First Trimester 2005 EPRI Project Report

“Consultant to EPRI Project Management on the
Fabrication of New Superconducting Materials”

EPRI Contract Agreement No. EP-P18263/C9013
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Brief History of Superconductivity

It can be argued that the story of superconductivity begins with the discovery of the particulate nature of the electron in 1897 by J. J. Thompson closely followed by the notion formulated in 1900 by Paul Drude that electrical conduction in metals arose from the free flow of these negatively charged particles within. Their “freeness”, evidenced by measurements of electrical conductivity, increased with decreasing temperature, and, although the Bohr model of the atom with its orbiting “planetary” electrons was still fifteen years in the future, its basic elements were already anticipated, and much speculation arose as to what would happen to the electrons in a metal at “absolute zero.” A key element of the Drude theory was that the reason the electrons were able to move arose from their being initially “excited” out of their orbits by ambient thermal energy. After this initial step, the electrical conductivity decreased because the electrons were more and more “banged about” or scattered by the atomic vibrations. On the other hand, if the temperature of the metal was made sufficiently high, the banging became violent enough that some actually escaped, thereby enabling Thompson’s very discovery of them.

Now, although the conductivity of all known metals decreased with temperature (this behavior actually defines the term “metal”) due to the weaker “banging about”, it was widely held that at low enough temperatures, the electrons should “freeze out,” snapping back into their maternal atomic orbits, and electrical conductivity would completely disappear. In other words, the “metallic state” would inevitably be destroyed, and vigorous exploration of the low temperature properties of metals began in Europe at the as the 20th century opened.

The liquefaction of helium in 1908 by Heike Kammerlingh Onnes in Leiden greatly abetted this search by allowing temperatures as low as 0.9 Kelvin to be produced, far closer to absolute zero than previously obtainable. A major hindrance to the unambiguous measurement of the electrical conductivity of metals at low temperature was the presence of impurities. By 1911, a research associate in Onnes’ laboratory was able to obtain ultrapure mercury metal by multiple distillation, and the very first measurement of its electrical properties immersed in liquid helium resulted not in a tendency toward zero conductivity, but the sudden appearance of zero resistance, in other words, a “perfect metal” for which Onnes coined the term “supraleitung,” or “superconductor.”

Little did they suspect that they had discovered not a perfect metal, but the complete destruction of the metallic state! It would be another four decades before this seemingly paradoxical and “impossible” situation was indeed what really was going on.

In the 1920s, Wolfgang Pauli invoked the concept of electron spin to explain a plethora of accumulated spectral data on atoms and molecules taken in an applied magnetic field.. This model required a “quantum dipole” interaction between neighboring electron spins that would eventually “pair them” into up and down magnetic dipoles, which today we call the Heisenberg exchange interaction, in order to produce the lowest total energy of an ensemble of electrons. When extended to the Drude model, it became clear by the 1930s that there was something “unstable” about the idea of a “gas” of electrons when quantum mechanics dictated there would always be an interaction of some kind between them. That is, at absolute zero, or close to it, electrons would inevitably pair through the Heisenberg antiferromagnetic exchange interaction producing an “energy gap,” thus lowering the overall energy, which then could only be overcome by thermal excitations at and above a given threshold temperature. Such behavior is what defines an “insulator.”

In the late 40s, evidence arose that the charge transported in the superconducting state of a metal involved pairs of electrons rather than just a single charge. Leon Cooper speculated the electrons were somehow spontaneously “paired” at the onset of superconductivity. But what was the source of the pairing interaction? It had been noticed that the superconducting transition temperature of a given metal or alloy depended on the isotopic mass of the nucleus, implying that the very thermal vibrations of the atomic lattice that produced electrical resistance were also involved in bringing on superconductivity. Careful measurements of the quantum nature of these vibrations revealed that there was always a small range of energies where they could produce a slight attractive interaction between pairs of electrons and not just scatter them.

Why then was superconductivity observed and not insulating behavior?

