PROGRESS IN SUPERCONDUCTIVITY: *THE INDIAN SCENARIO*

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India has made rapid progress in the field of high temperature superconductivity, beginning at the time of publication of the *Zeitschrift für Physik* paper by Bednorz and Müller. Phase I of the program was conceived by the Department of Science & Technology of the Government of India. It consisted of 42 projects in the area of basic research, 23 projects in applications and 4 short-term demonstration studies. The second phase started in October 1991 and will run through March 1995. It consists of 50 basic research programs and 24 application programs. The total investment, mainly consisting of infrastructural development to supplement existing facilities and hiring younger people, has amounted to about Indian Rupees 40 crores, equivalent to about US$ 13 million. The expenditure for the period 1992-1997 shall be upto about Rs. 27 crores, equivalent to about US$ 9 million. The basic idea is to keep pace with developments around the world.

It is noteworthy to remark that during the above-mentioned period several books have been published. Some of the titles are: ***Chemical Aspects of High Temperature Superconductivity,*** edited by C.N.R. Rao (World Scientific Publishing Company, Singapore, 1991), ***Superconductivity Today,*** C.N.R. Rao and T.V. Ramakrishnan (Wiley Eastern, 1992), ***Proc. of the International Conference on Superconductivity,*** edited by S.K. Joshi, C.N.R. Rao and S.V. Subramanyam, a Series (now in its 13th. volume) entitled ***Studies in High Temperature Superconductors,*** edited by A.V. Narlikar, ***Thallium-Based High Temperature Superconductors,*** edited by J.V. Yakhmi and A.M. Hermann (Marcel-Dekker, New York, 1994), ***Selected Topics in Superconductivity - A Flavor of Current Trends,*** edited by L.C. Gupta and M.S. Multani (as part of a nine-volume series on **Frontiers in Solid State Sciences,** World Scientific Publishing Company, 1993-1995), ***Physical and Material Properties of High Temperature Superconductors,*** edited by S.K. Malik and S.S. Shah (Nova Science Publishers, Inc., New York, 1992), ***Theoretical and Experimental Approaches to High Temperature and Conventional Superconductors,*** edited by L.C. Gupta (Nova Science Publishers, New York, 1991)

One of the highlights of our achievements is the discovery of borocarbides as superconductors. Prof. R. Nagarajan, the main discoverer of this new family, is giving a separate talk on this. So I shall not dwell on it. We shall outline below the main achievements of the past two to three years.

SYNTHESIS AND CHARACTERIZATION

Thin Films

The growth of high quality high-T_c superconductor films on semiconductor substrates is an important step towards the possible marriage of two technologies. A recent study by the Poona University group was the realization of Y-123/YSZ epitaxial configuration on Si (100) by pulsed laser ablation without the chemical removal of the native surface oxide. The crystalline characteristics of the deposited films have been studied by x-ray diffraction (XRD), high resolution transmission electron microscopy (HREM) and Rutherford backscattering (RBS) techniques. Typically, the superconducting films of thickness 500 nm deposited on silicon with 150 nm epitaxial Y-ZrO_2 buffer layer have T_c as high as 88 K and J_c of $2x10^5$ A/cm^2 at 77 K for a 5 μm bridge pattern (using the same KrF excimer laser as for pulsed laser deposition).[1]

The group has deposited superconducting thin films as well as buffer layers using the KrF excimer laser (λ = 248 nm). The substrates include Y-ZrO_2 , $LaAlO_3$, $LiNbO_3$, $Gd_3Ga_5O_{12}$ and Si (100). Detailed studies addressing such issues as epitaxy, interface reactions, grain structure and coupling have been carried out. Effects such as those of dopants, devices and other physical properties will be described later in this talk in the relevant sections. The characterization was done at the laboratory of one of the authors (MM).[2] A group at the Bhabha Atomic Research Center (BARC, Bombay) has been growing single crystal substrates.

Granularity of HTSC (bulk as well as thin) materials is a characteristic disadvantage of the layered superconductors. While one single crystal grain of an HTSC film can support a J_c $\geq 10^7$ A/cm^2 at 77 K, most bulk materials measurements show 3 to 4 orders of lower critical current density. Thin epitaxial films have improved these values considerably - but not quite close to the intrinsic value of a single crystal. A group at the Tata Institute of Fundamental Research has prepared Ag-doped (5 wt.%) and undoped Y-123 films by PLD.[3] The excimer laser fluence was 3 J/cm^2 The growth of the film was carried out at 200 mTorr oxygen, a target-substrate distance of 5 cm and a laser repetition rate of 10 Hz. A normal oxygen cool in 500 Torr oxygen was provided as post deposition oxygenation. The group found that Ag-doping considerably improves the microstructure, leading to larger and well-aligned grains with narrower grain boundaries. A 10 μm wide microbridge led to a J_c = $1.4x10^7$ A/cm^2 at 77 K on (100) $SrTiO_3$. Implications of this for devices is discussed in the appropriate section.

