THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Physical chemistry: Model's reputation restored

Citation for published version:

de Vries, MA & Harrison, A 2010, 'Physical chemistry: Model's reputation restored', *Nature*, vol. 468, no. 7326, pp. 908-909. <https://doi.org/10.1038/468908a>

Digital Object Identifier (DOI):

[10.1038/468908a](https://doi.org/10.1038/468908a)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Nature

Publisher Rights Statement:

Copyright © 2010 Macmillan Publishers Ltd. All rights reserved.

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Post-print of peer-reviewed article published by the Nature Publishing Group.

Published article available at: <http://dx.doi.org/10.1038/468908a>

Cite as:

De Vries, M. A., & Harrison, A. (2010). Physical chemistry: Model's reputation restored. *Nature*, 468(7326), 908-909.

Article published: 15/12/2010

Physical chemistry: Model's reputation restored**

M. A. de Vries^{1,*} and A. Harrison^{2,*}

^[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

^[2]Institut Laue-Langevin, 6 rue Jules Horowitz, F-38042 Grenoble, France.

^[*]Corresponding authors; M.A.V. e-mail: m.a.devries@ed.ac.uk; A.H. e-mail: harrison@ill.eu

Abstract

The mineral herbertsmithite - nominally $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ - has been hailed as a rare model for the study of an unconventional form of magnetism believed to play a key role in the mechanism of high critical temperature (high- T_c) superconductivity. However, concerns have been raised that chemical disorder in this material could produce defects in the array of magnetic atoms, disturbing or even destroying the model properties. A recent paper by Danna E. Freedman *et al.*^[1] clearly identifies the type of disorder present, and shows it to have little influence on the magnetic lattice. This represents an important step forward in establishing a simple, clean system to provide unambiguous insights into this important form of magnetism.

Main text

The magnetism of materials is ultimately derived from unpaired electrons each of which have a property called spin, s , with a value of $\frac{1}{2}$ that bestows on each of them a magnetic moment. In insulators, such moments or spins are localized on atoms, and commonly interact with their closest neighbours so that specific orientations are preferred. In most cases, an antiparallel – or antiferromagnetic - configuration of nearest-neighbour spins is favoured so when a lattice of such atoms is cooled, their spins usually freeze to form an ordered array. This is illustrated for the case of a square lattice in Fig. 1(a). However, under certain circumstances, quite different behaviour may ensue. Fig. 1(b) shows an array of corner-sharing triangles called a *kagome* lattice. It is clearly impossible to arrange each near-neighbour pair of spins so that they are simultaneously antiparallel: we say that such a lattice is *geometrically frustrated*. The lowest- energy arrangement might be expected to be that in Figure 1(c), where neighbouring spins are 120° to each other. However, P. W. Anderson pointed out for a number of lattices composed of triangles^[2] that when there is just one electron per atom – *i.e.* for $s = \frac{1}{2}$ - it is more favourable for neighbouring spins to pair up in a manner analogous to that in a chemical bond such as for H_2 . Quantum mechanics allows the spins in this valence bond to be simultaneously up-down and down-up, thus relieving the frustration by effectively allowing pairs of local moments to cancel-out themselves. Furthermore, such coupling may occur between all pairs of spins, so the overall picture is that of a liquid of valence bonds, resonating between all possible ways of making such bonds (Figure 1(d)). This state is called a quantum spin liquid or Resonating Valence Bond (RVB) liquid by analogy with Pauling's model^[3] of chemical bonding in organic molecules such as benzene, in which the chemical structure can also be described as a hybrid of different valence bond arrangements. It was proposed^[4] – again by Anderson – that the pairs of electrons bound into valence bonds in the RVB state are the superconducting charge carriers in the high- T_c layered cuprates.

Figure 1. Arrangement of magnetic moments, or spins in a tile from (a) a square antiferromagnet and (b) a kagome lattice illustrating the frustration of pairwise interactions leading to (c) a compromise configuration. (d) One of many possible ways of arranging ‘bonds’ in an RVB state or quantum spin liquid. (e) The structure of Herbertsmithite $[\text{ZnCu}_3(\text{OH})_6\text{Cl}_2]$, with two kagome layers of Cu^{2+} ions (blue) linked by O^{2-} ions (red) in OH^- groups, separated by layers with Zn^{2+} (grey) and Cl^- ions (not shown). The ‘!’ marks the Cu^{2+} defect on the interplane Zn site the corresponding Zn^{2+} on the kagome lattice (marked with an ‘x’) is not observed.

