

## CHAPTER - I V

## CHAPTER-IV

# CRYSTALLOCHEMICAL ANALYSIS OF CHARGE AND SPIN FLUCTUATION IN OXYGEN DEFICIENT AND DOPED $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$

### IV.1. Introduction

In the present chapter we analyze the mechanism of charge transfer in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  (YBCO) when its charge reservoir layer is perturbed. The perturbations considered are oxygen vacancies, their ordering, and trivalent and monovalent ion doping. Our crystallochemical analysis shows that the Cu(1) ions close to the oxygen vacancies or to the substituent ions are driven to an unstable charge state. The resulting charge fluctuation in the CuO basal plane is shown to induce antiferromagnetically coupled spin fluctuation in the  $\text{CuO}_2$  planes. The observed structural and superconducting features of the YBCO are explained based on these fluctuations.

### IV.2. Charge and Spin Degrees of Freedom in Oxygen Deficient YBCO

#### *IV.2.1. Oxygen coordination and charge states of Cu*

The structure of YBCO can accommodate varying oxygen concentration with  $y$  ranging between 0 and 1. The square pyramidal oxygen coordination of Cu(2) atoms in the conducting  $\text{CuO}_2$  sheets however is stable and does not change with the oxygen content. Any oxygen deficiency in the YBCO results in vacant oxygen sites in the Cu-O-Cu chains along the b-axis. The Cu ions nearest to any vacant oxygen site are left in a 3-fold oxygen coordination. Crystallochemical analysis [1,2] shows that  $\text{Cu}^{1+}$  can have only

a 2-fold oxygen coordination, whereas at least a 4-fold oxygen coordination is admissible to  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$ . Spectroscopic studies [3-5], however, rule out 3+ valence state of Cu. Near the vacancies, the emerging 3-fold oxygen-coordinated Cu(1) ions remain in an unstable charge state. The charge state of these ions can either temporally fluctuate between 2+ and 1+ and/or can spatially equilibrate with an appropriate number of  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$ , depending upon the viability of dynamic nonequilibrium ordering in the system as discussed later.

The  $\text{O}_7$  phase corresponds to an ordered phase with all the chains full and all the Cu(1) ions 4-fold coordinated. In such a configuration, Cu(1) ions have stable 2+ valence state. The  $\text{O}_{6.5}$  phase corresponds to another ordered phase with alternate full and vacant chains. In this case, half of the Cu(1) ions are 4-fold coordinated with 2+ valence and the other half are 2-fold coordinated with 1+ valence. Thus, in both the ordered phases (i.e.  $\text{O}_7$  and  $\text{O}_{6.5}$ ), the Cu(1) ions have stable charge states of either 2+ or 1+ in accordance with their coordination number. However, in phases with in-between oxygen concentrations, even though the sample is prepared under thermodynamic equilibrium conditions, some of the Cu(1) ions acquire an unstable coordination of 3-fold and hence an unstable charge state.

The superconducting range from  $\text{O}_7$  to  $\text{O}_{6.5}$  is sharply divided by two phases [6,7]: one with  $T_c \sim 90$  K from  $\text{O}_7$  to  $\text{O}_{6.85}$ , the ortho-I phase with a peak in  $T_c$  at about  $\text{O}_{6.93}$  [8], and another plateau with  $T_c \sim 60$  K from about  $\text{O}_{6.75}$  to  $\text{O}_{6.6}$ , the ortho-II phase (Fig. IV.1). We examine, next, the effect of unstable charge state on the charge and spin degrees of freedom in this two regimes of  $T_c$  vs oxygen content.

#### ***IV.2.2. Charge Fluctuation***

The charge transfer model [9] views the  $\text{CuO}_2$  sheets as the charge conductor planes while the basal CuO layers act as charge reservoirs transferring holes to the conductor layers. Thus, the stoichiometric

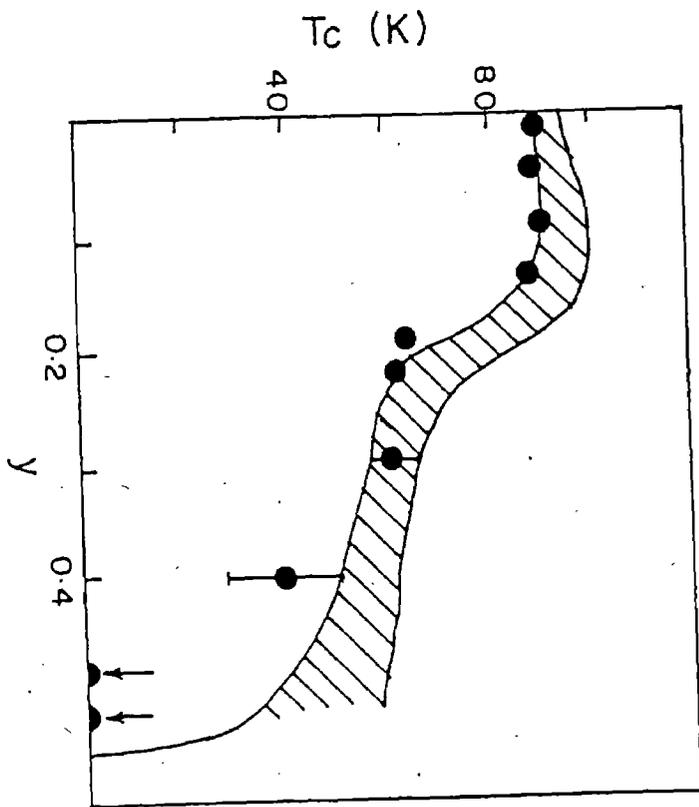
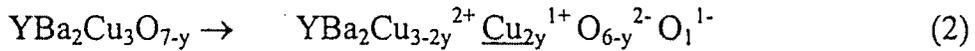
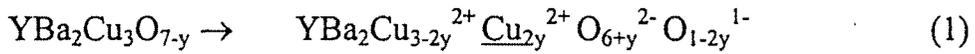


