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Symmetry Reduction in the Quantum Kagome Antiferromagnet Herbertsmithite

A. Zorko,[1,*] M. Herak,[2,†] M. Gomilšek,[1] J. van Tol,[3] M. Velázquez,[4] P. Khuntia,[5] F. Bert,[5] and P. Mendels[5]

[1] *Jožef Stefan Institute, Jamova c. 39, SI-1000 Ljubljana, Slovenia*
[2] *Institute of Physics, Bijenička c. 46, HR-10000 Zagreb, Croatia*
[3] *National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA*
[4] *CNRS, Université de Bordeaux, ICMCB, UPR 9048, 87 Avenue du Dr. A. Schweitzer, 33608 Pessac Cedex, France*
[5] *Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris-Saclay, 91405 Orsay Cedex, France*

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Employing complementary torque magnetometry and electron spin resonance on single crystals of herbertsmithite, the closest realization to date of a quantum kagome antiferromagnet featuring a spin-liquid ground state, we provide novel insight into different contributions to its magnetism. At low temperatures, two distinct types of defects with different magnetic couplings to the kagome spins are found. Surprisingly, their magnetic response contradicts the three-fold symmetry of the ideal kagome lattice, suggesting the presence of a global structural distortion that may be related to the establishment of the spin-liquid ground state.

Spin-induced breaking of crystal symmetry is a widespread phenomenon in one-dimensional antiferromagnets [1–3]. There, spin degrees of freedom can conspire to form singlets, i.e. valence bonds, leading to lattice dimerization known as the spin-Peierls transition. In higher dimensions, a similar lattice instability induced by magnetoelastic coupling can appear in geometrically frustrated magnets to relieve frustration by lifting the degeneracy of magnetically ordered ground states [4–10]. A more intriguing option though is a spin-Peierls-like transition due to spin paring in disordered but correlated spin states of frustrated lattices. The latter phenomenon was indeed theoretically predicted [11–13] and also found experimentally in a triangular-lattice compound [14] and a Shastry-Sutherland lattice representative [15], both featuring spin-singlet ground states. The two-dimensional quantum kagome antiferromagnet (QKA), a paradigm of correlated disordered spin states, seems to be resistant against valence-bond ordering, as a spin-liquid (SL) ground state preserving the lattice symmetry is predicted [16–18]. However, this state is only slightly energetically favorable as compared to a valence-bond crystal (VBC) [19], which breaks the translational symmetry and could lead to a lattice distortion if assisted by the magnetoelastic coupling. Since defects, inherently present in kagome materials, may be able to pin a VBC [20], it is interesting to pose the question of how much such perturbations to the QKA can modify its ground state.

From early investigations [21–23], randomness in the form of Zn-Cu intersite disorder is an issue well known for the so far most intensively studied QKA representative herbertsmithite, $ZnCu_3(OH)_6Cl_2$. The amount of disorder is sizable, as 5-8% of the Cu^{2+} ions end up at the Zn intersite even for the best polycrystalline samples and single crystals [21–24]. Additionally, the presence of Zn^{2+} vacancies at the intralayer kagome Cu site was suggested from early ^{17}O nuclear magnetic resonance (NMR) experiments [22], but was later disputed based on x-ray anomalous scattering [24] and NMR measurements on single crystals [25]. The defects behave like weakly coupled spin-1/2 entities [26] and represent the dominant contribution to thermodynamic quantities at low energies and low temperatures (T's) [27–30]. A recent inelastic neutron scattering study has helped to disentangle the kagome and defect excitation spectra and has revealed that the defects are correlated [30]. The important question of how much they affect the SL ground state of the kagome spins, however, remains unsettled [30–32].

Here we provide a novel insight into the problem of the interplay of defects and the kagome physics in herbertsmithite by combining bulk magnetic torque and local-probe electron spin resonance (ESR) measurements on single crystals. The torque magnetometry surpasses conventional magnetization measurements when determining the orientation of the principal axes of the magnetic susceptibility tensor, while high resolution and sensitivity of ESR allow individual inspection of different contributions to magnetism if these differ in g factors or line widths [34]. Indeed, in herbertsmithite, we clearly demonstrate with ESR the presence of two distinct types of defects that prevail at low T's. Unexpectedly, the corresponding g-factor anisotropy as well as the T-dependent orientation of the magnetic axes provide complementary evidence that both defect contributions break the three-fold symmetry of the kagome lattice, which reveals a global structural distortion.