Innovative design and development for producing *in situ* superconducting thin films and make property-structure-deposition parameter correlations have been made by a group at the Indian Institute of Science (I.I.Sc., Bangalore). A technique with the acronym HOST (High pressure oxygen sputtering technique) was developed and *in situ* superconducting Y-123 films have been successfully prepared. To prove the superiority of HOST over the conventional sputtering techniques, detailed investigations have been carried out on HOST plasma by studying the *I-V* characteristics and by carrying out Langmuir probe studies and optical emission spectrometry (OES). These studies have revealed that in high pressure oxygen plasma at elevated substrate temperatures, negative oxygen ion energy was extremely small and the number of ions near the substrate were also small. This clearly explains why the negative oxygen ions cannot disturb the composition of the films in HOST. It was also observed that the positive ion population was more in this technique and, hence, deposition rates were high.

Y-123 films have been deposited on MgO, $SrTiO_3$, and $LaAlO_3$ by HOST. Auger and RBS channeling studies have indicated that the films are stoichiometric and perfectly oriented. The films were uniform (better than 1 percent) over an area of I $cm.^2$. The challenging task of depositing large-area (60 mm or more) films has begun with the design of Facing Target Sputtering (FTS). Investigations have been carried out to study the effect of target diameter, target-substrate distance, operating pressure, inter target distance, *I-V* characteristics, Langmuir probe studies, negative bias voltage on the substrate, and a variety of other parameters are being studied for optimal deposition rate and quality.

A significant aspect of the research by another group at the I.I.Sc. has been the synthesis, purification and characterization of all the organometallic precursors needed for the CVD process. Initially, dipiraoxylmethanates (DPM) of Y, Ba and Cu were synthesized. These have been used by other investigators as well. More recently, a new β-diketonate precursor has been synthesized for each metals. These precursors, the keto-carboxylates, have been found to be very useful and, perhaps, better than the DPM precursors. The processes for the synthesis and purification of the various precursors have been scaled up to yield usefully large (10 grams) quantities. Due to polymerization-related problems with Ba precursors, only poor quality high-T_c have been obtained so far by MOCVD.

A group at the National Physical Laboratory (NPL, New Delhi) has achieved very good epitaxial films of the Y-123 system by the technique of dc magnetron sputtering. These films have been grown *in situ* on the following substrates: $SrTiO_3$ (100), $LaAlO_3$ (100), MgO (100), YSZ (100) and the *r*-plane of sapphire.[4] The sputtering gas consisted of a flowing mixture of argon and oxygen (in the ratio 2:1) at pressures varying between 200 to 1600 mTorr. The effects of sputtering gas pressure and the substrate temperature in the on-axis geometry (30 mm distance) were characterized by XRD, SEM, RBS, VSM, *R-T* and χ_{ac} -*T*.

The value of the critical current has been estimated as a function of the magnetic field using Bean's modified critical state model. The typical values of J_c at zero field and 12 kOe are $2.2x10^7$ and $1.6x10^6$ A/cm^2 at 77 K

Fullerenes and Related Systems

The Indira Gandhi Center for Atomic Research (IGCAR, Kalpakkam) group has synthesized C_{60} and C_{70} along with the alkali dopants, K and Rb. Some preliminary studies have also been made on co-doping K with Pb or Bi. The nominal compositions were PbK_2C_{60} and BiK_2C_{60} were prepared in the vapor phase reaction, starting with the stoichiometric constituents. XRD and χ_{ac}-*T* measurements indicate that while Pb and Bi are incorporated in the *fcc* lattice, there is no appreciable change in T_c unlike in the case of Tl-doped samples. On doping C_{60} samples with Yb it is seen that Yb_2C, Yb_3C_{60} and Yb_6C_{60} are formed. The observed superconductivity below 5.4 K is due to the *fcc* compound with the least Yb.(See ref.5 and citations therein)

The group of one of the authors (MM) in collaboration with the Poona University group has also been looking a Raman scattering from thin films of carbon-60 clusters with admixtures of the carbon-70. The 488 nm Ar^+ radiation in the backscattered geometry has been used to characterize the different bonding types. Diamond films have been the focus of study by the two groups with respect to novel synthesis techniques. We have achieved formation of diamond films by laser-induced reactive quenching at the liquid-solid interface between a suitability organic liquid such as cyclohexane (in view of its stereochemical aspects) and a well-characterized substrate such as tungsten. A nanosecond laser pulse is made incident on a thin layer of cyclohexane or decalin supported on a tungsten foil. An area of 5 mm x 5 mm is thermally shocked in the scan mode by the laser pulses. The evidence from glancing angle XRD, TEM and laser Raman spectroscopy show, conclusively, the formation of hexagonal and cubic diamonds on the surface of tungsten. The choice of the organic liquid is found to be crucial.

