

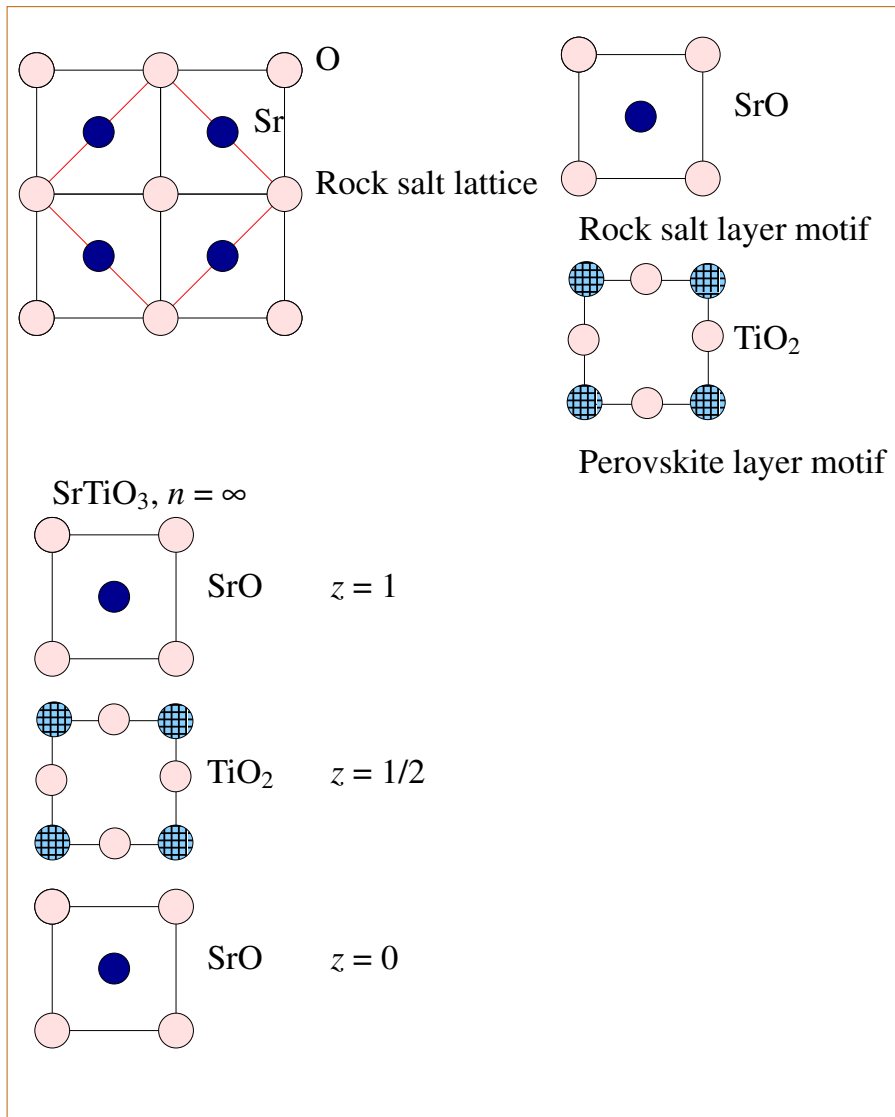
## MATRL 218/CHEM 227: Class XII — Superconductivity and High $T_C$ copper oxides