In our investigation we used several single crystals of masses m=5-17 mg with irregular shapes, similar to the one reported in Ref. 33. The crystals were grown following the published procedure [35]. High quality of the samples was verified by x-ray diffraction (XRD) and SQUID magnetometry. The direction of crystallographic axes was determined by XRD using a Laue camera in back-scattering geometry.

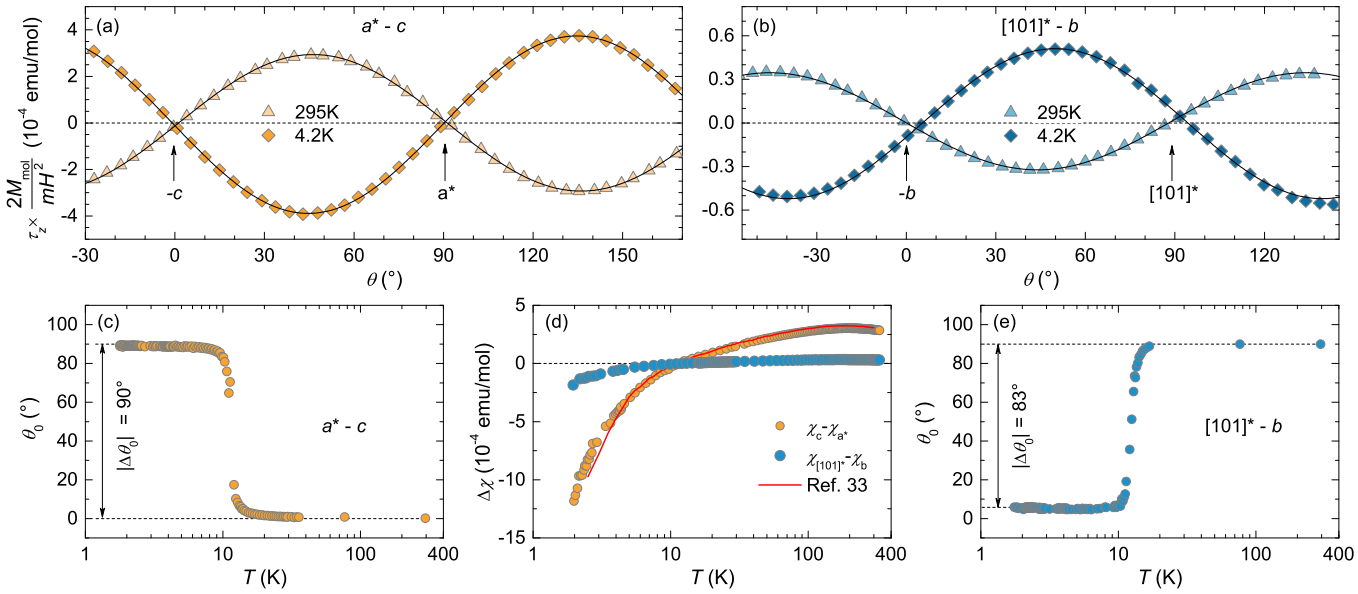

FIG. 1. (a), (b) The angular dependence of the magnetic torque τ_z in two different crystallographic planes. The solid lines represent fits with Eq. (1). The T-dependence of (c), (e) the corresponding magnetic-torque phase θ_0 and (d) the corresponding magnetic anisotropy for both crystallographic planes. The solid line in (d) represents the magnetization data published in Ref. 33. The dashed lines are a guide to the eye. In (e) they highlight the magnetic-torque phase change of $|\Delta\theta_0| \neq 90°$, which reveals broken symmetry with $\chi_{a^*} \neq \chi_b$ (see text for details).

