A Review On Superconductor Materials-Nickelates Analogous of Cuprates.

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Abstract - Quest for analogous materials to cuprates is underway. Recently, Harold Hwang group found superconductivity in nickelate material. This serves as a structural and electronic match for cuprate superconductors. With this discovery prospectus of cuprate family of superconductors is bright now. Hwang and his team successfully made neodymium strontium nickel oxide, $Nd_{0.8}Sr_{0.2}NiO_2$ Which shows superconductivity below 15 kelvins. In this case, previous knowledge of cuprates enables researchers to achieve this milestone. Although, chemistry of Ni and Co are different but near fermi level both share quite same electronic structure, which is dominated by the $d_{x^2-y^2}$ orbitals [10,11].

1.1 Brief History: Before the discovey of high temperaue superconductors, traditional superconductors in plathora were discovered, which can be explained on the basis of BCS theory (1957) given by John Bardeen, Leon Cooper, and John Schrieffer [1]. In 1911 superconductivity was found in mercury at 4 degree kelvin by H. Kamerlingh Onnes, at this temperature resistance suddenly disappears. After this in 1913 he won nobel prize for the same. In subsequent decades, 1941 niobium-nitride was found to superconducts at 16 Kelvin, many more followed. Muller and Bednorz in the year 1986 discovered high temperature cuprates which initiated a flurry of activity in the field of superconductivity. For more than 20 years mercury copper oxides held the record for highest critical temperature at 138 K. However in the past many other copper oxide materials have been found superconducting at much higher temperatures [2]. A brief timelines of evolution of many families of superconducting materials are given below.

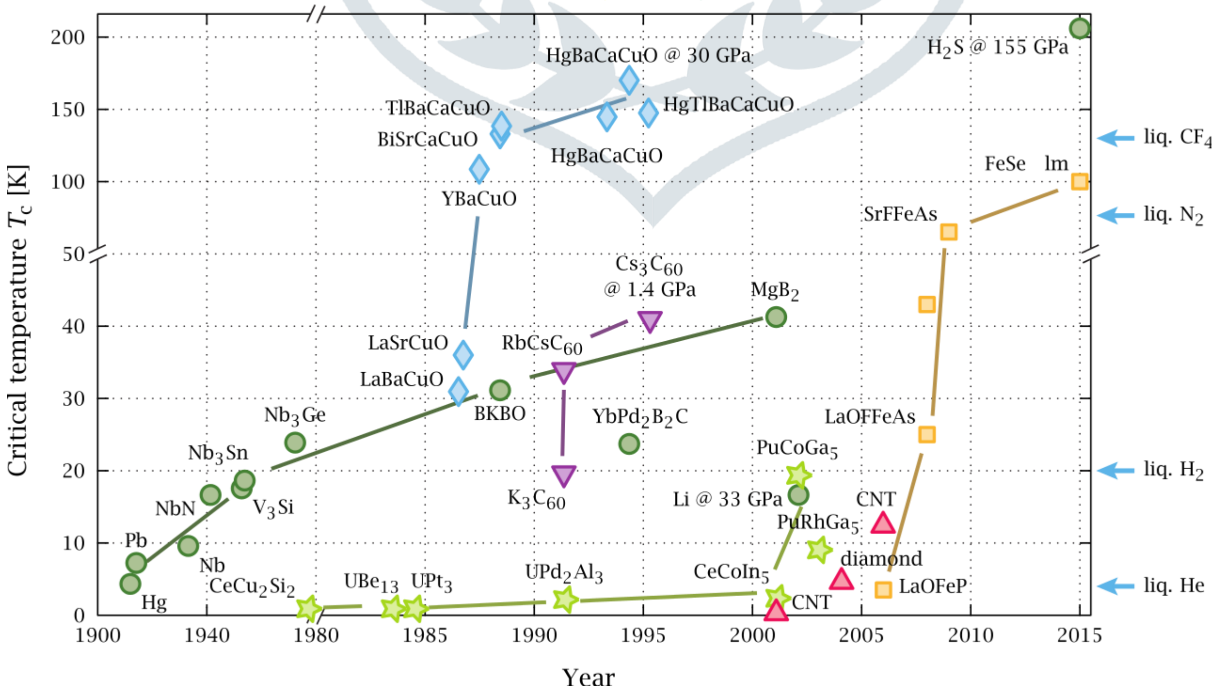


Figure 1.0: Timeline of superconductors - BCS superconductors - green circles, cuprates - blue diamonds, and iron-based superconductors - yellow squares.