Among simple lattices made from triangles, the $S = \frac{1}{2}$ kagome case has been regarded for some time as a prime candidate for a spin-liquid state. However, it is only recently that an undistorted realization of this highly-prized system has been found. The same group responsible for the paper highlighted here showed that the array of Cu^{2+} atoms (each of which have one unpaired electron) in herbertsmithite appeared to qualify (Fig. 1(e))^[5]. It was soon demonstrated that although there is a very strong antiferromagnetic coupling between the spins – with an energy scale of the order of 200 K – no freezing could be observed down to the lowest yet achievable temperature of 50 mK^[6]. This was consistent with some form of spin-liquid state. However, evidence was also found for disorder in the structure, raising concerns that this was not as clean a model system as might be hoped. Neutron

diffraction data, combined with elemental analysis using inductively-coupled plasma Auger electron spectroscopy (ICP-AES) on the stoichiometric compound $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, indicate that $\sim 1/4^{\text{th}}$ of the interplane Zn sites are occupied by a Cu^{2+} ion (marked by a “!” in Fig. 1(e)) and that in turn $1/12^{\text{th}}$ of the Cu sites on the kagome lattice are occupied by a Zn^{2+} ion (marked with an “x”). The actual level of site disorder was however estimated to be slightly lower, based on analysis of the magnetic susceptibility^[7] and heat capacity^[8]. Both exhibit a contribution from nearly-free spins (i.e. spins that interact only very weakly with the other spins in the material) that is attributed to the $s = 1/2$ of Cu^{2+} ions occupying one in every 5 interplane Zn sites.

Freedman *et al.* appreciated that this situation was unsatisfactory and that rigorous determination of the exact level of disorder should depend on structural and chemical methods only. They carried out new neutron diffraction, extended X-ray absorption fine-structure (EXAFS) and anomalous X-ray diffraction measurements. All their results show that $\sim 15\%$ of the Zn sites ($\sim 1/6^{\text{th}}$) is occupied by a Cu^{2+} ion. This convincingly dispels the last doubts about the concentration of Cu^{2+} ions (and $s = 1/2$ spins) on the Zn sites. It also confirms the earlier interpretation of low-temperature heat capacity and magnetic susceptibility that these defect spins interact only weakly with the other spins and hence have very little influence on the behaviour of the spins on the kagome lattice. What has come as a surprise is that the concentration of Zn^{2+} on the kagome Cu sites was found to be only $\sim 1(3)\%$. This is good news for the quantum magnetism community – it means that there are very few vacancies in the periodic array of spins forming the kagome lattice, allowing for a reliable comparison between theory and experiment. Paradoxically, the smaller-than- thought chemical disorder implies in the present case that the chemical formula is likely closer to $\text{Zn}_{0.85}\text{Cu}_{3.15}(\text{OH})_6\text{Cl}_2$ instead of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ as thought previously. This will doubtless be checked in other laboratories using the chemical analysis method of ICP-AES.

The results by Freedman *et al.* underline that as the first clean spin-liquid system for which the spin correlations and dynamics can readily be measured, herbertsmithite has great potential to reveal the character of spin-liquids, and explore the relationship between antiferromagnetism and superconductivity in layered transition metal compounds.

References

- [1] Freedman, D.E. et al. Site Specific X-ray Anomalous Dispersion of the Geometrically Frustrated Kagomé Magnet, Herbertsmithite, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. *Journal of the American Chemical Society* **132**, 16185-16190 (2010).
- [2] Anderson P.W. Resonating valence bonds: a new kind of insulator Mat. Res. Bull. 8 (1973) 1530160.
- [3] Pauling, L. Nature of the Chemical Bond (1960) Cornell University Press, Ithaca, New York.
- [4] Anderson, P.W. The resonating valence bond state in La_2CuO_4 and superconductivity,
- [5] Shores, M.P., Nytko, E.A., Bartlett, B.M. & Nocera, D.G. A Structurally Perfect $S = 1/2$ Kagomé Antiferromagnet. *Journal of the American Chemical Society* **127**, 13462-13463 (2005).
- [6] Mendels, P. et al. Quantum Magnetism in the Paratacamite Family: Towards an Ideal Kagomé Lattice. *Phys. Rev. Lett.* **98**, 077204 (2007).
- [7] Bert, F. et al. Low temperature magnetization of the $S = 1/2$ kagome antiferromagnet $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. *Phys. Rev. B* **76**, 132411 (2007).
- [8] de Vries, M.A., Kamenev, K.V., Kockelmann, W.A., Sanchez-Benitez, J. & Harrison, A. Magnetic Ground State of an Experimental $S=1/2$ Kagome Antiferromagnet. *Phys. Rev. Lett.* **100**, 157205 (2008).