CHAPTER: III

EPR Spectra Of De-oxygenated High-Tc Superconductors
3.1 Introduction: High temperature Superconductors (HTSC) are EPR silent but all important CuO$_2$ planes of the superconductors and also their constituents can be proved if the substances are deoxygenated. In this chapter CuO, BaCuO$_2$, CaCuO$_2$, Y$_2$Cu$_2$O$_5$, Y-123, Tl-2223 and Hg-1223 have been investigated. All kinds of the spectra are being reported and attempts have been made to identify the species giving the spectra and analyze them. Each substance after deoxygenation, does not always give the same spectrum and to understand the complexity and capriciousness of the spectra is the main aim of this study.

3.2 Experimental:

Substances were prepared by usual solid state reaction route. Details of each preparation is given below.

Substances were prepared by usual solid state reaction route by calcining the samples for 40 hours (BaCuO$_2$ and CaCuO$_2$ at 900°C, Y$_2$Cu$_2$O$_5$ and YBa$_2$Cu$_3$O$_7$ at 950°C) with three intermediate grindings. Some of the samples were heated for 70-80h. In some samples oxygen reduction was achieved by dynamic vacuum ($10^{-3}$ mm Hg) by maintaining the samples at 500°C for three days. In the Y-123 compound, oxygen reduction was achieved by heating the already prepared samples at 450°C in flowing nitrogen for two days. In all cases, the oxygen reduction was estimated by the weight loss of the samples.

The samples Bi-Sr-Ca-Cu-O were prepared by solid state reaction route. In this method Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO were mixed in the stoichiometric ratio Bi : Sr : Ca : Cu : O = 2 : 2 : 0.1 : 2 : 2 : 1 : 2, 2 : 2 : 2 : 3 and grinding thoroughly. The grinding material of Bi-2201, 2212 and 2223 were heated at 850°C, 840°C and 860°C respectively for 32 hours with four intermediate grindings and then slowly cooled to room temperature in five or
six hours. The sample of Bi-2201, 2212 and 2223 were pressed into pellets. Samples were deoxygenated by suddenly dropping the substance from a temperature a little higher than its preparation temperature into a liquid nitrogen bath.

The Tl-Ba-Ca-Cu-O HTSC samples were synthesized via a two step process. In the first step, high purity powders (99.99%) of BaCO₃, CaCO₃ and CuO were mixed in the ratio 2 : 2 : 3 and thoroughly ground. The resulting powder was calcined in air at 900°C for ~ 40h with three intermediate grindings. In the second step, the precursor (Ba-Ca-Cu-O) thus prepared was mixed with Tl₂O₃ to form a mixture with nominal composition of Tl : Ba : Ca : Cu : O = 2 : 2 : 2 : 3 and ground in a closed glove box. The resulting mixtures were pressed into pellets. The pellets were wrapped in Au-foil and transferred into a silica tube fitted with oxygen flowing system. It was finally sintered in a preheated programmable furnace at ~ 890°C ± 1°C in flowing oxygen for 1 to 1.5h and allowed to cool at the rate of 2°C per minute.

The bulk samples Hg-Ba-Ca-Cu-O were prepared by solid state reaction between stoichiometric mixtures of yellow HgO and precursor powders of Ba₂Ca₂Cu₃O₇. The precursor Ba₂Ca₂Cu₃O₇ was obtained by solid state reaction of stoichiometric quantities of BaO, CaO and CuO in air at 900°C for 48h with three intermediate grinding. The black precursor powders obtained were taken immediately into a dry and decarbonated glove box, where powders of HgO and Ba₂Ca₂Cu₃O₇ were ground well and pressed into a pellet. The pellet (3x3x100 mm³) was introduced into a quartz tube which was then evacuated and sealed. The sealed quartz capsule (6mm ID x 11mm OD x 150mm length) was placed in a long horizontal steel tube which was kept inside a furnace. The sides of steel tube were packed with
sand powder to contain Hg vapors if the tube were to explode. The samples were heated slowly to 800°C in 3-4h held at 800°C for 5h and then slowly cooled to room temperature in 5-6h.

In Tl-2223 and Hg-1223, deoxygenation were carried out by sucking out air continuously by vacuum pump from an open quartz or steel tube containing the substance maintained at different temperatures.