A second group at NPL has recently published a paper reporting on the observation of imperfect carbon cage structures of C_{60} by high-resolution scanning tunneling microscopy.[6] The imperfect carbon cages have been resolved to the finest detail, which, for the first time, provide adequate confirmation of a variety of defect structures predicted by molecular dynamics simulations. From the conductance spectra by in the STS mode, one observes that the gap between the HOMO and LUMO for the clusters is decreased with the presence of defects. From the value of 1.5 eV for the perfect cage, the imperfect cage can lead to gap values of 0.3 eV or even lower, perhaps to zero value.

Powders and Compacts

A new technique called the pyrophoric process has been developed to synthesize ultrafine powders of the Y-123 system. The nanoparticles (40 nm) and have been observed to sinter to 99% density by processing the pellets at much lower temperatures (880 C) and shorter lengths of time (1 hr.) than other processes, *viz.*, the conventional ceramic process or the coprecipitation technique.

C-axis oriented Y-123 whiskers have been synthesized to fabricate whisker-reinforced Y-123 composite, which show partial *c*-axis orientation after sintering and a J_c value of 1440 A/cm^2 at 77 K.

In collaboration with the University of Florida group, the author's (MM's) group at has invented the method of synthesizing high density (about 97% of single-crystal density) of Y-123 ceramics with a large Meissner fraction (90% unoptimized). The technique involves the use of microemulsions which has been the focus of many studies reported in the past decade by chemists as well as physicists. The microemulsion-derived powders sintered with explosive grain growth from about 40 nm to about $50x10^3$ nm (along the longer axis of the ellipsoids). There are ramifications for high *Jc* in bulk superconductors from these studies.

The IGCAR group has designed a vacuum calcination method for the synthesis of high temperature superconductors. The essence lies in decomposition of precursors (from the co-precipitation, citrate, or sol-gel routes) in the quick removal of the CO_2 which would otherwise react with the Y-123 to form $BaCO_3$, Y_2O_3, CuO and $Y_2Cu_2O_5$, depending on the temperature. The reduced pressure calcination circumvents this by more effective removal of the carbon dioxide. Presently, synthesis of upto 150 grams of Y-123 powder per batch has been standardized. The process parameters are well understood and there should be no difficulty in scaling up the process for 500 grams batch size. An annual production upto 100 kg of well-characterized material is well within reach.

A new semi-wet route to the synthesis of Pb-doped Bi-2223 powders free from contamination by the 2201 and 2212 stoichiometries has been developed. This process requires 48 hours to complete. By following the sequence of the thermochemical reactions, it is shown that Ca_2PbO_4 and 2212 formed in the early stages of reaction, in conjunction with CuO, play the most crucial role in accelerating the formation of the 2223 phase.[7]

The Defence Metallurgical Research Laboratory (DMRL, Hyderabad) has synthesized Y-123 powder which leads to sintered compacts with high current densities and levitation properties using quenched melt growth (QMG) and modified QMG techniques. The group has also prepared Y-123 sputtering targets of high quality.

Towards New Superconductors

It was recently shown that $YSr_2Cu_3O_7$, which is not otherwise possible to prepare under ambient conditions, can be stabilized by the incorporation of oxyanions such as carbonate, sulfate and phosphate. Such oxyanion derivatives of the 123 cuprates are rendered superconducting by the partial substitution of Y by Ca, Sr by Ba, or by the substitution of carbonate by nitrate. It has been noted that $YSr_2Cu_{2.8}(PO_4)_{0.2}O_y$ is stable in the orthorhombic structure, but the material is non-superconducting. The group has found that increasing the hole concentration through partial substitution of Y by Ca typically by 30 atomic percent renders the complex system superconducting (T_c 40 K). Once again, by incorporating the 0.2 phosphate group in the Cu site of orthorhombic $YBaSrCu_3O_7$, a stable tetragonal derivative with a transition temperature of 47 K has been prepared. The T_c increases to 70 K by 30 atomic percent substitution of Y by Ca. The IR spectrum of this system confirms the presence of the phosphate group in the C_{2v} symmetry. This observation is significant since no other stable 123-type cuprate is known to be formed in the Y-Ca-Sr-Cu-O system under the experimental conditions employed; let alone exhibit superconductivity.

