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DEPENDENCE OF TRANSITION TEMPERATURE ON HOLE CONCENTRATION PER CuO_2 SHEET IN THE BI-BASED SUPERCONDUCTORS

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Abstract

The recently observed variations of the transition temperature T_c with oxygen content in the Bi-based (2212) and (2223) superconductors are analyzed in terms of p^+, the hole concentration per CuO_2 sheet. This analysis shows that in this systems T_c increases with p^+ initially, reaching maxima at $p^+ = 0.2 \sim 0.3$, followed by monotonic decrease of T_c with p^+. The forms of these variations are similar to those observed in the $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_y$ systems, suggesting that p^+ may be an important variable governing superconductivity in the cuprate superconductors.

Among the cuprate high-T_c superconductors, $La_{2-x}Sr_xCuO_{4-\delta}$ is a prototype since the unit cell of this system contains only a single CuO_2 sheet [1]. The hole concentration or excess valence p^+ on the CuO_2 sheet in an ionic charge lattice represented by $La^{3+}_{2-x}Sr^{2+}_{x}(CuO_2)^{-2+p^+}O^{2-}_{2-\delta}$ is given by $p^+ = x - 2\delta$, meaning that p^+ can be varied by varying either x or δ [2,3]. With $\delta = 0$, T_c increases from 0 to 38 K as x increases from 0.06 to 0.15, T_c starts to decrease for $x > 0.15$ and superconductivity disappears for $x > 0.27$ [2,3]. This result indicates the existence of two superconducting states: a hole (carrier)-deficient state and hole (carrier)-excess state. For the hole-deficient state, T_c increases with holes concentration whereas for the hole-excess state, T_c decreases as the hole concentration increases.

For the (123) family of superconductors represented by $YBa_2Cu_3O_y$ [4], superconductivity vanishes for stoichiometric composition $y = 6.5$ and for $y > 6.5$, T_c increases with y, reaching 93 K for $y \sim 7.0$. In this system, each unit cell contains two CuO_2 sheets and a CuO chain. The question of where the excess holes resides leading to superconductivity has been studied by Tokura et al [5]. According to their analysis, the excess holes p given by $p = (2y - Q - 6)/3$ is distributed as $p_{sh} = (y - 6.5)/2$, and $p_{ch} = (y - 6.5)$ with $p = (2p_{sh} + p_{ch})/3$. In the above, Q is the total cationic charge (excluding Cu), and p_{sh} and p_{ch} respectively represent the excess holes in the CuO_2 sheets and CuO chain. They further suggested that holes associated with chains, p_{ch}, are localized and merely provide an insulating reservoir of charge whereas p_{sh} is the principal variable governing superconductivity. If p^+ represents hole concentration per CuO_2 sheet, then $p^+ = p_{sh}/2$ for the (123) system. By doping with La and Ca, Tokura et al. showed that T_c initially increases with p^+ for $p^+ > 0$, reaches maximum of $T_c \sim 85$ K at around $p^+ = 0.2$ and for $p^+ > 0.2$, a decrease of T_c is seen.

The idealized structure of the $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (2212) superconductor is quite similar to that of the (123) compound with Ca, SrO and double BiO layers replacing Y, BaO and CuO chain layers respectively. $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (2223) phase can be formed by inserting one more (CuO_2 + Ca) slab into the (2212) phase. From the structure similarities, one may expect that excess oxygen atoms are residing in the double BiO layer, playing the same role as the excess oxygen in the CuO chains for the (123) superconductor. However, the situation for the Bi (2212) phase is complicated. First of all, the exact location of the excess oxygen atoms in the compound is still unclear. Secondly, there are numerous deviations from the idealized structure and composition in the Bi and Tl superconductor systems, especially in the double Bi(Tl)O layers and the Sr(Ba)O layers. Deviations such as strontium deficiency [6] (Sr:Ca < 2:1 for the (2212) phase) also creates holes on the CuO_2 sheets. Attemp to vary the oxygen content will inevitably alter the structure to some extent. Thirdly, on synthesizing the high T_c (2223) phase, intergrowth with a low T_c phase often occurs in this system which makes quantitative study on a single phase difficult.

