Copper Tellurium Oxides - A Playground for Magnetism

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(Dated: August 18, 2017)

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 relatives of this mineral have been discovered and characterized [2]. Despite the existence of a large Curie-Weiss temperature of order 300 K, herbertsmithite does not order down to 20 mK [3].

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 undefined. 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 on a triangular lattice does order, with the spins rotating by $120^\circ$ 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...
of this mineral, along with a host of others, are unknown at this time.

Last year, in searching the mineralogical literature, I became aware of a review article on tellurium oxides [13]. Copper (desired since it is an S=1/2 ion) has a tendency to be associated with tellurium, and indeed there are several examples that can be found in this literature. Based on this, a search was done for interesting materials that might be worth synthesizing and studying for their magnetic properties.

Bluebellite (Cu₆IO₃(OH)₁₀Cl) and mojaveite (Cu₆TeO₄(OH)₉Cl) are recently discovered minerals found in the Mojave Desert [14]. Though the first has I⁵⁺ as opposed to Te⁶⁺ for the second, their crystal structures are similar, and also similar to another mineral discovered there, fuettererite (Pb₃Cu₆TeO₆(OH)_7Cl₃) [15], as well as the mineral sabelliite (Cu₂ZnAsO₄(OH)₃) discovered in Sardinia. In these four examples, the copper ions sit on a so-called maple leaf lattice (1/7-depleted triangular lattice). This lattice (with a coordination number of z=5) is intermediate from a frustration viewpoint between a triangular lattice (z=6) and a kagome (1/4-depleted triangular lattice with z=4), and is thought to be (barely) on the ordered side [27]. There has been one copper mineral with such a lattice that has had its magnetic properties investigated, spangolite (Cu₆Al(SO₄)(OH)₁₂Cl(H₂O)₃), whose susceptibility resembles that expected for a singlet ground state [28], with a small upturn at low temperatures due to about a 7.5% concentration of orphan spins (similar to what is observed in herbertsmithite). In all cases, though, the maple leaf lattice is distorted (Fig. 1). In Table II, these distortions are tabulated, with sabelliite the least distorted, and bluebellite the most. But for sabelliite, even though there is only one crystallographic Cu site (as compared to two for the others), significant site disorder exists in this material, with Zn on the Cu sites, and Sb on the As sites, making a synthetic variant a desirable goal.

We next come to a more promising mineral, quetzalcoatlite (Zn₆Cu₃(TeO₆)₂(OH)₆Y), with Y=Ag₉Pb₉Cl₉z+2p a neutral unit [17], found in the

### Table I: Table of various copper tellurium oxides. SG is the space group, Lattice is the arrangement of copper ions, and Ref is the associated reference to the literature.

| Formula unit                  | SG  | Lattice        | Ref   |
|-------------------------------|-----|----------------|-------|
| Cu₆IO₃(OH)₁⁰Cl                | R₃  | maple leaf     | [14]  |
| Cu₆TeO₄(OH)₉Cl                | R₃  | maple leaf     | [14]  |
| Pb₃Cu₆TeO₆(OH)₇Cl₃            | R₃  | maple leaf     | [15]  |
| Cu₂ZnAsO₄(OH)₃                | P₃  | maple leaf     | [16]  |
| Zn₆Cu₅(TeO₆)₂(OH)₉Cl          | P₃m | kagome          | [17]  |
| Mg₃Cu₂TeO₉(H₂O)₆              | P₃m | honeycomb      | [18]  |
| Cu₆TeO₆                       | Iₐ3 | hexagons       |       |
| Pb₂(Cu₃Sb)₁/₃(TeO₃)₆Cl        | P₄₁/₃ | hyperkagome | [21]  |
| PbCuTe₂O₆                     | P₄₁/₃ | hyperkagome | [22]  |
| Cu₂TeO₄                       | P₂₁/n | square lattice | [23]  |
| Sr₂CuTeO₆                     | I₄/m | square lattice | [24]  |
| Sr₂Cu₂TeO₇                    | Pbcm | orthorhombic   | [25]  |
| Cu₃Bi₃Te₂O₆Cl                 | Pcmn | kagome staircase | [26]  |

