Technical Memorandum

Ambature TM # 2014 - 05

To: Ron Kelly, CEO, Ambature Corp.

Cc: Ketan Patel, Richard Tucker

From: Davis H. Hartman

Date: 10/28/2014

Re: **A Notional View of the HTS Phase Transition**

Ron;

A proposed strategy to search for High Temperature Superconductors based on observed antiferromagnetic order and multiphase competition

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It is generally agreed that high temperature superconductivity (HTS) is driven by different mechanisms than low temperature superconductivity (LTS). LTS materials are metals, whose behavior in their normal conducting state is adequately described as a Fermi liquid, and whose superconducting properties are well quantified using the BCS theory[1]. The underlying material science of LTS is well understood; complex (albeit costly) devices and integrated circuits (like RSFQ digital logic) have been and still are implemented in moderate volume with high success.

At temperatures exceeding $\sim 40^{\circ}$ K traditional BCS style superconductivity in metals has not been observed, probably owing to competition from thermal carriers preventing the needed pairing and long quantum mechanical correlation. However, the discovery in 1987 of a new class of high temperature superconducting materials changed everything. These HTS materials are not conductors but ceramics, semiconductors or even straightforward Mott insulators. Their phase transitions, when observed, are not necessarily Type I. Millions of man-hours and billions of dollars have been spent in aggregated scientific efforts to understand how these materials function as superconductors. These efforts have thus far

[1] Bardeen, J., L. N. Cooper, J. R. Schrieffer, "Theory of Superconductivity", Physical Review, 108(5), pp. 1175-1204, 12/01/1957.

brought limited results. To date there is no complete theory akin to BCS that completely describes HTS material behavior, and new classes of materials with HTS qualities continue to be discovered, without theoretical explanation.

A different approach to the problem may be needed; one that has search formalism embedded within. In this white paper we explore the HTS state as the evolutionary outcome of a phase transition, rather than studying the steady state superconducting behaviors of a given material. That is, we ask the question "How does a material get to the desired normal-to-superconducting phase transition?" rather than asking "What does HTS look like?" The latter question begs the science while the former question tries to identify a search method.

The Phase Transition and Entropy

The onset of BCS superconductivity in a material is a Type I phase transition (the first derivative of the free energy is discontinuous at T_C). Phase transition ns occur in materials when an environmental change creates a more energetically favorable set of conditions for the material. Many phase transitions are thermodynamically reversible and the two states often can coexist in thermal equilibrium. As far as we can tell, the LTS phase transition is reversible and is adequately described thermodynamically by the theorem of Clausius and Clapeyron. HTS phase transitions appear to be more complex than LTS ones.

While they are taking place, phase transitions are extremely complex, chaotic and non-linear, as observing a microscopic view of water freezing will attest. Nevertheless, most phase transitions result in a dramatic increase or decrease in the ordering of a system. If energy is removed from a material system (for example by lowering ambient temperature) and a phase transition ensues, it will result in a more ordered state. So, when heat is removed from water for example, its free energy reduces until the final state of an aggregated crystal is favored by nature over a colder liquid, i.e., the liquid freezes. This final state is more ordered than the initial state. Conversely, if an appropriate amount of heat (latent heat of melting) is injected into ice via a thermal reservoir, a tipping point is reached where the crystal structure of the ice is deconstructed in an avalanche event and the material liquefies into a much more disordered state.

The entropy of a state is a measure of its order. Entropy is defined statistically as

$$S = k \cdot \log(\Omega). \tag{1}$$

Here Ω is defined as the density of final states. Ω is a measure of the number of distinct results a transition can have. For example, the density of states of a thrown die is six, since there are six possible outcomes. So, when a phase transition occurs as the result of the removal of energy, the entropy is reduced, or $\Delta S < 0$. Conversely, when energy is pumped into a material system, it can trigger a phase transition where $\Delta S > 0$. As mentioned earlier, an obvious example is ice melting.

It is not clear that, in the case of HTS, that competing states can or do coexist in thermal equilibrium. It may be that they compete for their place as a lowest energy solution. This subtle point deserves more consideration.

Density of States: Obviously, the more possible outcomes of an event, the less likely a single event is to occur. To predict the outcome of a change of state requires a full knowledge of all the possible outcomes, or the density final states.

It is often the case that many physical processes simultaneously take place or are energetically capable of taking place in a system. There is evidence that this occurs in many material systems potentially capable of an HTS phase transition. Ferri-magnetic or antiferromagnetic states have been observed to emerge in competition with superconductive transitions.