1.2 High temperature cuprates: Let us discuss briefly, some basic aspects of the structure and properties of high-T_c cuprate superconductors, mainly $La_{2-x} Sr_xCuO_4$, the first high-T_c superconductor discovered [3],[4] (though the original discovery was rather made on $La_{2-x}Ba_xCu_2O_4$). Some other high-T_c superconductors based on transition metals are also available. There are now several groups of high-T_c cuprate superconductors known. Besides the so-called "214" or LSCO system of the type $La_{2-x}Sr_xCu_2O_4$, with maximum critical temperature T_c - 40 K, there are also the systems $YBa_2Cu_3O_7$ (YBCO); materials on the basis of Bi, for example $Bi_2Sr_2CaCu_2O_8$ (BSCCO 2212); and similar systems based on Hg or Tl. The maximum values of T_c are as follows, YBCO and BSCCO have T_c - 90 K, while mercury and thallium-based materials have $T_c \sim$ 120–130K (under pressure, even up to ∼140–150 K).

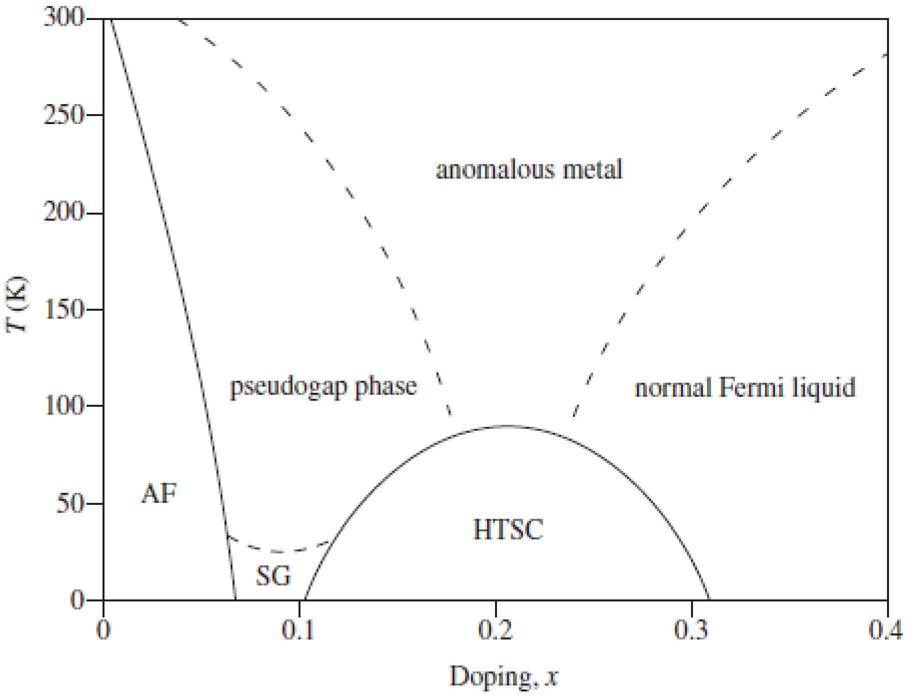


Figure 1.1: Schematic phase diagram of high-T_c superconducting cuprates. AF denotes the antiferromagnetic insulator phase; SG denotes the spin-glass phase; HTSC is the phase of high-temperature superconductivity.

All these systems have the same basic building blocks - two-dimensional CuO_2 layers shown for example in Figure1.2. In some cases the in-plane Cu ions are in elongated octahedra, for example in $La_{2-x} Sr_xCuO_4$ as shown in Figure2.3, in other systems, for example in $YBa_2Cu_3O_7$, the active layers contain fivefold-coordinated Cu in CuO_5 square pyramids, Figure1.3, and also, Cu ions are square-coordinated (note that these are typical coordination of Cu^{2+} in general, due to the very strong Jahn–Teller nature of these ions). The blocks sitting between such CuO_2 layers (sometimes bilayers or trilayers) play the role of charge reservoirs.