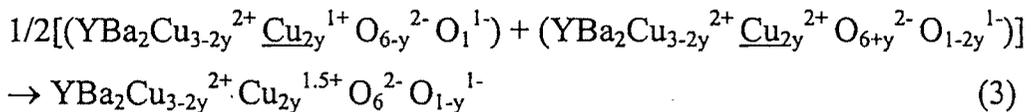
Fig. IV.1. Variation of  $T_c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  with  $y$  (hatched region : magnetic susceptibility data and closed circles : resistivity data) [8].

composition  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has one hole per unit cell, mostly located at the oxygen site in  $\text{CuO}_2$  planes.

So long as the concentration of oxygen vacancies are low in the oxygen-deficient YBCO system, so that they do not interact, the isolated random unstable 3-fold oxygen coordination around  $\text{Cu}(1)$  is inhibited to spatially equilibrate and stabilize to 4-fold and 2-fold ones as discussed in section IV.2.4. Thus, for each oxygen vacancy, there will be two nearby  $\text{Cu}(1)$  ions which are driven to unstable three fold oxygen coordination. The resulting unstable charge state of these  $\text{Cu}(1)$  ions can fluctuate between two stable charge states  $2+$  and  $1+$  as shown in eqns. IV.1 and 2 respectively (with charge fluctuating Cu ions underlined).



Balancing of the charge on the R.H.S. of eqns. IV.1 and 2 while keeping the total number of oxygens to  $7-y$  shows that, these Cu ions when driven to  $2+$  charge state, reduce the carrier concentration per unit cell from 1 in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase to  $1-2y$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  phase (eqn. IV.1). In the  $1+$  charge state however, these Cu ions restore the carrier concentration to 1 hole per unit cell irrespective of the oxygen deficiency  $y$  (eqn. IV.2). The charge fluctuation in the chains, thus leads to annihilation and creation of oxygen holes in the unit cell. On time average, for  $y$  number of vacancies, the number of holes  $n_h$  per unit cell will be reduced from 1 in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  to  $1-y$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  as shown in eqn. IV.3



The variation of the density of four fold ( $n_f$ ) and three fold ( $n_t$ ) coordinated copper sites in the basal plane and the carrier density  $n_h$  with oxygen vacancy concentration  $y$  is shown in Fig. IV.2. The present discussion pertains to the region  $0 < y \leq 0.25$  where spatial equilibration of the unstable Cu sites are prevented.

As  $T_c$  is known to scale with carrier concentration [10,11], such a fluctuation resulting in reduction of  $n_h$  is expected to suppress  $T_c$  with increasing  $y$ . On the contrary, the  $T_c(y)$  plot gives a plateau at  $T_c \sim 90$  K for the low values of  $y$ . It is thus clear that the carrier density cannot be the sole factor governing the  $T_c$ . Pressure dependence of  $T_c$  [12] indicates the existence of other parameters which seem to be related to local atomic coordination around Cu. The  $T_c$ , therefore is not expected to fall monotonically with decreasing  $n_h$ . The observed 90 K plateau for low values of  $y$  can be explained by considering all such parameters controlling  $T_c$  as  $n_h$  and local geometric distortion leading to unstable charge states. In fact, the 90 K plateau with the observed peak in it can be well explained if we consider charge fluctuation at these isolated unstable 3-fold coordinated Cu sites inducing antiferromagnetically coupled spin fluctuations in the  $\text{CuO}_2$  planes.

### *IV.2.3. Spin fluctuations*

Absence of  $\text{Cu}^{2+}$  electron paramagnetic resonance (EPR) signal [13], Pauli temperature-independent type Susceptibility [14], nuclear magnetic resonance [15] and neutron inelastic scattering studies [16] all point towards evidences of strong 2-dimensional antiferromagnetically coupled spin fluctuations in cuprate superconductors, the origin and mechanism of which have been largely speculative. From neutron inelastic scattering and nuclear spin lattice relaxation studies, the spin fluctuation seems to be intimately related to the occurrence of superconductivity.