When the Cu(1) site in orthorhombic $YBaSrCu_3O_{7-}$ (T_c = 80 K) is partly substituted by the carbonate ion (upto 50%), the crystal structure becomes tetragonal and electron diffraction pattern shows evidence for $2a$ x $2c$ superstructure; the material, however, is not superconducting. The same is true when Y is partly replaced by Ca as in $YCaBa_2Sr_2Cu_5(CO_3)O_y$. When the CO_3 group is partly by the NO_3 group as in the $YCaBa_2Sr_2Cu_5(CO_3)_{1-x}(NO_3)_xO_y$, the structure remains the same but superconductivity is retained. The IR spectroscopic studies show that both, CO_3 and NO_3 coordinate strongly and are not present as free ions in these oxyanion cuprate derivatives. Cu K-EXAFS studies on the carbonate and carbonato-nitrate derivatives confirm the presence of oxyanions in the place of CuO_4 units in the Cu-O chains.

Incorporation of the BO_3^{3-} stabilizes the $YSr_2Cu_3O_7$ but the borate derivative is not superconducting. Neither is superconductivity obtained by partial substitution of Y by Ca. Superconductivity appears, however, when Sr is partially replaced by Ba. Now, dramatically, 50 atomic percent replacement of Y by Ca remains superconducting. The borate ion is coordinated to Cu, reducing its point group symmetry. Observation of superconductivity in the borate derivatives prepared under ambient conditions is noteworthy.

The important point to note is that the cuprate family compounds are, essentially, being *fine-tuned* to observe subtle changes in the electronic properties. Such an approach can lead to an identifiable mechanism of the new ceramic superconductivity. It can also lead to higher or well-tailored transition temperatures. The derivative, $Tl_{0.5}Pb_{0.5}Sr_4Cu_2(SO_4)O_y$, has been synthesized with the same motivation. Infrared spectra show that the sulfate ion is present as a bidentate ligand as expected from the structural space group, P4/mmm. (See refs. 8, 9 and citations therein)

Coatings

Plasma spraying of high-T_c superconductors offers some scope for large scale processing. The results of work done at Bharat Heavy Electricals Ltd. (BHEL, Hyderabad) are reported. Essentially, in the plasma spray process, feed stock material in the form of powder is injected into a high-temperature, high-velocity, plasma stream. The temperatures have been estimated to be in the region of 4000-12,000 K while the velocities may lie in the vicinity of 100-200 m/s. These fast-moving molten droplets form a deposit (coating) when they are suddenly stopped by a relatively cold substrate. We can, therefore, see that the heat and momentum transfer from the plasma jet to the powder particles are of crucial importance for achieving good coatings. The arc current, plasma gas composition and flow, and particle size of the feed stock powder are the primary parameters which need to be optimized. Substrate distance from the gun nozzle and the substrate temperature are also relevant parameters as they dictate the speed with which solidification takes place on impact and govern porosity and micro cracks in the deposited coating.

Tapes

BHEL has also been engaged in the design and development of tapes. Silver-sheathed tapes were fabricated using the Bi-2223 system. The tapes were processed to final thickness by direct rolling as well as by repeated rolling with intermediate heat treatment. The rolling reduction rate was also varied to find its effect on the final properties. The critical current measured at 77 K could be enhanced from 2770 A/cm^2 for directly rolled tapes to 12,500 A/cm^2 by repeated rolling under identical conditions. In repeatedly rolled tapes the J_c - B variations were found to be much lower in comparison to the directly rolled tapes. Texture evaluation using angular dependence of the magnetoresistance showed the *a-b* plane orientation to be along the rolling direction..

The powder-in-tube technique using an Ag sheath has emerged as the only viable method for fabricating long lengths of flexible HTSC tapes. The Bi:Pb ratio in the above 2223 system was 1.8 : 0.4. The average particle size of the powder was about 2 μm. The BHEL group has now completed angular magnetoresistance (AMR) studies to garner useful information regarding the texture in the tape described above.The magnetic field is provided by suitably chosen gap distance between two NdFeB permanent magnets. The gap is adjusted so that the uniform field is more than H_{c1} of the Bi-2223 system (where Bi is partially substituted by Pb). The fixture for changing the field direction is such as to change the angle (θ) between the transport current (in the plane of the tape) direction and the applied magnetic field direction. The range covered is $0 \leq \theta \leq 180$. The BHEL group has completed a study along with the Argonne National Laboratory and the Regional Research Laboratory (Trivandrum) on the influence of initial composition and processing parameters on the critical current density of BPSCCO PIT process tapes.

