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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

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ABSTRACT

We employ a very useful quantity, the electronegativity, to classify the superconductor. The value of the group average electronegativity to separate superconductor into two categories is 2. Each category has unique chemical bond features. The high-T_c oxide superconductor belongs to the second category with group average electronegativity being larger than 2. Their unusual bond nature also gives new insight into some essential factors beneficial to enhance superconductivity.

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Although up to now the superconducting mechanism of the high-T_c oxide superconductor (HTOS) has not yet been solved, it is quite evident that the HTOS has many unique features in contrast to the conventional BCS superconductor. For example, HTOS is near the boundary of semiconductor or insulator, and the superconducting coherence length is of the order of the lattice parameter or somewhat larger. Besides, there are common features of the chemical bonding among the known HTOS, i.e. intermediate valence state of the metal ions (M), $M-O-M$ cluster configuration (O = oxygen ions) and the existence of some kind of locally pair correlation of carriers. It is a natural question that is there simple "coordinate" to differentiate the HTOS from the conventional BCS superconductor?

According to Pauling [1], the properties of a substance depend in part upon the type of bonds between the atoms of the substance and in part upon the atomic arrangement and the distribution of the bonds. The electronegativity can be used approximately to make quantitative statements on the bond nature in solids. Thus we introduce the average electronegativity of a compound ($\bar{\chi}$) as the rough scale describing the overall nature of the bonds in HTOS. $\bar{\chi}$ is defined as

$$\bar{\chi} = \sum_i a_i \chi_i$$

where χ_i is the electronegativity of the ith element in a compound and a_i is the atomic percent of the ith element in this compound. See Table 1 for example.

Table 1

Average electronegativity for some compounds in HTOS

Compound	$\bar{\chi}$
$T\ell_2 Ba_2 Ca_2 Cu_3 O_{10}$	2.52
$Bi_2 Sr_2 Ca_2 Cu_3 O_{10}$	2.56
$YBa_2 Cu_3 O_7$	2.58
$YBa_2 Cu_4 O_8$	2.60
$La_{1.85} Sr_{0.15} CuO_4$	2.65
$Ba_{0.6} K_{0.4} BiO_3$	2.64

Taking twenty examples of the HTOS, we have made the arithmetic mean of them, which are named as the group average electronegativity ($\bar{\chi}_g$). It is found that the $\bar{\chi}_g$ of the HTOS is approximately 2.6 and that there is a tendency of roughly increasing T_c from 2.7 to 2.5 of the about value of $\bar{\chi}$. The group average values of electronegativity of some well-known superconducting groups are shown in Table 2. It is noteworthy that except the HTOS and K_3C_{60} group $\bar{\chi}_g$ are all smaller than or near 2. It is well-known that all superconducting elements concentrate in a narrow range from 1.3 to 1.9 of the values of the electronegativity [2]. According to Pauling, the most obvious correlation of the electronegativity scale with the chemical properties of the elements lies in the division of the elements into metals and nonmetals. The value $\chi = 2$ is approximately the point of this separation with the metals being elements having smaller electronegativity than

2. It seems certain that there are two kinds of superconductors with $\bar{\chi}_g \lesssim 2$ for the first category and $\bar{\chi}_g > 2$ for the second. It is expected that the metallic bond plays the prevailing role in the superconductivity of the first category. In comparison with the superconducting elements the superconductors of the first category have higher T_c mainly through ℓ, $\ell \pm 1$ hybridization of the conduction bands [3,4] (ℓ: angular momentum) and the soft mode of phonons.

Table 2

Group average electronegativity

Type	$\bar{\chi}_g$
$A15$	1.71
La_2C_3 structure	2.00
Chevrel	2.07
$Nacl$ structure	2.13
$HTOS$	2.59
K_3C_{60} group	2.42

In contrast to the first category, the nature of bonds in HTOS is complex. Here the electronegativity difference of the elements playing the leading role in a superconductor is another important coordinate. As pointed out by Pauling [5] Cu and O differ in electronegativity by 1.6 units, corresponding to covalent bond nature with 47% partial ionic character [1]. In $Ba_\chi K_{1-\chi}BiO_3$, Bi and O differ in electronegativity by 1.7 units, corresponding to covalent bond nature with about 51% partial ionic character. This is in the language of hybrid bond between a normal covalent bond and an extreme ionic bond. It is certainly a rough approximation. However, it is important to stress from this description that the behaviour of the carriers in the HTOS (or the superconductor in the second category) is radically changed from the first category in which there are pure conduction electrons. If there are still conduction character of the carriers in the HTOS, they are quite different from the metallic bond situation. For instance, Pauling has suggested resonating bonds in $Cu - O$ chains [5]. Anyway, there are effective carriers which have mobility to a certain extent by some ways of resonance or tunneling. This is one side to this question. On the other side of the shield, there are local character of the carrier and the localized carrier pair correlation due to the nature of the chemical bond in the HTOS. Recently, S. Sugai et al. [6] have shown the direct evidence of the existence of some kind of local pair correlation from the detailed analysis of the Raman spectra. The coexistence of the itinerant character carriers and the localized bipolarons has been suggested from their experiment. This is consistent with the picture derived from the argument of electronegativity. Therefore, instead of the pure conduction band picture for the superconductors of the first category, the effective electronic picture of the superconductors of the second category is the combining picture of two subsystems. One of them is the carrier subsystem of itinerant character (electrons or holes) and the other subsystem is the bound pairs or the bipolarons. Here, the hybridization is between the two subsystems.

It is important to emphasize that $\bar{\chi} \sim 2.6$ and about 50% partial ionic character are not the sufficient conditions for achieving high T_c in the HTOS. A decisive factor is the appropriate value of the hybridization strength between the two subsystems. According to a previous paper of mine [7] if this hybridizzation strength is zero, then the superconductivity of the whole system is determined only by the BCS parameter of the carrier subsystem of the itinerant character, Δ_s^{ph}. Generally, Δ_s^{ph} is very small in the HTOS [9] and thus high T_c is not possible in this pure case. Our essential viewpoint is that the hybridization between the two subsystems makes the effective attractive interaction between the effective carriers stronger than the pure BCS coupling as in the superconductors of the first category. So it is very important for achieving high T_c to have appropriate hybridization between the two subsystems. Doping can change this hybridization strength. In a recent work by Wang [8], he estimated the value of parameter (h) describing the above-mentioned hybridization strength in $La_{2-x}Sr_xCuO_4$. It has been found that h gradually decreases to zero as x goes up to about 0.3. According to the above viewpoint this is consistent with the experiment that the superconductivity of $La_{2-x}Sr_xCuO_4$ disappears in the region of $x > 0.3$.

To sum up, from the value of the group average electonegativity of the HTOS, they belong to another category of the superconductors and are different from the pure BCS case. The bond nature is a hybrid between a normal covalent bond and an extreme ionic bond. Also, there is resonating bond nature. The important factors for achieving high T_c in the HTOS are $\bar{\chi} \sim 2.6$, about 50% partial ionic character and the appropriate hybridization strength in this system having two subsystems.

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