As discussed earlier, the charge fluctuations between 2+ and 1+ charge states of Cu in the CuO chains annihilate and create holes (eqn. IV.3) in the

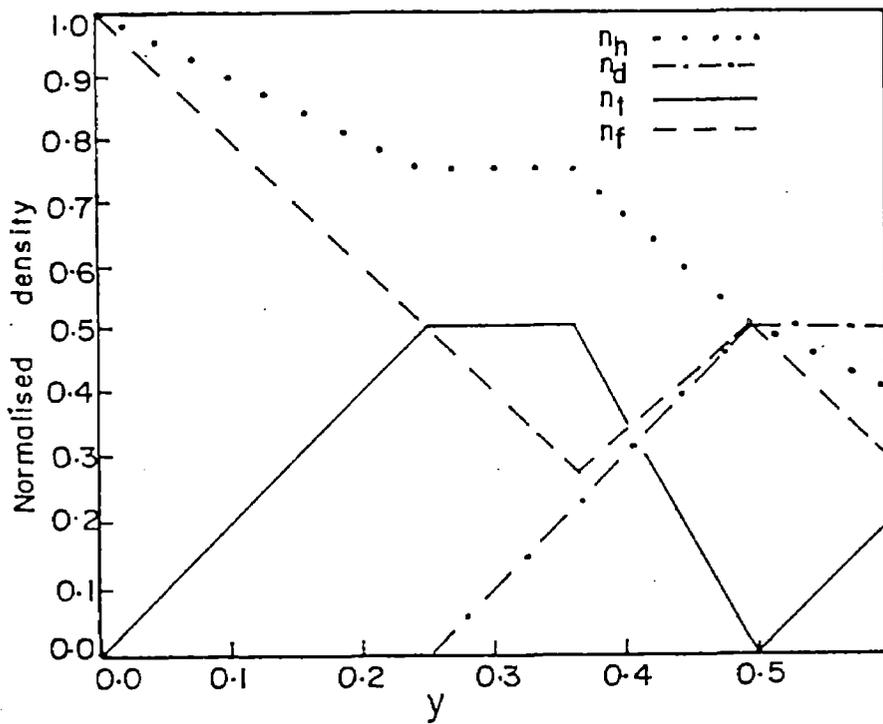


Fig. IV.2. Variation of number of charge carriers  $n_b$ , 2-fold, 3-fold and 4-fold coordinated Cu(1) sites per unit cell in  $YBa_2Cu_3O_{7-y}$  with  $y$ .

CuO<sub>2</sub> planes. This persistently ongoing annihilation and creation of holes at the oxygen sites bridging the Cu ions switches the magnetic interactions from ferromagnetic to antiferromagnetic inducing spin fluctuations. For these spin fluctuations to take place and to be sustained, it is necessary that the system remains in a metastable state. In YBCO type systems, such metastability is achieved by having unstable 3-fold oxygen coordinated Cu ions in the lattice. In La- or Bi/Tl-based systems the lattice mismatch as well as the deviation from the ideal charge states of the intercalating cations lend the cuprates a metastable state. It is also necessary that the metastable sites do not mutually interact and spatially equilibrate, a condition that prevails for low vacancy concentrations in YBCO type systems.

Though the mechanism of superconductivity is still obscure, many authors [17,18] have suggested that antiferromagnetically coupled spin fluctuations play a decisive role in the mechanism. These fluctuations are believed to provide the coupling between cooper pairs in the superconducting state [19,20]. Such a coupling competes with the monotonic fall of T<sub>c</sub> due to the depletion of carrier concentration [21]. Such an override accounts for the 90 K ortho-I plateau with the peak in it for  $y \sim 0.1$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> (Fig. IV.1). It is also interesting to note that the normal state resistivity peaks for samples with oxygen content which shows the highest T<sub>c</sub> [8] (Fig. IV.3). As discussed earlier, the antiferromagnetically coupled spin fluctuation dominates in these concentration regime. Therefore, the scattering of the charge carriers in the normal state due to these fluctuations is expected to be high leading to high resistivity. Similar implication arises in low T<sub>c</sub> superconductors where bad metals are seen to be good superconductors because of the usual electron-phonon interaction.

#### ***IV.2.4. Spatial equilibration***

Increasing vacancy concentration beyond a critical value  $y_c$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub>, the large density of unstable 3-fold coordinated Cu(1) ions start

