CHAPTER - I

SUPERCONDUCTIVITY : VIEWS FROM DIFFERENT ANGLES

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1.1 INTRODUCTION

The end of the 19th century witnessed three great discoveries. Rontgen discovered X-rays, Bequerel discovered radioactivity and Thompson discovered the electron within the period 1895 to 1898. These enabled the physicists and the chemists to know precisely the structure of building block of matter and the chemists to precisely analyse the nature of the chemical bond and the nature of chemical reactions. This was a formidable and challenging task that opened the 20th century. When we have reached almost to the end of the 20th century a very surprising and pleasing repeatation appears to be occurring by way of again three new epoch making discoveries with which we will probably enter the 21st century. These are high temperature superconductivity, hydrogen generation technique by using catalytic decomposition of water and coordination chemistry of synthetic oxygen carriers. The human life and welfare of the future human generations and the assurance and retention of the livability of earth are intimately associated with these discoveries. With high temperature superconductivity, the problems of power and energy may be dramatically solved. An abundant, unending supply of clean fuel will be available with hydrogen generation technology. The source, that is, water, is abundantly available, the catalyst is not consumed in this reaction, and the energy liberating oxidation of hydrogen will regenerate water. Even with combustion reaction there is no generation of any pollutant and by product of catalytic decomposition is oxygen. The whole process is so clean that the threat of pollution associated with all known convensional energy processes will be permanently dispensed with. The synthetic oxygen carriers may function as human blood which is so vital for sustaining the life. It is a surprising coincidence that the element oxygen has a fundamental, important role in all the above three gifts to humanity. In the first and the last, it is concerned with the triplet oxygen and in the second with oxygen atom converted to oxide ion. Probably the dawn of the 21st century will bring a very happy hope of well-being, happiness and prosparity to the human race and an assurance of perpetuation of the human race through the centuries to come.

The opening of the year 1990 which heralded the last decade of the 20th century has been assigned a very hectic scientific programme by the destiny. The fore-runner of this activity was the publication of Bednorz and Muller's[1] paper announcing the discovery of lanthanum cuprate and the leap of Tc by a very small increase of 7^{o} (i.e.30 K) and an immediate rise of Tc in 1,2,3 bulk ceramic oxides from liquid helium through liquid neon to liquid nitrogen 80 K[2]. New materials based on thallium and bismuth have further shifted Tc 120 K within a span of less than two years. The synthetic and analytical efforts culminated into huge amount of work covering preparatory methods, new compositions, and study of physical properties of the materials. The chemists and physicists have given this new material to the engineers and technologists to develop new technology based on HTSC. Ceramic superconductors with Tc ∿90 K using abundantly available liquid nitrogen* as a cryocooler has been identified as a landmark in the progress of science and technology for the 21st century.

The high hopes and a very quick rise in Tc in 1988 created a hope that if progress takes place at the same pace and rapidity, liquid water superconductors are lingering at our door and it is anybody's game just to catch them. Necessarily it may be a ceramic oxidic composition. The dawn of the last decade of the 29th century has cautioned us that it may not be as easy as man thought it to be in the beginning. This is not a discouraging note. The only indication is that we must prepare a very large number of compositions and use novel methods to examine them. This brings together the chemists first to initiate the process and to hand over the materials to the physicists to study them. The chemists must prepare innumerable compositions

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* Liquid helium is scarce and almost 50 times costly compared with liquid nitrogen.

and after screening the aspects of structure and bonding transfer the selected candidate materials to the physicist to have thorough investigation, choose a few bests from the lot and finally to handover to the engineers and technocrats to choose the one that they would find suitable for end uses. In the Acharya P.C. Memorial lecture delivered by Prof. C.N.R.Rao[3] in the 24th Convension of Chemists at Kolhapur on 23rd November 1987, said "It is noteworthy that superconductivity has really moved into the domain of chemistry, since the chemistry of these oxides has much to do with their superconducting property."

Although the physicists have immediately pushed them into this challenging area, unfortunately, even at the world level, there is very little involvement of chemists in HTSC. It is necessary that more chemists join this field to bring the success in vision. Indian scene as far as involvement of chemists is concerned, is quite discouraging. It is necessary to attract more chemists and involve them in a well-organized national programme. Much of the work in India is merely confined to a few advanced national institutes and a very little at the level of universities. Abundant creative young talent is fortunately available but unfortunately no infra structure is available in universities. The nature of work at many places is borrowing a pellet of ceramic superconducting material and studying some property. This hardly can lead to any progress. Many may not like this statement but truth need not be very palatable.

There are many haunting areas and issues with HTSC which a chemist would like to study. These are stated as follows :

(1) The preparatory technique for getting still higher Tc material.

(2) The molecular structure of ceramics.

(3) The nature of chemical bond.

