_d , we propose two recipes for sampling the phase diagram.

The first option is to apply pressure, keeping the chemical compositions. To investigate this avenue, we have calculated the structures of KL and HD at experimental volumes and at compressions up to 12% (Fig. 5). These compressions correspond to pressures of ≈ 7.9 GPa for both KL and HD, which is experimentally accessible. In both cases, the Cu-O-Cu angle decreases systematically, and J_1 increases by up to 140% (KL) and 80% (HD), as shown in Fig. 5. Thus, by applying pressure we should be able to drive KL into the PM regime, and even approach the boundary with the FM phase, while applying pressure to HD will drive it deeper into the FM regime.

The second option combines both structural and chemical changes. One can preserve homogeneity by substituting Zn in KL with Cd. Due to the larger ionic radius, this substitution may be difficult to realize and might require high-pressure synthesis. Indeed, our calculations show that while such a compound would be locally stable, the

Cu-Cd plane would be considerably expanded and the Cu-OH-Cu angle would flatten to 112° – 113° , which renders J_1 antiferromagnetic [37]. This compound, however, would also be highly compressible and would return to a structure similar to KL at a pressure of about 20 GPa. One expects that J_1 should already be ferromagnetic at this pressure, while at the same time, we note that since the $5d$ level in Cd lies considerably lower compared to the $4d$ level in Zn, the J_d is expected to reduce. Both conjectures are confirmed by our calculations. Indeed, at $P = 20$ GPa the representative point in the phase diagram appears close to HD at $P = 0$, while at $P = 13.6$ GPa it is close to KL at $P = 0$ (Fig. 2). Thus, synthesizing $\text{CdCu}_3(\text{OH})_6\text{Cl}_2$ and applying external pressure provides us a vehicle to traverse a vast extent of the phase diagram encompassing a large range of J_d , especially deep into the paramagnetic phase.

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Paramagnetism in the kagome compounds (Zn,Mg,Cd)Cu₃(OH)₆Cl₂

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I. DENSITY FUNCTIONAL THEORY CALCULATIONS

A. Prediction of high pressure structures

We predict high pressure structures using the Vienna ab initio simulation package (VASP) implementation [1, 2] of DFT within the generalized gradient approximation (GGA) [3]. We base our calculations on the structures of Krause *et al.* [4] for kapellasite, and of Malcherek *et al.* [5] for haydeeite. We obtain a $P = 0$ GPa relaxed structure by fixing the experimental volume and relaxing all lattice and internal structural parameters. The DFT calculated pressure at this volume, due to the well known underbinding of the GGA exchange correlation functional, is $P_{\text{offset}} = 1.54$ GPa for kapellasite and $P_{\text{offset}} = 0.93$ GPa for haydeeite. We then proceed to reduce the volume in steps of 3%, relaxing all lattice and internal structural parameters. The physical pressure values are obtained by subtracting P_{offset} from the calculated pressure at each reduced volume.

B. Determination of Hamiltonian parameters

The calculations were performed with the full potential local orbital (FPLO) basis set [6] and the GGA functional [3]. Total energies for sets of different spin configurations were calculated with GGA+U using the atomic limit double counting correction [7], and we employed orthogonal projection of the Cu 3d densities. We would like to note that the results are very sensitive to (i) the choice of exchange correlation functional (LDA or GGA), (ii) the double counting correction in the LDA+U approach, and (iii) the choice of projection scheme for the Cu 3d orbitals in the FPLO basis. In Ref. [8] the calculations were performed with the LDA exchange correlation functional and the around mean field double counting correction was chosen for the LDA+U functional. With this setup the ferromagnetic contribution in J_1 for kapellasite is strongly suppressed, however, with the same setup the results of our two groups agree [9].

We fix $J_H = 1$ eV and vary U . Tables I and II show the result of fitting to 9 spin configurations of an orthorhombic $\sqrt{2} \times \sqrt{2} \times 1$ supercell with $P1$ space group, containing 6 inequivalent copper ions. A $6 \times 6 \times 6$ k mesh was used after confirming that an $8 \times 8 \times 8$ k mesh yields identical results. The error given in Tables I and II reflects the statistical error of fitting 9 energies to 5 unknowns (reference energy and four exchange couplings). We have also performed calculations with $2 \times 2 \times 1$ supercells of kapellasite and haydeeite yielding 46 distinct total energies from 12 inequivalent copper ions. The two approaches proved to be precisely equivalent so that the computationally less demanding smaller supercell was chosen for the final computations. Very small fitting errors indicate that the Cu²⁺ spins are well localized and their interaction is very well described by the chosen Heisenberg model.