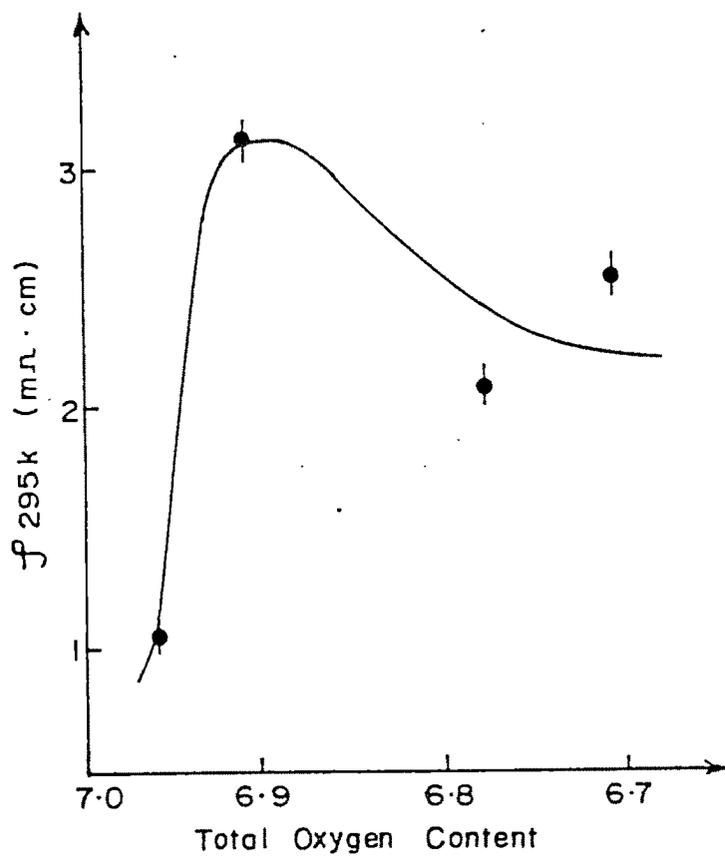
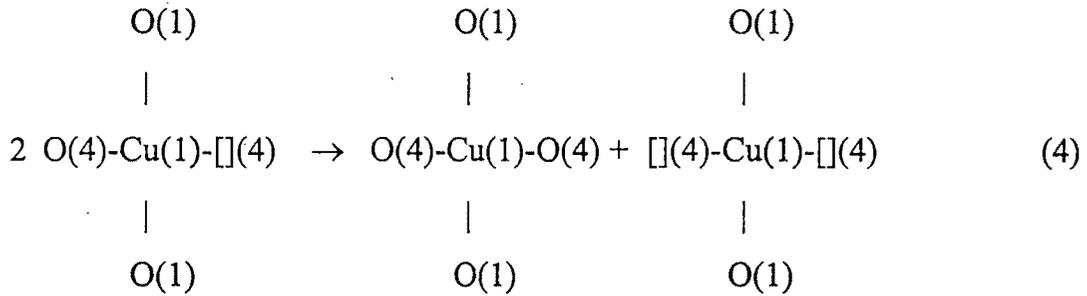


Fig. IV.3. Variation of room temperature resistivity  $\rho_{295k}$  with total oxygen content of  $YBa_2Cu_3O_{7-y}$  showing a maximum near  $y \sim 0.1$  [8].

mutually interacting because of their proximity. Oxygen diffusion process would then drive two such Cu(1) ions to stabler 4-fold and 2-fold coordination as shown in eqn. IV.4



Such a rearrangement of the oxygen ions is expected to result into lowering of the free-energy. The valence states of the 2-fold oxygen coordinated Cu will be 1+ while those of the 4-fold ones will be 2+ as discussed earlier.

From the physical evidences of the appearance of a distinct second phase, the ortho-II plateau at  $O_{6.75}$  [6,7], we may take the corresponding vacancy concentration 0.25 as the  $y_c$  where the vacancy-vacancy interaction leading to the spatial equilibration as shown in eqn. IV.4 sets in. The large separation ( $\sim 11.7\text{\AA}$ ) between the Cu-O chains along the c-axis precludes any interaction amongst vacancies and consequent possible ordering in this direction [22]. Hence, we may without loss of generality, assume the vacancy ordering to be confined to the basal ab-plane. Then the stochastically probable distance  $a_v$  between two vacancies, depending upon the lattice constants in the ab-plane and the vacancy concentration  $y$ , will be given by  $a_v = (ab/y)^{1/2}$ . Fig. IV.4 shows the variation of average distance between vacancies with the vacancy concentration. As stated earlier,  $y = 0.25$  marks the beginning of the ortho-II phase. This is therefore, the critical vacancy concentration  $y_c$  where the intervacancy distance  $a_v$  equals the vacancy interaction length  $\xi_v$ . Hence, the critical vacancy interaction length  $\xi_v$ , where the spatial ordering can set in, will be equal to  $[ab/y_c]^{1/2}$ . With  $y_c = 0.25$ , and the corresponding  $a = 3.82 \text{ \AA}$ ,  $b = 3.38 \text{ \AA}$ ,  $\xi_v$  turns out to be  $\sim 7.71 \text{ \AA}$ . We

