

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

–Supplemental Material–

Yasir Iqbal,¹ Harald O. Jeschke,² Johannes Reuther,^{3,4} Roser Valentí,² I. I. Mazin,⁵ Martin Greiter,¹ and Ronny Thomale¹

¹*Institute for Theoretical Physics and Astrophysics,
Julius-Maximilian's University of Würzburg, Am Hubland, D-97074 Würzburg, Germany*

²*Institut für Theoretische Physik, Goethe-Universität Frankfurt,
Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany*

³*Dahlem Center for Complex Quantum Systems and Fachbereich Physik,
Free University of Berlin, D-14195 Berlin, Germany*

⁴*Helmholtz-Zentrum Berlin for Materials and Energy, D-14109 Berlin, Germany*

⁵*Center for Computational Materials Science, Naval Research Laboratory, Code 6390,
4555 Overlook Ave, SW, Washington, DC 20375, United States of America*

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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)

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)

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 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 $108^\circ - 109^\circ$. 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,

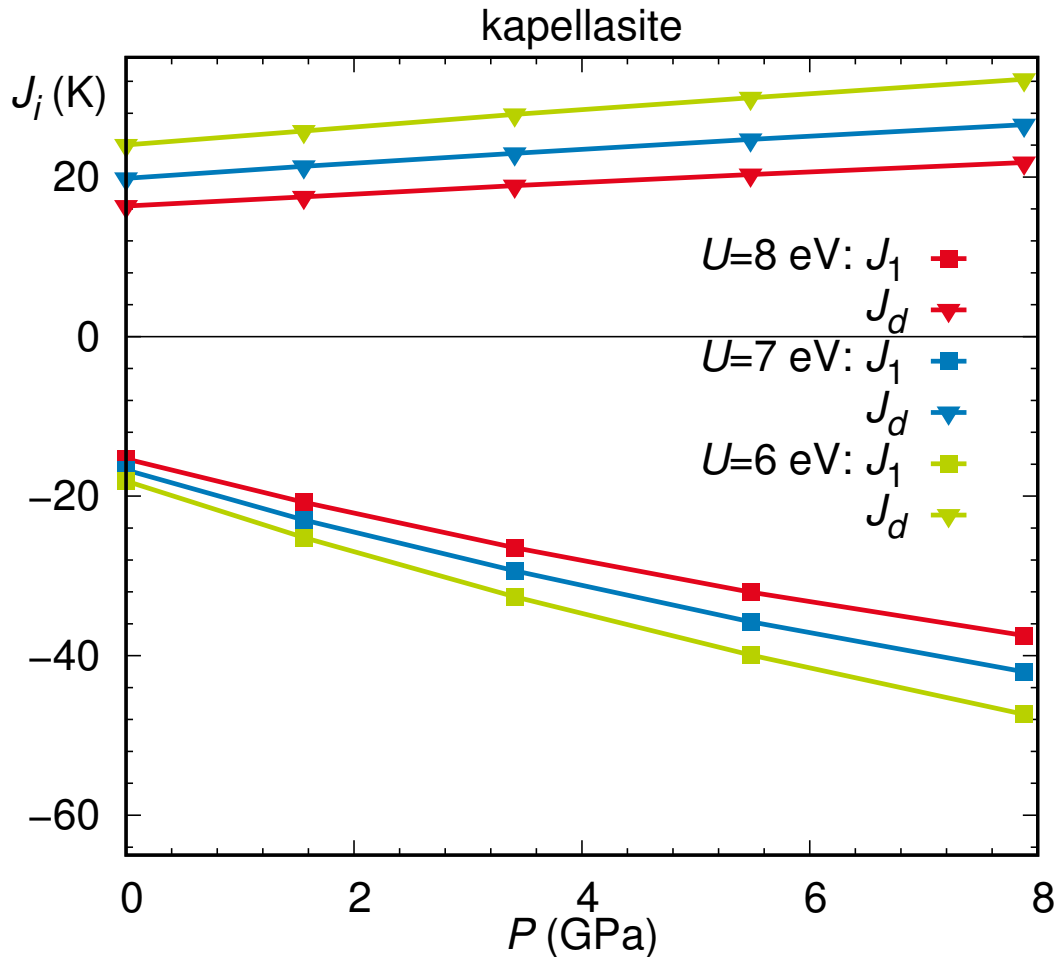


FIG. 1: Exchange couplings of kapellasite. The two significant Heisenberg Hamiltonian parameters for kapellasite are given as function of applied pressure and for three different values of the onsite interaction strength U .

