Herbertsmithite: pressure evolution of a spin liquid

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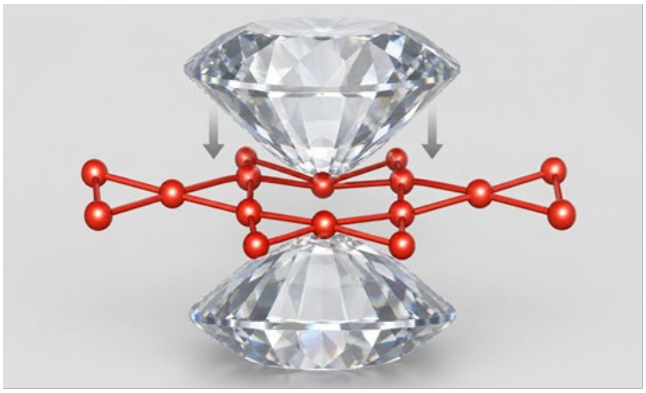
Abstract

Frustrated interaction geometry of magnetic moments can lead to unusual types of magnetic order and even to novel phases, such as quantum spin liquid where spins are dynamically correlated without forming a symmetry-broken long-range-ordered state. This theoretical prediction was extensively studied in various transition-metal compounds, including the Cu^{2+} mineral herbertsmithite, $Cu_3Zn(OH)_6Cl_2$, with a kagome network of interacting Cu^{2+} ions [1].

Whereas herbertsmithite lacks long-range magnetic order down to lowest temperatures, this observation received a conflicting assessment in the previous literature. On the one hand, a structural disorder of the magnetic Cu^{2+} and nonmagnetic Zn^{2+} ions was invoked as a plausible reason for the suppression of magnetic order. On the other hand, the occurrence of a pressure-induced transition toward a magnetically ordered state above 2.5 GPa [2] speaks in favor of a genuine spin-liquid scenario where competing interactions are detuned by the applied pressure, and magnetic order is stabilized. Abrupt structural changes around the critical pressure of 2.5 GPa [2] and at higher pressures [3,4] have been reported, but their origin could not be revealed.

Here, we revise pressure-dependent crystal structure and magnetism of herbertsmithite using single-crystal x-ray diffraction in a diamond anvil cell combined with high-pressure magnetometry. Contrary to the previous studies, we find that herbertsmithite evolves monotonically up to at least 10 GPa with no visible changes in its low-temperature magnetic behavior. It means that a disordered magnetic ground state persists above 2.5 GPa, at odds with the earlier findings. The reduction in the Cu-O-Cu bond angles at elevated pressures weakens nearest-neighbor magnetic couplings and increases the role of weaker interaction terms that should eventually stabilize magnetic order. The absence of this pressure-induced magnetic order in the experiment favors structural disorder as the driving force of the apparent spin-liquid behavior in herbertsmithite.

Intriguingly, at pressures above 10 GPa where monoclinic distortion was reported in the earlier studies [3,4], a robust trigonal symmetry is observed in our data. However, the *c*-parameter shows an anomalous increase upon compression. The possible origin of this negative anisotropic compressibility will be discussed.



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[2] D.P. Kozlenko *et al.* Phys. Rev. Lett. **108**, 187207 (2012)
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[4] Y. Luo *et al.* Phys. Chem. Chem. Phys. **25**, 25130 (2023)