The two significant exchange couplings, J_1 and J_d , obtained in this way, are shown visually in Fig. 1 for kapellasite and in Fig. 2 for haydeeite. Evolution of couplings with pressure, and with onsite interaction U is very smooth. The ferromagnetic nearest neighbour coupling in the kagome plane is larger in haydeeite compared to kapellasite while the antiferromagnetic exchange J_d coupling Cu²⁺ ions across the hexagons of the kagome lattice is slightly larger in kapellasite than in haydeeite. J_1 varies more strongly with pressure than J_d , reflecting its sensitivity to the bond angle. Increasing the onsite interaction U from $U = 6$ eV to $U = 7$ eV and $U = 8$ eV leads to a smooth decrease in absolute value of both exchange couplings. The other two exchange couplings are not shown in the figure; J_2 is very small at ~ 0.5 K and insensitive to pressure, while J_4 is nearly exactly zero within computational error.

TABLE I: Kapellasite exchange couplings. All structures except the one marked “exp.” are predicted as described in the text.

P (GPa)	J_1	J_2	J_4	J_d
GGA+U, $U = 8$ eV, $J_H = 1$ eV				
0 (exp.)	-12.59(3)	-0.55(3)	-0.17(3)	16.16(4)
0	-15.27(2)	-0.55(2)	-0.08(3)	16.40(4)
1.6	-20.78(2)	-0.50(2)	-0.04(3)	17.57(4)
3.4	-26.41(2)	-0.48(2)	0.01(3)	18.87(4)
5.5	-32.02(2)	-0.49(2)	0.04(3)	20.28(4)
7.9	-37.48(2)	-0.53(2)	0.07(2)	21.80(3)
GGA+U, $U = 7$ eV, $J_H = 1$ eV				
0	-16.65(4)	-0.56(4)	-0.02(4)	19.89(6)
1.6	-22.94(4)	-0.50(4)	0.03(4)	21.33(6)
3.4	-29.37(3)	-0.48(3)	0.09(4)	22.95(5)
5.5	-35.79(3)	-0.48(3)	0.13(4)	24.71(5)
7.9	-42.06(3)	-0.52(3)	0.16(4)	26.58(5)
GGA+U, $U = 6$ eV, $J_H = 1$ eV				
0	-18.05(6)	-0.53(6)	0.10(7)	24.00(9)
1.6	-25.22(6)	-0.46(6)	0.17(6)	25.80(9)
3.4	-32.57(5)	-0.42(5)	0.23(6)	27.81(9)
5.5	-39.93(5)	-0.43(5)	0.28(6)	29.98(8)
7.9	-47.13(6)	-0.46(6)	0.28(7)	32.33(10)

TABLE II: Haydeeite exchange couplings. All structures except the one marked “exp.” are predicted as described in the text.

P (GPa)	J_1	J_2	J_4	J_d
GGA+U, $U = 8$ eV, $J_H = 1$ eV				
0 (exp.)	-21.27(2)	-0.57(2)	-0.13(3)	12.72(4)
0	-28.39(2)	-0.55(2)	-0.02(3)	14.06(4)
1.8	-33.94(2)	-0.51(2)	0.03(2)	15.42(3)
3.5	-39.50(2)	-0.50(2)	0.08(2)	16.97(3)
5.6	-45.07(2)	-0.51(2)	0.12(2)	18.71(3)
7.9	-50.50(3)	-0.52(3)	0.08(3)	20.65(4)
GGA+U, $U = 7$ eV, $J_H = 1$ eV				
0	-31.23(3)	-0.57(3)	0.05(4)	16.60(5)
1.8	-37.57(3)	-0.53(3)	0.11(3)	18.26(5)
3.5	-43.92(3)	-0.52(3)	0.16(3)	20.14(4)
5.6	-50.30(3)	-0.53(3)	0.21(3)	22.25(4)
7.9	-56.56(2)	-0.57(2)	0.25(3)	24.59(4)
GGA+U, $U = 6$ eV, $J_H = 1$ eV				
0	-34.15(5)	-0.57(5)	0.17(5)	19.52(7)
1.8	-41.38(6)	-0.52(6)	0.25(7)	21.52(9)
3.5	-48.64(4)	-0.50(4)	0.31(5)	23.81(6)
5.6	-55.94(4)	-0.52(4)	0.36(4)	26.36(6)
7.9	-63.13(4)	-0.57(4)	0.40(4)	29.18(6)