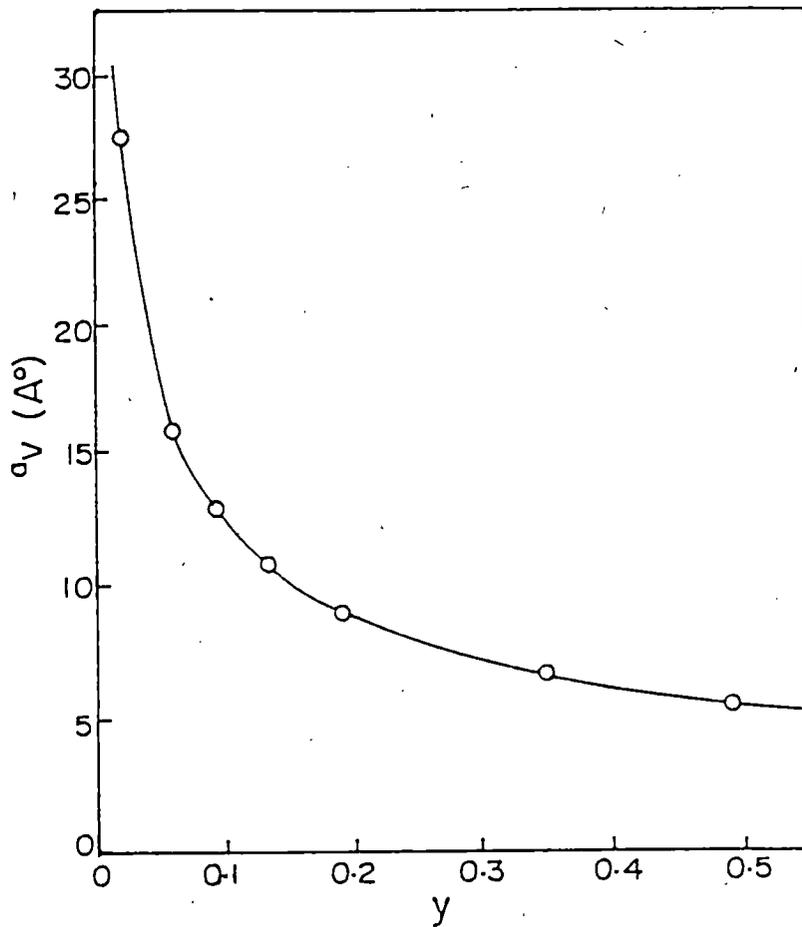
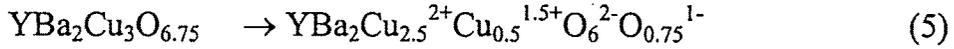
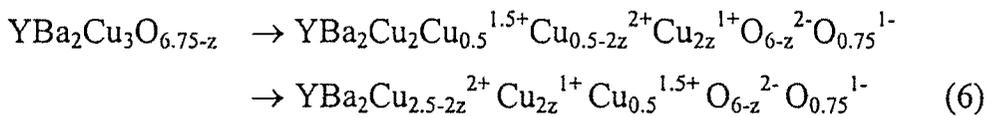


Fig. IV.4. Variation of the average intervacancy length  $a_v$  with  $y$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ .

stipulate that so long as the average intervacancy length  $a_v$  at different  $y$ 's is greater than this  $\xi_v$ , the isolated unstable 3-fold oxygen coordinated Cu charge states will temporally fluctuate. With this  $O_{6.75}$  phase taken as the reference point, eqn. IV.3 changes to



The  $2y$  number metastable 3-fold oxygen coordinated Cu(1) ions in the chains for  $y$  number of vacancies correspond to 0.5 Cu(1) ions for 0.25 oxygen vacancies in  $YBa_2Cu_3O_{6.75}$ . These Cu ions in the chains fluctuate between  $2+$  and  $1+$  charge state. On time average they present a stochastic charge state of  $1.5+$  as shown in eqn. IV.5. With further depletion of oxygen, say by  $z$  from 6.75 to  $6.75-z$ , we notice from eqn. IV.6 that while the number of 3-fold coordinated Cu ions remain unaltered on organization of vacancies by way of proximity eqn. IV.4, the number of 4-fold Cu ions decrease by  $2z$  and that of the 2-fold ones increase by  $2z$ .



thus keeping the number of holes as well as the number of the fluctuating 3-fold coordinated Cu sites per unit cell unaltered (Fig. IV.2).

The  $T_c$  depends on the number of charge carriers, as well as on the interaction energy between the charge carriers leading to the formation of Cooper pairs ( $T_c = K\omega_D e^{-1/\lambda\rho_F}$ ). If, as pointed out earlier, antiferromagnetic coupled spin fluctuations are responsible for such interaction leading to high  $T_c$  as in cuprates, we find here that the concentration of unstable 3-fold coordinated Cu-sites which triggers these fluctuations remain constant. Thus, in addition to density of states at the Fermi energy  $\rho_F$ , depending upon the carrier concentration  $n_h$  remaining constant, the interaction parameter  $\lambda$ ,

depending upon the concentration of unstable 3-fold coordinated Cu sites also remains constant, providing a  $T_c$  independent of oxygen concentration. Of course, with depletion of oxygen from the chains, the number of charge carriers has dropped from a maximum value of one hole per unit cell at  $O_7$  to 0.75 holes per unit cell in this  $O_{6.75-z}$  regime before it stays constant. So long as these nonequilibrium ordering conditions prevail with unvarying number of charge carriers and arrested coupling of the charge and spin fluctuations, the  $T_c$  remains flat but at a reduced value (Fig. IV.1). This is the observed 60 K ortho-II plateau [6-9,23].

