CHAPTER - 2

THE COPPER OXIDE SUPER CONDUCTOR
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2.1 General Properties of the High $T_c$ Material

In the last three decades, High $T_c$ superconductivity has been discovered in a family of cuprate compounds [1]. Even if several physical details, such as the critical temperature ($T_c$), change from material to material, there are properties which are common features. These properties involve solid state structure. Antiferromagnetism and superconductivity is of great importance.

Starting from the crystalline point of view, all the high temperature superconductors (HTSC) have a similar solid structure, in which every copper atoms are at the centre of tetragonal structure composed by oxygen atoms. Moreover several CuO$_2$ layers appear in the crystal structure and between these layers are the transition elements (such as La or Ba). A typical example of such is La$_{2-x}$Sr$_x$CuO$_4$ ($T_c=39K$) such structure is given in fig. 2.1. In which La atoms lies between layers of CuO$_2$ atoms (one layer per unit cell). A more complex material is YBa$_2$Cu$_3$O$_7$ ($T_c=92K$), in which there are two neighboring Cu$_2$O planes per unit cell. This is also shown in fig 2.1. The presence of Cu$_2$O layers in all compounds led to the belief that a lot of the important physics is contained in these two dimensional systems. This is supported by the fact that the Cu – O
in plane bond length is about $1.9 \text{\AA}^0$ while the distance between planes is about $6.6 \text{\AA}^0$ and so the interlayer coupling can be neglected.

![Crystal Structures of La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_{6+x}$](image)

**Fig: 2.1 Crystal Structures of La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_{6+x}$**

All the high $T_C$ superconductors originate from the doping of an Antiferromagnetic character of undoped system is given by the copper which in the solid has a valance Cu$^{+2}$ and has a hole in $3d$ shell, namely has a net magnetic moment. The oxygen is magnetically neutral and due to his mediation there is a net superexchange coupling between the in plane Cu atoms [25]. Since there is an effective odd number of electrons per copper atom a metallic behavior should be expected, but due to the strong correlations the undoped system is an Antiferromagnetic Mott insulator. In the case of La$_2$CuO$_4$, doping is achieved in two different ways; substituting La$^{+3}$ with Sr$^{+2}$ or inserting O$^{2-}$. These two different kinds of doping lead to quite different properties in the
material. The Sr substitution is equivalent to adding holes in CuO$_2$ layers (i.e. extracting electrons) while the oxygen insertion increases the number of electrons. Moreover the additional O$^{2-}$ ions are mobile and are able to screen a change imbalance, leading to rather different physical features.

An analysis of the phase diagram shown in Fig.2.2 of the considered materials shown that by hole-doping the Antiferromagnetic long range order of the ground state is immediately lost (close to $\delta\sim0.03$) and superconductivity appears (close to $\delta\sim0.08$). $T_C$ reaches its maximum value at $\delta\sim0.15$ which is usually called optimal doping. When electron doping is considered Antiferromagnetic long range order is stable up to $\delta \sim 0.11$, 0.12 and susceptibility occurs immediately after and superconductivity occurs immediately after.

![Phase diagram of doped La$_2$CuO$_4$](image)

**Fig. 2.2 Phase diagram of doped La$_2$CuO$_4$**
A very important similarity between high $T_c$ materials is given by the symmetry of the superconducting gap. In a BCS superconductor the gap has $s$-wave symmetry, isotropic in momentum space. There is now a wide consensus that in high $T_c$ superconductors the pairing occurs in a $d_{x^2-y^2}$ symmetry. Experimentally this was detected by SQUID measurements in Josephson junction between BCS and high $T_c$ superconductor [26]. The critical temperature varies a lot, ranging from 24 K (Nd$_{1.85}$Ce$_{0.15}$CuO$_4$) to 133K for the case of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ [27], which represents the compound with the highest $T_c$ discovered up to now. These values must be compared with the critical temperature of the standard BCS superconductor which is typically less than 4K. So even if their critical temperatures are rather different they share the common properties of being too high for conventional superconductors.

Fig. 2.3; $\alpha$ exponent and critical temperature as a function of doping for La$_{2-x}$Sr$_x$CuO$_4$
2.2 Isotope Effect

In BCS type superconductors the pairing between the electrons is given by an effective attractive electron interaction which originates from the electron phonon interaction. This evidence was experimentally achieved through isotope effect measurements on $T_C$ [29]. In a conventional superconductor the dependence between the critical temperature and the isotope mass is $T_C \propto M^\alpha$ where $\alpha \sim 0.5$. The oxygen isotope measurement in YBa$_2$Cu$_3$O$_{6+\delta}$ showed that the value of $\alpha$ exponent is less then 0.1 [30]. This value is by far too small to think that the electron-phonon interaction alone can be responsible for the pairing. For La$_{2-\delta}$Sr$_\delta$CuO$_4$ the behavior of the exponent $\alpha$ is much more complex and depends on doping [28, 31]. In fig2.3 $T_C$ and the exponent $\alpha$ are plotted as a function of doping for this material.