II. ORIGIN OF EXCHANGE PARAMETERS

Cu^{2+} is usually a textbook case for the Hubbard model. Cu electrons are strongly localized with hopping $t \ll U$, and the standard superexchange perturbation theory works very well. Most experimental papers interpret haydeeite (HD) and kapellasite (KL) in terms of this theory, specifically, in terms of the Goodenough-Kanamori-Anderson rules, which stipulate that at the bond angle $\phi = 90^\circ$, the superexchange process Cu-O-Cu is completely suppressed and the only remaining interaction is ferromagnetic and generated by the Hund’s rule coupling on oxygen (the fact

TABLE III: Hypothetical Cd-kapellasite exchange couplings. All structures are predicted as described in the text.

P (GPa)	J_1	J_2	J_4	J_d
GGA+U, $U = 8$ eV, $J_H = 1$ eV				
0.6	36.96(5)	-0.10(3)	-0.46(5)	7.15(7)
3.2	23.82(4)	-0.09(2)	-0.33(5)	8.04(6)
4.8	17.13(4)	-0.08(2)	-0.27(4)	8.55(6)
7.6	6.98(3)	-0.08(2)	-0.20(4)	9.38(5)
9.8	0.25(3)	-0.08(2)	-0.15(4)	9.99(5)
13.6	-9.95(3)	-0.08(2)	-0.11(3)	11.00(5)
20	-23.31(3)	-0.09(2)	-0.11(3)	12.54(4)
GGA+U, $U = 7$ eV, $J_H = 1$ eV				
0.6	42.37(7)	-0.10(4)	-0.46(8)	8.77(11)
3.2	27.39(6)	-0.08(3)	-0.31(7)	9.90(9)
4.8	19.74(5)	-0.08(3)	-0.25(6)	10.53(9)
7.6	8.10(5)	-0.07(3)	-0.15(6)	11.58(8)
9.8	0.37(5)	-0.07(3)	-0.11(5)	12.34(7)
13.6	-11.39(4)	-0.08(2)	-0.06(5)	13.62(7)
20	-26.83(4)	-0.09(2)	-0.08(4)	15.53(6)
GGA+U, $U = 7$ eV, $J_H = 1$ eV				
0.6	48.46(10)	-0.09(5)	-0.41(11)	10.69(16)
3.2	31.40(9)	-0.074(5)	-0.23(10)	12.13(14)
4.8	22.67(7)	-0.07(4)	-0.13(8)	12.93(11)
9.8	0.42(7)	-0.06(4)	0.00(8)	15.20(11)
13.6	-13.14(7)	-0.07(4)	0.05(8)	16.78(11)
20	-31.05(6)	-0.08(3)	-0.01(6)	19.14(10)

that in these materials the angle is actually rather far from 90° is usually swept under the rug). This coupling is proportional to $t_{pd}^4 J_O / \Delta_{pd}^4$ (where t_{pd} is the hopping and Δ_{pd} is the charge transfer energy). Note that the usual antiferromagnetic superexchange is proportional to $t_{pd}^4 / \Delta_{pd}^2 U$, which is larger by a factor $\Delta_{pd}^2 / U J_O$ for $\Delta_{pd}^2 / U J_O > 1$. Thus, near-cancellation of the assisted hopping via different O orbitals is a necessary requirement for ferromagnetic superexchange. There are two ways to look at this situation. One can assume a coordinate system where \tilde{x} and \tilde{y} are along the Cu-O and O-Cu bonds in the trimer, in which case the “left” Cu electron can only hop to the O $p_{\tilde{x}}$ orbital, and the “right” one only to the O $p_{\tilde{y}}$ one. Since these are mutually orthogonal, there is no net assisted Cu-Cu hopping. Another way is to assume the system where x is along the Cu-Cu bond and y is perpendicular to it. In this case, there is assisted hopping *via* each of the orbitals, but the two contributions are equal in magnitude and opposite in sign, so they cancel out. As the angle becomes larger than 90° , the Cu- p_x -Cu hopping becomes larger than Cu- p_y -Cu one and cancellation becomes incomplete. In typical transition metal oxides if the angle is larger than $\approx 95^\circ$ this effect is significant.