Purity of the prepared substances verified by XRD were taken on Philips model (PW 1710) diffractometer. They tallied with the earlier reported XRD patterns of these substances. In most of the cases, XRD were taken before and after deoxygenating of the samples and no significant difference was found in the relative intensity, line profile and the width the diffraction lines in the two conditions. Only in the case of Bi-2223 (quenched from 860°C to liquid nitrogen temperature) two new, but very faint lines appeared in the quenched samples over and above the unquenched one. As will be shown later, this is the one substance which after quenching gave EPR spectrum with systematic angular variation. It is inferred that comparatively bigger crystallites of the deoxygenated material is found in this case which may explain angle dependent spectra as well as the appearance of two new faint XRD lines in the quenched samples. The two new faint lines may be due to superlattice associated with ordered distribution of isolated (CuO)₄ unit or ordered oxygen vacancies. On the basis of two new lines, it is difficult to determine parameters of superlattice or ordered oxygen vacancies in the quenched samples. The two faint lines should not be collected with any impurity. Transition temperature (Tc) of all the samples were measured by D.C. four probe technique. None of the as prepared samples gave EPR spectra suggesting their superconducting nature due to EPR silence. Only after deoxygenation, they gave EPR spectra.
Weight of the samples were measured before and after deoxygenation. In a few cases, the weight loss was found to be 2-3% and in others, no weight loss was registered. The weight loss was attributed to the loss of oxygen content. Both kinds of the deoxygenated samples, with or without weight loss, gave EPR spectra. In cases, where weight loss was registered, it was inferred that some Cu-Oxygen bonds have ruptured and oxygen ejected out of the bulk and in cases where there was no weight loss but still giving EPR spectra, it was inferred that some oxygen ions have been displaced from their equilibrium positions. It is assumed that on deoxygenation, CuO$_2$ planes of the superconductors are broken in to fragments of various sizes. Small fragments of CuO$_2$ plane which are magnetically isolated from the bulk due to Cu-O bond breaking or displacement of oxygen ions from their equilibrium positions give EPR spectra. They are situated as small islands in the bulk. This is Y, the deoxygenation does not bring about any significant change in the XRD patterns, as monitored earlier. Even in transition temperatures (Tc’s), the deoxygenation does not bring about significant change. It is thought that the super conducting current path which is broken by the Cu-O bond breaking or displacement of oxygen ions from their equilibrium sites is short-circuited by the neighbouring continuous super conducting paths. Small fragments of CuO$_2$ plane which are responsible for producing EPR spectra come from different CuO$_2$ planes and from different places in the planes of the micro crystallites of the material, which are themselves oriented at random and hence the spectra have mostly powder characteristics. In some cases, when the deoxygenated pieces are bigger in size, they have characteristics of crystal spectra.
EPR spectra were recorded on JEOL (JES-RE2X) X-Band ESR spectrometer with 100KHz field modulation. All the spectra were recorded at room temperature.

3.3 Results and Discussion:

EPR spectra were recorded for more than 100 samples, from different batches of preparation and from different portions from the same batch. The aim was to record all the variety of the spectra in these samples. Different samples of the same compounds gave different spectra, some of which were repetitive, but some spectra of the samples of different compounds were also similar. It was understandable, because every spectra came from CuO₂ plane of the super conductors which is broken in to fragments of various sizes on deoxygenation. Breaking of CuO₂ sheet by quenching is a statistical process and every time the fragments should not be same hence variation in the spectra in different cycles. In all, 20 different types of spectra could be observed and for ready reckoning. Spectra obtained in these compounds have been shown in Fig. 7.1-7.6