TOWARDS DEVICES

The etch kinetics of Y-123 films have been investigated for fabrication of 2 µm width microbridges by photolithography. The films have been etched to form different patterns of micron dimensions. It has been shown that Y-123 could be patterned down to micron dimensions by controlled wet etching using EDTA as an etchant and by lift-off technique. Lift-off technique requires fewer number of processing steps and avoids exposure to chemical etchants. EDTA is an admirably suitable etchant. The critical current density has been found to increase with decreasing linewidths which is due to decreasing number of weak links in the active microbridge area.

The same group at the Indian Institute of Technology (IIT, Kharagpur) has now been able to grow 5 monolayer thick 2201 and 2212 phases of BSCCO either singly or one on top of the other by the atomic layer deposition (ALD) process . In this method, the group has sequentially evaporated Bi and Cu from K-cells and SrO and CaO from e-beam guns onto MgO (100) substrates heated to 700 C. During the deposition, oxygen gas containing 10% atomic oxygen (generated by dc. discharge inside a U-shaped tube with a very fine hole in the bent portion which allows the atomized gas into the chamber) was allowed to impinge on the heated substrate. The 2201 film was deposited first on the substrate followed by the 2212 film so as to prevent interdiffusion and consequent reaction between the MgO and the 2212 film. The films have been found to be perfectly *c*-axis oriented. Tunneling measurements are in progress.

The group has also deposited BSCCO 2201 and 2212 films on PLZT-coated $Si/SiO_2/Si_3N_4$ substrates by the ALD process. The PLZT, depending on its processing conditions, can be used either as a dielectric or a conductor. *In situ* RHEED analysis shows excellent *c*-axis growth of the PLZT layer. Further studies on Si/PLZT/BSCCO/PLZT/BSCCO films are in progress.

Some degree of success has been obtained by a group at NPL in the design, fabrication of an rf-SQUID.[10] It is well known that a dc-SQUID is difficult to synthesize because of the requirement of two weak links having the same critical current. Moreover, the observation of an rf-SQUID behavior does not require a direct contact, so the problem of contact resistance can be eliminated. These SQUIDs were prepared from screen-printed films of Y-123 and Bi-2223 (with a small contamination of the 2212 stoichiometry). The voltage-flux characteristics of both the SQUIDS show oscillations with the period of the flux quantum,ϕ_o. These oscillations correspond to the area of the SQUID loop and are observed upto 85.1 K in the Y-123 system (central hole of 350 µm radius with a suspended microbridge of dimensions 200x400

μm^2) and upto 98 K in the Bi-2223 system (with a central hole of 40 μm with a microbridge of 150x120 $\mu m^{2)}$. The field sensitivity of the first system comes out to be $\sqrt{S_B} = \sqrt{(S\phi/A)} = 5.2 \times 10^{-12}$ T/Hz in the white noise region. For the second system the corresponding value is 7.9×10^{-12} T/Hz. The latter system is also found to be more stable with several thermal cycles between liquid nitrogen and ambient temperatures that the former system.

The IGCAR group has developed SQUID sensors using the Nb-Al_2O_3-Nb sensor using the slit wafer geometry. A whole set of photomasks involving a minimum feature size of 4 μm has been designed and fabricated. This device geometry enables fabrication of SQUID sensors with an integrated input coupling coil which couples the picked-up signal into the SQUID. The coupling efficiencies exceed 80-85%, a value difficult to achieve with other types of device design. Since the fabrication foundry can handle wafers upto 75 mm diameter, a large number of devices can be obtained in each batch.

The Poona University group has succeeded in using Zn doping for tuning of the operating temperature of a bolometer based on Y-123 thin films.[11] The advantage of Zn doping lies in the fact that $(1/R)(dR/dT)$, which is the highest at the mid-point of the resistive transition for the new ceramic superconductors, does not decrease substantially as for other dopants. Thus the T_{co} can be tailored to specific values, such as, for example, at the boiling point of liquid nitrogen. In fact, T_c is hardly affected upto doping level of $x = 0.3$ which drives the transition temperature down to 52 K.

