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THE PHENOMENOLOGY OF HIGH TEMPERATURE CERAMIC
SUPERCONDUCTORS: STRUCTURE, OXIDATION STATES AND
SUPERCONDUCTIVITY

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ABSTRACT

We present a brief overview of the phenomenology of high temperature oxide superconductors particularly aimed towards understanding which general structural and/or electronic features determine the superconductivity. A systematic study of the phenomenology in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system shows that structural features as well as oxidation states affect strongly the superconductivity and that in certain regions of the phase diagram universal relations exist which relate certain structural features to the superconducting transition temperatures.

Although the study of high temperature oxide superconductors has proceeded at a feverish level for the last two years, to date no clear-cut consensus has emerged regarding the main phenomenological features which determine the superconductivity.^{1-3]} In general, two approaches are being used; in one correlation are searched between the different systems, in the other a variety of systematic changes are induced in one particular system and their effect on the superconducting properties are studied.

The general structural feature which is present in all high temperature oxides is the presence of Cu-O and/or Bi-O planes with a distinct asymmetry in the coordination of Cu or Bi and the O ($\text{Ba-K-Bi-O}^{4,5}$], La-Cu-O^{6-8}], Y-Ba-Cu-O^{9-22}], $\text{Bi-Ca-Sr-Cu-O}^{23-32}$], $\text{Tl-Ca-Ba-Cu-O}^{33-39}$]). In addition, all systems contain some sort of doping which changes the formal oxidation state of Cu from 2+ to 3+ or that of O from 2- to 1-. For instance, in the case of the La_2CuO_4 family, the dopant can be a

metal ion such as Sr or in the case of $\text{YBa}_2\text{Cu}_3\text{O}_y$ family the role of the dopant is taken by the oxygen deficiency. It may be argued, by comparing different systems, that the transition temperature increases with increasing number of closely packed Cu-O planes;^{40-42]} for instance, the La_2CuO_4 type superconductors have one closed packed plane and a T_c of ~ 40 K, $\text{YBa}_2\text{Cu}_3\text{O}_y$ has two closed packed planes and a T_c of ~ 90 K. Similar effects have been claimed earlier in multilayered superconductors of Pb/Ga, Sn/Ge or Al/Ge where the T_c was found to increase with the number of layers.^{43]} However, controlled studies are difficult to perform in order to vary the number of closely spaced planes and only three closely spaced planes in a variety of inter-grown configurations have been realized to date.^{41]} The main reason for this, is that the number of closely spaced planes are determined by the metallurgy, stoichiometry and thermodynamics of a particular compound and therefore are not controllable at will. Moreover, to date the detailed structure (particularly the oxygen ordering) of some of the compounds (BiCaSrCuO and TlCaSrCuO) is not uniquely determined and therefore the conclusions should be taken with some caution.

A possible alternate approach is to perform well-controlled changes in a particular system which contains all the hopefully relevant features.^{44]} This approach has been quite successfully used in the $\text{YBa}_2\text{Cu}_3\text{O}_y$ system. The reasons this system is particularly attractive are the following: a) the transition temperature is quite high, b) a large number of substitutions which have varied degrees of influence on the superconductivity can be performed, c) changes in the oxygen stoichiometry can easily be accomplished by a variety of means and perhaps most importantly d) almost single phase compounds can be prepared which allows a very precise and detailed determination of the structure.

As is well-known by now, the superconductivity in this system occurs in the single phase compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $\delta < 0.5$. The structure consists of two dimpled Cu-O planes surrounding an Y plane and these units weakly linked together by "fence" like Cu-O chains as shown in Fig. 1.^{9]} This structure is commonly known in the literature as the "1-2-3 phase". Based on the valency of the constituents, an oxygen stoichiometry of 6.5 implies that the formal oxidation state of copper is $2+$ and that of oxygen, $2-$. An increase in the oxygen stoichiometry above this value, naively implies the existence of some Cu^{3+} or some O^{1-} (in practice, it is hard to distinguish these two cases experimentally). The fundamental question therefore is which of the structural

features (if any) are "responsible" (i.e. crucial) for the superconductivity and whether the existence of trivalent Cu or monovalent O is crucial.

