

**Recent Progress Towards Developing a High Field, High- T_c
Superconducting Magnet for Magnetic Suspension
and Balance Systems.**

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I. INTRODUCTION.

The initial discovery of the high- T_c superconducting ceramics in 1986 [Bednorz and Müller], rapidly followed by the subsequent development of compositional families which exhibited zero resistance transition temperatures at 90 K [Wu], 125 K [Hermann], and recently as high as 132 K [Hongbao et al., Chandrachood et al.], heralded predictions for major breakthroughs in mankind's technical mastery of the universe. Images of high-speed magnetically levitated trains racing across the continent or inexpensive electricity transported thousands of miles over resistanceless power lines littered the pseudo scientific literature to popularize these new observations. As had been the case when the first type-I low- T_c superconductors were identified in 1911 [Onnes], a more thorough investigation of the intrinsic properties of these materials fostered sobering attitudes within the technical and engineering communities as practical limitations to the application of this technology were identified.

In the 50 years succeeding the discovery of superconductivity, the physical foundations upon which an understanding of the onset and preservation of the resistanceless conductive state were constructed. This arduous research path led to the commercialization of superconductors for applications as diverse as low field magnetometry, high field magnetism, and charged particle acceleration throughout the 1960's, -70's, and -80's. Although superconductors remain a modest industry by global business standards, their reliability and unique performance capabilities in medical and extremely high-cost experimental physics apparatus has demonstrated feasibility for their integration into complex systems where down time spells disaster.

There is a clear need for the development of the high- T_c superconductors. Relieving the constraint of systems operation at liquid helium cryogenic temperatures makes the application of superconducting devices more broadly possible on the basis of overall system cost and simplicity. At present, NASA has identified interest in applying high- T_c superconducting magnets to the following aerospace technology applications: vibrational isolation, high accuracy pointing, and magnetic suspension in wind tunnel testing. The most challenging system requirements for these application orientations will be found in the suspension and balance systems used in conjunction with cryogenic wind tunnels. Levitation is required in this test apparatus to remove aerodynamic interference caused by a mechanical support under conditions of dynamic or unsteady testing. Superconducting magnets for this application will have to be capable of maintaining DC fields on the order of 6 - 8 Tesla, in addition to an overlapping large amplitude ac sinewave field at 5 Hz, superposed by higher frequency (50 Hz to 60 Hz) 0.1% maximum field strength signals which are critical to system control.

This paper will briefly review superconducting magnet and high- T_c superconducting oxide ceramic materials technology to identify areas of fundamental impasse to the fabrication of components and devices that tap what are believed to be the true potential of these new materials. Fortunately a great knowledge base on the subject of superconductivity and superconductive devices has already been acquired through the development of low- T_c superconductor components. However, the high- T_c ceramics pose problems in fundamentally different areas which have to be solved. We will map out an experimental plan designed to research process technologies which, if suitably implemented, should allow us to overcome many of these deficiencies. We will conclude with an assessment of where and on what regimes magnetic system designers should focus their attention to advance the practical development of systems based on these new materials.

II. FUNDAMENTAL CONSIDERATIONS TO THE DESIGN OF SUPERCONDUCTING MAGNETS.

The superconductive state is a thermodynamic phase of material systems susceptible to "delicate" and complex internal electronic interactions. The phase space mapped out by the superconducting state is defined through the following parameters of state: temperature, T , magnetic field, H , and current density, J . Critical values for each of these parameters mark the transition of the material from its superconducting phase to its *normal* resistive phase. The critical values for each of these state parameters are dependent upon the thermodynamic weighting of the other state variables through a system of Lagrangian constraints. That is, the highest critical load that can be sustained by this thermodynamic phase, be it thermal, magnetic, or electrical, is obtained through the application of minimal stress on the other two state variables.

Zero electrical resistance can be maintained at the highest temperatures in the absence of any applied or generated magnetic field, and through the passage of minimal current densities. The superconductive phase will persist under the weight of high magnetic fields at the coldest temperatures and with minimal current densities, and so on and so forth. While both temperature, T , and magnetic field, H , are fundamental thermodynamic state variables defined by the internal dynamics and energies intrinsic to a specific materials system, critical current densities, J_c , are far more susceptible to influences extrinsic to the material system and can generally be increased through improved materials processing.

The objective in designing and constructing a high field superconducting magnet is essentially to run the gambit. It is necessary to construct a superconductive surface topology which allows the material system to sustain its thermodynamic phase through the application of maximal stress on at least two, and many times all three of the state parameters. **Figure 1** shows a topological design using a tape/ribbon conductor. The tape is constructed to have a surface coverage of superconducting material. As diagrammed, the poles of the magnet will be subject to considerable thermodynamic stress. Maximum magnetic load will be fundamentally limited by the effects of strain produced in this "stress node" of the magnet. Magnetic field densities in the superconductor will be greatest in those regions where the radial field lines loop back down through the core of the magnet. A high current will induce a strong magnetic field. The ultimate field density in the core of the magnet is proportional to the current passing through the coil and defined by a *shape factor* which relates the surface current paths to the induced field strength. The generation of these fields which penetrate through the superconductor, will in turn *pinch-off* the critical current densities passing through the conductor at these stress points in the coil, and, as a result, start limiting the maximum field.

