Intrinsic peculiarities of real material realizations of a spin-1/2 kagomé lattice

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Abstract. Spin-1/2 magnets with kagomé geometry, being for years a generic object of theoretical investigations, have few real material realizations. Recently, a DFT-based microscopic model for two such materials, kapellasite $Cu_3Zn(OH)_6Cl_2$ and haydeeite $Cu_3Mg(OH)_6Cl_2$, was presented [Janson O, Richter J and Rosner H *arxiv:0806.1592*]. Here, we focus on the intrinsic properties of real spin-1/2 kagomé materials having influence on the magnetic ground state and the low-temperature excitations. We find that the values of exchange integrals are strongly dependent on O—H distance inside the hydroxyl groups, present in most spin-1/2 kagomé compounds up to date. Besides the original kagomé model, considering only the nearest neighbour exchange, we emphasize the crucial role of the exchange along the diagonals of the kagomé lattice.

Two-dimensional (2D) magnets with a kagomé lattice arrangement of magnetic ions (Figure 1) are geometrically frustrated due to a triangular-like arrangement of nearest neighbours (NN) leading to an unusual highly degenerate classical ground state (GS) [1]. Strong quantum fluctuations arising from spin-1/2 ions can lift the classical degeneracy and drive the system into a magnetically disordered quantum paramagnetic state, which might be applied for future quantum computational applications [2]. Nonetheless, in real materials couplings to further neighbours [3, 4] and between the kagomé layers [5] are always present and influence the GS and the thermodynamics.

In a recent paper [4] we have performed DFT calculations for two new natural isostructural materials with spin-1/2 kagomé lattice — kapellasite $Cu_3Zn(OH)_6Cl_2$ [6] and haydeeite $Cu_3Mg(OH)_6Cl_2$ [7, 8]. The local density approximation (LDA) yields a metallic solution (left panel in Figure 2) in contrast to the experimentally observed insulating behaviour due to underestimation of strong on-site correlations for the Cu^{2+} sites. To account for this deficit, we carried out an effective one-band tight-binding (TB) fit of the LDA bands (Figure 2, right panel) and subsequently mapped the resulting transfer integrals t_i to an extended Hubbard model and to a Heisenberg model with $J_i = 4t_i^2/U_{eff}$. This mapping provides an estimate for the antiferromagnetic (AFM) part of the exchange. To obtain the values for the total exchange, consisting of AFM and ferromagnetic contributions, we have performed supercell calculations for various spin arrangements. The correlations were treated in the LSDA+U approximation. We have found that besides the standard kagomé model based on NN interactions (J_1), an additional coupling along diagonals of kagomé hexagons (J_d) is relevant (Figure 1). Since the absolute values of J_1 and J_d change only the overall temperature scale, their ratio $\alpha \equiv J_d/J_1$ is crucial for the GS and low-energy excitations.
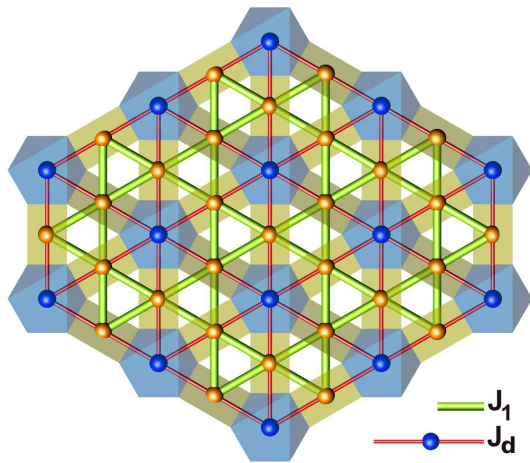
Figure 1. Kagomé layers in the crystal structure of kapellasite (haydeeite). CuO_4 plaquettes are shown in yellow, ZnO_6 (MgO_6) octahedra are shown in blue. The relevant exchange paths are highlighted.
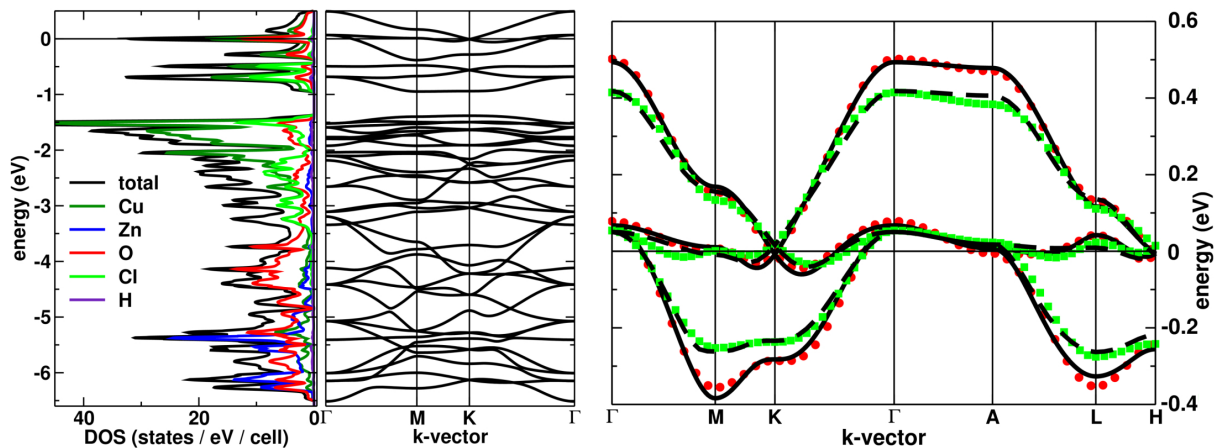