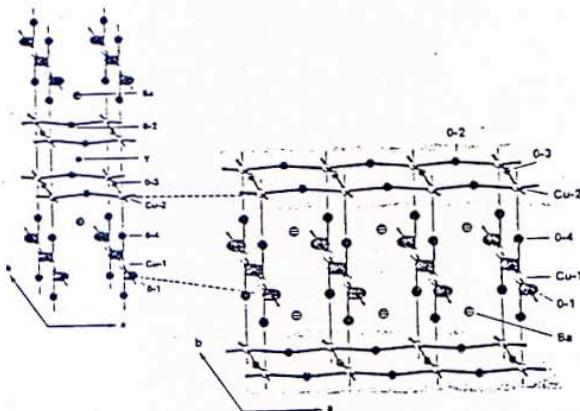


Figure 1 Orthorhombic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ showing the full structure (above) and the coupling by the Cu-O "fence" of the Cu-O planes. The occupied oxygen site on the chain is labeled O1, the unoccupied O5, the bridging oxygen O4 and the oxygens in the plane are O2 and O3. Cu in the chains are labeled Cu1 and in the plane Cu2.

The answer to many of these type of questions lie in a series of well-controlled experiments in which the structure and superconductivity for various oxygen deficiencies and metal ion substitutions have been performed.

Figure 2 shows the resistivity of two $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples, one slowly cooled and another quenched from a high temperature.^{45]} The slow cooled sample shows a low oxygen deficiency and normal state resistivity and a high T_c , whereas the quenched sample has a higher oxygen deficiency and normal state resistivity, and a depressed T_c . Detailed studies show that the transition temperature decreases to zero close to an oxygen stoichiometry of 6.5 (i.e. only Cu^{2+} or O^{1-} present) and close to the occurrence of the orthorhombic to tetragonal phase transition. Recent gas evolution experiments^{46]} have shown that in fact, for low enough vacancy concentration in the Cu-O planes which do not disrupt conduction, the T_c and the orthorhombic-tetragonal phase transitions are determined mostly by the concentration of oxygens in the Cu-O chains.

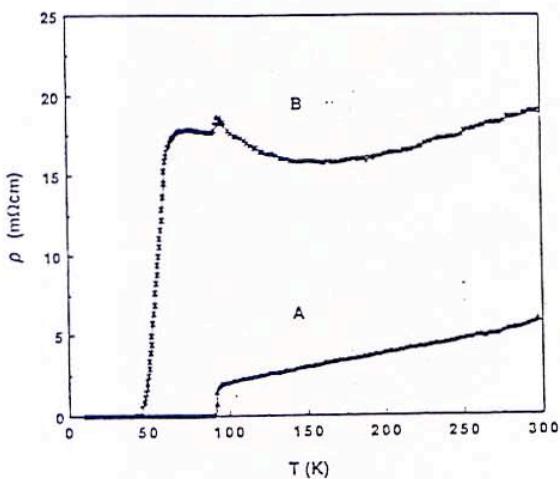


Figure 2 Resistivity versus temperature for a slowly cooled sample (A) and the same sample after quenching from a high temperature (B).

A variety of other experiments, especially in the $\text{La}(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_y$ ^{47]} and the $\text{Nd}(\text{Ba}_{2-x}\text{Nd}_x)\text{Cu}_3\text{O}_y$ ^{48]} systems show that again the superconducting transition temperatures are correlated with the concentration of oxygen in the Cu-O chains.