#### ***IV.2.5 Structural phase transition***

In the 60 K ortho-II plateau, as the oxygen stoichiometry decreases below 6.75, the 4-fold oxygen coordinated Cu(1) ions get depleted with an equal increase in the number of 2-fold oxygen coordinated Cu(1) ions, leaving the concentration of 3-fold coordinated Cu sites intact (Fig. IV.2). The average distance between 2-fold oxygen coordinated Cu(1) ions in their charge state  $1+$  goes on decreasing. Beyond a certain critical value of  $z$  corresponding to a critical distance between  $Cu^{1+}$  ions, it can be seen that the concentration of 3-fold coordinated Cu sites no longer remains constant but decreases rapidly due to oxygen vacancy reordering. As can be seen from Fig. IV.5, this critical distance is the distance between two 2-fold coordinated Cu(1) ions separated by two 3-fold coordinated Cu(1) ions. This is seen to be  $3b$ . We may, in this circumstance, calculate the corresponding critical value of  $z$  by setting  $(ab/z_c) = 3b$  or  $z_c = 0.113$ , giving the oxygen content per unit cell as  $O_{6.75-z_c}$  i.e.  $O_{6.637}$ . Below this oxygen concentration, the 3-fold coordinated Cu(1) ions get converted to 2-fold ones if a bridging oxygen is removed (Fig. IV.5a) or to 2-fold and 4-fold ones if the bridging oxygen migrates to a neighboring chain, filling the vacancy between two nearby 3-fold coordinated Cu-sites (Fig. IV.5b). Thus, this region of oxygen concentration marks the spatial reorganization of the remaining 3-fold Cu ions to 4-fold and 2-fold ones. In this ordering process, alternate chains

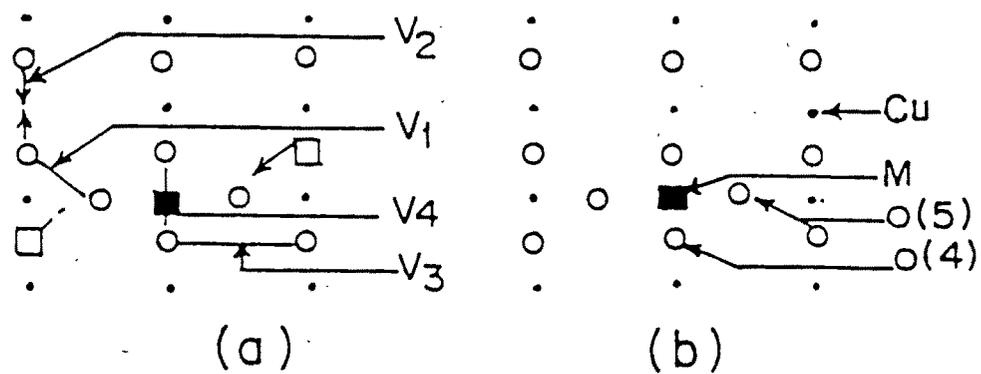


Fig. IV.5. Conversion of two 3-fold coordinated Cu(1)-sites to (a) 2-fold coordinated sites on oxygen removal, and (b) 4-fold and 2-fold coordinated sites on interchain oxygen diffusion.

become full and empty of oxygen in accordance with the basal plane energetics [24], reducing the number of 3-fold oxygen coordinated Cu ions to zero, with only 2-fold coordination in one chain and only 4-fold coordination in the neighboring chain. Such a transformation is complete at  $y = 0.5$  (Fig. IV.2), embarking upon the second ordered phase with doubling of the a-axis in the unit cell.

From this ordered structure, further removal of oxygen, leads to further random oxygen vacancies giving rise to 3-fold oxygen coordinated Cu sites. As a result, the charge fluctuations at these sites build up with concomitant spin fluctuations in the  $\text{CuO}_2$  planes which provide the interaction between Cooper pairs. The coupling, to some extent, will compensate for the rapid monotonic decrease of  $T_c$  with fall of carrier concentration. Hence, another plateau, the anti ortho-I phase, which has been speculated by Ceder et al. [25] is expected to arise.

### **IV.3. Charge Fluctuation Mechanism in Trivalent Metal Ion Substituted YBCO**

The trivalent metal ions like Fe, Ga, Al, Co, etc. generally prefer 6-fold oxygen coordination. Substitution of these ions at the site of the square planar (4-fold) Cu(1) ion (site specific occupancy is discussed in chapter-II) perturbs the potential field distribution in the CuO basal plane. This effects oxygen rearrangement in the basal plane by the following two processes

- (i) Transfer of an oxygen from the nearest Cu site to the M site (Fig. IV.6a)
- (ii) Incorporation of extra oxygen from the gas phase (Fig. IV.6b).

