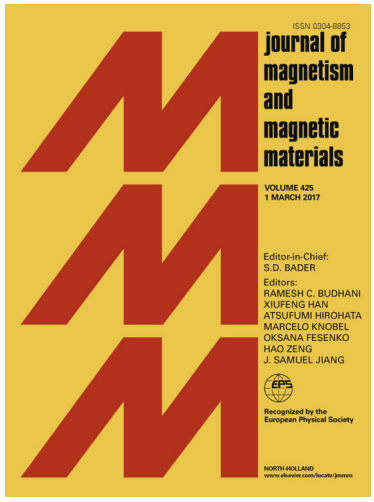

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Copper Tellurium Oxides - A Playground for Magnetism

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A variety of copper tellurium oxide minerals are known, and many of them exhibit either unusual forms of magnetism, or potentially novel spin liquid behavior. Here, I review a number of the more interesting materials with a focus on their crystalline symmetry and, if known, the nature of their magnetism. Many of these exist (so far) in mineral form only, and most have yet to have their magnetic properties studied. This means a largely unexplored space of materials awaits our exploration.

In 2005, Dan Nocera's group reported the synthesis of the copper hydroxychloride mineral, herbertsmithite [1]. A number of years later, they were able to report the growth of large single crystals [2]. Since then, a number of relatives of this mineral have been discovered and characterized [3]. Despite the existence of a large Curie-Weiss temperature of order 300 K, herbertsmithite does not order down to 20 mK [4].

The reason these events have significance is that these minerals could be a realization of an idea proposed by Phil Anderson back in 1973 [5] that was based on an early debate in the field of magnetism between Louis Néel and Lev Landau. Néel had proposed the existence of antiferromagnetism, where there are two sub lattices of ferromagnetic moments oppositely aligned. This state was subsequently seen by neutron scattering (which resulted in a Nobel prize for Néel, and later for the neutron scatterer, Clifford Shull). But at the time, there was great skepticism about the existence of this state. The reason is that it is not an eigenstate of the spin operator (unlike ferromagnetism). There was suspicion that the true ground state would be a singlet. We now know that the origin of the Néel state is broken symmetry [6], and that fluctuations are usually not enough to destabilize long range order. But Phil realized that if the spins sat on a non-bipartite lattice, matters could change. Imagine a triangle with Ising spins. Then if two spins are anti-aligned, the direction of the third spin is undetermined. Phil speculated that instead of Néel order, the spins instead paired up to form singlets, and this would be preferred in two dimensions (where thermal fluctuations have a tendency to suppress order) and for low spin (where quantum fluctuations are more important). This is particularly obvious for S=1/2, where a singlet bond has an energy of -3J/4 compared to -J/4 for an antiferromagnetic bond. But to avoid the energy loss from the unpaired spin, these singlets should fluctuate from bond to bond, much like Pauling's model for how double carbon bonds in benzene rings resonate from one link to the next (hence the name, resonating valence bonds).

Most attention has been given to the Heisenberg model, given the more important role of fluctuations in this case. But we now know that the near neighbor Heisenberg model on a triangular lattice does order, with the spins rotating by 120° from one sub lattice to the next [7]. This is most clear from exact diagonalization studies, where precursors of the broken symmetry state, and associated magnon excitations, are evident in the eigenvalue spectrum [8]. But for the kagome case, the spectrum is qualitatively different, with no signature of these effects [9]. Over the years, a number of numerical studies have been done, either purporting a valence bond solid (an ordered array of singlets), or various types of quantum spin liquid states (gapped Z_2, gapless U(1), chiral, etc., where the group corresponds to an emergent gauge group associated with the symmetry of the spin liquid). The uncertainty is connected to the fact that all of these states have energies comparable to one another. The real interest, though, is that these solutions are characterized by fractionalized excitations (typically free spin 1/2 neutral fermions known as spinons, or gauge flux excitations known as visons). Proving the existence of such excitations is a major challenge in physics [10, 11].

This brings us to real materials. Many of them either have contributions over and beyond that of a near neighbor Heisenberg model (longer range exchange, anisotropic exchange, Dzyaloshinskii-Moriya interactions, etc.) or distorted lattices, all of which can in principle either change the nature of the ground state, or promote or destabilize order. Hence the interest in finding as many materials as possible that have frustrated lattices for their magnetic ions, and then characterizing these materials. In that context, we can often allow Mother Nature to do the hard work for us. Many minerals are known which have the appropriate magnetic lattices, making them ideal sources for finding desired materials. In fact, Dan Nocera's group had first synthesized the iron jarosite minerals (where the iron ions sit on a kagome lattice), but realized that the same would not apply to a copper (S=1/2) version, since Cu^{2+} would not go onto the Fe^{3+} site. Hence the turn to herbertsmithite once they had seen that structure in the mineralogical literature. In that context, there is one mineral where copper goes into a jarosite-type structure, osarizawaite [12], but in this case, the copper kagome lattice is strongly diluted by Al^{3+} ions. The magnetic properties