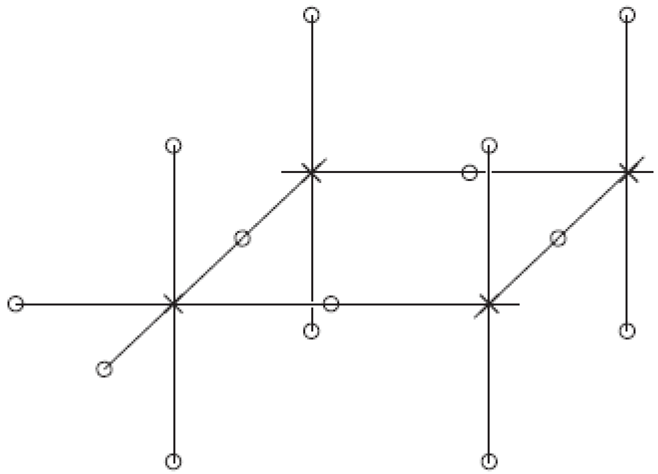
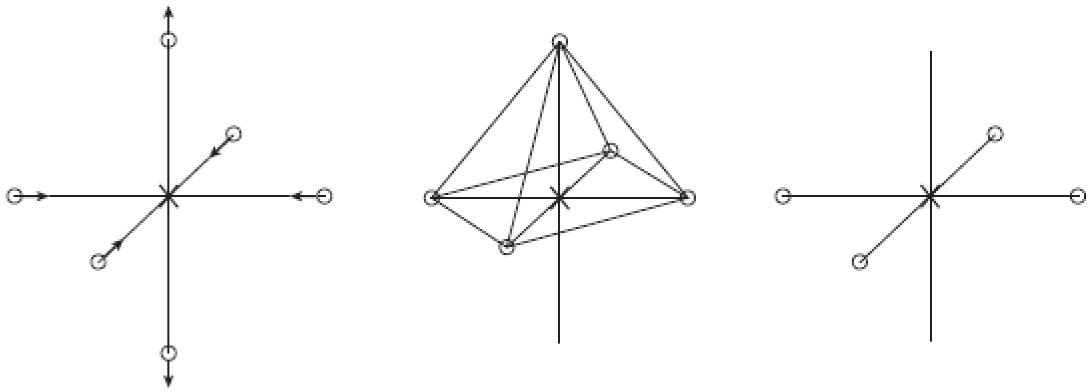


Figure: 1.2 Basic building block in high temperature cuprate superconductors, CuO_2 layers



(a) (b) (c)

Figure 1.3 Possible coordination of Cu in high-T_c cuprates, (a) elongated octahedron, (b) square pyramid (fivefold coordination), (c) square (fourfold coordination).

A change in composition, for example the substitution of Sr^{2+} for La^{3+} in $La_{2-x}Sr_xCu_2O_4$, leads to hole doping of CuO_2 planes, and starting from a certain hole concentration superconductivity appears. The schematic phase diagram of high-T_c cuprate superconductors has already been shown in Figure 1.1 for the example of $La_{2-x}Sr_xCu_2O_4$, but its general structure is very similar in other systems of this class as well [5],[6]. For $x = 0$ we have a Mott insulator with magnetic $Cu^{2+}(d^9)$ ions with $S = ½$, which order magnetically. Hole doping in both cases leads to the appearance of the superconducting phase. In all cases of high-T_c cuprates the superconducting phase lies in close proximity to such magnetic phases and is dome-shaped, reaching the maximum at a certain doping level and decreasing in the over doped regime.

In 2008 a second big class of superconductors with transition metal elements and with high transition temperatures, reaching - 55 K, was discovered [7], the iron-based high-T_c superconductors.

There are similarities and differences between this class of materials and high-T_c cuprates. Both are layered (two-dimensional) systems. In both there is usually a magnetic state close to the superconducting one. The general shape of the phase diagram is also similar, Figure 1.1. But there are also important differences between them. One is that, in contrast to cuprates, here the doping may be isovalent, and it can be replaced by pressure. Also, whereas the undoped cuprates are Mott insulators [8], with strong electron correlations which apparently persist to the superconducting composition, the Fe-based systems are commonly metallic. The electron correlations in them are weaker – probably they are still present, but definitely not as strong as in cuprates. Magnetism in them is presumably mostly of itinerant character, resembling density waves [9].