A number of studies [7-11] have shown that T_c in the Bi superconductors is sensitive to oxygen stoichiometry. For example, Morris et al [9] observed increase in T_c with the decrease of oxygen content for the (2212) phase. They varied oxygen content by annealing the samples at different oxygen pressures [9]. We used a TGA (Thermogravimetric Analysis) apparatus to heat a $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (2212) sample to < 850°C and subsequently quench the samples in Ar gas [10]. This method is relatively simple. Since the sample treatment was carried out at atmosphere pressure, it is less destructive than other methods and the weight variation can be monitored in-situ with 1 μg sensitivity. By varying the quenching temperature, we were able to affect the oxygen content by different levels and we observed an increase of T_c of 25 K as a result of loss of 0.09 oxygens per formula unit. By the same technique, we studied a Pb-doped Bi superconductor consisting of the (2223) phase with an admixture of the (2212) phase [11]. Here we observed that with loss of oxygen, T_c of the (2212) phase <u>increased</u> from 70 K to 90 K, whereas that of the (2223) phase <u>decreased</u> from 107 to 90 K. These results suggested that the as-prepared Bi (2212) phase is in the hole-excess state whereas the Bi (2223) phase is in the hole-deficient state. For an as-prepared Tl (2223) phase sample, T_c has been observed to decrease with decrease of oxygen content [12,13] whereas for an as-prepared Tl (2201) phase sample [14], T_c increases with decrease of oxygen content.

At first glance, the above findings on the variation of T_c with hole concentration in the (2212) and (2223) phases of the Bi superconductors do not fit into a consistent picture. Furthermore, the T_c's of the Bi (2201), (2212), (2223) and (2234) phases are quite different viz. 10, 85, 110 and 90 K respectively and these results need to be understood. Here we show that when the observed findings of the variation of T_c with oxygen content in the Bi superconductor are analyzed in terms of p^+, the hole concentration per CuO_2 sheet, a consistent picture emerges. In addition, the variation of T_c with p^+ in

Bi and possibly in Tl superconductors is quite similar to that shown in the $La_{2-x}Sr_xCuO_{4-\delta}$ and the $YBa_2Cu_3O_y$ superconductors, providing a consistent picture for the four families of the cuprate superconductors.

The Bi (2223)+(2212) phase sample we prepared is not a simple mixture of two compounds. As mentioned in the previous paragraph, during the formation of the (2223) phase, intergrowth of the (2212) phase occurs. Therefore the double Bi-O layers are often shared by the (2212) and the (2223) phases. If we assume that excess oxygen atoms are residing in the double BiO layers, the amount of the holes provided by the excess oxygen atoms will be shared by two CuO_2 sheets in the (2212) phase case and by three CuO_2 sheets in the (2223) phase case. According to literature [15,16], δ in $Bi_2Sr_2CaCu_2O_{8+\delta}$ varies from 0.15 to 0.6 for the as-prepared (2212) phase sample. With the consideration of the holes created by strontium deficency [6], we assume there is 0.8 holes per formula unit. Then in average, the hole concentration per sheet, p^+, is given by $p^+ = 0.8/n$. This gives $p^+ = 0.4$ and 0.27 for the (2212) and (2223) phases respectively. Using these two values for the as-prepared samples, the variations of T_c with p^+ for the (2212) and (2223) phases based on our data [10,11] are shown in Fig. 1. A different choice of δ shifts p^+ at which the maximum T_c is observed. However general shape of the curve remains the same. Fig. 1 shows that the as-prepared Bi (2223) is in a carrier-deficient state whereas the as-prepared Bi (2212) phase is in a carrier-excess state. This explains the opposite directions of the T_c variation observed in the (2223) and (2212) phases as a result of loss of oxygen [7-11]. According to the above scheme, one may explain that T_c for the (2234) phase with four CuO_2 sheets is lower (90 K) than that for the (2223) phase because of the smaller p^+ value and the low T_c (~ 10 K) for the (2201) phase with one CuO_2 sheet because of the larger p^+ value. In addition, the as-prepared Bi (2234) and (2201) phase samples are expected to belong to carrier-deficient and carreir-excess states respectively if the structure of the double BiO layer and the SrO layers remains the same as that for the (2212) and (2223) phases. We note that Urland and Tietz [15] have reported the variation of T_c with p^+ for the Bi (2212) phase. T_c variation was achieved by varying Sr:Ca ratio and oxygen content. They showed that as p^+ increases from 0.1 to 0.6, T_c first increases from 73 to 80 K, remaining at 80 K for $p^+ = 0.2 \sim 0.4$, then falling for $p^+ > 0.4$. Their results suggest that for a single Bi or Tl phase, the variation of T_c with p^+ may follow the same shape as that in Fig. 1. Recently, similar results have been reported by Yoshizaki et al [17] and Torrance et al [18] respectively in Y doped, and Na and K doped Bi (2212) samples. Maximum T_c's were found at $p^+ = 0.15 \sim 0.25$. In the case of La doped (2201) $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ compound [19], Groen et al showed that the as-prepared (2201) phase is in a carrier-excess state. Maximum $T_c = 28$ K was observed at $p^+ = 0.3$ and for $p^+ < 0.21$, the sample became non-superconductor.