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 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

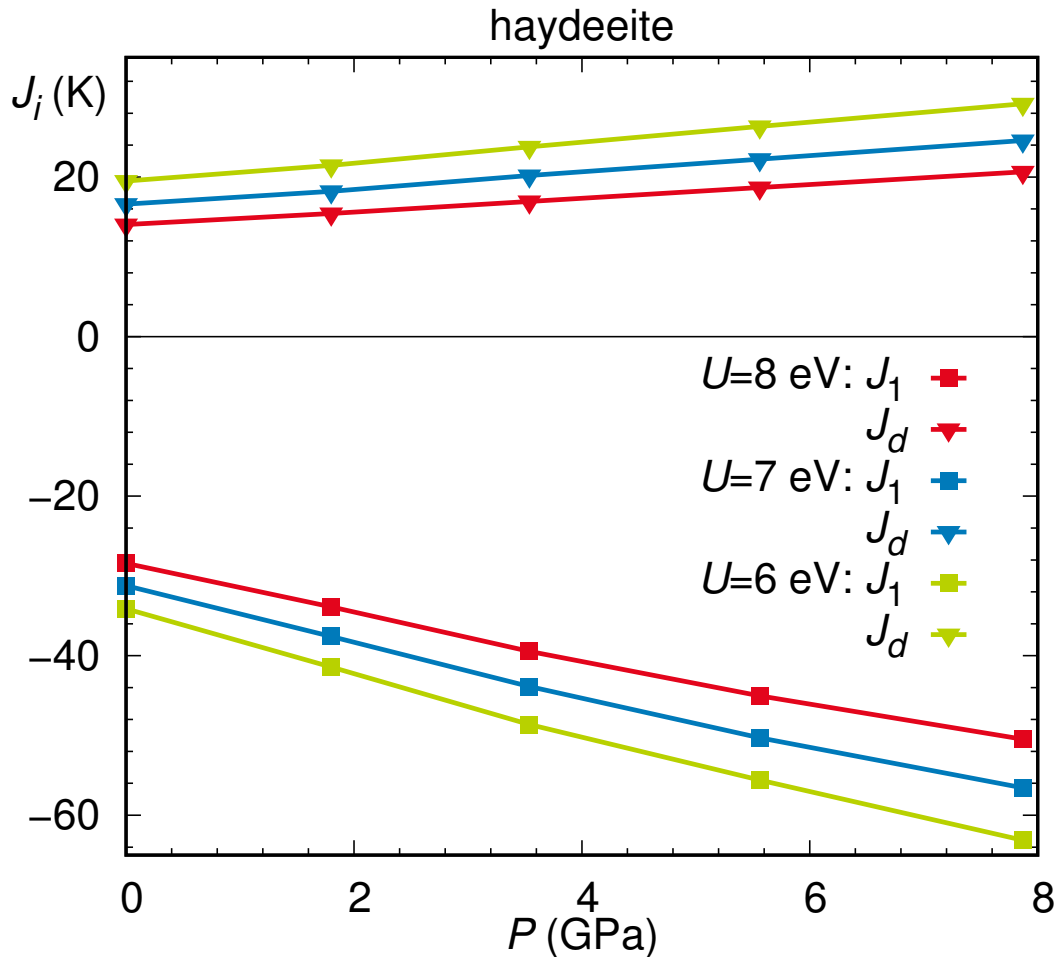


FIG. 2: Exchange couplings of haydeeite. The two significant Heisenberg Hamiltonian parameters for haydeeite are given as function of applied pressure and for three different values of the onsite interaction strength U .