For many years, the thermodynamics of the superconducting state implied it was pervasive and macroscopic in nature, but clearly could not, like a liquid-solid phase transition, be explained by classical mechanics. John Bardeen guessed superconductivity might be a manifestation of a quantum macroscopic state under which the electron pairing occurred in momentum space instead of “real” space, and, by virtue of the uncertainty principle, perfect localization in momentum space results in perfect delocalization in “real” space. J. Robert Schrieffer, Bardeen’s graduate student, was able to statistically solve the Hamiltonian for Avogadro’s number of electrons under an arbitrarily weak attractive interaction, a mathematical tour-de-force, which showed superconductivity was due to the “real” space motion of a macroscopic quantum state containing net charge. But there clearly was a destruction of the metallic state, because the lower energy of the paired state resulted in a gap that required external thermal or optical excitation to restore it. In fact, it is now clear that semiconductors and insulators could in principle become superconductors if the pairing gap were greater than the single electron band gap, although no such materials actually exist (yet).

The BCS theory, awarded the Nobel Prize in 1972, and its subsequent refinement and extension, is arguably the most elegant and far-ranging accomplishment of 20th century condensed matter physics. In its most generalized form, using the framework of quantum electrodynamics, it describes the pairing of fermions interacting through a boson field. For superconducting materials, the fermions are electrons or holes, and the boson field is comprised of lattice vibrations or phonons. In the case of neutron stars, the fermions are spinning neutrons and the boson field arises from strong force-field leaking out from the quark interactions within. The BCS theory also provides the framework for high temperature superconductivity. The problem is we don't yet know the nature of boson field…is it due to magnetic excitations or some type of exotic lattice vibrations, or perhaps the collective excitation of the plasma of holes themselves?

The bottom line is that the "robustness" of the BCS state depends exponentially on the strength of the fermion-boson interaction. In the case of electrons and phonons (lattice vibrations), if this interaction is really strong, a crystallographic phase transition to a lower energy lattice structure, resulting in an even number of electrons within each unit cell, is likely to occur before superconductivity can set in and we wind up with a semiconductor or insulator. Nonetheless, a good hunting ground for new superconducting materials are systems which are on the verge of undergoing a crystallographic or magnetic phase transition and may succumb to superconductivity first.

Technical Rationale for the Present Project

It is against this background that EPRI and Stanford contracted to undertake a three year search for new superconductors in previously unexplored transition metal oxides, concentrating initially on the fabrication and properties investigation of metastable cubic copper oxide (CuO). Copper monoxide is found in nature as the mineral tenorite whose crystal symmetry is monoclinic, not cubic, whereas its closest neighbor electronically, nickel monoxide, is cubic. Thus, there is reason to suspect that if metastable cubic copper oxide, or a nickel-copper oxide solid solution, could be synthesized, it may exhibit strong electron-phonon interaction may be in play trying to "get it back" to the monoclinic structure it "wants to be," and "something interesting," like superconductivity, might emerge if the structure can be properly doped to produce a few free carriers.

Why pursue this research at Stanford?

For the following reasons:

1. The idea to explore the cubic copper oxide system comes from Ted Geballe, Emeritus Professor, and founder of the Geballe Laboratory for Applied Materials (GLAM) in the Stanford Applied Physics Department, who has discovered more superconductors than any other living scientist.

2. GLAM, and its staff, are in the forefront of thin film fabrication of novel structures, many of them metastable. They have contributed enormously to the advanced of coated conductors through the development of IBAD-MgO which is now the buffer layer of choice on the SuperPower commercialization path to 2G wire and tape.
3. The combination of molecular beam epitaxy, in-situ high and low electron diffraction, x-ray and ultraviolet photoemission spectroscopy, IR and visible Fourier spectroscopy, sample substrate preparation, and ion-beam assist during growth (IBAD), all in the same physical apparatus, exists no where else on the planet. This system is called the Molecular Beam Growth (MBG) system.
4. The presence of the ion assist beam is a key element of the MBG for this study. The process was developed by IBM in the early 1980s. It consists of directing an energetic beam of heavy inert gas ions, typically argon or xenon, along a pre-chosen unit cell direction of the symmetry type one is hoping to grow the film. Any atoms deposited that lie along this direction are knocked away and are not incorporated in the growing film. The notion of IBAD acting as an "atomic sandblaster" is a good analogy.
5. The team of investigators, as follows
    a. Ted Geballe, Emeritus Professor,
    b. Mac Beasley, Professor of Applied Physics and former Dean of the Stanford School of Arts and Sciences,
    c. Bob Hammond, Research Professor, who designed and built the laboratory and equipment described above,
    d. Assisted by Gertjan Koster, Visiting Professor from the University of Twente, Hideki Yamamoto, Senior Scientist on sabbatical from the National Institute of Metals, Japan, and Wolter Siemons, PhD Candidate, Stanford and Twente Universities,
    all in all, an excellent combination of senior and junior researchers.