The magnetic torque τ_z was measured along the z laboratory axis on a home-built apparatus in a fixed magnetic field of $\mu_0 H = 0.2$ T (μ_0 is the vacuum permeability) rotating in the xy laboratory plane [36]. This complements previous high-field torque measurements that were performed for fixed directions of H as a function of the field strength [37]. In our experiment, the field was rotated in two different planes, the first one containing the a^* and c crystallographic axes [Fig. 1(a)], and the second one comprising the [101]* and b axes [Fig. 1(b)]. Here, c denotes the axis perpendicular to the kagome planes. All measured angular dependences of τ_z are typical of systems with a magnetic response linear in H, where [36]

$$\tau_z = \frac{m}{2M_{\rm mol}} H^2 \left(\chi_{x'} - \chi_{y'}\right) \sin(2\theta - 2\theta_0). \qquad (1)$$

Here, $M_{\rm mol}$ is the molar mass of the sample, $\chi_{x'}$ and $\chi_{y'}$ are the maximal and minimal susceptibility values within the xy plane, θ is the angle between H and x axis, while the torque phase θ_0 represents the angle between the x' and x axes. From the torque amplitude one obtains the susceptibility anisotropy $\Delta\chi_{xy} = \chi_{x'} - \chi_{y'}$ in the measured xy plane while θ_0 tracks the rotation of the magnetic easy axis within the xy plane.

From measurements in the a^*-c plane [Fig. 1(a)], we find that at high T's, i.e., for the intrinsic kagome spins that dominate the magnetic response of herbertsmithite above ∼100 K [26], the magnetic easy axis is oriented along c ($\chi_c > \chi_{a*}$). Around the crossover temperature of $T_0 \approx 12$ K, θ_0 changes by 90° [Fig. 1(c)], revealing that $\chi_c < \chi_{a*}$ for the defect spins, which are dominant at low T's. Thus the bulk easy axis c is replaced by the bulk easy plane ab below T_0, in agreement with previous bulk susceptibility measurements [Ref. 33; see Fig. 1(d)]. At first glance, similar information is obtained from measurements within the [101]*-b plane [Fig. 1(b)]. The sign of $\chi_{[101]^*} - \chi_b$ changes from positive to negative at T_0 on decreasing T [Fig. 1(d)], as expected, because the [101]* direction contains a small part of the c component. However, unexpectedly, the torque curves for 4.2 and 295 K cross zero at notably different θ_0 [Fig. 1(b)], revealing a total change of the torque phase $|\Delta\theta_0| = 83°$ around T_0 [Fig. 1(e)]. This change is incompatible with threefold crystal symmetry yielding $\chi_{a^*} = \chi_b$, which can only supports the torque-phase change of 90° [36]. The measurements thus irrefutably disclose a deviation from the uniaxial symmetry. Note that, for randomly and independently distributed defects, an average uniaxial global symmetry should be preserved in bulk magnetic measurements, even if defect possess lower local symmetry. A torque phase change that differs from 90° is thus a fingerprint of a reduced crystal symmetry.

In order to further inspect this surprising bulk symmetry reduction, we performed complementary ESR measurements at the NHMFL, Tallahassee, Florida on a custom made ESR spectrometer operating at 240 GHz. A single broad ESR line (labeled B in Fig. 2) was observed at high T's for $\mathbf{H}||\mathbf{c}$ and $\mathbf{H}\perp\mathbf{c}$, with the line width and g factors [36] in agreement with previous data from polycrystalline samples [38]. The ESR intensity $I(T)$, which is proportional to the magnetic susceptibility $\chi_{\rm ESR}$ [39],