### Table II: Table of copper maple leaf lattices, 1/7-depleted triangular lattices with a sub formula unit of Cu₆X, with X sitting in the middle of the hexagonal hole. S is the smallest, L/S their ratio.

| Formula unit                  | X  | S  | L  | L/S   |
|-------------------------------|----|----|----|-------|
| Cu₆IO₃(OH)₁⁰Cl                | I  | 2.899 | 3.900 | 1.345  |
| Cu₆TeO₄(OH)₉Cl                | Te | 2.999 | 3.572 | 1.191  |
| Pb₃Cu₆TeO₆(OH)₇Cl₃            | Te | 3.033 | 3.322 | 1.095  |
| Cu₂ZnAsO₄(OH)₃                | Zn | 3.028 | 3.166 | 1.046  |
| Cu₆Al(SO₄)(OH)₁₂Cl(H₂O)₃      | Al | 3.004 | 3.214 | 1.070  |

FIG. 1: Crystal structure of mojaveite [14]. View is along c, with z ranging from 0.2 to 0.5. The two different crystallographic Cu sites are shown as blue and cyan, with Cl as green, Te as gold and oxygen as red.
FIG. 2: Crystal structure of quetzalcoatlite [17]. View is along c, with z ranging from 0.25 to 0.75. Cu is blue, Cl green, Te gold and oxygen red.

same Blue Bell claims as bluebellite. Interestingly, this was the first mineral whose crystal structure was determined at the Advanced Photon Source at Argonne (studied there because of the small size of the crystals). It exhibits a perfect kagome net of copper ions (Fig. 2), with Cl ions sitting at the center of the hexagonal holes. The stacking of the kagome planes is AA (as opposed to ABC stacking in herbertsmithite), thus similar to kapellasite, which is a polymorph of herbertsmithite (both have the same space group). Like herbertsmithite, these layers are separated by Zn ions (Fig. 3), but here, the Zn ions have tetrahedral coordination \((\text{ZnO}_2\text{(OH)}_2)\). Because of this, the disorder seen in herbertsmithite (where Cu can sit on the Zn sites) should be absent in this mineral. Moreover, the Cu-O-Zn-O-Cu pathway connecting successive kagome layers is quite tortuous, implying weak coupling between the layers. But there is still some disorder because of the variability of the Y unit (ideally one would have AgCl dimers along the c axis). Turning to the planar properties (Fig. 2), unlike herbertsmithite where one has Cu-O-Cu superexchange pathways, here Te intervenes, leading to weaker couplings of the form Cu-O-Te-O-Cu or Cu-O-O-Cu (super-superexchange). Because of this, the anticipated Curie-Weiss temperature should be significantly smaller than herbertsmithite. Still, as one of the few known materials where Cu ions fall on a perfect kagome lattice, one would hope that the available crystals could be studied for their magnetic properties, and an attempt at synthesis would be a desirable goal as well.

The next mineral in Table I is leisingite \((\text{MgCu}_2\text{TeO}_6\text{(H}_2\text{O})_6)\). Here, the copper ions form a perfect honeycomb lattice \((\text{z}=3)\), with Te ions sitting in the hexagonal holes (Fig. 4). The Cu ions are connected by a superexchange pathway, but the Cu-O-Cu bond angle is 93.5°, which is near the crossover from F to AFM behavior. The layers are AA stacked, being...
connected by Mg(H₂O)₆ octahedra with Mg ions sitting below the Te ions. But again, disorder is present, with Fe sitting on the Mg sites, and some Mg sitting on the Cu sites. Again, a synthetic variant is highly desirable.

Jensenite (Cu₃TeO₆(H₂O)₂) is mentioned in passing. Like leisingite, it is composed of layers of Te and Cu forming a honeycomb lattice (but in this case, it is distorted) separated by other layers which contain isolated copper dimers. Mcalpineite has the same formula unit as jensenite (except for the waters), but has a cubic space group instead. Although known in mineral form [29], it has been synthesized as well by a variety of techniques [20, 21, 22]. It is composed of a lattice of corner-sharing copper hexagons whose normals point in different directions (a different lattice of hexagons has been seen in frustrated spinels like ZnCr₂O₄ [33]). This material, which has been studied by a number of groups, has been called a ‘spin web’ compound [31] with a Néel temperature of 61 K [30].