Annealing under reduced atmosphere precludes exotic oxygen, and oxygen rearrangement is effected through the process (i). In this case, the two nearby Cu(1) ions which contribute one of their coordinating oxygen are left in a 3-fold coordination. As discussed earlier, the charge state of these Cu ions will be unstable and will fluctuate between two stable charge state  $1+$  and  $2+$ , creating and annihilating holes in the  $\text{CuO}_2$  planes. If the oxygen

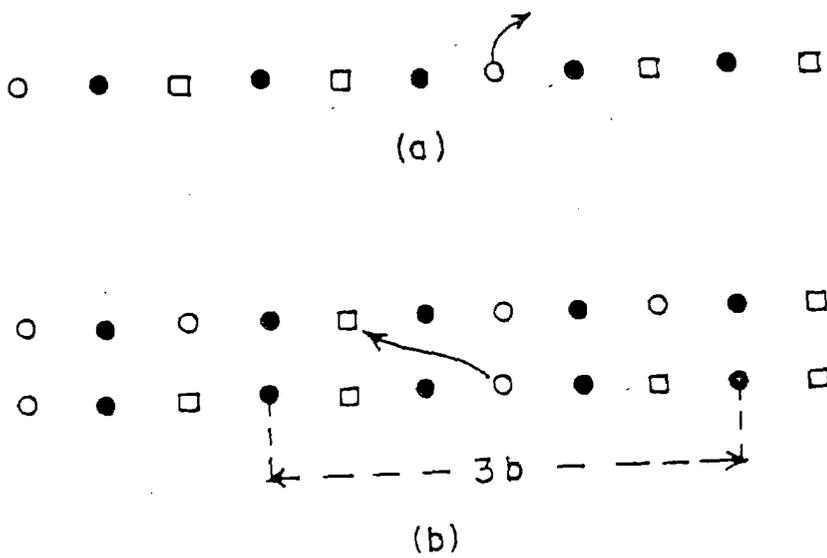
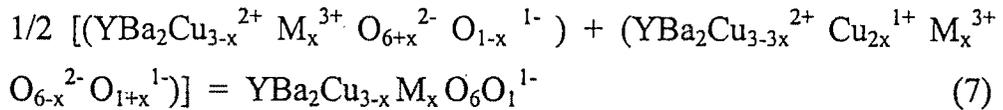


Fig. IV.6. Oxygen configuration around M : (a) Oxygen transfer from CuO chain, (b) Incorporation of exotic oxygen

content is kept at  $O_7$ , the time average of the two fluctuating charge states and their corresponding carrier concentrations leave the total hole density unaffected as shown in eqn. IV.7.



The  $T_c$  is known to scale with carrier density [10], and hence is expected to remain unaffected with trivalent metal ion doping. Experimental findings show it, but up to a certain critical value  $x = x_c \sim 3\%$  [26,27].

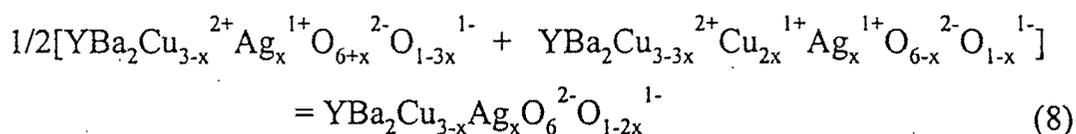
For  $x > x_c$ , probability of two or more M ions occupying neighbouring sites in the basal plane increases. If it takes place along the a-direction (Fig. IV.6b), the oxygen at O(5) site bridging the two M ions can come from the gas phase. This would however leave two neighbouring Cu sites in unstable 3-fold coordination. On the other hand, if clustering of metal ions occurs along the b-direction, no exotic oxygen is needed: two stable 2-fold coordinated  $Cu^{1+}$  sites per M ion will be favoured driving the system to equilibrium and  $T_c$  will be suppressed.

The non-variance of  $T_c$  at the orthorhombic to tetragonal transition [26,27] points to non-importance of CuO chains for superconductivity. But the presence of differently oriented orthorhombic domains [28,29] suggests that even in the tetragonal phase, short CuO chains still exist. The 3-fold coordination (Fig. IV.6) arising due to oxygen vacancy in the chains is a non-equilibrium state for Cu which sustains charge and spin fluctuations, needed for superconductivity. Since these unstable coordination develop at the M-cluster boundaries by displacement of an oxygen from the CuO chains, these chains, even in small fragments, seem necessary for superconductivity to occur in the M-doped YBCO systems.

#### IV.4. Charge Fluctuation Mechanism in Monovalent Ion Substituted YBCO

The substitution of monovalent ions such as Ag and Au for Cu in the CuO basal plane of YBCO has been confirmed by many authors [30-33]. We consider the effect of doping Ag at the Cu(1) site in the YBCO structure, as it has been studied extensively by many and also forms a part of the present study elaborated in chapter-V.