Figure 2. Left panel: total and atom-resolved densities of states of kapellasite $Cu_3Zn(OH)_6Cl_2$ (left) and the corresponding band structure (right). Right panel: band structure of antibonding $dp\sigma$ bands crossing the Fermi level and the effective one-band tight-binding fit for different O—H distances (experimental: 0.78 Å, LDA bands — dashed lines, TB fit — green squares; optimized: 1 Å, LDA bands — solid lines, TB fit — red circles).

One focus of this paper is to emphasize the influence of side groups (which are commonly neglected in model physics) on different exchange paths. A key issue of theoretical investigations of real materials is the construction of a relevant model, which describes experimental data and has predictive power. For cuprates, that are insulators with a $3d^9$ Cu^{2+} configuration, the extension from the initial Heisenberg idea to consider only spin degrees of freedom (Heisenberg model) to a multiband Hubbard model with a separate treatment of Cu $3d$ and O $2p$ orbitals became computationally feasible only recently. On the other hand, the famous Goodenough-Kanamori-Anderson (GKA) rules formulated quite early on an empirical basis provide a simple intuitive picture for the exchange interactions based on geometrical quantities. Due to the simplicity of the GKA rules, they are violated in many cases. A natural way to search for a possible origin of these phenomena is to improve the model by including ligand fields effect. In general, such models are very difficult to evaluate. Even in case of simple systems like $CuGeO_3$ the models are quite complicated and contain many parameters [9].

