Structural and Doping Correlations to High Temperature Superconductivity in Copper Oxides

Keith D. Kepler Literature Seminar February 20, 1992

The discovery of high temperature superconductivity [1] in copper oxide compounds was announced by Bednorz and Müller [2] in mid-1986 and confirmed late that year at the University of Tokyo [3] and the University of Houston [4]. Their observation of a superconducting transition temperature onset (T_c) at 35K in a La-Sr-Cu-O ceramic led to a frantic search for compounds with an even higher T_c and won them the1987 Nobel Prize in Physics.

Today, there are over one hundred known high temperature superconductors. The most thoroughly studied of these are the copper oxide materials $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+x}$. Most of the copper oxide compounds have similar features which include planes of superconducting CuO_2 layers separated by 'charge reservoir' layers [4], complex temperature vs. doping phase diagrams [6], and brittle, polycrystalline morphology. The materials can be synthesized in many ways [7] with the most common goals being the production of single crystals [8], thin films [9] or polycrystalline pellets.

Bardeen, Cooper, and Schrieffer (BCS) theory of normal low temperature superconductivity [10] has not proven to be very useful in modeling the new superconductors, though the low temperature and high temperature superconductors do share some characteristic BCS properties [11]. As a result of this breakdown in theory, an extensive amount of research has been done to develop a clearer picture of the superconducting state in the copper oxides.

Much of the research has concentrated on the structural and electronic properties of these materials. Also studied has been the changes in these properties as the compound has been increasingly doped. The phase diagram of the $La_{2-x}Sr_xCuO_4$ compound (Figure 1) illustrates the many states involved in the superconduction transition of most copper oxide superconductors. As BCS theory predicts, the compound must at least be metallic before superconduction can occur. From the structure of $La_{2-x}Sr_xCuO_4$ (Figure 2) an electronic band diagram based on Cu-3d, O-2p overlap in the superconducting copper oxide layers can be constructed [12]. The observed antiferromagnetic insulating state has been successfully modeled by assuming the unpaired spins (tetragonal, d^9 copper atoms) interact cooperatively (antiferromagnetically) to lower the systems energy and open a gap in the antibonding sigma Cu-3d, O-2p orbital [13].

La_2CuO_4 is doped with Sr to make it superconducting. Sr has one less electron than La so electrons are removed from the top of the antibonding orbitals (CuO layers are oxidized). As doping increases the correlation splitting begins to collapse. In a small dopant range the ceramic insulator becomes a metallic superconductor as the Fermi level falls into an antibonding energy band. Angle resolved resonance PES and other spectroscopic techniques have shown evidence for O-2p character around the Fermi level for copper oxides [14]. The states at the Fermi level should contribute the most to the superconduction properties of the materials.

The $YBa_2Cu_3O_{6+x}$ system consists of the typical CuO_2 planes separated by O-Cu-O chains. A two-tiered T_c dependence on oxygen doping level is observed in the phase diagram. By calculating the oxidation state of the copper in the planes from crystallographic data at different doping levels, a direct correlation between the copper oxidation state and T_c is observed [16(a,b)]. This correlation is commonly found in the copper oxide compounds. This two-tiered dependence has been assigned to two oxygen ordering phases (Ortho I, Ortho II) that form as $YBa_2Cu_3O_{6+x}$ is doped [17].

The structural, doping and pressure experiments all seem to point to the importance of the oxidation state and covalent delocalization of the CuO_2 layers in determining the superconducting state. The structure and extent of oxidation required for superconduction depends on the compound. All of these components help determine the nature of the energy band diagram. A better understanding of this diagram and its origins may help the development of a new theory of the high-temperature superconductivity mechanism. This new theory may be similar to BCS or may be based on completely different ideas.

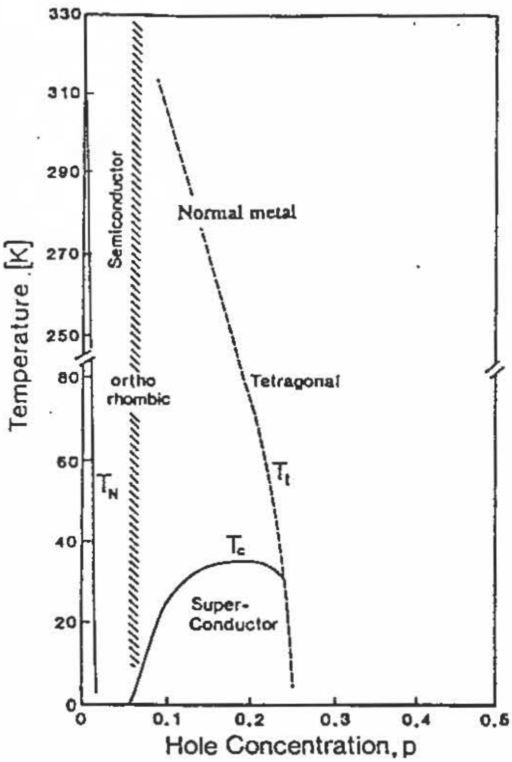

Figure 1

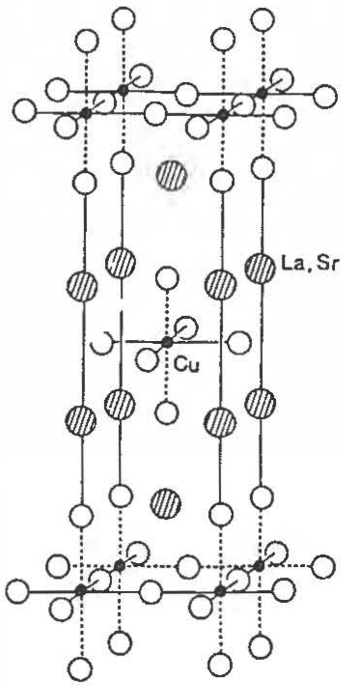

Figure 2

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