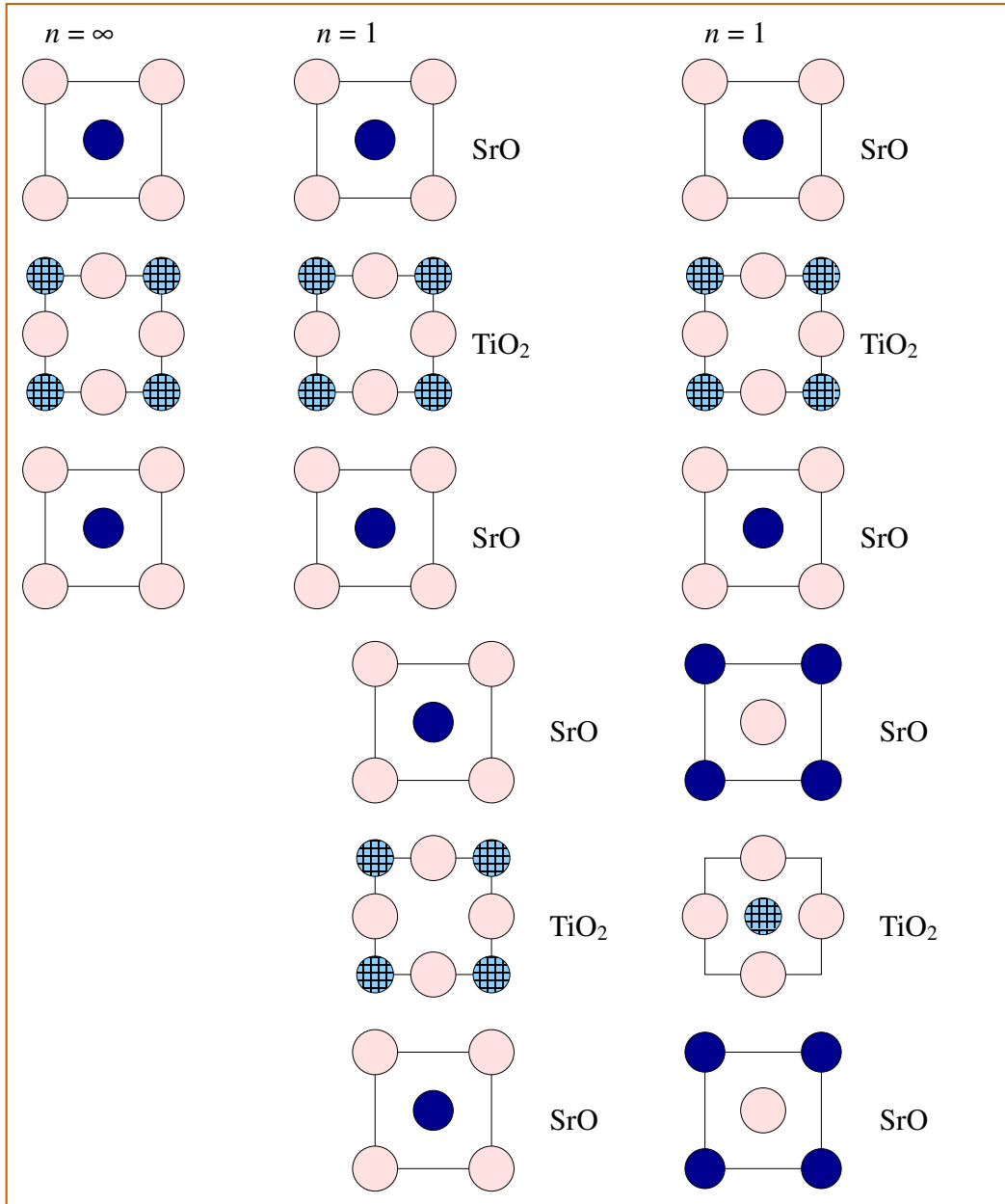
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The Ruddlesden-Popper phases:

Ruddlesden-Popper phases are intergrowths of perovskite slabs with rock salt slabs. First described in the system Sr-Ti-O, the general formula of the  $n^{\text{th}}$  member of the phase is  $(\text{SrTiO}_3)_n(\text{SrO})$ , and is also written,  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ . The perovskite structure is one end-member of the R-P series ( $n = \infty$ ) and the  $\text{K}_2\text{NiF}_4$  structure is the other end-member ( $n = 1$ ). The  $n = 0$  member is rock-salt.