However, our calculations as well as the experimental results, indicate that the crossover from the antiferromagnetic to ferromagnetic J_1 in these materials occurs at the bond angle of 108° – 109° . Moreover, as discussed in Ref. [8] and confirmed in our calculations, shifting H away from O makes the interaction at a given angle less ferromagnetic, suggesting an important role of H orbitals.

In the literature one can find two seemingly contradicting predictions regarding adding to the standard 4-orbitals (two Cu d and two O d) another bridging orbital. On one hand, Geertsma and Khomskii considered a $\phi = 90^\circ$ case [10] when O p orbitals are bound to another orbital, such as in our case hydrogen, in their case germanium, or, in the simplest case with the same symmetry, to O s . In that case the p_y orbital couples with H, but p_x does not. As a result, the cancellation described above is incomplete and there is some residual antiferromagnetic superexchange, which can either overcome the weak ferromagnetic coupling, as in Ref. [10], or considerably reduce it. Furthermore, this theory predicts that at $\phi = 90^\circ$ moving H toward O must enhance the tendency to antiferromagnetism.

On the other hand, Hay *et al.* [11] considered a similar problem (using O s and the additional bridging orbital, which is not important) as a function of ϕ and concluded that the full cancellation between all Cu-O-Cu hopping processes occurs not at $\phi = 90^\circ$, but at a larger ϕ_c [for the $\text{Cu}_2(\text{OH})_2\text{Cl}_4^{2-}$ radical they found numerically $\phi_c \approx 108^\circ$, but the actual value must be system-dependent, and, in particular, may be smaller for our materials]. This is not in contradiction with Ref. [10]; indeed Hay *et al.* explicitly emphasize that it is only at ϕ_c that the antiferromagnetic exchange completely cancels out; for both larger *and* smaller angles there is residual antiferromagnetic coupling, in

