Chemistry of the Modern Superconductors

Tanya Prozorov Literature Seminar October 19, 2000

In 1911 H. Kamerlingh Onnes observed that electrical resistance of mercury vanished below 4.2 K. He named this phenomenon "superconductivity".[1] One of the most important parameters of a superconductor is the transition temperature, T_c. Any conceivable application of superconductors is only possible well below T_c. Progress towards the higher T_c, however, was slow. As of 1973 the highest T_c was only about 24 K in intermetallic Nb_3Ge. From the chemical point of view, the history of superconductivity is a series of discoveries of materials with more and more complicated structures. This can be considered as a "chemical evolution" of these materials from simple to complex ones (Figure 1).[2] The path to radically higher transition temperatures was opened with the discovery in 1986 of superconductivity at ~35 K in "LaBaCuO" (mixed lanthanum-barium-copper oxide).[3] The T_c was improved to 92 K in less than one year after the synthesis of "YBCO" ($YBa_2Cu_3O_{7-\delta}$).[4,5] This new class of superconductors is now called "high-T_c superconductors" (HTSC) to distinguish from the conventional "low-T_c" materials. There are many classes of relatively high T_c superconductors, such as heavy fermions (UPt_3), borocarbides, or alkali-doped fullerenes, which will not be discussed here.[1]

Figure 1

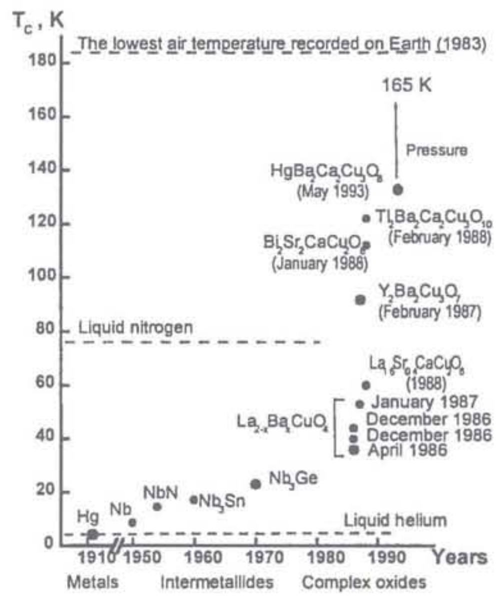
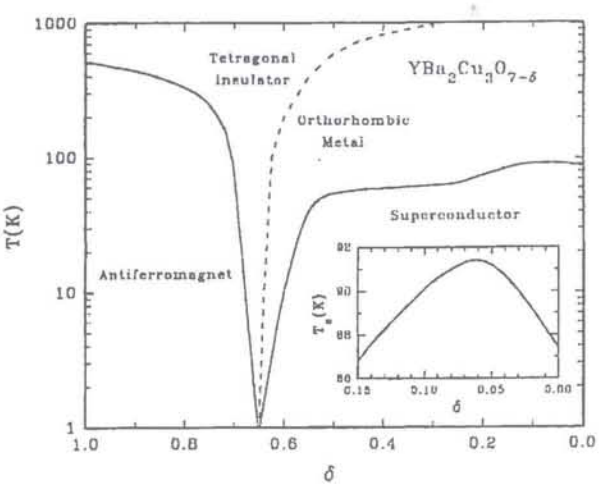


Figure 2



Poor conductors in the normal state, HTSC cuprates become superconducting due to CuO_2 layers, which contain non-stoicheometric charge carriers.[6] Currently, more than 50 individual layered superconducting cuprates are known.[7,8] The most thoroughly studied are $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8-\delta}$ materials. It should be emphasized that there is no accurate theory currently available for the appearance of superconductivity in HTSC. Despite obvious similarities, it could well be that superconductivity in HTSC is of different origin as compared to the low-T_c materials. Much of the chemical research has concentrated on the changes in structural and electronic properties of these materials upon changing the oxygen doping or fluorination, since both change concentration of the charge carriers. The generic phase diagram of HTSC (Figure 2) consists of antiferromagnetic part at low carrier concentration and a relatively narrow region of superconductivity, bound from above by metallic-like type of behavior.[6,7]

Chemical substitution has a dramatic effect on superconducting properties of HTSC, mostly due to the effect of lanthanide contraction. Currently, almost all the Rare Earth (RE) analogues of the $[RE]Ba_2Cu_3O_{7-\delta}$ system have been synthesized by isomorphous replacement of yttrium.[8,9] The differences in the magnetic moments of R^{3+} ions, energies of their stabilization by the ligand crystal field, and possible oxidation states (+4, +3, +2) along with the geometrical factors, provide additional degrees of freedom in the synthesis of superconducting materials. Interestingly enough, superconducting transition in $YBa_2Cu_3O_{7-\delta}$ is accompanied by the structural transformation from tetragonal to orthorhombic structure. The direct observation of d-orbital holes and Cu-Cu covalent bonding confirmed the "hole-doped" nature of these materials.[10] There is also a class of superconducting cuprates in which carriers are electrons ($[RE]_{1.85}Ce_{0.15}CuO_{4-\delta}$). Only very recently it was proven that these materials exhibit the same type of superconductivity as their hole-doped counterparts.[11]

The original theory of superconductivity[12,13] conceived by Bardeen, Cooper and Shrieffer (BCS) was rigorously proven for most of the low-Tc superconductors by studying, for example, the isotope effect. It was shown for conventional superconductors, that the transition temperature decreases with the increase of the ion mass. In HTSC, however, the isotope effect is either absent or unclear, mostly due to complicated crystal structure. Proximity of the antiferromagnetic phase has prompted various models, based on the spin-fluctuations mediated attractive electron-electron interaction.[1,14] Still, it is one of the greatest challenges of modern science to give a correct theoretical picture of the high-Tc cuprates.[15-19]

Interestingly, the metallic behavior in the materials formed from "non-metallic constituent elements" was proposed in the same year the superconductivity was discovered.[20] Almost seventy years later, the first organic superconductor was made and characterized.[21] Modern organic superconductors exhibit some properties very similar to the HTSC cuprates.[22-24] The latter includes the layered structure and short coherence lengths.[25] The extreme purity, low dimensionality, and large crystal size of organic superconductors permit the use of exotic physical methods, such as Shubnikov-de Haas oscillations, for the direct measuring of the Fermi surface.[2,22]

The latest findings allow researchers to improve and tune the conductivity in organic molecular solids.[26] Extended study of superconductivity in organic solids can help to better understand the related phenomena in high-Tc cuprates, and vice versa.

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