We now consider different stacking depictions of the perovskite ( $\text{SrTiO}_3$ ,  $n = \infty$ ) phase and  $\text{K}_2\text{NiF}_4$  ( $\text{Sr}_2\text{TiO}_4$ ,  $n = 1$ ) phases.



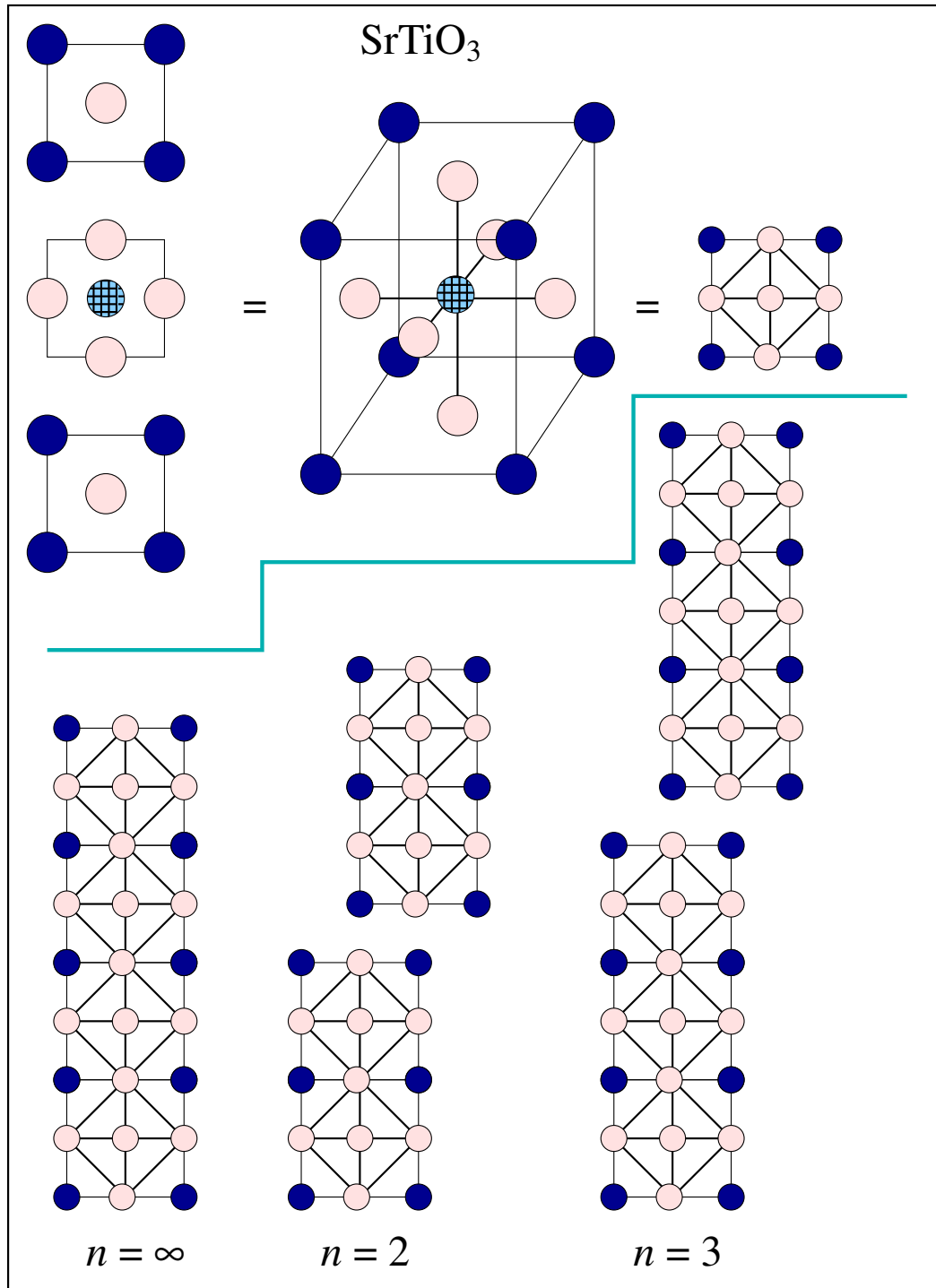


Along the  $c$  axis (the stacking direction), we notice for SrTiO<sub>3</sub> ( $n = \infty$ ), the repeat sequence is ...[SrO][TiO<sub>2</sub>][SrO][TiO<sub>2</sub>]....