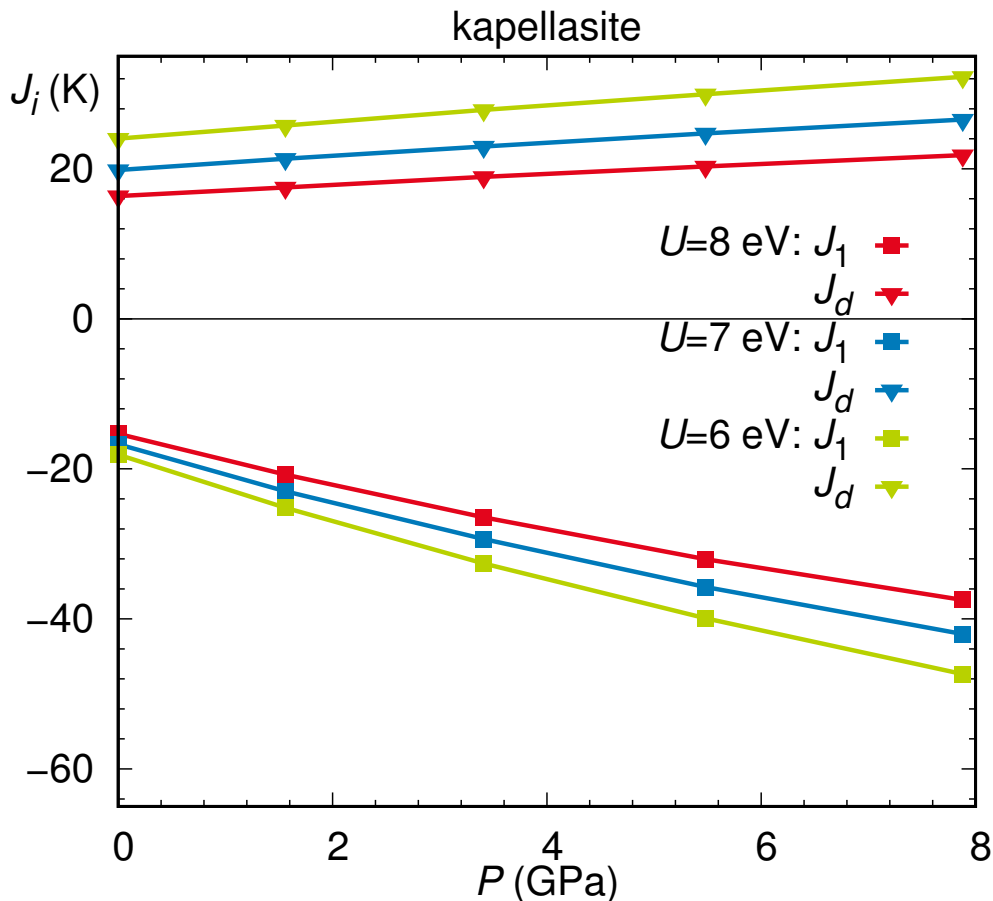


FIG. 1: Exchange couplings of kapellasite. The two significant Heisenberg Hamiltonian parameters for kapellasite are given as function of applied pressure and for three different values of the onsite interaction strength U .

accord with the Geertsma and Khomskii theory. However, at $\phi = 90^\circ$ the Cu- p_y -Cu hopping is the stronger the shorter the O-H bond is, and to restore the balance one needs to enhance Cu- p_x -Cu hopping by flattening ϕ . So, at least qualitatively (quantitative analysis is underway and will be published elsewhere), Hay *et al.* theory seems to explain why the large bond angles in HD and KL nonetheless generate net ferromagnetic coupling.

Yet another paradox manifests itself in comparing the J_d values for HD and KL. It is generally believed that this exchange is provided by hopping from Cu (*via* O) to Zn or Mg. However, as discussed below, this may be not the case. Indeed, Cu-(Zn,Mg) hopping can proceed either to the s orbitals of Zn or Mg, or to d orbitals of Zn. The $5s$ orbitals of Zn are considerably more diffuse than the $3s$ orbitals of Mg, and much closer to the Fermi level. Since J_d in the simple Hubbard theory should be proportional to the square of the overlap integrals and inversely proportional to the energy separation, we estimate that J_d in HD should be nearly an order of magnitude smaller than in KL, even without taking into account an additional hopping channel *via* $3d$ orbitals of Zn. In the experiment, as well as in the calculations, the difference is less than a factor of two. A closer look, however, shows that this naive reasoning doesn't apply here. Indeed, an inspection of the crystal structure shows that the Cu-O₂-(Zn,Mg)-O₂-Cu multimer is planar, as shown in Fig. 4. The bond angle is about 100° considerably closer to 90° than the Cu-O-Cu angle. Had it been exactly 90° , the hopping from the $x^2 - y^2$ Cu orbital, where the actual hole resides, to the (Zn,Mg) s orbital would be zero by parity (see Fig. 4(b)). For 100° , it should be strongly suppressed. For Zn, there is an additional option of hopping via $3d$ orbitals. However, as Fig. 4(c) shows, $dp\sigma - pd\sigma$ hopping is again forbidden by symmetry. The $dp\sigma - pd\pi$ hopping is allowed, but the two oxygens are antiphase and cancel each other (see Fig. 4(d)).

Keeping in mind the H effect, one may conjecture that 100° may be rather close to full cancellation. Our numerical results provide for the effective (after integrating out O) Cu(d)-Zn(d) hopping a value of about $\tau \approx 40$ meV, which is nearly an order of magnitude smaller than for the Cu-Cu one. Thus, we conclude that the mechanism providing for sizeable J_d in HD and KL, as compared to herbertsmithite, is more complex than it has been anticipated so