(4) The chemical composition and stereochemistry of desired and undesirable phases.

(5) Critical and crucial procedural details of enriching the desired orthorhombic phase.

(6) The role of triplet oxygen.

(7) Stereochemistry of copper with cooordination number 4 and 5.

(8) Valence fluctuation of Cu^{I}, Cu^{II}, Cu^{III} and fractional valencies.

(9) To develop new chemical techniques in which a purer precursor will be obtained which will improve I_c although T_c may only marginally change. This needs uniformity of the composition. Since fusion method is not applicable only method left for this may involve uniformity at molecular level at precursor stage in chemical method.

(10) Orthorhombic-tetragonal interconversion.

(11) Reactivity of HTSC material with other chemical species and environmental factors.

(12) Shifting of the domain of activities in appropriate direction on the basis of feedback from the physicists and engineers.

(13) Trying new compositions and new materials.

(14) Results of the study of relation between Fe/O or Cu/O in oxygen carrier biological function to be used as a guide for study of Cu/O relation in HTSC.

The present project aims at application of precipitation from homogeneous solution (PFHS) in preparation of 1,2,3 and related cuprate materials, and also to use metal acetylacetonates as the precursors. There is abundant scope for application of new synthetic routes in this field.

1.2 PAST AND PRESENT OF SUPERCONDUCTIVITY

Onnes observed in 1911 that at 4 K the electrical resistance of mercury completely vanished.[4] He called this property as superconductivity possessed by matter in the new state. In 1920's and 1930's higher transition temperatures were observed with intermetallic compounds and alloys. In 1941 Ascherman <u>et al</u> observed Tc near 18 K in NbN[5]. Organic and nonmetal superconductors were speculated in 1937 by London.[6] A very high rise in Tc (185 K) was claimed by Ogg[7] in 1946 in very cold alkali metal-ammonia solutions which claim could not stand. Further during 1950's empirical theoretical foundations were laid down. The study of energy gap in electronic spectrum laid to the <u>B</u>ardeen, <u>C</u>ooper, <u>S</u>chrieffer (BCS) theory[8]. During 1960's applied superconductivity was born with the discovery of Josephson effect[9] and gave directions to an "off the beaten path" theory and experiment which laid to true HTSC in 1986. In 1972 superconductivity was discovered in $PbMo_6S_8$ and it opened a new field of ternary superconductors.[10] The empirical rules for binary material became invalid and synthesis part of superconductors grew more complicated and sophisticated. This obviously involved more chemists and material scientists in the search of new materials.

1.3 SOME NOVEL ASPECTS OF SUPERCONDUCTIVITY

1.3.1 Organic Superconductors

Search for superconductors in organic materials was a new field which was opened in 1964, when Little generated interest in organic and one dimensional superconductivity and predicted that specific molecular arrangements would push Tc to room temperature.[11,12] Much work was done in synthesis of tailored molecules and biological molecules but all early reports proved to be false. In 1969 Ladik predicted room temperature superconductivity in DNA molecule.[13] Wolf in 1972 reported Tc near 140 K in bile cholates.[14] Heeger[15] in 1973 reported Tc of 77 K in (TTE-TCNQ) molecules. In 1971 Cope attributed the exponential nature of the nurve muscle response as well as the exponential growth statistics of E. coli as an indication of Tc as high as 300 K[16]. In all the above cases the high speculations turned out to be miserable at laboratory level and the organic superconductivity started fading out. When this was happening, the work by Jerome on (TMTSF-PF_6) came in 1980.[17] A host of such compounds have been studied taking Tc under pressure to not more than 8 K in ß-$(BEDT\text{-}TTF)_2I_3$.[18] It is believed that in these materials 'p' wave pairing interactions are present and their superconductivity is not due to electron-phonon interaction.

1.3.2 Layered Superconductors

In 1964 Ginzburg proposed layer structures as new HTSC materials[19] and the exitonic mechanisms in layered or two dimensional materials. The work during the next nine years gave theory of exitonic superconductivity in 1972. The 1980 report of Tc at 3 K in eutectic Ir-Y[20] arroused interest in multilayered metallic systems with no further success. In 1983 Oguschi et al reported Tc as high as 200 K in Nb layer growth on Si.[21] However, it did not gain acceptance.