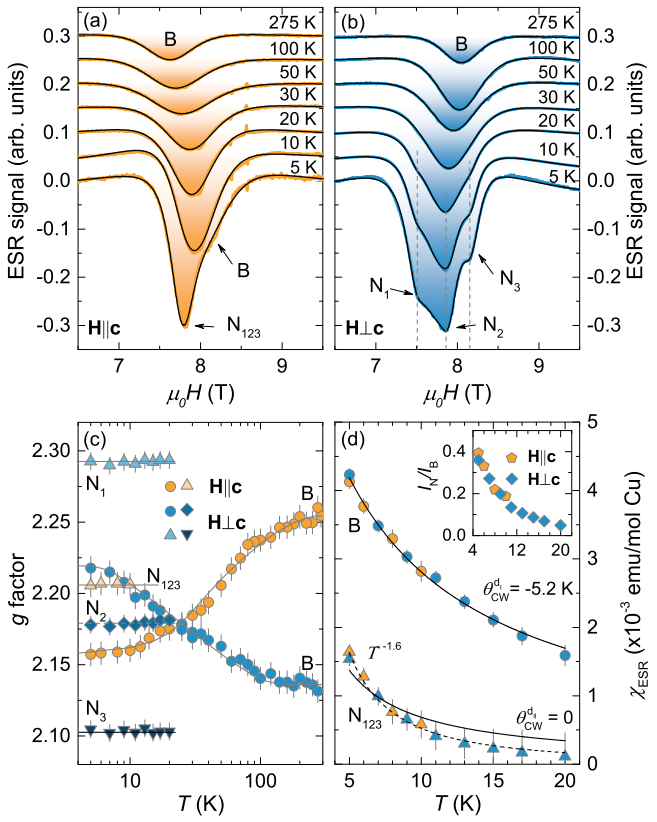

FIG. 2. The ESR spectra for (a) $\mathbf{H}||\mathbf{c}$ and (b) $\mathbf{H}\perp\mathbf{c}$, which are displaced vertically for clarity. The fits (solid lines) disclose a single broad (B) ESR component at high T's, while an additional narrow component (N_{123}) is found for $\mathbf{H}||\mathbf{c}$ and three additional components (N_1, N_2 and N_3) for $\mathbf{H}\perp\mathbf{c}$ at low T's. The positions of the latter are indicated by dashed lines. (c) The T-dependence of the g factors of individual components. The lines are a guide to the eye. (d) The ESR susceptibility of the B and N components and their measured ratio (inset). The solid lines show fits with the Curie-Weiss model, the dashed line corresponds to a power-law dependence.

was previously found to scale with the bulk susceptibility rather than with the kagome susceptibility in powder samples [38]. This remains the case for single crystals [Fig. 2(d)]. The corresponding crossover of the ESR spectra from high T's (kagome spins) to low T's (defects, labeled d_I) is clearly observed by the variation of the ESR line widths [36, 38] and g factors [Fig. 2(c)] between 100 and 10 K. The change of the g factors corroborates the crossover from the high-T c easy-axis to the low-T ab easy-plane-like behavior also found by the torque magnetometry. We note that the existence of a single broad ESR line, instead of separated lines from the kagome spins and the defect spins, is due to exchange narrowing [40] and reveals that the coupling J^{d_I} between the two spin species is larger than $J_H = \Delta g \mu_B \mu_0 H/k_B \approx 2$ K, where $\Delta g \sim 0.3$ is the g-factor anisotropy typical for Cu^{2+} [41], μ_B the Bohr magneton and k_B the Boltzman constant.

In contrast to powder ESR spectra [38], additional, narrower components appear at low T's in single crystals – a single narrow component (N_{123}) below ∼10 K for $\mathbf{H}||\mathbf{c}$ [Fig. 2(a)] and three similarly intense narrow components (N_1, N_2 and N_3) below ∼20 K for $\mathbf{H}\perp\mathbf{c}$ [Fig. 2(b)]. Since the relative intensity of the N components with respect to the broad B component is the same for the two field orientations, $I_{N_{123}}/I_B = (I_{N_1} + I_{N_2} + I_{N_3})/I_B$ [inset in Fig. 2(d)], a single additional defect site in the crystal structure of herbertsmithite is required. The ESR intensity of these new defects (labeled d_{II}) amounts to ∼40% of the B component at 5 K, where the latter is mainly assigned to d_I defects. Therefore, we can write $\chi^B_{ESR} = \chi^k + \chi^{d_I}_{ESR}$ for the B component, where χ^k denotes the intrinsic kagome susceptibility, while for the N component $\chi^N_{ESR} = \chi^{d_{II}}_{ESR}$. After separating the two defect contributions [36], we find [Fig. 2(d)] that $\chi^{d_I}_{ESR} \propto 1/(T - \theta^{d_I}_{CW})$, with the Weiss temperature $\theta^{d_I}_{CW} = -5.2$ K, in agreement with the above conclusion $J^{d_I} \gtrsim J_H$. In contrast, $\chi^{d_{II}}_{ESR}$ increases much faster with decreasing T, possibly even faster than the Curie law ($\theta^{d_{II}}_{CW} = 0$), as a phenomenological T^{-p} ($p = 1.6$) dependence works even better [Fig. 2(d)]. This, together with the much smaller line width of the N components [36] and the fact that they are not exchange narrowed for $\mathbf{H}\perp\mathbf{c}$, reveals that the exchange coupling $J^{d_{II}}$ associated with the d_{II} defects is small, i.e., $|J^{d_{II}}| \ll J_H$.