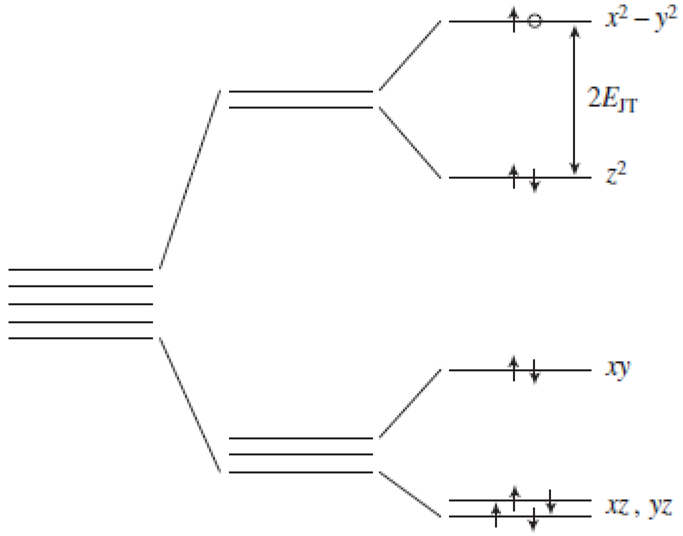
1.3 Nickelates analogous to cuprates (Superconducting below 15 K):

Search for analogous materials to cuprates is underway. Recently, Harold Hwang group found superconductivity in nickelate material [10]. This serves as a structural and electronic match for cuprate superconductors [11]. With this discovery prospectus of cuprate family of superconductors is bright now. Hwang and his team successfully made neodymium strontium nickel oxide, $Nd_{0.8}Sr_{0.2}NiO_2$

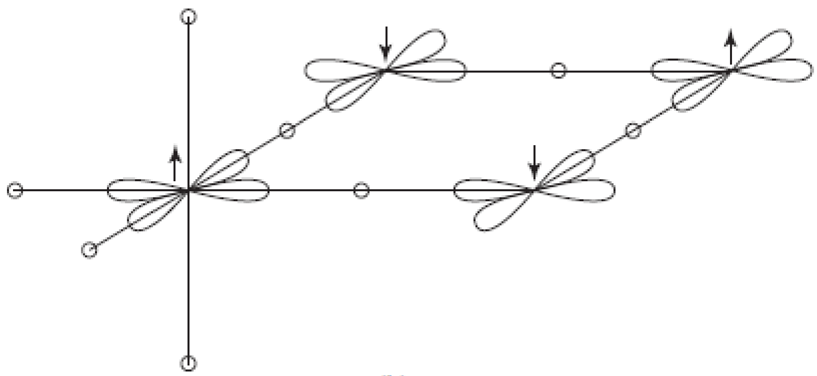
Which superconducts below 15 kelvins. This discovery is not achieved by chance, previous knowledge of cuprates enables researchers to achieve this milestone. Although, chemistry of Ni and Co are different but near the fermi level both share same electronic structure, which is given by $d_{x^2-y^2}$ orbitals. Let us see some more detail about cuprates and physics involved.

The basic material for high-T_c cuprates, which was actually kind of the first such superconductor discovered, is layered perovskite $La_{2-x}Sr_xCuO_4$. Its main building blocks, CuO_2 layers, are present in most other high-T_c materials of this type. These layers are very important for superconductivity. One can change carrier concentration in these layers to achieve the superconducting state. There are many examples available related to this discussed below. High temperature copper oxide materials are studied extensively.

Undoped La_2CuO_4 is a Mott insulator with $Cu^{2+}(d^9)$ ions, that is with one hole in the *d*-shell, with spin 1/2, arranged in CuO_2 layers in a simple square lattice. There is antiferromagnetic ordering of *G*-type (checkerboard spins up and down) at T_N of about 317 K. Cu^{2+} ion is a famous Jahn–Teller ion having one hole in the doubly degenerate e_g orbitals. This causes strong tetragonal distortion, which puts two e_g electrons on the z^2 orbital, the hole remaining in the $x^2 - y^2$ orbital, see Figure 1.4. In the process of this distortion the two apex oxygens move away from the basal plane, see Figure1.3. This distortion can be so strong that one of these oxygens can be removed, leaving Cu^{2+} in a fivefold coordination, Figure1.3. May be, even both apex oxygens can move away, and Cu will remain square-coordinated.