Moreover, a plot of two types of quenching experiments (fixed times different temperature, or fixed temperature different times), the $\text{La}(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_y$ and $\text{Nd}(\text{Ba}_{2-x}\text{Nd}_x)\text{Cu}_3\text{O}_y$ systems are found to scale universally above a $T_c \sim 50$ K, with the chain occupancy (i.e. number of O in the O1 chain site - number of O in the empty O5 sites).^{49]} Below this T_c , the different types of experiments diverge from each other. Whether this universal behavior above 50 K is of fundamental importance or accidental requires further studies. At this point it should be stressed that the concentration of oxygens in the chains is simultaneously related to the overall oxygen stoichiometry, and structural parameters such cell and bond lengths, etc. Because of this, it is difficult to ascertain unequivocally which of these parameters is key in determining the superconductivity. Therefore, it is necessary to search for universality between the different types of experiments; i.e. the various kinds of quenching and substitutions. Moreover, if a definite statement is to be made detailed structural models, *experimentally determined* are necessary.

The substitutions of a number of rare earths in the Y site show very little effect on the superconducting properties. However, three elements (Ce, Pr, Tb) have not been successfully incorporated into the superconducting 1-2-3 phase. These are also the elements that form mixed valent compounds and are occasionally found in the tetravalent state, unlike Y which is always trivalent. Fig. 3 shows the temperature dependence of the resistivity for a series of samples in which Pr is substituted in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system.^{50]} Again, as a function of increasing x the normal state resistivity increases and the T_c decreases. These changes are quite similar to changes which occur with increasing oxygen deficiency δ in the $YBa_2Cu_3O_{7-\delta}$ system as described above. It is tempting to assign all these changes to a change in the amount of Cu^{3+} or equivalently O^{1-} present in the sample. As the Pr concentration increases the amount of Cu^{3+} (or O^{1-}) decreases and therefore the resistivity increases and the T_c decreases. Unfortunately, no detailed neutron refinements are presently available in this system to make a definite statement as far as the role of Pr valency as opposed to the oxygen ordering is concerned. It should be stressed again that in all cases a variety of phenomena occur simultaneously and therefore assigning changes in the superconductivity to one particular feature may be misleading.

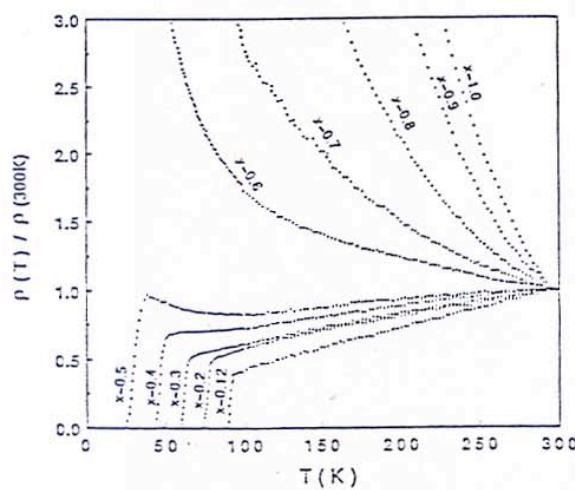


Figure 3 Relative resistivity (normalized to room temperature) as a function of temperature for selected $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples. Notice the systematic decrease of T_c and increase of normal state resistivity with increasing x .

This brief review has outlined some of the main issues in the field of ceramic superconductors. Namely, which is the main feature which determines the superconductivity; a definite structural feature (bond length, cell edge, oxygen ordering, etc.) or electronic feature, particularly the presence of Cu³⁺ or O¹⁻. In order to ascertain which of these features is critical it is argued that universality in behavior among a variety of different well-controlled experiments should be searched. Experiments to date imply that both the formal oxidation state of Cu or O as well as the oxygen ordering are of importance. Above a T_c of ~ 50 K, the superconducting transition temperatures obtained in quenching and substitution (Nd, La) experiments seem to scale universally with the oxygen chain order parameter. Below this T_c no universal behavior is found.

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