Additional insight into the two defect contributions at low T's is provided by the angular dependence of the g factors within the kagome planes at 5 K (Fig. 3). The B component is angle independent within the experimental

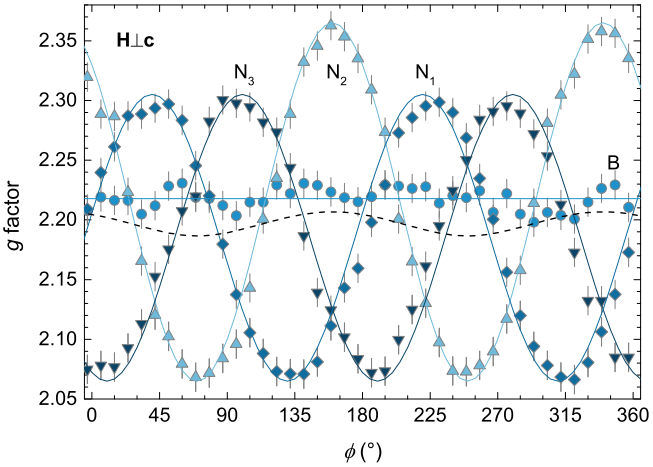

FIG. 3. The angular dependence of the g factors for $\mathbf{H}\perp\mathbf{c}$ at 5 K. The B component is angle independent (horizontal line), while the N components behave according to the model $g_j(\phi) = \left[g^2_{j,\min}\cos^2(\phi-\phi_j) + g^2_{j,\max}\sin^2(\phi-\phi_j)\right]^{1/2}$ (solid lines). The dashed line corresponds to the average $\sum_j g_j(\phi)/3$ and demonstrates the breaking of uniaxial symmetry. The $\mathbf{H}\perp\mathbf{c}$ measurements in Fig. 2(b) were taken at $\phi = 30°$.

uncertainty, as would be expected for the three-fold symmetry of the kagome lattice. The three N components, corresponding to the d_{II} defects, each show the expected 180° periodicity and a relative shift of 60°. However, as one of the three components exhibits a notably larger g-factor anisotropy than the other two, the three-fold symmetry of the crystal structure is evidently broken. This is the second unambiguous fingerprint of symmetry reduction in herbertsmithite. For the N defect component we find an average g-factor anisotropy of $\Delta g_{ab}^{d_{II}} = 0.02$ within the kagome planes (see the dashed line in Fig. 3), while for the B defect component we can estimate its upper bound, $\Delta g_{ab}^{d_I} \lesssim 0.01$.

Further assessments of $\Delta g_{ab}^{d_I}$ can be done based on simulations of the magnetic-torque phase θ_0 [36]. At high T's, the torque is determined by the susceptibility of the kagome spins, while below T_0 it is mainly given by defects. Since $\chi_{ESR}^{d_I} \gg \chi_{ESR}^{d_{II}}$ at $T_0 \approx 12$ K [inset in Fig. 2(d)] where θ_0 abruptly changes [Figs. 1(c), (e)], only the dominant d_I defect contribution is considered. If $g_a^{d_I} = g_b^{d_I}$, which would be in accordance with the three-fold kagome-lattice symmetry, only a change of $|\Delta\theta_0| = 90°$ could occur in any crystallographic plane [36] at the temperature where $\Delta\chi_{xy}^{k} = \Delta\chi_{xy}^{d_I}$. Allowing $g_a^{d_I} \neq g_b^{d_I}$ leads to $|\Delta\theta_0| \neq 90°$ for the $[101]^*$-b plane while leaving $\Delta\theta_0 = 90°$ for the a^*c plane, because c remains a magnetic eigenaxis [36]. This is in perfect agreement with the experiment [Fig. 1(c), (e)]. Within this model, the experimentally observed phase change of $|\Delta\theta_0| = 83°$ is reproduced for $\Delta g_{ab}^{d_I} \sim 0.003(1)$ [36]. Such a small g-factor anisotropy, nevertheless revealing a symmetry reduction also for the broad ESR component, can obviously not be resolved by ESR. The magnetic-torque measurements thus nicely complement ESR measurements by exposing the symmetry reduction also for the other type of detects. We note that both, the unexpected torque-phase change [Fig. 1(e)] and the g-factor irregularity (Fig. 3) were observed in all investigated crystals. Thus, the symmetry reduction reflected in the magnetism of defects is obviously an intrinsic feature of herbertsmithite.