Along the  $c$  axis (the stacking direction), for Sr<sub>2</sub>TiO<sub>4</sub> ( $n = 1$ ), the repeat sequence is ...[SrO][SrO][TiO<sub>2</sub>][SrO][SrO][TiO<sub>2</sub>]....

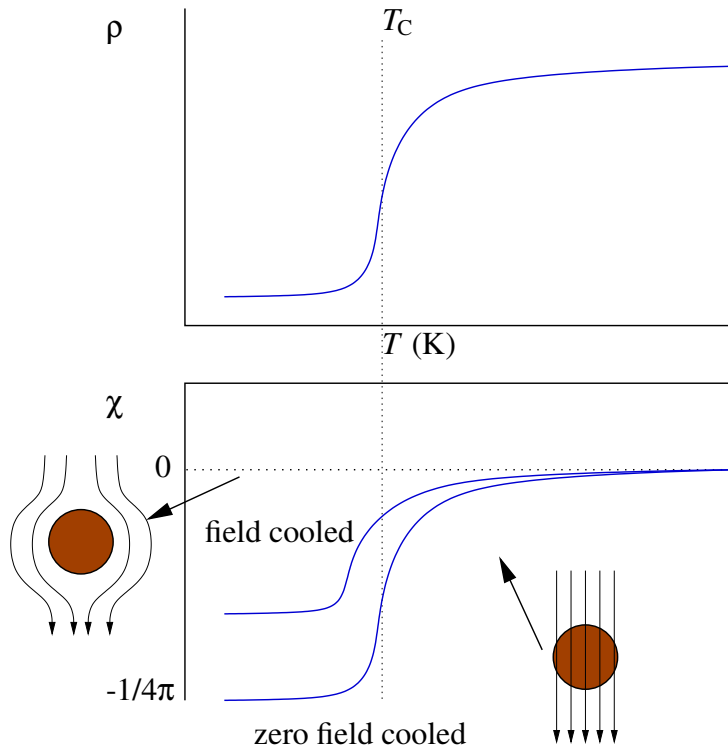
For Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> ( $n = 2$ ), the repeat sequence must be ...[SrO][SrO][TiO<sub>2</sub>][SrO][TiO<sub>2</sub>][SrO][SrO][TiO<sub>2</sub>][SrO][TiO<sub>2</sub>][SrO][SrO]....

There is an alternate way of visualizing these structures, making use of octahedra:



## Superconductivity

In 1908, Kamerlingh Onnes liquefied He for the first time, and in 1911 he used it to cool mercury to about 1.5 K. At 4.2 K, the resistance of his Hg specimen dropped suddenly from about  $0.1 \Omega$  to  $10^{-5} \Omega$ , and by 3 K had dropped to  $1/10^6$  its value at room  $T$ . This marked the discovery of superconductivity. Typical temperature dependence of the electrical resistivity and the magnetic susceptibility of a superconductor are shown below:



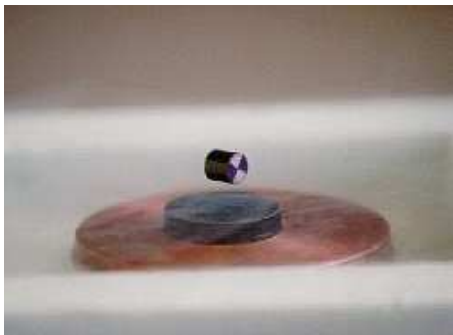
Not only does the electrical resistivity go to zero, but because of the *Meissner effect* any magnetic lines of force are thrown out by the superconductor, making superconductors strong diamagnets (perfect, even, when the magnetic susceptibility becomes  $\chi = -\frac{1}{4\pi}$ ).