The spectra obtained in various cases have been analyzed in terms of Cu-octamers, Cu-tetramers, Cu-dimers and Cu-monomers. There is a signal appearing at near zero field, which could not be identified because it did not have any structures. It may be due to a fragment bigger the Cu-octamer. It is believed that when the substances are quenched, CuO₂ is broken into fragments of different sizes. The smaller fragments are octamers, tetramers, dimmers and monomers and the bigger fragments are not accessible by EPR because probably the original AFM order remains intact in them. The identified fragments also do not appear in one variety. This may be due to different type of association with surrounding oxygen ions. For example, a Cu-tetramer (CuO)₄ may be completely isolated or attached with one oxygen
Fig. 7.1: EPR spectra of Bi-2201 (a) quenched from 8400°C to LNT, 1) Cu-octamer, 2) Cu-tetramer, 3) Cu-monomer (b) air sucked out at 840°C for 12 hours. Dots indicate fine structure components of Cu-tetramer.
Fig. 7.1(c): Hyperfine structure of octamer shown in Fig. 1a. Dots represent 25 hyperfine components.
Fig. 7.2: EPR spectrum of Bi-2212 after sucking out air at 855°C for 12 hours. Dots indicate 4 fine structure components of Cu-tetramer.
Fig. 7.3: EPR spectra of Bi-2223 (a) a representative spectrum when the substance was quenched from 860°C to LNT. Dots indicate the 4 fine structure components of Cu-tetramer and M represents signal due to Cu-monomer. (b) and (c) when air was sucked out at 840°C for 12 hours. In (c) the two signals are separated but in (b) they (1&2) are coincident. The fixed signal (2) is due to Cu-monomer and the moving signal (1) may be due to Cu-tetramer.
**Fig. 7.4:** EPR spectra of Y-123 (a) after sucking out air at 300°C for 12 hours, (1) Cu-octamer (2) Cu-dimer. 4 small dots indicate 4 f.s. components of one kind of tetramer and 4 circles indicate 4 f.s. components of another kind of Cu-tetramer. (b) air sucked out at 860°C for 12 hours. Two arrows indicate two f.s components of Cu-dimer, 4 circles indicate 4 f.s. components of Cu-tetramer and M shows Cu-monomer signal (c) air sucked out at 400°C for 12 hours. Two arrows indicate two f.s. components of Cu-dimer, 4 dots indicate 4 f.s. components of Cu-tetramer and M shows Cu-monomer signal. (d) air sucked out at 860°C for 24 hours. Arrow shows unsplit Cu-dimer. 4 dots shows 4 f.s. components of Cu-tetramer and M- shows Cu-monomer signal with $g_{11}$ & $g_1$. 
Fig. 7.5: EPR spectra of Ti-2223 (a) air sucked out at 100°C for 12 hours; 4 dots show 4 f.s. components of Cu-tetramer; M represents monomer with $g_{11}$ & $g_1$. (b) air sucked out at 300°C for 12 hours; $\uparrow$ represents Cu-cluster bigger than Cu-octamer; two vertical arrows represent two f.s. components of Cu-dimer; $\leftrightarrow$ represents unsplit Cu-tetramer. M, monomer (c) air sucked out at 300°C for 24 hours. Overlapping big cluster ($\downarrow$) and Cu-octamer (1) signals. 2 represents Cu-dimer. 8 dots represent f.s. components of two sets of Cu-tetramers; difficult to isolate them. (d) air sucked out at 450°C for 12 hours. Overlapping big cluster ($\downarrow$) and Cu-octamer (1) signals. 2 represents Cu-dimer. 8 dots represent f.s. components of two sets of Cu-tetramers; difficult to isolate them. Part of the spectrum shown at higher gain. (e) air sucked out at 450°C for 24 hours. 2 dots represent f.s. components of Cu-dimers.
Fig. 7.6: EPR spectra of Hg-1223 (a) air sucked out at 350°C for 24 hours shows 13 line hyperfine structure of Cu-tetramer, (b) air sucked out at 400°C for 36 hours shows unresolved Cu-tetramer signal (c) air sucked out at 350°C for 12 hours (different batch from that in (a), 4 dots show 4 f.s. components of Cu-tetramer) (d) spectrum of the precursor of Hg-1223, i.e. Ca$_2$Sr$_2$Cu$_3$O$_8$ heated at 900°C for 5 days; shows monomer signal with $g_{\perp}$ & $g_{\parallel}$. 
ion at the top acquiring square pyramidal form or two oxygen ions giving it a distorted octahedral form. Alternatively, the electronic structure of CuO₂ might change from substance to substance due to different types of insulator plane present in the immediate vicinity of CuO₂ plane. For Cu-monomers, difference in g-values may be due to different environment of Cu²⁺ ions.