Summary of Activity During 2004

The contract for this project was let in the summer of 2004. Most of the activity in the last trimester of 2004 involved staffing and repair and acquisition of equipment, and is covered in the associated Form 112 and invoice documents pertaining to this period.

First Trimester 2005 Activities and Results

- January
  The vacuum pump on the ion beam assist gun was sent out for repair. During this time, a research plan was put in place once the MBG was back on line. Some initial calculations were performed on the stability of cubic CuO which are still currently underway. Some of the effort of the team was diverted to formulating reports to the DOE Wire Development Workshop on project other than the EPRI work.
- February

Repair was completed on the IBAD gun and the unit re-installed. Some initial tests were performed which showed the monoclinic form of CuO could be epitaxially deposited on single crystal substrates of strontium titanium oxide (STO). STO, a cubic perovskite, is a very commonly employed substrate, along with MgO, for the deposition of other perovskites such as the family of high temperature superconducting layered copper oxide compounds. As in January, the junior staff was required to prepare talks for the March APS and MRS meetings reporting on other activities in GLAM.

- <u>March – April</u>
  Experiments on the MBR unit began in earnest during this period. Here are the principal results obtained so far.
    1. It appears that cubic CuO may actually grow heteroepitaxially on STO and MgO substrates for the first three or four unit cell layers without the need for an assist beam (IBAD), before reverting to the more stable tenorite structure as growth continues. High intensity x-ray diffraction measurements are currently underway using facilities of the Stanford Synchrotron Radiation Laboratory (SSRL) to directly confirm this suspicion.
    2. When the assist beam is turned on during growth on STO and MgO, in situ reflection high energy electron diffraction (RHEED) suggests a cubic phase is "trying" to grow, but the data needs further refinement and different ion beam impingment angles need to be explored.
    3. However, when an amorphous substrate is employed instead of single crystal STO or MgO, no oriented films of CuO can be grown at any ion beam parameters of energy or direction. This is unlike other systems such as IBAD-ed MgO deposited on a-SiN which grows cubically oriented (this finding was a key claim in the "Stanford patent" on coated conductors). It seems as though the successful growth of thick cubic CuO films will require a combination of initial heteroepitaxial formation of the first few atomic layers followed by IBAD.

<u>Second Trimester 2005 Planned Activities</u>

1. Continue to explore conditions for the heteroepi + IBAD growth of "high crystalline" quality thick CuO films, whereas at present mixed cubic-monoclinic phase intergrowth is being obtained.
2. Explore "seeding" the growth of cubic CuO with the addition of small amounts of Ni (NiO is cubic, and very old literature (in German) implies the cubic symmetry of NiO is preserved up to 40% substitution by Cu before transitioning to monoclinic. In line with searching for superconductivity in the vicinity of a phase transition, this "cross-over" point might prove interesting. Surprisingly, not many investigations seem to have been made on the properties of Cu-Ni-O solid solutions.
3. Initial attempts will be made to "dope" the CuO films during growth with monovalent ions such as F and Na (the former should yield electron transport and

the latter holes). If successful, optical, electrical transport and magnetic measurements will be performed.

4. Concurrent with the above, it is intended to explore the phase stability of cubic CuO and Cu-Ni-O solid solutions using commercial total energy quantum chemistry programs under Stanford license. That is, we will attempt to understand the “width” of the metastable energy valley surrounding the cubic symmetry and the strength of lattice vibration fluctuations attempting to transition to the more stable tenorite phase.