In these cases the possible final states are mixed. They are expressed in the form of a "density matrix". For each candidate final state there is a corresponding Hamiltonian describing the physics of that state and possibly soluble Eigenstates of the system. Each Hamiltonian component represents the energy of a state of the system. The final states of each state are associated with a probability of occurrence within the mixed state system. The sum of all these possible states is r, and is expressed as the density matrix, whose elements are,

$$\rho_{n'n} = \sum_i w(i)\ a^{*(i)}_n\ a^{(i)}_{n'} \tag{3}$$

Here the *w(i)* are weight values for each candidate transition and the a_n are the wave function coefficients. In a mixed state, the system will transition to the most energetically favorable one. In general, that state will fluctuate with time and environmental factors. If the energy of the candidate states is comparable, then predicting the final state can be difficult. However, if in a given material system there are two candidate states with only two comparable state probabilities, then one could be invoked if the other state can be frustrated. We explore the possibility of seeking out new HTS materials by searching for competing states and means of frustrating the unwanted state.

Antiferromagnetic Behavior

Antiferromagnetic behavior has been associated with materials exhibiting high temperature superconductivity, such as copper oxide materials like YBCO. In these materials, antiferromagnetic order is either frustrating the onset of HTS or vice versa. In other cases, antiferromagnetic order has been observed as traveling waves, called "density waves", or "spin density waves", (ferrimagnetic order) [2,3].

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2 "No mixing of superconductivity and antiferromagnetism in a high-temperature superconductor", I. Bozovic, G. Logvenov, M. A. J. Verhoeven, P. Caputo1, E. Goldobin & T. H. Geballe, *Nature* 422, 873-875 (24 April 2003)

Antiferromagnetic order is the anti-alignment of spin magnetic moments in a material, at the unit cell level, resulting in perfectly anti-aligned moments and null magnetic field. It is a very highly ordered state of the material. When antiferromagnetic order occurs, there forms a magnetic unit cell of spin anti-alignment that is different and often larger than the chemical unit cell. The order is the result of the overlapping of the Bloch wave functions to the extent that Pauli exclusion principal prohibits two neighboring atoms in the same state to coexist; hence neighbors share their symmetric position wave function $\psi(r,t)$ but swap their spin wave function (anti-symmetric) $\sigma(i)$, rendering the total wave function anti-symmetric as required. A quasi-fictitious field called the exchange field is introduced to account for this behavior, but it is, to our limited understanding, the outcome of a selection rule that is known to exist but it is not really known why.

We approximate a copper or oxygen atom with the quantum mechanical model of Hydrogen-like atoms, whose wave function contains a radial part, an azimuthal part and a spin-dependent part

$$\Psi_{E,l,m}(r,\theta,\phi,\sigma) \cong f_{n,l}(r) \circ Y_{l,m}(\theta,\phi) \circ S_i(r,\sigma). \tag{4}$$

Here $S_i(r,\sigma)$ represents the anti-symmetric electron spin wave function, $Y_{l,m}(\theta,\phi)$ are spherical harmonics and the radial part $f_{n,l}(r)$ is most generally expressed in terms of the confluent hypergeometric function of the first kind $F(a,b,z)$ as,

$$f_{n,l}(r) = N_{n,l}\left(\frac{2Z\rho}{n}\right)^2 \cdot F(-n+l+1, 2l+2, 2Z\rho/n) \cdot e^{-(Z\rho/n)} \tag{5}$$

Here n, l and m are principal and angular momentum quantum numbers, Z is the element atomic number, $\rho = r/a_o$, a_o is the Bohr radius (5.3×10^{-11} meters) and N_{nl} is a numerical constant.

We consider the behavior of $f_{n,l}(r)$ in different orbital states, to estimate the degree of wave function overlap that might occur in a material with a given interatomic spacing. It is theorized that this overlap has bearing on whether antiferromagnetic ordering can occur or is frustrated. Figure 1 shows $f_{n,l}(r)$ for

[3] Henley, C. L., "Antiferromagnetic and frustrated order", http://www.lassp.cornell.edu/clh/p654/MM-5.3.pdf

n=1/l=0 (1s radial state; Figure 1a), *n=2/l=1 (*2p radial state; Figure 1b) and for *n=3/l=2 (3d* radial state; Figure 1c). As the radial state increases (corresponding to a larger atom; for example copper), the wave function extends over more area.