Analysis of the spectra (shown in Fig. 7.1-7.6) have not been very rigorous because angular variation of the spectra could not be plotted except in one case of Bi-2223. Octamers could be identified by hyperfine splitting into 25 components and then their often occurring g-values, tetramers by their fine structure splitting into four components with proper intensity and their g-values and occurrence of parallel and perpendicular components. Assignment of EPR spectra of particular copper-clusters has been based on the hyperfine and fine structure of specific spin state of clusters. The electronic spin of individual Cu-ion = ½ and its nuclear spin = 3/2. It is assumed that the electronic spins of all the Cu-ions in a cluster align ferromagnetically and so also the nuclear spins. For example in a Cu-tetramer [(CuO)₄] the total electronic spin S=2 and the total nuclear spin I=6 which may give 2S=4 fine structure components and 2I+1=13 hyperfine structure components. It is conjectured that compounding of electronic and nuclear spins is due to the fast motion of the electrons/holes in the skeletal framework of (CuO)₄ network. The Cu²⁺ ion in a 3d⁹ system and its behaviour can be described in terms of one hole and one electron in the fifth d-subshell of the third orbit and henceforth, the term hole will be used. Ferromagnetic coupling of spins probably ensures the lowest energy state of the system. This assumption seems to be justified as it works to explain the EPR spectra obtained here and also in earlier cases. However, a rigorous theoretical treatment is required.
In most of the cases, there is fine structure splitting but practically no angular variation in it or in the g-values of the complexes. The hyperfine structure has been observed only in Cu-octamer signal (Fig. 7.1c). The reason may be that the small pieces of deoxygenated materials are in crystalline state and they are distributed in a random fashion as already mentioned in section 2. A few cases, which show a little deviation will be specially mentioned here. In Fig. 7.1b, there is no angular variation in the g-value but a slight and erratic (not corresponding to any one of the crystal symmetries) variation in the D-value. The value of $g=2+\xi \Delta$, where $\xi =$ spin orbit coupling constant and $\Delta$ involves matrix elements connecting the ground and excited states via the orbital angular momentum operator. $D=D_{so} + D_{ss}$, where $D_{so}$ is the contribution of the spin-spin interaction. $D_{so} = \xi^2 \Delta$, but $\Delta$ used here may differ from the one used in the definition of $g$. In $g$, $\Delta$ connects states of the same multiplicity but in $D_{so}$, it may connect states of different multiplicities also. Usually, both come out to be equal in magnitude. It may be argued that both in $g$ and $D$, the spin-orbit coupling part is averaged out to a small constant value and the small variation seen in $D$ is due to spin-spin interaction. Due to some order left in the distribution of the crystallites, spin-spin interaction causes slight but erratic angular dependence. In Bi-2223, quenched by dropping the substance from 860C into liquid nitrogen bath, angular variation of the fine structure components could be plotted (Fig 7.3a and 7.7) and spin Hamiltonion parameters could be determined. In the case of Bi-2223, deoxygenated by air sucking at 840c for 12h, there is a large variation in the g-value but no fine structure splitting (Fig 7.3b, c and 7.8). It seems that in these two cases larger crystallites of deoxygenated materials capable of showing regular angular variation were formed. In liquid nitrogen
Fig. 7.7: Angular variation of the spectrum of Bi-2223, a representative spectrum of which was shown in Fig. 7.3a.
quenched Bi-2223, small crystallites showing angular dependence could be selected out. But they were so small that they could not be handled easily in the experiment and hence one crystallite was embedded in wax which was cut into a rectangular block of convenient size and its angular variation could be studied. This was repeated for many crystallites. The angular variation of the spectrum in zy plane has been plotted in Fig. 7.7. In the case of Bi-2223, deoxygenated by sucking out air, no such crystallite could be picked out. There was variation in the g-value but the absence of the fine structure splitting may be attributed to one of the following reasons i.e. dipolar interaction, fast motion or cubic symmetry around the series giving the EPR signal.

It seems that on quenching by liquid nitrogen there is chance of getting small crystallites but with very low probability. Sucking out air from the substance maintained even at low temperatures of 100-400°C is quite efficient method of deoxygenation. The air quenching seems to be quite inefficient.