1.3.3 Oxides and Hole Carrier Superconductors

The fore-runner of the work in oxide superconductors was the 1964 prediction by Cohen of semiconducting type materials exhibiting superconductivity.[22] In 1964 Hein reported superconductive 'p' type GeTe.[23] Schooley et al were the first group to report ceramic superconductors -

$SrTiO_3$ in 1965.[24] It must be noted that although Tc was below 1 K, it was the first peroveskite material which gave proper direction to the research in HTSC. Johnston's discovery of superconductivity in $LiTiO_3$ at Tc of 13 K[25] was a great feet of achievement since the earlier belief that Tc for oxidic materials was very low was removed. Sleight and coworkers discovered $PbBiBaO_3$ with Tc 14 K.[26] This material had an interesting property which made is useful as sensors of electromangetic radiation. Next eleven years this ternary oxide was studied in great details and although no elevation of Tc was observed, it became apparent that the time was pregnant with new materials waiting to see the light of the world. In 1978 superconductivity for the first time became a headline in the news with the Russian report[27] of Tc of 140 K in cuprous chloride. This report was condemned as completely false containing cooked results as Mathias[28] thought, however, Chu[29] was of the opinion that there may be some truth in these reports. It is quite surprising that eight years prior to real discovery of HTSC, a storm in the news-world has once taken place and calmed down. In 1980, reports on CdS[30] and TiBe[31] with Tc at 150 K and 295 K appeared but these were highly nonreproducible and were rejected. The real breakthrough came from Bednorz and Muller[1] in 1986 with lanthanum cuprate with Tc at 30 K and Wu's yttrium cuprate[2] with Tc at 94 K in 1987. The fate of earlier claims of high Tc was so bad that Bednorz and Muller were hesitating for several months to publish their work. The new results were reproducible and within a short time innumerable new materials in the range of Tc upto 90 K were synthesized and studied. As is very often seen, along with the believable reproducible claims, came a few high sounding non-reproducible reports.[32] In the world of science it may be tempting to put the claim. Although it is a bad practice to do so, one can correct oneself by withdrawing the claim explaining the cause of getting spurious results. However, the spirit of putting a false claim and then not withdrawing it must be condemned since it misguides the host of researchers and pollutes the literature. In the history of chemistry and physics a few such shameful incidences have occured but these must be taken as the moral degradations of a few individuals. During the last four years the excitement in HTSC appears to be slightly passified. In fact the high rise of Tc from 23 K to 30 K to 90 K was a quick scientific achievement but the expectation of maintaining the same rate of rise was hardly in keeping with scientific temper. Over the last four years new materials containing Pb and Bi and Tl have been prepared with rise of Tc to 140 K. When we look at these aspects of HTSC results, we are compelled to ask ourselves a few questions :

(1) What shall be the next mark of progress ?

(2) Will it be a search for new materials with higher and higher Tc ?

The answer to second question may be that it will be absolutely necessary to carry out a search for new materials, new properties, new methods of getting materials and a careful monitoring of certain new parameters. It may be that in this search we will get better materials with almost the same Tc. Answer to the first question is that it may be anybody's game. An accidental blind-shooting may give new material with the next target Tc, the water superconductor with Tc 373 K.

It may also be a feature of applying the hitherto discovered new materials to new technologies. When we know that liquid helium superconductors were a workable technology in the production of superconducting magnets, for advanced instrumentation with so scarce coolant liquid helium, the abundantly available liquid nitrogen as a coolant may be very easy for commercial exploitation. It is no wonder that for levitation train we need not wait for high Tc but should try to put the known material to use.

Much more important than the above two aspects is that the last four years have given us a new scientific insight. With more work, we have become friendly with new materials which have revealed as many secrets of their structure and behaviour as has shown by the history of super conductivity. Scientific world must renew its commitment and recognise the importance of those individuals who are ready to leave the trodden path and delve into the fearful and apparently nonrevealing forest. It is necessary to note that the woods are full of delicious fruit!

1.3.4 Rôle of δ Oxygen

The accidental association of oxygen with the three great discoveries for 21st century may not be ignored as not significant. There is something more in it. The haemoglobin (blood) oxygen and ceramic superconductor δ oxygen have striking behavioural similarity.

The formation of oxide ion O^{2-} from O_2 molecule involves absorption of large amount of energy.

$$\frac{1}{2} O_{2(g)} \rightarrow O_{(g)} \qquad E = 248 \text{ k J mol}^{-1}$$

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad E' = 752 \text{ k J mol}^{-1}$$

$$(E+E') = 1000 \text{ k J mol}^{-1}$$

If oxygen from air has to react with Fe^{2+} in haeme frame and get converted to O^{2-} giving Fe^{3+} initially will have to spend energy to bind the oxygen in the blood purification in lungs. Further this will not be easily available for glucose oxidation in organs unless some process is found out to convert O^{2-} to O_2. This is avoided by avoiding $Fe^{2+} \rightarrow Fe^{3+}$ reaction and oxygen merely dissolved in blood is transported as triplet oxygen. A man has 5 L blood and solubility of oxygen in blood is 200 ml L^{-1}. This solubility is not a small value. The solubility of oxygen in water is

3 ml L^{-1}. This way if water is the solvent for oxygen in mans body at least 300 L water must be circulating through veins. The use of complex containing 2.5 g Fe^{II} does wonders in our body and oxygen merely by physical process goes to organs and oxygen is not acting chemically. Similar role can be given to Cu ion also. The blood of snail is copper based blood. The oxygen carrier role can be played by both copper and iron.