The $\alpha$ increases up to the large value of $\alpha \sim 0.5$ for doping $\delta = 1/8$ but then decreases by a factor of 5 at optimal doping, reaching the same order of magnitude of one detected in YBa$_2$Cu$_3$O$_{6+\delta}$.

The 1/8 anomaly is still an open problem. In a present compound, namely La$_{2-\delta}$Sr$_\delta$CuO$_4$, it was found [32] that at $\delta = 1/8$ a structural phase transition from a low temperature orthorhombic (LTO) phase temperature tetragonal (LTT) phase occurs. This phase transition involves a tilting of the oxygen octahedral and clearly phonons must play an important role. For La$_{2-\delta}$Sr$_\delta$CuO$_4$ there is no evidence for such a phase transition, but
may be the system is approaching such instability. The 1/8 anomaly involves even the critical temperature since there is local minimum of $T_c$ at this doping fraction.

The experimental measurements of the $\alpha$ exponent show that the isotope effect is very small at optimal doping for both the compounds. These results suggested that may be the pairing could be given by the strong electronic correlations and not only by the electron-phonon interaction.

### 2.3 Phase Separation

The coexistence between holes and electrons in the CuO$_2$ layers has been a very discussed issue over the years. Several authors [10, 11] suggested that superconductivity could be connected with the phase separations of electrons and holes in these layers.

Phase separation was observed in the oxygen doped compounds using Neutron Powder diffraction NPD [33] and Nuclear Magnetic Resonance NMR [34]. The experimental data showed that the system is separated in an oxygen rich and in an oxygen poor region. The NPD experiments found phase separation at $T<320K$ and for an oxygen insertion greater than 0.05. Similar results were obtained by NMR [34]. No evidence of phase separation has been found in the hole-doped compounds.

In order to understand the appearance of phase separation in the oxygen doped compounds it is important to recall that the inserted oxygen ions are mobile in the solid. As a consequence these ions are able to screen the long range coulomb repulsion due to the charge imbalance connected with the phase separation instability. This is not the case
of the hole doped compounds. The interplay between this effect and superconductivity is still an open question.

2.4 Magnetic Properties

Through Neutron Scattering and Nuclear Magnetic Resonance (NMR) experiments it is possible to careful analyze the change of the magnetic properties of HTSC material upon doping. Measurements of the Neutron Scattering cross section provide informations on the spin-spin structure factor of the sample.

Fig 2.4 Left: Spin fluctuation in the dynamical spin structure factor at $\delta=0.14$. Right: Linear dependence of peak position on doping

As a consequence of Antiferromagnetic long range order, the undoped compound shows a sharp peak in the spin structure factor at the Antiferromagnetic wave vector, $Q = (\pi, \pi)$. In the case of the La$_{2-x}$Sr$_x$CuO$_4$, as the sample is doped with Sr, this peak broadens and at a doping $\delta > 0.05$ disappears and incommensurate spin fluctuation arises close to the $Q$ point [35-37].
At positions ($\pi, \pi \pm 2\varepsilon\pi$) and $(\pi \pm 2\varepsilon\pi, \pi)$, the dependence of the incommensurability $\varepsilon$ with doping [37] is linear for $0.05 < \delta < 0.12$ and after saturates as in fig 2.4 A striking feature is that the angular coefficient of the linear relation between the incommensurability and the doping fraction is exactly $2\pi$.

X-ray diffraction measurements [38] has shown that similar incommensurate peaks occur in the charge structure factor but close to the $\Gamma = (0, 0)$ point with an incommensurability which is twice the spin structure one. This behavior has been explained by a domain walls ordering of holes in CuO$_2$ layers as is shown in Fig. 2.5. The half filled hole stripes separate Antiferromagnetic regions which are correlated with a $\pi$ shift across a domain wall. The modulation connected with the charge is then at low momenta, close to the $\Gamma$ point, while the spin structure presents a spin density wave at incommensurate momentum close to the Antiferromagnetic wave factor.

Fig. 2.5 Spin and hole structure at a doping $\delta=1/8$. The hole stripes are half filled. The antiferromagnetic regions are correlated by a $\pi$ shift across a domain wall.
Mook and his coworkers [40] showed that even in YBa$_2$Cu$_3$O$_{6.6}$ these features are present suggesting that they are a very general property of HTSC. In La$_{2.8}$Sr$_5$CuO$_4$ the width of the incommensurate spin fluctuations becomes particularly narrow at the doping $\delta = 1/8$. Neutron scattering experiments and $T_C$ measurements at this doping fraction in La$_{1.6}$Nd$_{0.4}$Sr$_5$CuO$_4$ [39] showed that this property occurs together with the anomalous suppression of superconductivity (an effect which was already discovered in La$_{2.6}$Ba$_5$CuO$_4$ [41].

Nowadays a satisfactory theoretical explanation of 1/8 anomaly is not present. Even if several theories involving frustrated phase separation by the repulsive Colombian interaction [42] and segregation in stripes of charges and spins have been proposed, it is not completely clear their relation with superconductivity, the high value of $T_C$ and pairing mechanism.