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 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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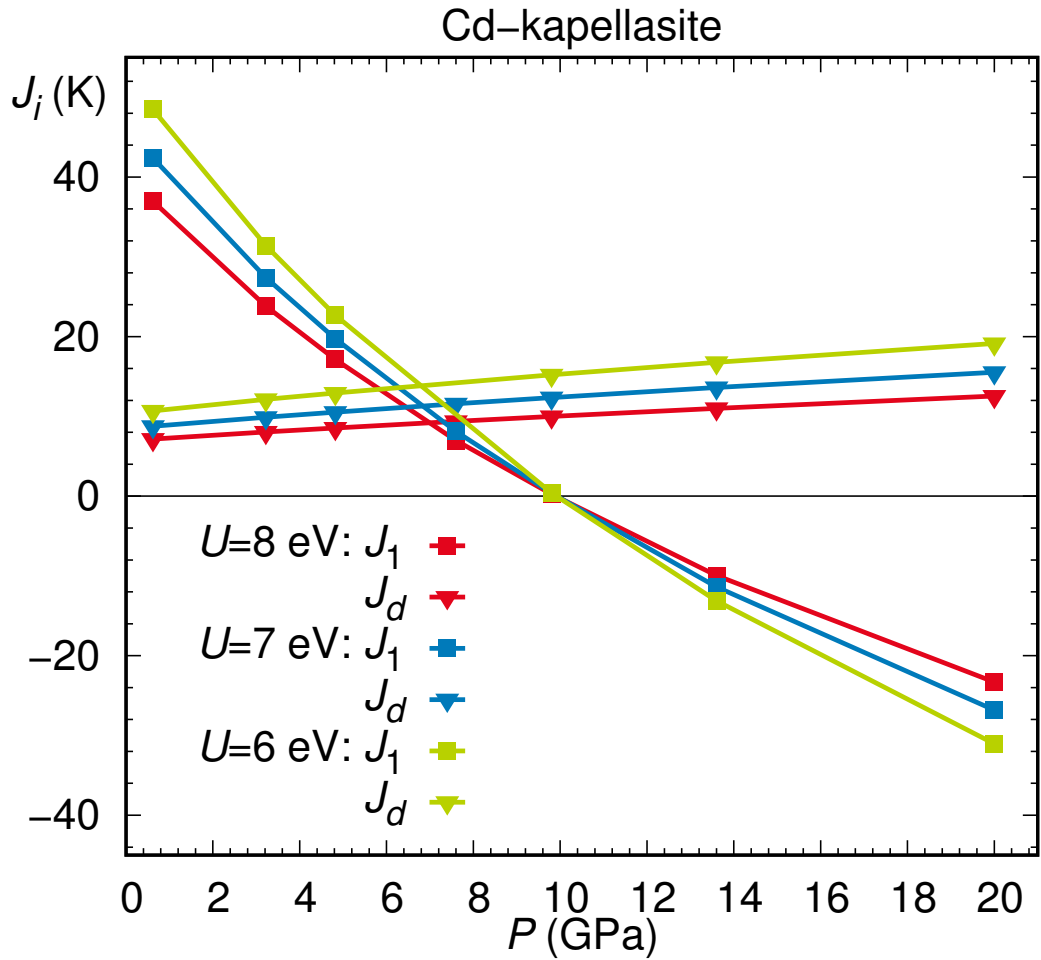


FIG. 3: Exchange couplings of hypothetical Cd-kapellasite. The two significant Heisenberg Hamiltonian parameters for Cd-kapellasite are given as function of applied pressure and for three different values of the onsite interaction strength U .

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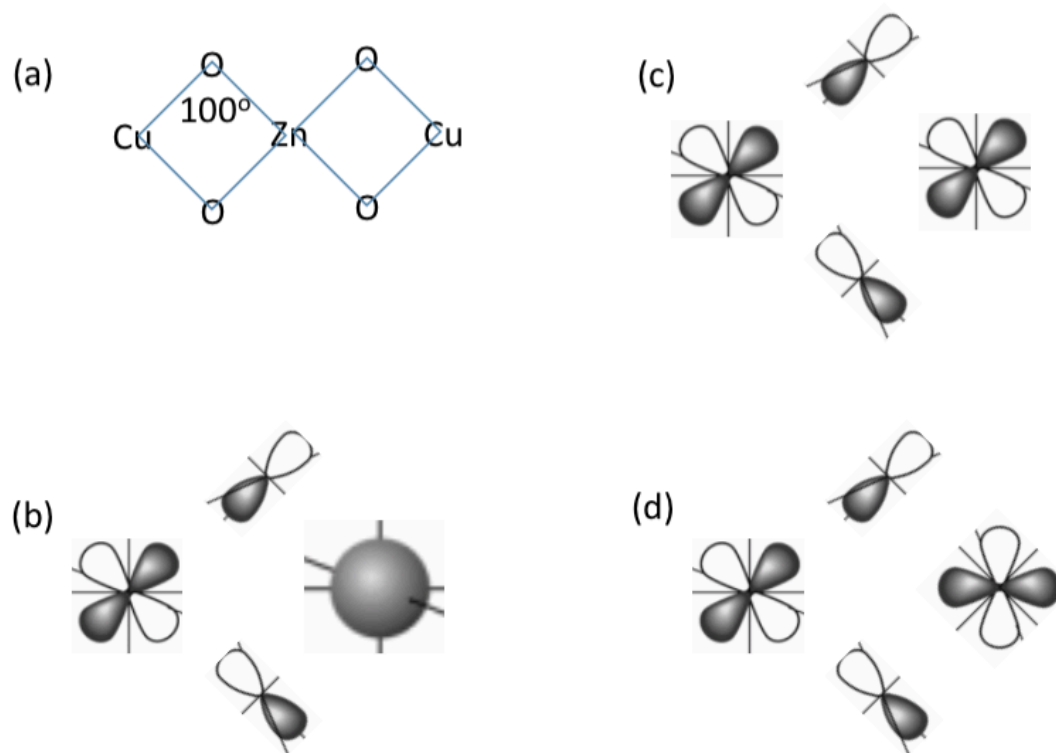


FIG. 4: Orbitals and hopping pathways.