(a)



(b)

Figure1.4: (a) Crystal field splitting of *d* levels of Cu^{2+} in La_2CuO_4, (b) $x^2 - y^2$ hole orbitals occupied inLa_2CuO_4.

The hole occupancy of the ($x^2 - y^2$) orbital is very much usual for most known materials having Cu^{2+} configuration. But the axes of these distorted CoO_6 either octahedra or pyramids or squares need not be in the z-direction.

In the oxide La_2CuO_4 the situation in this sense is, all long axes of the CuO_6 octahedra are parallel to the z-axis, that is the hole orbitals are all of $x^2 - y^2$ type. And, as the JT splitting of these orbitals is quite large, one usually considers only $x^2 - y^2$ orbitals, skipping the z^2 orbitals. Thus, in this system the holes are in nondegenerate $x^2 - y^2$ levels, and these cuprates can be explained by the simple nondegenerate model called Hubbard model.

One can reduce this three-band model or d–p model to the non-degenerate Hubbard model [12]. As the state Cu^{3+}, which one would get by hole doping, corresponding to a very small or negative charge-transfer gap. This means that doped holes will predominantly go to the p-orbitals of oxygens, that is inspite of the state $Cu^{3+}(d^8)$ we would have $Cu^{2+}(d^9)$ L, where L is the ligand oxygen hole. The state $Cu^{2+}(d^9)$ has spin 1/2, the ligand hole L around it also has an unpaired spin 1/2, and due to the strong d–p hybridization this ligand hole would form a bound singlet state with Cu^{2+}. This is known as the Zhang–Rice singlet state [12].

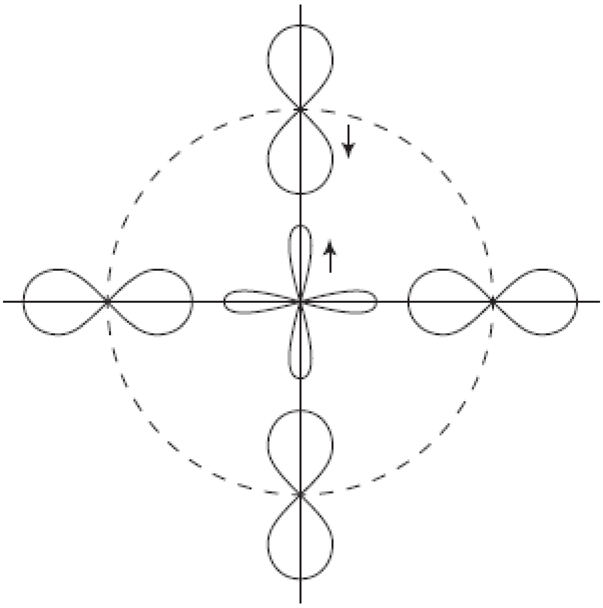

(a)

Figure: 1.5 (a) Hybridization of an $x^2 - y^2$ hole orbital of Cu with four p orbitals of surrounding oxygens, showing the formation of Zhang–Rice singlets.

When we dope the Mott insulator material La_2CuO_4, by increasing the Sr content x, first of all the antiferromagnetic order is suppressed very quickly, and it becomes metallic in nature. This metal phase is also a high-T_c superconductor. The typical behaviour of T_c in these systems is dome-shaped, T_c increases initially with doping, passes through a maximum, and then starts to decrease and disappears in the over doped regime. A typical phase diagram for high T_c superconductors is shown in Figure 1.1, where different phases are, the AF insulator; an intermediate phase which behaves as spin glass, and the superconducting phase HTSC. For over doped systems we usually have a more or less normal metal state described by the standard Fermi-liquid theory. But in the intermediate concentration range, close to optimal doping, the properties of the normal state above T_c are unusual, the resistivity does not behave as in conventional metals, etc. This phase is of an anomalous metal. And yet another special state is observed typically for smaller x, the pseudo gap phase [13], in which both transport and magnetic properties are anomalous.

Conclusion – These new materials can act as replacement of cuprate family of superconductors. Nickelates superconducts at 15 K, which is far low than what cuprates offer. Further, more investigation of this material is required to explore different phases of it. One has to see what mechanism is responsible to achieve superconductivity in these materials.

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