Here, we present the results of a DFT-based modeling for $Cu_3Zn[Mg](OH)_6Cl_2$. In these compounds, the leading exchange interactions are strongly dependent on the position of H
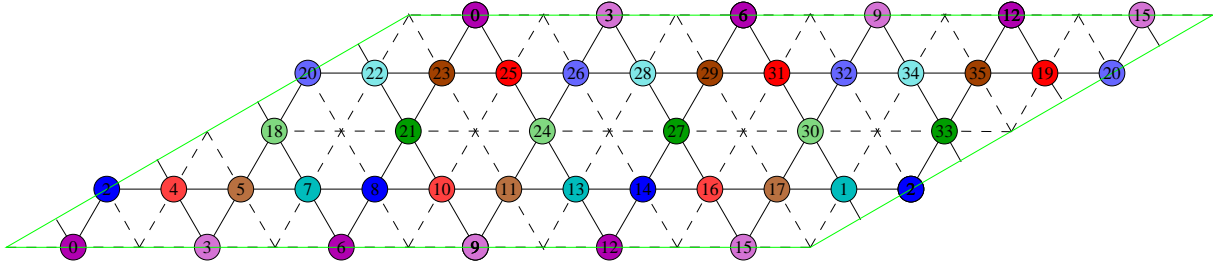
Figure 3. Finite kagomé lattice of $N = 36$ sites. The solid lines represent the NN bonds J_1 and the dashed lines the diagonal bonds J_d. The coloured circles indicate the spin orientations of the twelve-sublattice classical GS relevant for $J_d > 0$. Along the chains formed by diagonal bonds there is an antiparallel (Néel) spin alignment (e.g. the spins at the light and dark green circles). On each triangle formed by NN bonds J_1 (e.g. spins on sites 21, 22, 23) there is a 120° spin arrangement. In addition, two antiparallel (Néel) spin-sublattices are perpendicular to one other group of two Néel-like sublattices, i.e. ● ⊥ ● ; ● ⊥ ● ; ● ⊥ ● .
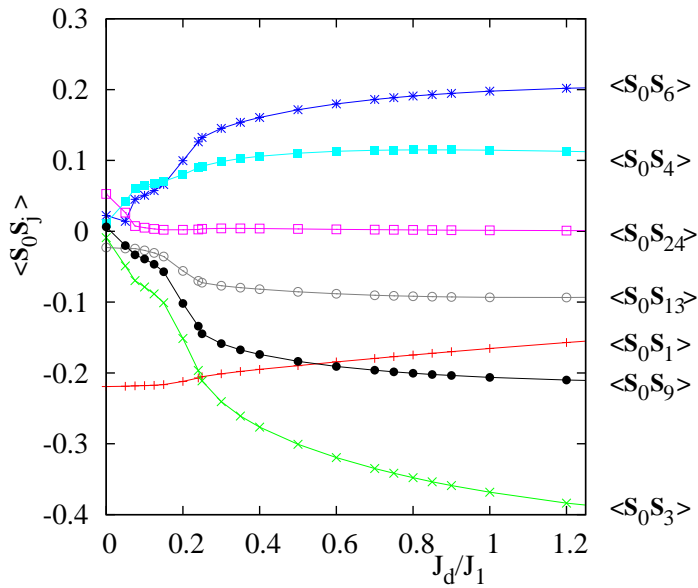

Figure 4. GS spin-spin correlation $\langle \mathbf{S_0 S_j} \rangle$ in dependence on $\alpha = J_d/J_1$ for the finite lattice of $N = 36$ sites shown in Figure 3. The site indices $j = 1, 3, 4, 6, 9, 13, 24$ correspond to those of Figure 3.

atoms — the simplest possible side groups.

For haydeeite, the experimentally defined H position yields an unusually short O—H distance (d) of 0.78 Å (for kapellasite the H position has not been reported). Therefore, in LDA calculations we relaxed the H position which resulted in an optimized $d \approx 1$ Å for both systems. In order to elucidate the influence of d on the exchange integrals, we have studied the range $d = 1.0 \pm 0.3$ Å which covers the experimental errors (that are large due to weak x-ray scattering by H atoms). The details of our calculations are described in [4]. We find that d has a strong influence on the NN exchange J_1, while J_d is almost unaffected. Obviously, this modifies their ratio α and consequently the physical properties. The underlying reason is the shift of oxygen states down in energy caused by the shortening of an O—H bond. In consequence, Cu—O hybridization decreases. Therefore, for a fixed Cu—O geometry, a decreased d reduces the AFM contribution to the total exchange. This is supported by a strongly reduced bandwidth (which is related via $t_i^2 \sim J_i^{AFM}$ to the AFM exchange) for a reduced d (Figure 2, right panel) and fits

well the results of supercell calculations. There, we find a quasi-linear $J_1(d)$ dependence with a positive slope for both compounds. J_1 is 2.5 times larger for $d = 1$ Å than for $d = 0.8$ Å in kapellasite (2.5 meV versus 1 meV), while it changes the sign in haydeeite (0.7 meV versus -0.2 meV).