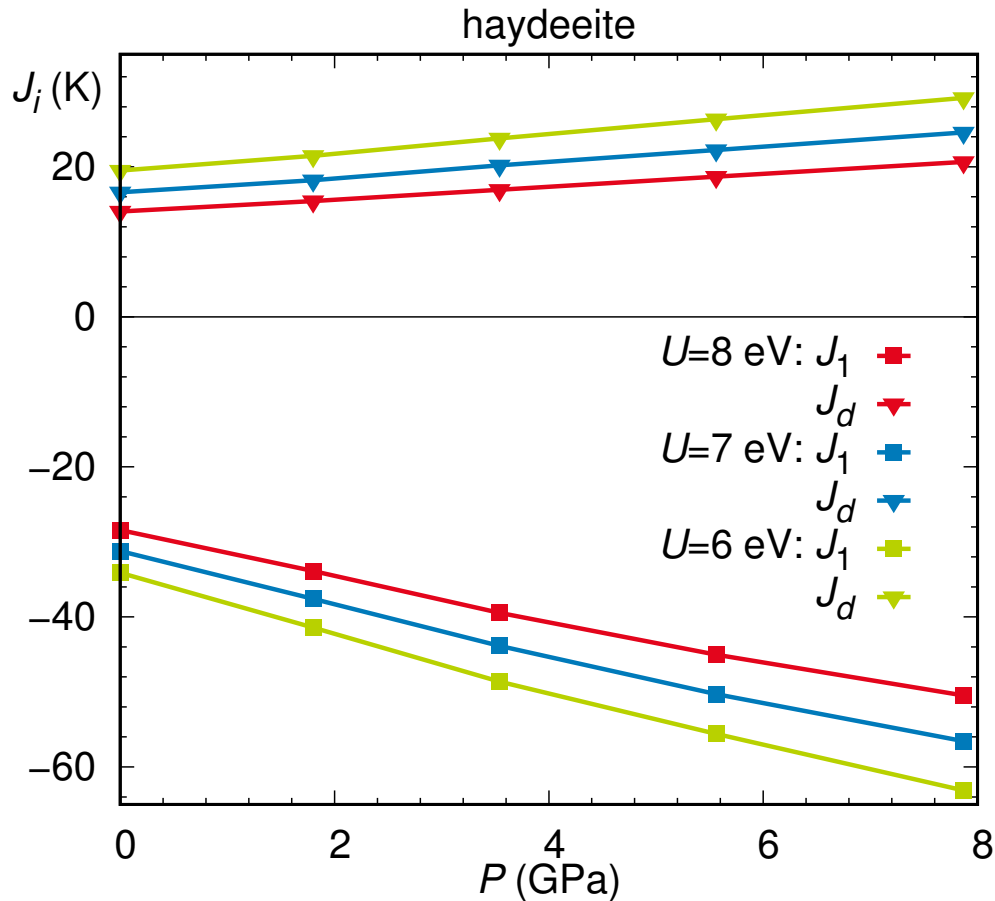


FIG. 2: **Exchange couplings of haydeeite.** The two significant Heisenberg Hamiltonian parameters for haydeeite are given as function of applied pressure and for three different values of the onsite interaction strength U .

far, and does not reduce to just providing a hopping path *via* a central atom. This makes it very difficult, if at all possible, to anticipate the trends in the exchange parameters after material modifications and makes *ab initio* calculations indispensable. As a last remark, it should be mentioned that for a systematic investigation of the effects of, for instance, substitution of the central atom, experimental estimates are not necessarily superior to the theoretical estimates, due to the problems related to site disorder in the samples.