As Ag is monovalent, its incorporation in the YBCO lattice increases the hole concentration unless oxygen content is reduced. The  $\text{Ag}^{1+}$  however has a linear 2-fold oxygen coordination unlike the Cu(1) ions which have 4-fold square planar oxygen coordination. The doping of Ag at Cu(1) site thus creates oxygen vacancies along the CuO chains leaving the two nearby Cu(1) ions in 3-fold oxygen coordination. As discussed earlier, the 3-fold oxygen coordination leads to an unstable charge state for Cu(1) ions. In this unstable charge state, these ions fluctuate between two stable charge states 1+ and 2+ with consequent annihilation and creation of oxygen holes in the unit cell. Thus the carrier concentration is affected as shown in eqn. IV.8.



With additional y number of oxygen vacancies, 2y number of Cu(1)'s in the Cu-O chains acquire 3-fold oxygen coordination and are driven to a unstable charge state, fluctuating between 1+ and 2+ [34]. The remaining  $1-3x-2y$  Cu's in the chains still have 4-fold oxygen coordination, and hence have stable valence of 2+. Thus, with silver concentration of x and oxygen vacancy concentration of y in the system with formula unit  $\text{YBa}_2\text{Cu}_{3-x}\text{Ag}_x\text{O}_{7-2x-y}$ , the number of oxygen holes per unit cell is  $1-2x-y$  as shown in eqn. IV.9.

$$\begin{aligned}
& 1/2[\text{YBa}_2\text{Cu}_{2-x}^{2+}\text{Cu}_{1-3x-2y}^{2+}\text{Cu}_{2x}^{1+}\text{Cu}_{2y}^{1+}\text{Ag}_x^{1+}\text{O}_{6-x-y}^{2-}\text{O}_{1-x}^{1-} \\
& + \text{YBa}_2\text{Cu}_{2-x}^{2+}\text{Cu}_{1-3x-2y}^{2+}\text{Cu}_{2x}^{2+}\text{Cu}_{2y}^{2+}\text{Ag}_x^{1+}\text{O}_{6+x+y}^{2-}\text{O}_{1-3x-2y}^{1-}] \\
& = \text{YBa}_2\text{Cu}_{3-x}\text{Ag}_x\text{O}_{6-x-y}^{2-}\text{O}_{1-2x-y}^{1-} \tag{9}
\end{aligned}$$

The Ag induced charge fluctuation, and the consequent spin fluctuation due to annihilation of holes, is expected to cause an increase of  $T_c$  as explained earlier. The time averaged carrier concentration however shows a decrease with increasing Ag content (eqn. IV.8 and 9) and hence should cause a decrease in  $T_c$ . The observed conflicting reports [35-38] on the  $T_c$  variation with Ag content, perhaps are a consequence of these two competing effects, the predominance of which would crucially depend on the sample preparation condition as discussed in chapter-V.

Ag does not induce disordering of oxygen chain site occupancy. Only vacancies are introduced into the chains which are rigidly bound to the Ag ions because of their fixed 2-fold oxygen coordination. The orthorhombic structure of YBCO is therefore kept intact at lower concentration of Ag. Perfect orthorhombic structure was found in  $\text{YBa}_2\text{Cu}_{3-x}\text{Ag}_x\text{O}_{7-y}$  [39] even for  $x$  upto 0.4, whereas the solubility limit of Ag was found to be 0.03. Though, there exists conflicting reports about the solubility limit of Ag in the YBCO in substitution process, the change in lattice parameters, which can arise only due to substitution, has been reported in the literature [30-33]. The formation of a solid solution between silver and YBCO in substitutional process changes the dimension of the unit cell [31] because the size of the Ag ion is much larger than that of a copper ion.

#### IV.5. Conclusion

Focusing our attention to the extensively studied YBCO system, we have thus attempted to demonstrate that a state of metastability is essential for superconductivity. A dynamic nonequilibrium state brought about by charge instability at the Cu(1) sites due to the oxygen coordination incompatibility in

oxygen-deficient YBCO systems is shown to induce charge fluctuation in the charge reservoir layers. Substitution of Cu(1) ions by metal ions with different charge state and oxygen ion coordination also leads to similar conclusion as far as the charge state instability at the neighbouring Cu(1) sites are concerned. In the absence of spatial equilibration of the defects created on oxygen removal, the carrier concentration is shown to depend on the charge fluctuation. Antiferromagnetically coupled spin fluctuations attendant with nonequilibrium state charge fluctuation have been shown to play a very significant role in compensating for the eventual drop of  $T_c$  with falling carrier density. Indeed, a coupling between the charge fluctuation and the concomitant antiferromagnetically coupled spin fluctuations has been experimentally demonstrated through simultaneous preferential substitution of  $Zn^{2+}$  and  $Ga^{3+}$  at the Cu(2) and Cu(1) sites, respectively [40].

Considering the structural aspect, it is shown that though orthorhombicity may not be indispensable to lend superconductivity to high  $T_c$  systems in general, presence of CuO chain fragments seem necessary to sustain fluctuating 3-fold coordinated Cu charges in YBCO systems. Work on the mechanism and quantitative assessment of the contribution of charge and spin fluctuation as compared to that of carrier density toward  $T_c$  is necessary. It is thus imperative that theories based upon only spin or only charge mechanism would not suffice. Instead, both these factors must be considered together to evolve a theory that is general and consistent with the established experimental data.

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