As shown in Fig. 7.9(a), an isolated Cu-tetramers is formed by breaking of eight Cu-oxygen bonds in its immediate neighbourhood. It has been generally accepted that there is some degree of covalency in the Cu-O bond. If it is supposed that there is 12.5% of covalency in the Cu-O bond, the breaking of eight bonds is equivalent to the loss of an electron or the advent of a hole in the isolated (CuO)₄ network. With these assumptions, two obvious questions arise: (1) what is the ground state of individual Cu²⁺ ions in the tetramer and (2) how is the ferromagnetic coupling realized in the system? In the isolated Cu-tetramer, the Cu²⁺ ions with 3d⁹ configuration probably remains in the usual ground state ⁵D₅/₂. This can explain the observed total electronic spin S=2 and total nuclear spin I=6. If the hole would have occupied one of the Cu²⁺ sites, it would have converted to 3d⁸
Fig. 7.9: (a) CuO$_2$ sheet of a superconductor. The dotted enclosure shows an isolated Cu-tetramer in which eight Cu-oxygen bonds in the immediate neighborhood have been broken. A and B in this figure represent Cu-tetramers in each of which one hole has entered and C where there is no hole. (b) the spin alignments in A, C and B in (a) above.
configuration and its ground state would have been $^3F_4$. In that case, it would not be possible to obtain the total electronic spin=2 i.e. from a combination of $s_1=1$, $s_2=1/2$, $s_3=1/2$ and $s_4=1/2$ representing the spins of the four Cu$^{2+}$ ions in the tetramer. The hole probably resides on the oxygen sites only. The state of affairs is better represented by Fig. 7.10.

The hole introduced as a result of isolation of the Cu-tetramer from the bulk hops among the positions 1', 2', 3', 4'. Hopping is possible because all the oxygen sites are equivalent. The hole probably takes short sojourns in $P_x$ orbitals of sites 2' and 4' and $P_y$ orbitals of sites 1' and 3' due to proximity. As the hole jumps from site 1' to 2' it forces the hole of the Cu$^{2+}$ (3$d^9$ system) at the position 2 to rush towards the Cu$^{2+}$ at the position 3. Again when the hole jumps from site 2' to 3', it along with hole displaced from the copper position 2 forces the hole on the copper position 3 to rush towards the position 4 and so the process goes on. As a result the four holes associated with the four Cu$^{2+}$ ions start circulating along the outer Cu-O-Cu-O-Cu- circuit, thus compounding the electronic spins ($S=2$) and the nuclear spins ($I=6$). The time taken to complete one round of the circuit should be much smaller than the precessional time of the holes. In this process, the hole negotiating the oxygen circuit (1', 2', 3', 4') does not combine with the holes in the outer Cu-O-Cu-O-Cu circuit. The ferromagnetic coupling of the electronic spins of the four holes among themselves and also of the nuclear spins of the four Cu-ions, probably ensures minimum energy state.

The EPR lines observed here are broad and unsymmetrical. Two reasons may be adduced to it:

1. The cross relaxation between the four FM coupled holes of the four Cu-ions (see Fig. 7.10) and the single hole hopping through the oxygen sites. For EPR transitions, the relaxation time of the four coupled holes may be
Fig. 7.10: Location and motion of a hole introduced as a result of isolation of the Cu-tetramer from the bulk. 1, 2, 3, 4, are the Cu-positions and 1', 2', 3', 4' are the oxygen sites. The $p_x$ and $p_y$ orbital of each oxygen is also shown.
much smaller than those of the single hole. The relaxation processes in the
ingle hole may be so fast as to widen its signal beyond detection, but it may
in turn, broaden the signal due to the four coupled holes of the four Cu-ions.

2. The material of each sample investigated here are of two types: (a) The
islands of isolated Cu-clusters giving EPR spectra and (b) the bulk material
having unbroken CuO2 sheets which is EPR silent. The bulk material is
metallic at the temperature of investigation (300K) as seen by the
temperature vs. resistance measurement and the metallicity or conduction
electrons/holes of the major fraction of the material part (b) may widen and
distort the signal due to the minor fraction (a), which is the sole signal giving
species.