In the above, we have shown that the variation of T_c with p^+ for the Bi (2212) and (2223) phases may be represented by Fig. 1. Moreover the shape of the curve in Fig. 1 is similar to that for the (123) [5] and $La_{2-x}Sr_xCuO_{4+\delta}$ [2,3] superconductors although the magnitude of p^+ corresponding to the maximum T_c is somewhat different for different families of superconductors. According to previous experimental results [12,13,14], it is likely that the variation of T_c with p^+ for the Tl-based superconducting phases may follow a pattern similar to that in Fig. 1 with maximum T_c = 125 K. These results suggest that p^+ (excess valence per CuO_2 sheet) may be an important variable for the cuprate superconductors and these results should form the major test for any successful theory of superconductivity.

It is interesting to note that without the hole reservoir, T_c for $La_{2-x}Sr_xCuO_{4-\delta}$ is below 40 K. With CuO chain, double BiO layers and double TlO layers as hole reservoirs, T_c increases to 93 K, 110 K and 125 K respectively. It appears that the key to the differences in T_c is the interaction between the hole reservoir part and the CuO_2 sheets. Bishop et al [20] argued that although superconductivity itself takes place on the CuO_2 sheets, the attractive pairing mechanism is not two-dimensional but may require dynamic coupling of these sheets to the surrounding polarizable environment in order to understand the difference in the T_c's of the four families of superconductors.

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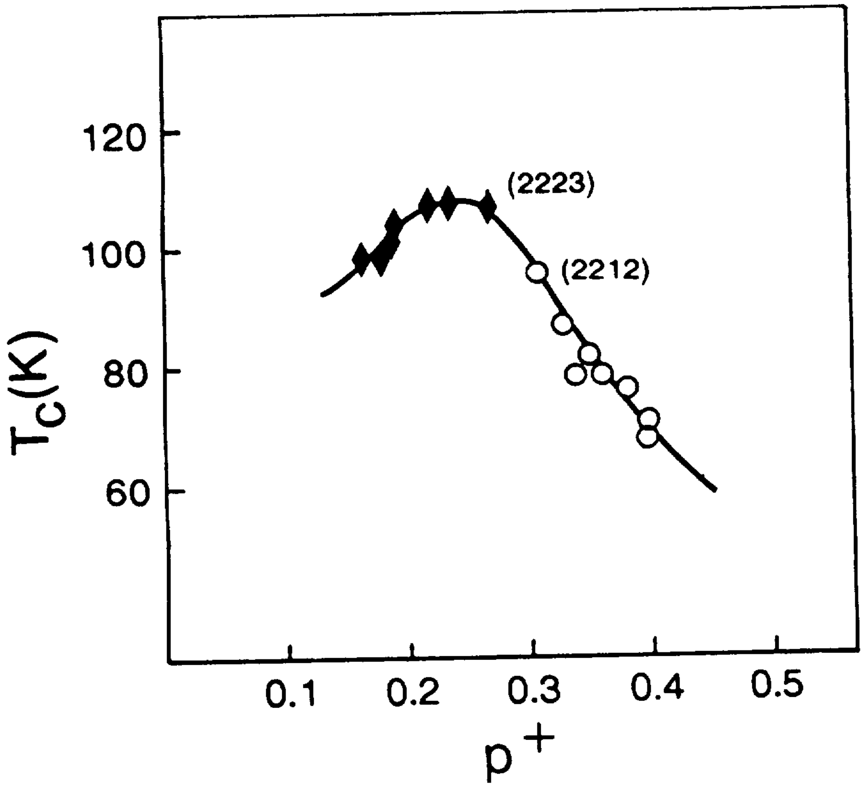

Fig. 1. The variations of T_c's with p^+ for the Bi (2212) and (2223) phases.