If one takes a kagome lattice and then stretches it along the c axis, one gets a hyperkagome structure, with corner sharing triangles arrayed in a cubic space group. The mineral choloalite (Pb₃(Cu₅Sb)₁/₃(TeO₃)₆Cl) has this lattice [21], with the same P4₁32 space group as the well known spin liquid iridate, Na₄Ir₃O₈ [34]. A simpler synthetic material, PbCuTe₂O₆, has the same hyperkagome lattice and space group [22]. No magnetic ordering has been seen by NMR and µSR down to 20 mK [35], though thermodynamic data indicate some type of transition occurring at 0.87 K [22], perhaps related to impurities [35]. Because of the distorted nature of the lattice, modeling this material is somewhat challenging, but exchange couplings have been proposed based on electronic structure calculations [22]. A Sr variant is known that orders at 5.5 K [36].

The first attempt to make Cu₃TeO₆ was by high temperature hydrothermal synthesis [20]. CuTeO₄ has been made under similar conditions [23], though Cu₃TeO₆ is thermodynamically more stable. The interest in CuTeO₄ is that it exhibits a square lattice net for the copper ions (Fig. 5). But unlike a typical cuprate, the Cu-O-Cu bond angles are either 122.5° or 126.1°, more similar to Herbertsmithite than other cuprates. This buckling of the CuO₂ planes is due to an attempt to lattice match with a TeO₂ layer. Interestingly, the copper ions are nearly octahedrally coordinated, with short, medium and long Cu-O bonds which are 14% different in length for Cu₂ ions, and 18% different for Cu₁ ions. Despite these differences from other cuprates, the electronic structure is remarkably similar, with a predicted magnetic ground state which is a quasi-2D Néel state [37]. It has been proposed that replacing Te⁶⁺ by Sb⁵⁺ could hole dope this material, potentially leading to a superconducting phase [37]. Experimenally, only the structure is known, and beyond the original synthesis paper [24], the only reports in the literature is finding it as a secondary phase.

In the material Sr₂CuTeO₆ [24], the Te ions move down into the plane (Fig. 6). So, though the copper ions again form a square net, the exchange pathway is Cu-O-Te-O-Cu (or Cu-O-O-Cu) as in quetzalcoatlite. This material is rather straightforward to synthesize, and a number of variants are known (with Ba instead of Sr, or W instead of Te). The Sr variant orders at ~80 K [24], but the Ba analoge does not appear to order (for the W version, the Ba analogue orders at ~30 K, but the Sr one does not). These maetrials have been extensively studied, as well as modeled by DFT calculations [38]. Crystals have been large enough to do both elastic [39] and inelastic [40] neutron scattering. One finds a simple Néel lattice, but with interactions significantly reduced from the layered cuprates due to the super-superexchange nature of the magnetic coupling.

SrCuTe₂O₇ has two types of Te sites (one 4+, one 6+)
The Cu ions sit on an orthorhombic lattice, either being connected by a Cu-O-Sr-O-Cu pathway (long direction) or an orthogonal Cu-O-Te-O-Cu pathway (Fig. 7). There are, though, four different layers containing copper (Z=4). No evidence for magnetic order has been found, but typically, an upturn is seen in the susceptibility at low temperatures, indicating the presence of orphan spins. Similar behavior is seen in Pb and Ba variants.

The last material we mention is Cu₃BiTe₂O₈Cl [26], similar to the mineral francisite, Cu₃BiSe₂O₆Cl. The lattice formed is a distorted version of a so-called kagome staricase, with the copper kagome layers strongly buckled. Francisite itself has been synthesized and studied quite a bit [41–43], and orders at 27.4 K, but the order is complicated due to the low symmetry of the lattice.