In superconducting ceramic cuprates all the critical difference comes from orthorhombic-tetragonal interconversion as a function of oxygen containt of cuprates. The δ -oxygen decides the preference. Hence superconductivity must be an attribute of free, triplet δ -oxygen in the cuprate.

When coming to HTSC cuprates are preferred over ferrates as δ -oxygen carriers because of magnetic consideration. Something diamagnetic is preferred. Here again -oxygen is triplet oxygen.

Does it merely represent a coincidence? No it may not! Probably attempts to understand both the phenomenon and the behavioural similarity are needed!!

1.4 FUTURE OF SUPERCONDUCTIVITY

Extensive preparatory and characterization work has been reported during the last four years and it is known that basic need for superconductivity is existence of defect layered perovskite cuprate compound with orthorhombic structure. It has been realised that even the minute changes of composition and ordering of oxygen vacancies cause considerable effect. The whole lot of experimentation has indicated that the key to resolving problems related to superconductivity lies in being able to prepare tailormade compositions. The dependance of existance of superconductivity in 1,2,3 compounds with 6.5 oxygens assuming all coppers a Cu^{2+} with more or less oxygen in the range O_6 to O_7 explains beyond doubt that it is a decisive issue. It has been observed that going from O_7 to $O_{6.6}$. There is a drop of 50 K in Tc and when oxygen is still reduced, the orthorhombic-tetragonal transition takes place and the property disappeares. This needs more studies. All are agreeing on one issue that in case of $Y\ Ba_2Cu_3O_{7-x}$ repeated sintering at 850°- to 950°C, grindings followed by oxygen annealings below the tetragonal to orthorhombic transition temperature i.e. 700°C is an essential part of the preparatory technique Heating below 1000°C brings about the reaction and grinding breaks up the grain boundries and introduces oxygen. Defects in between grains as well as intragranular ones which produce weak links result in lowering of critical current. Other defects are effective pinning centres and can increase the critical current. The work on single crystals and thin films is not discussed here. The 90 K superconductivity in 1,2,3 compounds is attributed by several groups to the existence of one dimensional chains of CuO which are sand-

-witched between the two dimensional CuO_2 planes. When the samples are quenched from 900°C the crystals are tetragonal and the oxygen vacancies are disordered. One dimensional chains are not formed and the superconductivity disappears. The recent report[33] on La-Ba-Cu-O material with tetragonal structure has no one dimensional feature and no oxygen vacancies in copper containing planes and still Tc is 90 K. This must be studied in more details.

There are a few reports of Tc > 100 K. Some of these reports indicate that superconductivity could exist under some highly metastable conditions at temperatures approaching room temperature. Since these reports are in connection with multiphase systems, the concentration gradients, strain and other non-equilibria which can be trapped between different coexisting phases may be important with respect to techniques of growing multilayered systems and must be investigated thoroughly.

Reports so far indicate the data regarding heat capacity, tunneling and far-infrared spectroscopy is conflicting. The anomaly regarding heat capacity was explained on the basis of presence of some non-superconducting metal present in the sample. But this raises an another issue that diffraction patterns, sharp transitions, large shielding and Meissner signal are inadequate to define a good sample. The results of optical studies on far-infrared absorption are ambiguous and reflectance data finds only limited analytical value.

Further studies on single crystal systems will be needed. It seems that 90 K superconductor has come to stay and prediction of very high Tc somehow appears unsound. The structural features associated with 1,2,3 superconductors which are unique must be proved non essential with further preparatory work and structural investigations. The spirit of science does not permit anybody to say positively that certain thing will not happen. We will have to wait till an altogether new kind of material exhibits sufficiently high Tc as a surprise coming from some chemists work-bench. The whole exercise of mending or repreparing new theories will have to be started because what is important is the material Theories exist only to explain its behaviour. It is surprising paradox that theoreticians who are reluctant to accept new facts lead the way to new materials which successively contradicts their own assumptions and findings!

1.5 CONCLUDING REMARKS

It can be said that Tc $\sim$ 90 K is a platue on the Tc profile and we must be prepared to exploit hitherto made progress to develop the technology for today. If we get the next higher platue soon it will be well and good!! However even if higher Tc appears a distant light today any efforts done in that direction enrich us with more precise knowledge!!!

This real dividend is more valuable than the last step of achievement in the quest of HTSC.

New preparatory techniques to improve Ic must be developed. It should not be ignored that Tc aims at getting high T_C value where ohmic resistance almost vanishes Ic maximises current carrying capacity for which only all the efforts are done!

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