Examining the g-value of the spectra, it will be very glaring that they deviate
considerably from the usual g≈2 range. Experimental values of g obtained
by the relation \( h\nu = g_{\text{experimental}} \beta H_{\text{observed}} \). But the true g-values may be quite
different from the \( g_{\text{experimental}} \). As there is ferromagnetic coupling of the spins
in the Cu-clusters, or say, spin-clusters, the effective field (\( H_{\text{eff}} \)) may be quite
different from the applied field (\( H_a \)) due to demagnetization effects. The
demagnetization field strength depends upon the shape and size of the
sample. In such cases the resonance absorption condition is written as \( h\nu = g\beta \)
(\( HB \))\(^{1/2} \) where B= magnetic induction or for cylindrical shape of the samples,
\( h\nu = g\beta (H+2M) \) where M = intensity of magnetization. As M is positive, for
the ferromagnetic sample it may happen that the effective field is of such a
value that will keep the g-values in the proximity of 2 as required by the
small zero field splitting occasionally identified for some of the samples in
this work.
The species of Cu-clusters that occur in our spectra are octamers, tetramers, dimers and monomers but never the species like trimers, pentamers, hexamers etc, probably, the later ones are not structurally and energetically favoured. The most frequently occurring species is the tetramer and appears at the lowest quenching temperature. It is understandable because $(\text{CuO})_4$ acts as the unit cell of the two-dimensional $\text{CuO}_2$ plane and on violent treatments done for deoxygenation, the breaking of $\text{CuO}_2$ plane into units seems to be quite natural.

The isolated Cu-tetramers seen in this study and the earlier seem to be of great significance. As mentioned earlier that the breaking of eight Cu-O bonds in the immediate vicinity of $(\text{CuO})_4$ is equivalent to the introduction of a hole in it, the following equality should hold good:

\[
\text{Isolated (CuO)}_4 = (\text{CuO})_4 \text{ of the actual superconductor + a hole inside it.}
\]

Further as the conductivity in the superconductors is through holes, the study of the behaviour of isolated Cu-tetramers may throw light on the properties of the bulk superconductors and may provide clue to the mechanism of high temperature superconductivity.

As had been noted in our earlier studies, Cu-tetramers are obtained in non-superconductors also like $\text{CaCuO}_2$, $\text{BaCuO}_2$ etc, but the Cu-tetramers obtained in the superconductors are different from those obtained in non-superconductors. A four one-half spin system is essentially 16 fold degenerate and by Heisenberg isotropic exchange splits into six components: one pentet, three triplets and two singlets. In superconductors, the pentet has been found to be ground state but in non-superconductors, singlet is the ground state.
Fig. 7.11: (A) Coupling Between The Two (CuO)$_4$ Units With Holes Via Spin Fluctuations In The Intervening Unit Having No Hole.
(B) Symmetry of The Condensate May Be $d_x^2 - y^2$. 
A mechanism of superconductivity may be visualized on the basis of $(\text{CuO})_4$ units. At least the symmetry of the pair condensate and the coherence length can be well understood as explained in the Figure 7.11.

In the Fig. 7.11(A), the holes contained in the boxes (Cu-tetramers) 1 and 2 may couple via the spin fluctuations in the box 3 having no hole inside it. Under the influence of 1 and 2 whose spins are in opposite directions, the spins in the box 3 may continuously change direction, thus working as a contact person. The space between 1 and 3 or 3 and 2 is the length of a box which in most superconductors is of the order of $3.8\text{A}^0$, therefore the coherence length for coupling between 1 and 2 may be of the order of $15-16\text{A}^0$ as is the value for in-plane coherence length. In Fig. 7.11 (B), 1 and 3 and 4 and 5 again may couple giving a semblance of d wave pairing. In Fig. 7.11(A), the spin directions of the FM coupled Cu ions in the boxes 1 and 2 are opposite to each other and hence spins of the holes trapped in these boxes will also be opposite to each other and hence the pairing will give a singlet state as expected.

At least, in all the magnetic theories of superconductivity, involving magnons, magnetic polarons, spin bag, spin fluctuations, the $S=2$ systems represented by cu-tetramers is a potential candidate for consideration.

It seems that in the consideration of mechanism of high temperature superconductivity, especially in the magnetic mechanisms, the $(\text{CuO})_4$ can play an important role. For example in the spin-bag theory, spin fluctuation theory, magnetic bipolaron, magnon theories physical quasiparticles can be taken as Cu-tetramers with spin = 2 instead of spin = $1/2$ fermions. The magnetic coupling will be stronger for the tetramers with total electronic spin ($S=2$) than for the spin =1/2 particle and may explain the higher transition temperatures.
REFERENCES