A novel approach has been adopted by a group at the Banaras Hindu University (BHU, Varanasi) for enhancing the intergrain and intragrain critical currents in bulk Y-124. The low intragrain critical current densities are due to inadequate flux pinning in the native cuprate high temperature superconductors. This situation can be remedied by developing appropriate flux pinning centers such as by local structural perturbations are strong and isolated, and their sizes are comparable to the short coherence lengths (0.4 - 3 nm). It has been found that the Y-124 dissociates above 915 C (for times as short as 10, 30 and 60 seconds) and the dissociated/transformed phase is always based on Y-124 even though it contains minority phases such as Y-123, Y-125, interfaces of these with the parent matrix phase, and stacking faults. The 30-second dissociated sample exhibits critical current densities about 11 times higher than for the virgin Y-124 at 77 K. The correlations with the microstructures have been described and discussed. The same group, along with the group at NPL (New Delhi) has observed the rf-SQUID effect in thin films (obtained by spray pyrolysis) of Tl-Ca-Ba-Cu-O. Two films have been chosen for the SQUID characterization. One is mainly the 2122 phase with needle-like grains.The other consists of the well-connected platy phase of the 2223 stoichiometry. The SQUID has been operated in the flux-locked-loop mode. The 2223 stoichiometry thin film exhibits better flux noise performance.

At the Central Electronics & Engineering Research Institute (CEERI, Pilani) a superconducting magnetic resistor and S-FET device-like structures have been developed using the sputtering technique.

PHYSICAL MEASUREMENTS

In spite of the tremendous efforts by researchers around the globe, the mechanism of high-T_c superconductivity has thus far remained a mystery. Amongst the different approaches followed to unfold the mechanism, an important one has been the study of the influence of intelligent substitutions in the new ceramic superconductors different microscopic and macroscopic aspects of superconductivity. Within the broad context of this approach, the role of magnetic impurities has been of particular interest. Unfortunately, in the high transition temperature superconductors it has been difficult to isolate the direct positive or adverse effects of dopants (magnetic or otherwise) from their indirect effects realized *via* their influence on such aspects as the orthorhombicity, oxygen stoichiometry, oxygen-vacancy ordering, etc.. A few facts have emerged from the vast body of substituent data which need not be reiterated here. But it may be noted that theoretical attempts to understand dopant effects on T_c depression are scarce. It has been argued that the depression of the transition temperature can be understood to be due to spin flip scattering within the Abrikosov-Gorkov theory formulated for the strong coupling situation if it is assumed that (1) the Cu^{2+} on CuO_2 planes are highly localized and antiferromagnetically correlated even in the superconducting state and are, therefore, harmless, (2) a vacancy or an extra spin produced by a dopant acts as a magnetic scatterer.[12]

The IIT Kharagpur group has studied the electrical transport properties on the Y-123 films grown by rf. magnetron sputtering for understanding the dimensionality and inter-layer coupling between CuO_2 layers. The films (200 nm thick) on MgO or $SrTiO_3$ substrates, had a J_c of $1.5\text{x}10^6$ A/cm^2 at 77 K. The temperature dependence of the nonlinear current-voltage characteristics near the superconducting transition temperature have been analyzed for dimensionality crossover from 2D to 3D as suggested by the Kosterlitz-Thouless (KT) transition. The resistivity behavior near the transition temperature has been found to be governed by the activated thermal dissociation of the vortex-antivortex pairs as revealed by the exponential dependence of resistance on $\sqrt{T}$. However, deviation at temperatures away from T_c have been observed and are under investigation.

A group at I.I.Sc. along with the IGCAR group has made an interesting study of pressure-induced bandgap reduction, orientational ordering and reversible amorphization in single crystals of C_{70} using the techniques of photoluminescence (PL) and Raman scattering. These researchers were the first to measure the pressure-induced red-shift of the bandgap using the PL technique. These experiments yielded dE_G/dP = 0.138 eV/GPa. Later, the optical reflectivity and optical absorption measurements have confirmed this value. Using the bulk modulus K_o of 18 GPa, the hydrostatic deformation potential, which is related to the electron-phonon coupling constant, is $d_0 = dE_G/d(ln V)$ = 2.5 eV. The measurement on C_{70} indicates the hydrostatic deformation potential to be 2.15 eV. The slope changes in the pressure dependence of the peak positions and linewidths of the Raman modes associated with the intramolecular vibrations at 1 GPa mark the known *fcc* rhombohedral orientational ordering temperature. Group theory predicts 53 Raman-active modes corresponding to the species $12A_1' + 22E_2' + 19E_1'$ of the point group D_{5h} for the C_{70} molecule. In solid C_{70}, the selection rules predict many more Raman-active modes. Solid C_{70} transforms to an amorphous phase at P 20 GPa which reverts back to the starting crystalline phase on decompression, as evident from the