Uses of superconductors:

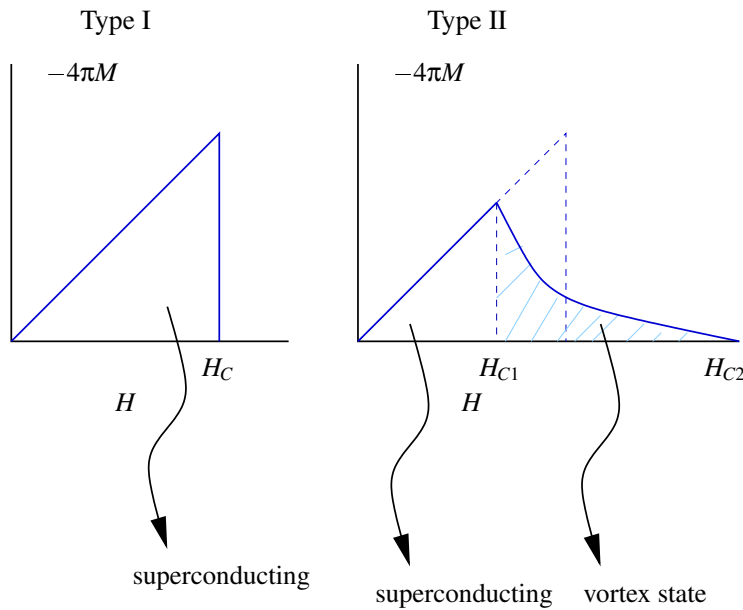
Used in electromagnetic coils in high field magnets in NMR, MRI *etc.*

Power transmission (high currents through thin wires)

Magnetic levitation

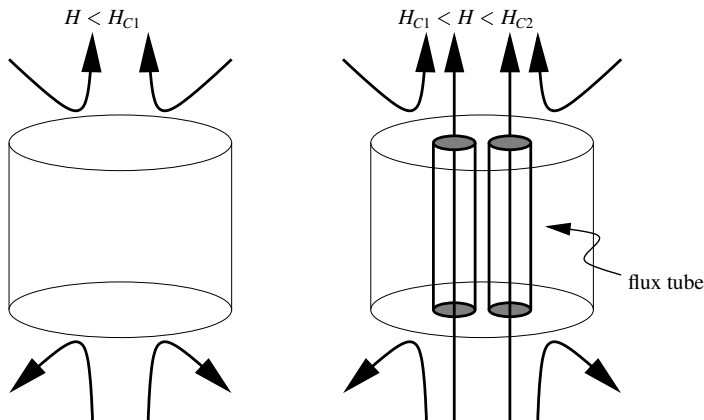


Type I and type II superconductors:



In type I superconductors (pure metals), the superconductivity is destroyed by small magnetic fields; above some critical magnetic field  $H_C$ , the material is no longer superconducting. Typical critical fields are of a 1000 Oe.