There are many other copper tellurium oxides that are not mentioned here, perhaps the best known being the perovskite CuTeO₃, the Se variant of which is a ferrimagnet. Interestingly, it has been recently modeled by Byung Il Min’s group [44], he being a former student of Art’s that I had the pleasure of working with when I was a postdoc of Art’s. Many materials not mentioned here exhibit chains instead, or more complex lattices. Variants are also known where Sb replaces Te. Certainly, Mother Nature has been kind to us in providing a wonderful playground of unexplored materials. It is up to us to do the exploring.

I know that if Art were still with us, he and his group would likely take on the challenge of trying to better understand this fascinating class of materials. Ironically, the motivation behind the study of spin liquids is the original work of Phil Anderson as outlined at the beginning of this article, and the two of them were well known for not seeing eye to eye (Art being a student of Slater’s, and Phil of van Vleck’s). In that context, I cannot resist showing a cartoon I presented to Art on his 80th birthday (Fig. 8) motivated by a quote from Martin Peter that succinctly illustrates the complex relation between Art and Phil [46]. I should end by saying that the physicist I came to be was shaped by the melding of the influences that these two individuals had on me, both of which I am eternally grateful to.

Work supported by the Materials Sciences and Engineering Division, Basic Energy Sciences, Office of Science, US DOE. The author would like to thank Antia Botana, who was instrumental in the work on CuTeO₄, and as an aside, is a ‘grandchild’ of Art’s (having been supervised as a postdoc by two people who were supervised as postdocs by Art, myself and Warren Pickett). And my thanks to Ruqian Wu, Bruce Harmon and Sam Bader for this opportunity to honor Art’s memory.