Raman lines associated with the intramolecular vibration and the PL. This implies that the C_{70} molecules are stable at least upto 31 GPa. This is in contrast to the irreversible amorphization in solid C_{60} at pressures greater than 22 GPa. The workers have rationalized this difference on the basis of different pressure dependence of the c-c distance between neighboring molecules.[13]

It is worth recalling a study made by two members of IGCAR along with the Texas group of C.W. Chu, the Princeton group and the Lawrence Livermore group.[14] They found a correlation between the local charge-density and superconductivity through positron annihilation studies. The temperature dependence between 10 and 300 K of the positron lifetime was measured in the $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ with 0.8, M Zn or Ga and x = 0.0 to 0,07. In the undoped and Ga-doped samples, the positron lifetime in the Bloch state, τ_b , was observed to decrease below T_c. In the Zn-doped samples, a dramatic x-dependent temperature variation of τ_b was observed below the transition temperature for $x = 0.01$ to an increase of the lifetime for $x > 0.02$. It is established from the experimental data that the positron density distribution (PDD) plays a crucial role. A decrease in lifetime is observed when the positrons probe the chains and an increase is observed when the positrons probe the CuO_2 layers. The decrease in the lifetime below the transition temperature implies an increase in electron density at the site of the positron, viz., the Cu-O chains. A simple physical picture to understand this is to invoke that there is a local transfer of electron density between the layers and the chains in the superconducting state. Such a proposal can account for the temperature dependence in the Zn- and Ga-doped systems if we take the PDD into account correctly. The calculated PDD shows that the weight of the positron density shifts from the Cu-O chains to the CuO_2 layers due to Zn doping. A transfer of electron density from the layers to the chains will in this case lead to a decrease in the electron density at the site of the positron and this can account for the observed increase in the lifetime below the transition temperature. In the Ga-doped system, the PDD is seen to be on the chains and a decrease in the lifetime is seen below the critical temperature; once again this is consistent with the notion of electron density transfer from the layers to the chains. Besides, this model explains the observed decrease in $\Delta\tau_b$ with increased doping concentration. An electron transfer from the layer to the chain in the superconducting state can be viewed as an increase of the charge state of Cu in the layers from 2+ to 3+. With partial replacement of Cu by Zn or Ga such a charge transfer can be expected to be suppressed, leading to a decrease in the magnitude of the $\Delta\tau_b$ with increased Zn or Ga doping.This basic approach has been extended to a number of HTSC systems and a comprehensive paper.

The group at the Saha Institute of Nuclear Physics (SINP, Calcutta) has been active in theory as well as experiment. A recent study involves the resistivity anisotropy in Y-substituted Bi-2212 system.[15] The group has grown undoped and doped Bi-2212 single crystals and measured the resistivity in the *ab*-plane and along the *c*-axis. The normal state ρ_{ab} is linear in T with positive slope for all samples. The data are interpreted in terms of the Matthiessen rule: $\rho = m^*/(ne^2\tau_{imp}) + m/ne^2\tau_{ph})$. The $x = 0$ and $x = 0.1$ samples show a metallic temperature dependence which agrees with the prediction made earlier by Kumar and Jayannayar for the *c*-axis resistivity, $\rho_c(T)$, and the resistivity anisotropy, ρ_c/ρ_{ab}, at room temperature. The value of the relaxation time that emerges from the fittings of the data to the Matthessen rule is almost of the same order ($\sim 10^{-14}$ sec) as obtained from optical conductivity measurements by Romero *et al.*.

The SINP group has also studied the excess conductivity of the Bi-2212 system as a function of the carrier concentration. The analysis shows that the system is highly anisotropic and the interlayer coupling strength decreases very rapidly with the decrease of the hole concentration. In the low-hole concentration region, T_c depends strongly on the interlayer coupling as compared to that in the optimum- and heavily-doped region. From the value of the interlayer coupling, out-of-plane coherence length and dimensional crossover temperature are estimated.

The Madras University group has been involved in Mössbauer[16] and Positron Angular Correlation[17] studies. A recent study focused on the 1D-ACPAR measurements on the Y-123 (with varying oxygen content) and the Y-124 systems have been analyzed. It is revealed from this work that the Umpklapp components of the second and third Brillouin zones appear in all superconductors. In the insulating compounds of the Y-123 system, they are less prominent. Otherwise the band structure features of all these samples are strikingly similar. In conclusion, the authors note that there is qualitative accord between the measured and calculated spectra, signifying the reasonable description of the ground state and the Fermi surface of the new superconductors.