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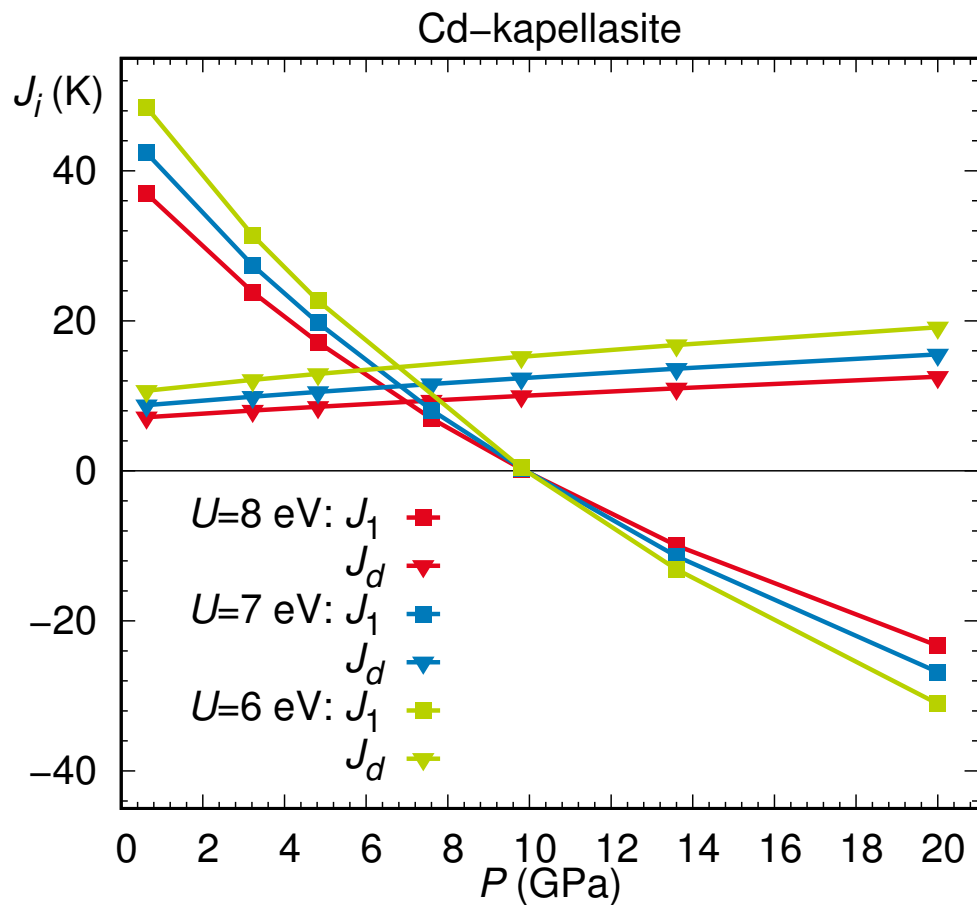


FIG. 3: Exchange couplings of hypothetical Cd-kapellasite. The two significant Heisenberg Hamiltonian parameters for Cd-kapellasite are given as function of applied pressure and for three different values of the onsite interaction strength U .

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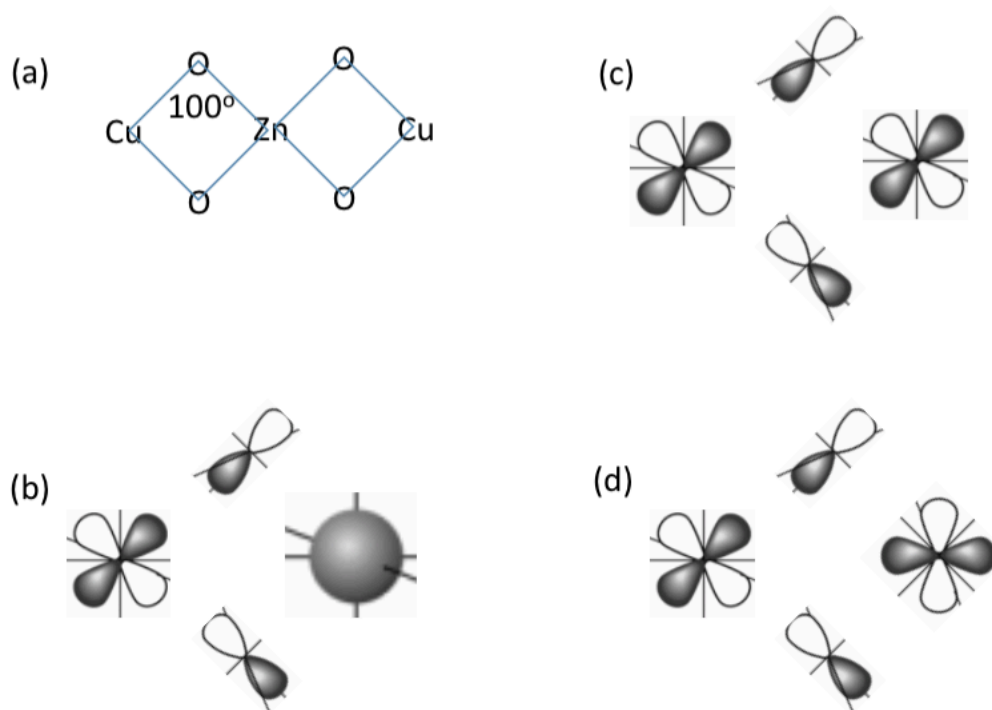


FIG. 4: Orbitals and hopping pathways.