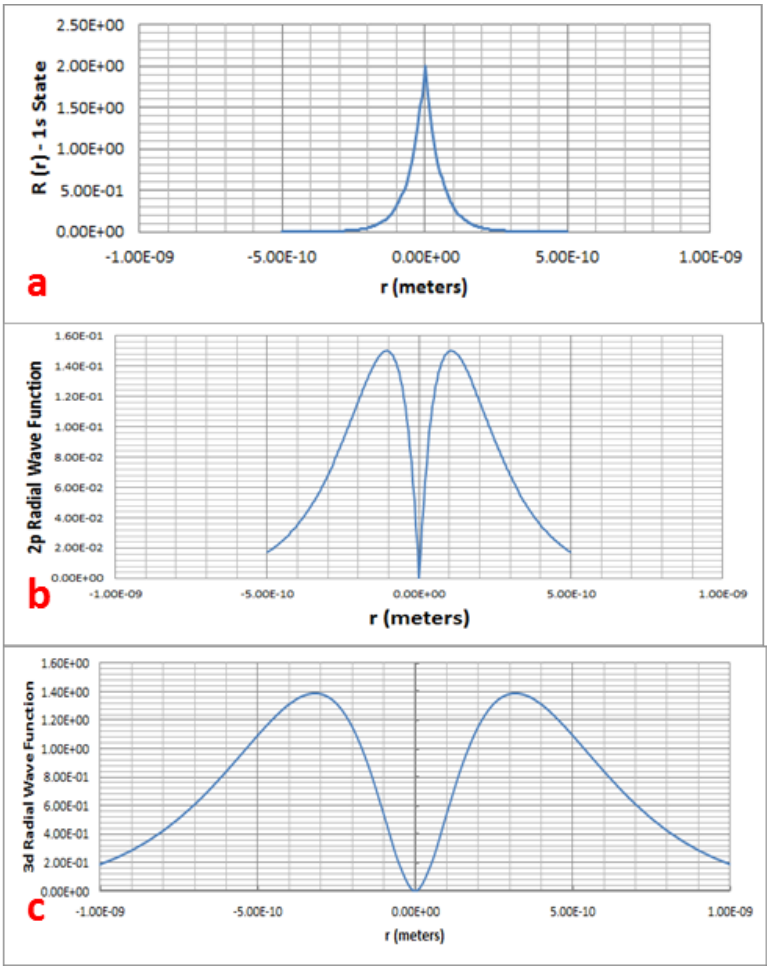

Figure 1: Radial wave functions for the 1s, 2p and 3d states of a Hydrogen-like atom. The wave function extends as the state increases.

Next, we place these wave functions at the site of three atoms of a lattice with interatomic separation d_0. Figure 2 shows how the wave functions of the neighboring atoms begin to overlap for spacing d_0 of 15 Å and 5 Å. In these figures we plot the sum of three wave functions to depict the effect of proximity on the aggregated picture. However, in the Bloch picture, the radial wave function of the aggregated system is the [symmetric] product of the individual wave functions, summed over all space. This summation of displaced products, plotted in Figure 3, is proportional to the correlation function for the Bloch atoms. This is a measure of the interatomic spacing (d_0) for which antiferromagnetic order will or will not occur. When d0 is smaller than this correlation distance, antiferromagnetic order is possible; larger interatomic spacing would not be likely to support antiferromagnetic order because the radial wave functions are not correlated. This means that the exchange field within the material would be driven to change. These argumeents are admittedly subjective. However it is hoped they can be tool for searching the vast material space for HTS onset that is otherwise frustrated by the competing antiferromagnetic transition.