The group of at the Center for Advanced Technology (CAT, Indore), a group at TIFR and co-workers at the Bhabha Atomic Research Institute (BARC, Bombay) have been concentrating in the past few years on the dc and ac hysteresis effects on granular samples of the new ceramic superconductors. A recent study involves the minor ac hysteretic study of Y-123. The results have implications for intergrain and intragrain response for hard type-II superconductors. When the external dc field B_{dc} is zero, hysteresis is seen as B_{ac} is raised from zero and higher odd harmonics are observed in the magnetization. The absence of even harmonics is indicated by the symmetry of the hysteresis loop. When B_{dc} is non-zero a response is also observed at higher even harmonics and the concomitant asymmetry of the minor hysteresis loop is stressed to be the signature of the field-dependent critical current density $J_c(B)$. It is shown for the first time that the shape of these loops is a function of the history of application of the cycling field. A model based on the two-component nature of an HTSC pellet has been put forward to explain the ac and dc history effects.[18,19]

THEORY

Prof. S.S. Jha has worked out a mathmatical outline of the generalized pairing theory for the layered HTSCs for, both, singlet and triplet pairing. For the spin-singlet case, a distinction is made between intra-layer and inter-layer pairing by using different coupling constants (phenomenological) for the two situations. The actual nature of the exchange mechanism (whether electronic charge fluctuations, spin fluctuations, ionic excitations, etc.) are not specified. It is shown how superconductivity at high Tc can arise in this type of materials. The singlet pairing theory appears to be more promising. It is suggested that no single exchange mechanism may be operative and the phonon exchange mechanism may be only playing a supporting role.[20]

Prof. G. Bhaskaran has clarified the application of RVB theory to HTSCs. The author introduces basic ideas of RVB theory by defing the RVB state and the nature of excitations. Some exactly solvable models having the RVB ground states are given, followed by approximate methods (mean field theory and slave boson gauge theory). The theory is then applied to explain some general properties of HTSCs, the interlayer tunneling mechanism and to calculate the NMR relaxation times.[21]

NEUTRON SCATTERING

Neutron profile refinement has been carried out for most polycrystalline HTSCs at the DHRUVA reactor at Trombay. The results of these investigations are reviewed within the context of the current structural models and some novel structural features are highlighted.[22]

SUPERCONDUCTING SYSTEMS

Superconducting Generator

Recognizing the important role of superconductivity in future technologies and products such as generators, BHEL has taken up the development of a 5 MVA Superconducting Generator under the National Superconductivity Program. As a forerunner to this, a 200 KVA laboratory model of the generator has been successfully developed at the Corporate R&D Headquarters at Hyderabad. The prototype is undergoing several commissioning trials. The rotor has been wound with Nb-Ti wire, producing peak magnetic field of 4 Tesla. For cooling the rotor windings, a closed-cycle liquid helium plant with liquid nitrogen pre-cooling system has been installed. The potential advantages of the Superconducting Generator are reduction in size and weight, improvement in efficiency, possibility of operating at larger capacities and higher voltages, and improvement in steady-state stability.

Superconducting High-Gradient Magnetic Separator

Magnetic separations is one of the largest industrial applications of magnetism, next to motors and generators. It is used for separation of paramagnetic and diamagnetic particles as well as non-magnetic materials, and finds extensive applications in mineral processing industries. The magnetic field intensity achievable through conventional magnetic separators is upto about 2 Tesla, and the magnetic field gradient is of the order of $1x10^3$ or $2x10^3$ Tesla/meter. With the advent of superconducting magnets, even larger magnetic field gradients such as about 10^5 Tesla/meter are achievable with negligible increase in power consumption. In view of these advantages, this area was promoted in India also. Projects for the design & development and laboratory trials of superconducting high-gradient magnetic separators have achieved some degree of success at BHEL & NPL[23] and the Atomic Minerals Division of the Department of Atomic Energy have now been completed. The system has been installed and successfully operated at the Corporate R&D Division of BHEL at Hyderabad.

At BHEL, using the superconducting high-gradient magnetic separator, a number of experiments have been carried out on ball clay, magnesite, synthetic rutile and iron ore slime. Iron oxide impurities in ball clay could be brought down from 1.5% to 0.5% from 1.0% to 0.5% in magnesite, from 2.5% to 0.5% for synthetic rutile, enrichment of iron ore slime enrichment to 70% from 60%, all processes in a single pass. These results have proved the efficacy of the system in separating weakly magnetic impurities of micron size from crushed basic minerals. The throughput is about 1 ton/hour for the crushed mineral ore while it about 5 tons/hour for the slurry.

This development marks the first step in the endeavors towards commercial application of superconducting technology in an industrial environment. Another prototype equipment development has been started by BHEL and the Electronics Corporation of India Ltd. (ECIL, Hyderabad)

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