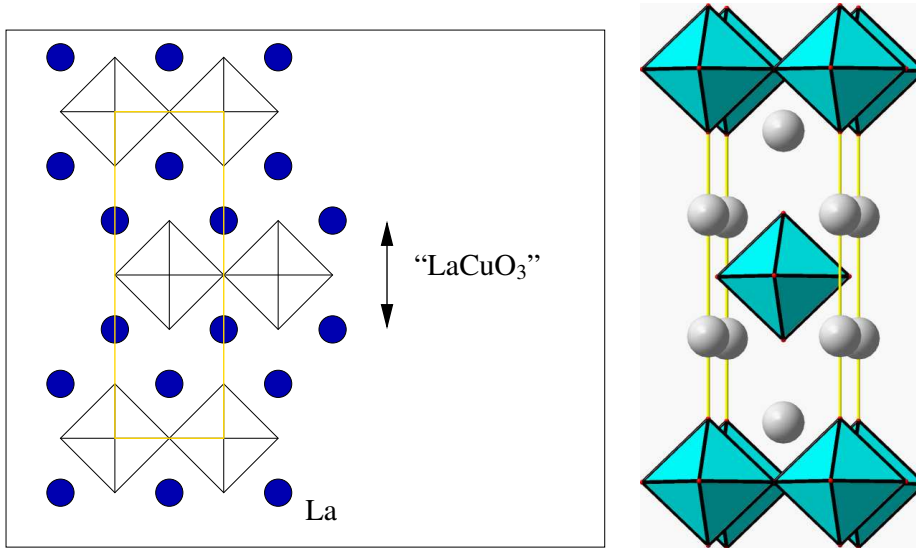
In type II superconductors, above the first critical field  $H_{C1}$ , the material is no longer a pure superconductor. It is in what is called the vortex state, comprising regions that are superconducting, interspersed with "flux tubes" that are normal (not superconducting). The magnetic field can penetrate the superconducting sample through the flux tubes, which often form an ordered lattice.



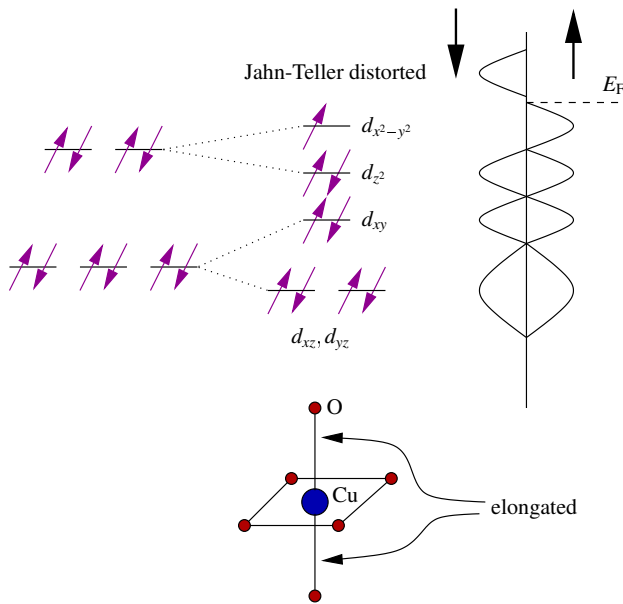
Examples of type II superconductor are most superconducting alloys and intermetallics (such as the so-called A15 compounds) and the high  $T_C$  copper oxide superconductors. The record for the second highest critical field  $H_{C2}$  is held by the Chevrel phase  $PbMo_6S_8$  of 54 T at 4 K. Such materials are good candidates for forming superconducting solenoids.

$La_{2-x}A_xCuO_4$  ( $A = Sr, Ba$  etc.):

The compound  $La_2CuO_4$  has the  $K_2NiF_4$  structure, which is the structure of the  $n = 1$  Ruddlesden-Popper phase  $(SrTiO_3)_1(SrO)$ . A sketch as well as the “real” structure are shown below:



The large spheres are the  $La^{3+}$  ions. The formula suggests that in  $La_2CuO_4$ , Cu is in the +2 oxidation state.  $Cu^{2+}$  has 9 d electrons. Since it is octahedral, we would expect the crystal field diagram and the DOS to look as follows:

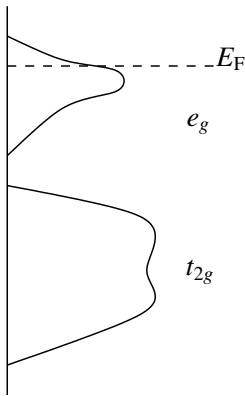


The  $d^9$  configuration is Jahn-Teller active. A Jahn-Teller active atom or ion has degenerate electronic states, and whose degeneracy can be lifted through a suitable structural distortion. In the case of a compound like  $\text{La}_2\text{CuO}_4$ , the degeneracy of the  $d^9$  Cu is lifted by distorting the  $\text{CuO}_6$  octahedra through elongation of the apical bonds. Jahn-Teller distortions of this kind (called 4-in, 2-out) split the  $t_{2g}$  and  $e_g$  levels by stabilizing those orbitals that have a z component. Thus, among the  $t_{2g}$  levels,  $d_{xz}$  and  $d_{yz}$  are stabilized, and  $d_{xy}$  is destabilized. Among  $e_g$  levels,  $d_{z^2}$  is stabilized and  $d_{x^2-y^2}$  is destabilized.

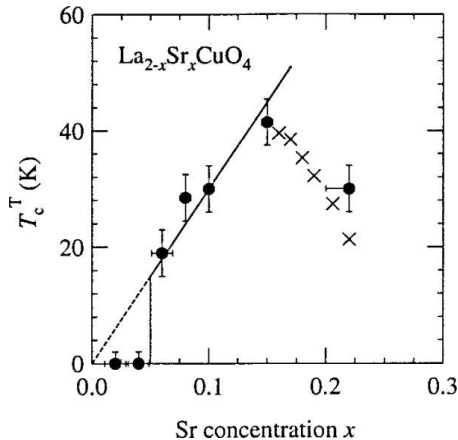
To construct the electronic structure of  $\text{La}_2\text{CuO}_4$ , we must first recognize that it is J-T active, and then we must switch on spin-polarization (because  $d^9$  is magnetic for the first row transition metals). The combination of the JT distortion and the spin-polarization gives an insulator. Experiments confirm that  $\text{La}_2\text{CuO}_4$  is in addition, antiferromagnetic.

Changing (increasing) the oxidation state of Cu, by substituting some of the  $\text{La}^{3+}$  by suitable divalent ions  $\text{A}^{2+}$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ ) results in the system becoming a non-magnetic metal.<sup>1</sup> In addition, it displays superconductivity. This was the discovery of Bednorz and Müller in 1996 in the system  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ .

Schematic DOS of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  is shown below:



The phase diagram for the system  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  is shown below:



Note various special aspects of the perovskite derived structure that are essential for superconductivity to manifest in this system. Firstly, substitution at the A site (Sr-for-La) can be used to change the oxidation

<sup>1</sup>Why does it become non-magnetic? Firstly, a system with only 1 unpaired electron is not a very strong magnet, so it does not need a great deal to switch off the magnetism. Secondly, the process of making some of the electrons mobile through the Sr-for-La substitution results in (a) the magnetism being further weakened and (b) the bands become broader, switching off the magnetism completely.

state at the B site (Cu). If the substitution were made at the B site, the electronic structure is “interrupted” and superconductivity cannot easily exist. The second feature is the presence of the  $\text{CuO}_2$  square lattice that permits very disperse bands to be formed between Cu  $d_{x^2-y^2}$  orbitals and O  $p_x$  and  $p_y$  orbitals (remember Assignment 5). This is considered to be an important ingredient of superconductivity.

For high  $T_C$  superconductivity in the layered copper oxides, some other important criteria include:

That Cu forms quite covalent bonds with O, particularly when its oxidation state is high (between 2 and 3).

That Cu, being near  $d^9$  is not very magnetic. Fe, Co and Ni compounds in the same structure and oxidation state are magnetic. Magnetism and superconductivity are usually competing states.

Many other layered copper oxides (than the system  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$ ) are now known that display superconductivity with high transition temperatures. Take a look at the link provided (<http://www.ill.fr/dif/3D-crystals/superconductors.html>) on the teaching website.

The most studied example, is the triple perovskite (with oxygen defects)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \sim 0.05$ ) that has a critical temperature of 92 K.