[1] M. P. Shores, E. A. Nytko, B. M. Bartlett and D. G. Nocera, J. Am. Chem. Soc. 127, 13462 (2005).
[2] S. Chu, P. Muller, D. G. Nocera and Y. S. Lee, Appl. Phys. Lett. 98, 092508 (2011).
[3] M. R. Norman, Rev. Mod. Phys. 88, 041002 (2016).
[4] P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. S. Lord, A. Amato and C. Baines, Phys. Rev. Lett. 98, 077204 (2007).
[5] P. W. Anderson, Mat. Res. Bull. 8, 153 (1973).
[6] P. W. Anderson, Phys. Rev. 86, 694 (1952).
[7] D. A. Huse and V. Elser, Phys. Rev. Lett. 60, 2531 (1988).
[8] B. Bernu, C. Lhuillier and L. Pierre, Phys. Rev. Lett. 69, 2590 (1992).
[9] P. Lechminiant, B. Bernu, C. Lhuillier, L. Pierre and P. Sindzingre, Phys. Rev. B 56, 2521 (1997).
[10] B.Bernu, C. Lhuillier and L. Pierre, Nature 464, 199 (2010).
[11] B. Savary and L. Balents, Rep. Prog. Phys. 80, 016502 (2017).
[12] G. Giuseppetti and C. Tadini, Neues Jahrb. Mineral. Monatsh. 9, 401 (1980).
[13] A. G. Christy, S. J. Mills and A. R. Kampf, Mineral Mag. 80, 415 (2016).
[14] S. J. Mills, A. R. Kampf, A. G. Christy, R. M. Housley, R. E. Reynolds and J. Marty, Mineral. Mag. 78, 1325 (2014).
[15] A. R. Kampf, S. J. Mills, R. M. Housley and J. Marty, Amer. Mineral. 98, 506 (2013).
[16] F. Ohmi, C. Sabelli and R. Trosti-Ferroni, Eur. J. Mineral. 7, 1331 (1995).
[17] P. C. Burns, J. J. Pluth, J. V. Smith, P. Eng, I. Steele and R. M. Housley, Amer. Mineral. 85, 604 (2000).
[18] S. M. Margison, J. D. Grice and L. A. Groat, Canad. Mineral. 35, 55 (1997).
[19] J. D. Grice, L. A. Groat and A. C. Roberts, Canad. Mineral. 34, 896 (1978).
[20] L. Falck, O. Lindqvist and J. Moret, Acta Crystal. B 34, 896 (1978).
[21] A. E. Läm, L. A. Groat, J. D. Grice and T. S. Ercit, Canad. Mineral. 37, 721 (1999).
[22] B. Koteswararao, R. Kumar, P. Khuntia, S. Bhowal, S. K. Panda, M. R. Rahman, A. V. Mahajan, I. Dasgupta, M. Baenitz, K. H. Kim and F. C. Chou, Phys. Rev. B 90, 035141 (2014).
[23] L. Falck, O. Lindqvist, W. Mark, E. Philippot and J. Moret, Acta Crystal. B 34, 1450 (1978).
[24] D. Iwanaga, Y. Inaguma and M. Itoh, J. Solid State Chem. 147, 291 (1999).
[25] J. Yeon, S-H. Kim, M. A. Hayward and P. S. Halasyamani, Inorg. Chem. 50, 8663 (2011).
[26] R. Becker and M. Johnsson, Solid State Sci. 7, 375 (2005).
[27] D. Schmalfuss, P. Tomczak, J. Schalenburg and J. Richter, Phys. Rev. B 65, 224405 (2002).
[28] T. Fennell, J. O. Piatek, R. A. Stephenson, G. J. Nilsen and H. M. Ronnow, J. Phys.: Condens. Matter 23, 164201 (2011).
[29] C. Carbone, R. Basso, R. Cabella, A. Martinelli, J. D. Grice and G. Lucchetti, Amer. Mineral. 98, 1899 (2013).
[30] M. Herak, H. Berger, M. Prester, M. Miljak, I. Zivkovic, O. Milat, D. Drobac, S. Popovic and O. Zaharko, J. Phys.: Condens. Matter 17, 7667 (2005).
[31] G. Caimi, L. Degiorgi, H. Berger and L. Forro, EPL 75, 496 (2006).
[32] Z. He and M. Itoh, J. Magn. Magn. Matls. 354, 146 (2014).
[33] S.-H. Lee, C. Broholm, W. Ratcliff, G. Gasparovic, Q. Huang, T. H. Kim and S.-W. Cheong, Nature 418, 856 (2002).
[34] Y. Okamoto, M. Nohara, H. Aruga-Katori and H. Takagi, Phys. Rev. Lett. 99, 137207 (2007).
[35] P. Khuntia, F. Bert, P. Mendels, B. Koteswararao, A. V. Mahajan, M. Baenitz, F. C. Chou, C. Baines, A. Amato and Y. Furukawa, Phys. Rev. Lett. 116, 107203 (2016).
[36] N. Ahmed, A. A. Tsirlin and R. Nath, Phys. Rev. B 91, 214413 (2015).
[37] A. S. Botana and M. R. Norman, Phys. Rev. B 95, 115123 (2017).
[38] H. Rosner, M. Schmitt, O. Janson, A. Tsirlin, D. Kasinathan, U. Nitzsche, K. Koepernik, S. Golbs, M. Schmidt and W. Schnelle, http://www2.cpfs.mpg.de/web/docs/scientreport/report2009_data15.pdf
[39] T. Koga, N. Kurita, M. Avdeev, S. Danilkin, T. J. Sato and H. Tanaka, Phys. Rev. B 93, 054426 (2016).
[40] P. Babkevich, V. M. Katukuri, B. Fak, S. Rols, T. Fennell, D. Pajic, H. Tanaka, T. Pardini, R. P. Singh, A. Mitrushchenkov, O. V. Yazyev and H. M. Ronnow, Phys. Rev. Lett. 117, 237203 (2016).
[41] P. Millet, B. Bastide, V. Fashchenko, S. Gnatchenko, V. Gapon, Y. Ksari and A. Stepanov, J. Mater. Chem. 11, 1152 (2001).
[42] M. Pregelj, O. Zaharko, A. Gunther, A. Loidl, V. Tsurkan and S. Guererro, Phys. Rev. B 86, 144409 (2012).
[43] I. Rousochatzakis, J. Richter, R. Zinke and A. A. Tsirlin, Phys. Rev. B 91, 024416 (2015).
[44] M. A. Subramanian, A. P. Ramirez and W. J. Marshall, Phys. Rev. Lett. 82, 13203 (1999).
[45] B. H. Kim, H. Choi and B. I. Min, New J. Phys. 12, 073023 (2010).
[46] M. Peter, Physica B 172, viii (1991).