The next step towards a physically relevant picture of real materials is to evaluate the influence of α onto the GS and the low-lying excitations. Here, we use a J_1-J_d spin-1/2 Heisenberg model on the kagomé lattice (J_1-J_d model). The classical GS of the pure kagomé system ($J_d = 0$) is known to be highly degenerate. The additional diagonal bond J_d reduces this degeneracy drastically and selects non-coplanar classical GS's with twelve magnetic sublattices (see Figure 3) among the huge number of classical GS's existing for $J_d = 0$. For the quantum spin-1/2 model we have calculated the GS by exact diagonalization for the finite lattice shown in Figure 3.

Obviously, the quantum GS spin-spin correlations are drastically affected when including J_d. While for $J_d = 0$ all spin correlations except the NN correlation function $\langle \mathbf{S_0 S_1} \rangle$ are close to zero we find a well pronounced short-range order for $\alpha \gtrsim 0.25$, that corresponds to the classical magnetic structure. For $\alpha \gtrsim 0.55$ the strongest spin correlations are $\langle \mathbf{S_0 S_3} \rangle$, $\langle \mathbf{S_0 S_6} \rangle$, $\langle \mathbf{S_0 S_9} \rangle$, and they belong to the chains formed by J_d bonds. The NN correlation function $\langle \mathbf{S_0 S_1} \rangle$ monotonously decreases with J_d. The correlation function $\langle \mathbf{S_0 S_{24}} \rangle$ belongs to two sites located on sublattices being perpendicular in the classical GS, and it is almost zero for $\alpha \gtrsim 0.55$. This leads to the conclusion that even in the quantum model the GS might have a non-coplanar magnetic structure giving rise to enhanced chiral correlations.

To summarize, we have shown the relevance of the ligand field for the low-energy physics by example of two spin-1/2 cuprates with a kagomé lattice geometry. We found that there are two relevant exchange integrals in both materials. The ratio $\alpha = J_d/J_1$ is strongly dependent on the O—H distance and has a drastic impact on the physical properties: the quantum GS of a corresponding spin-1/2 Heisenberg J_1-J_d antiferromagnet on the kagomé lattice exhibits strong magnetic correlations along J_d bonds for $\alpha > 0.5$, whereas the other correlations remain weak. Therefore, the low-energy excitations might be $S = 1/2$ spinons causing an effectively one-dimensional low-temperature physics as has been discussed previously for other 2D models such as the crossed-chain model [10] as well as for the anisotropic triangular lattice [11]. As the physical properties are related to α which is strongly dependent on the O—H distance, the H position should be reinvestigated experimentally with better accuracy. Generally, a precise determination of the position of side group atoms is crucial for an accurate model derivation. We suggest that the dependence of exchange integrals on side group positions can be used to tune a magnetic ground state under changed conditions like external pressure.

References

[1] Lhuillier C, Sindzingre P and Fouet J B 2001 *Can. J. Phys.* **79** 1525–1535
[2] Levi B G 2007 *Physics Today* **60 (2)** 16–19
[3] Harris A B, Kallin C, and Berlinsky A J 1992 *Phys. Rev. B* **45** 2899
[4] Janson O, Richter J and Rosner H *arxiv:0806.1592*
[5] Schmalfuß D, Richter J and Ihle D 2004 *Phys. Rev. B* **70** 184412
[6] Krause W, Bernhardt H J, Braithwaite R S W, Kolitsch U and Pritchard R 2006 *Mineral. Mag.* **70** 329–340
[7] Schlüter J and Malcherek T 2007 *Neues Jahrbuch für Mineralogie — Abhandlungen* **184** 39–43
[8] Malcherek T and Schlüter J 2007 *Acta Cryst. B* **63** 157–160
[9] Geertsma W and Khomskii D 1996 *Phys. Rev. B* **54** 3011–3014
[10] Starykh O, Singh R and Levine G 2002 *Phys. Rev. Lett.* **88** 167203
[11] Coldea R, Tennant D, Tsvelik A and Tylczynski Z 2001 *Phys. Rev. Lett.* **86** 1335