It seems reasonable to attribute the d_I defects with a sizable Weiss temperature $\theta_{CW}^{d_I} = -5.2$ K to Cu^{2+} spins at the Zn intersites, which are expected to be coupled to the kagome spins. Namely, the exchange couplings between the kagome layers that amount to several kelvins run through the intersites [42]. Moreover, pairs of such defects are correlated across the kagome layers at low temperatures [30]. On the other hand, the d_{II} defects are rather exceptional, as they appear quasi-free ($\theta_{CW}^{d_{II}} \sim 0$). Furthermore, they differ substantially in g factors from the d_I defects [Fig. 2(c)], implying a different local environment. The Zn^{2+} vacancies at the kagome sites, if present, could potentially be responsible for such defects by inducing local magnetization patterns in the surrounding spin liquid [20, 43, 44]. If such vacancies are absent [24] one could reconcile the existence of the d_{II} defects by a local effect the interplane Cu^{2+} spins might have on the kagome planes by perturbing the intrinsic spin liquid. Such a local perturbation can pin a spinon kagome-lattice excitation [45], as recently found in the related kagome compound Zn-brochantite [46, 47].

Trivially, Cu^{2+} at the Zn intersites could profoundly affect the intrinsic kagome physics by inducing random bonds on the kagome lattice [31]. However, the required amount of disorder is unlikely realized in herbertsmithite and there is no apparent reason why the *global* three-fold crystal symmetry should be broken. The same should apply to *local* Jahn-Teller distortions of the perfect octahedral environment at the Zn intersites induced by the Cu^{2+} spins [48]. Then, the important question arises of whether the observed global symmetry reduction is in any way related to the establishment of the SL ground state, which could provide a global driving force. Namely, the symmetry reduction in herbertsmithite may arise from local distortions if these are effectively coupled through the correlated electronic state of the system. In this case, the lattice distortion should appear around the temperature where strong spin correlations pertinent to the SL state develop, i.e. around 50 K, where the kagome susceptibility exhibits its maximal value [22, 25, 49]. Even though our investigation could not directly determine the possible onset temperature of this distortion – this would require unfeasible magnetic-torque measurement within the kagome plane [36] – further arguments that favor this scenario can be found in enhanced ^{35}Cl NMR relaxation rate at 50 K [25, 50] and in a pronounced change of the quadrupolar frequency between 50 and 100 K at the ^{17}O site next to defects [25].

The discovery of the symmetry reduction in herbertsmithite is interesting in the context of a striped spin-liquid-crystal state, which was recently proposed as an instability of the Dirac SL on the kagome lattice that breaks the uniaxial lattice symmetry, and also reduces the gauge symmetry from $U(1)$ to Z_2 [51]. The only synchrotron XRD report at low T's published up to date failed to detect any obvious structural phase transition in herbertsmithite [35]. However, the rather small values of Δg_{ab} suggest that deformation of the hexagonal structure may be very small. On the other hand, a recent infrared reflectivity investigation reported an anomalous low-T broadening of a low-frequency phonon mode [52]. Although this was interpreted as possibly signaling $p6$ chirality symmetry breaking [53] in the SL ground state, it could also be related to a structural deformation.

In conclusion, our study has revealed that two types of intrinsic magnetic defects exist in herbertsmithite at low T's, which differ significantly in their interactions with the surrounding kagome spins. The strongly exchange-coupled defects are identified by the broad ESR component with a Curie-Weiss T-dependence of the susceptibility, while the second defect type, corresponding to

the narrow ESR components, is characterized by much weaker coupling and a steeper increase of their susceptibility on decreasing T, possibly beyond the Curie model. Explaining the nature of the unexpectedly narrow ESR response of the latter defects and their apparent isolation from the kagome spins should be a key avenue in future studies of the interplay between the defect and the intrinsic kagome physics in herbertsmithite. Moreover, both types of defects have provided evidence of a global symmetry reduction of the kagome lattice in herbertsmithite at low T's. This changes the perspective on herbertsmithite and may have implications for the selection of its ground state. In order to better understand this intriguing discovery, refined *ab-initio* calculations of relaxed structures in the presence and absence of the intersite disorder could potentially be highly informative, since the energy difference between perfect and defect structures is minimal [54].

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* andrej.zorko@ijs.si
† mirta@ifs.hr

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