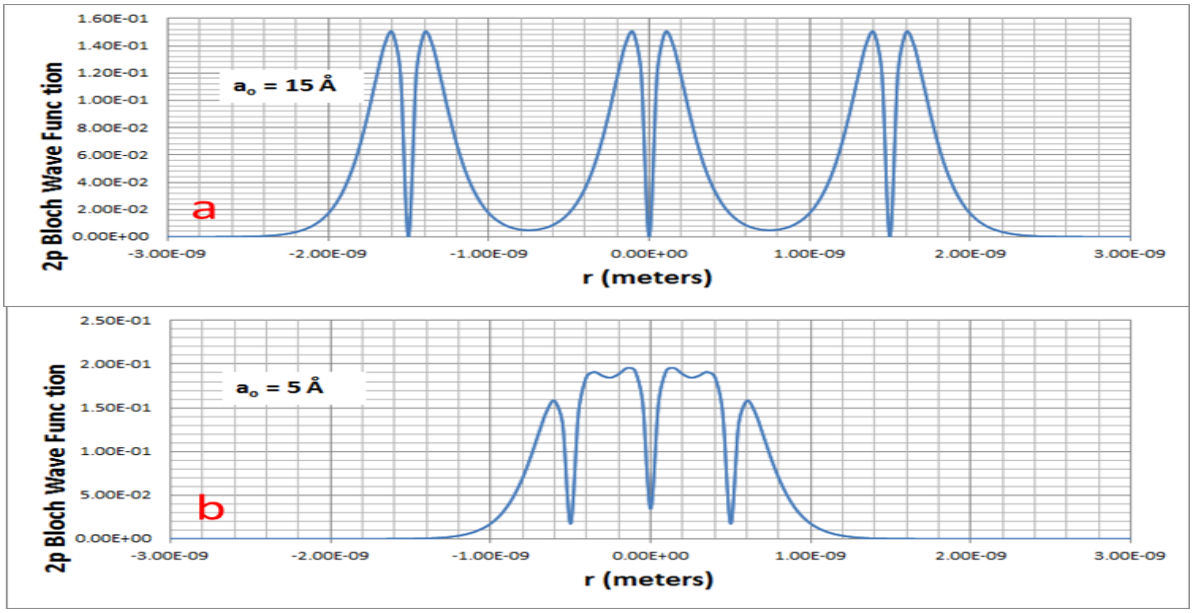

Figure 2: Overlap of Bloch wave functions (summation mode) as interatomic spacing changes from 15 angstroms (a) to 5 angstroms (b).

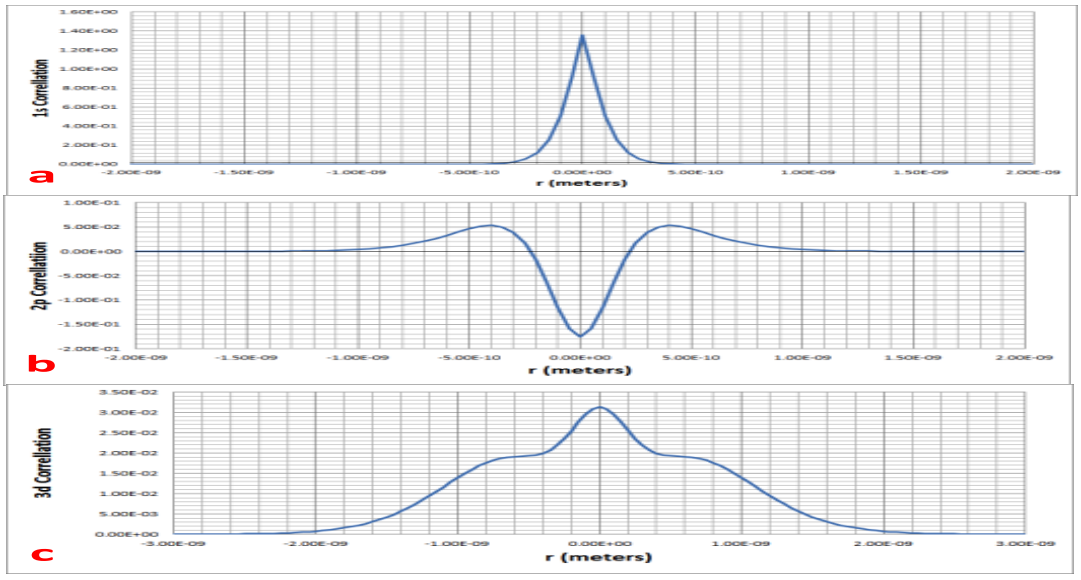

Figure 3: Product-mode radial wa ve functions, integrated over space to yield correlation of wave functions between Bloch sites.

Summary

While this exercise serves to illustrate in a very simple way, the overlapping of wave functions making up an aggregated system, it is a qualitative look at the problem. The notion that magnetic order (antiferromagnetic, ferromagnetic, ferromagnetic, etc.) is associated with onset of superconductivity in materials is not new. Nor is the idea that the phase transition leading to HTS should be scrutinized more completely. The overlapping of wave functions in HTS onset involves a complex series of phase coherent events (which I made no attempt to include in this illustration). Pairing of charge carriers in BCS is a dominating second order event which, in some metals is energetically favorable to transport of charge carriers in a normal metal. To date, I do not think that anyone has comparable knowledge of pairing in HTS materials, or if there is any one pairing mechanism.

The question "What does HTS look like?" may not be answerable any time soon. However, looking for ways to probe (both experimentally and theoretically) the nature of the normal-to-HTS phase transition may prove fruitful in the short run. To do this, Ambature should find credible research partners and engage with them both experimentally and theoretically. Ambature's a-axis deposition and growth techniques can provide new parametric design levers for producing novel HTS candidate materials.

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09/10/2014