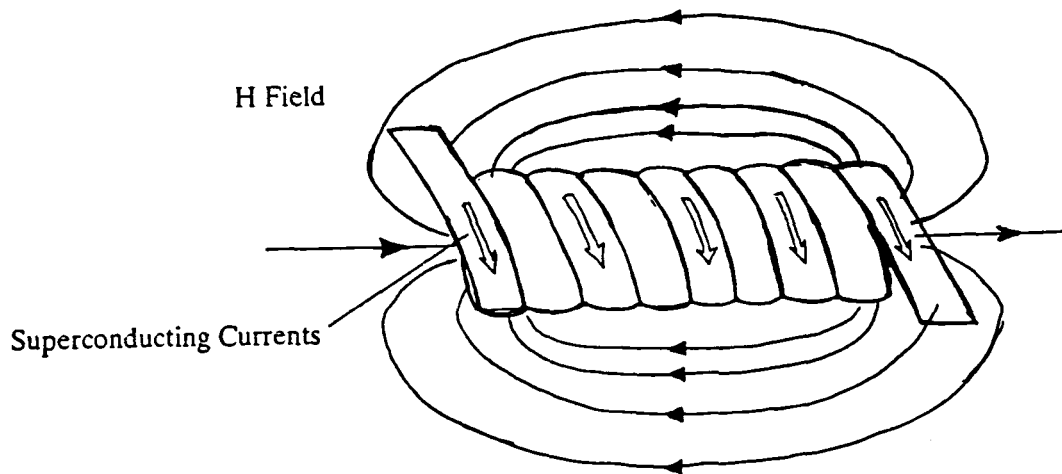


Figure 1. Magnetic coil based on a ribbon composite-conductor design. The high- T_c superconducting ceramic is either embedded as a sheet within the ribbon, or is applied as a surface coverage to the structure.

It is therefore necessary for the superconductor to be magnetically hardened at the poles. When magnetic flux bundles, fluxoids, penetrate the superconductor they will interact with the supercurrents through Lorentz forces. Greater fluxoid densities, will activate the frequency of these interactions. This interaction will deflect the supercurrents from their intended path and exert an equal and opposite force upon the fluxoid. (See **Figure 2**). Fluxoids will move in response to this force, and if they drift through the material they will dissipate their energy into the superconductor. Their energy is ultimately converted to heat, which in turn applies greater

stress to this thermodynamic phase of the material. However, if the fluxoids are *pinned* by potentials greater than the interaction energy of the Lorentz forces, their movement will be prevented and less heat is dissipated into the system.

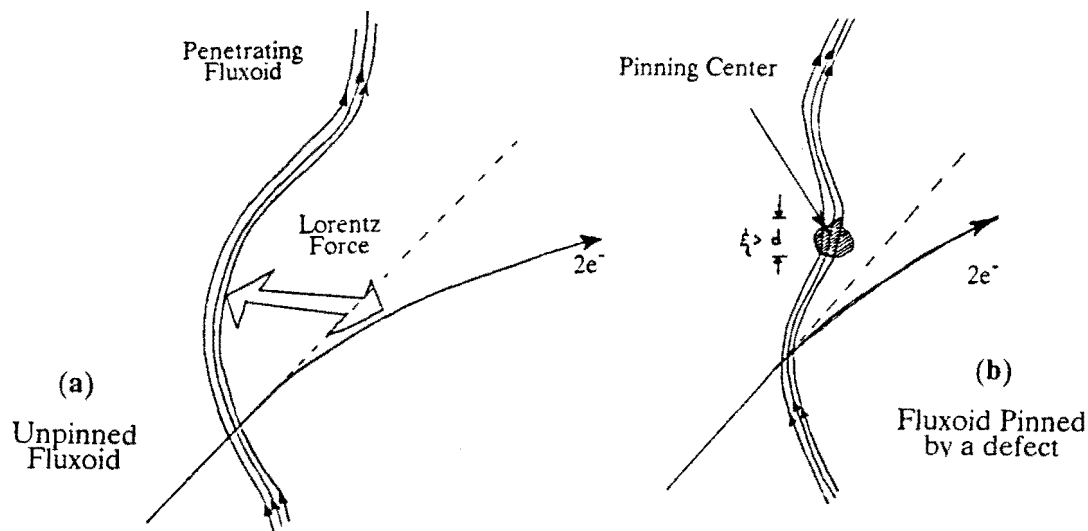


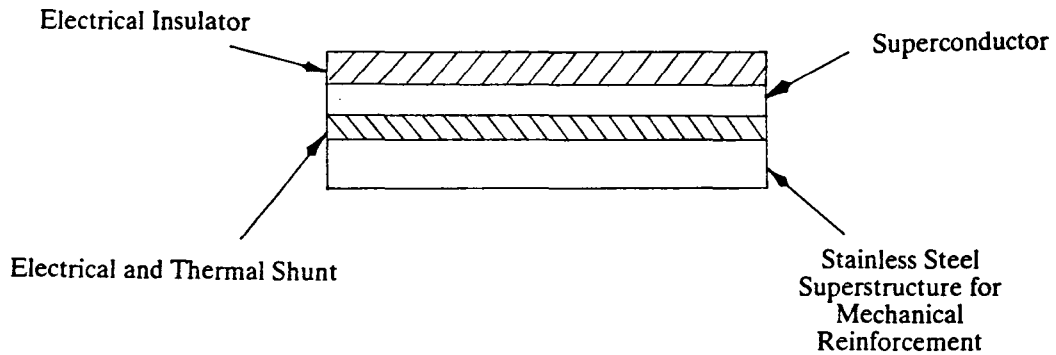
Figure 2. Lorentz force interaction between a penetrating fluxoid and supercurrents within the conductor (a). Fluxoids can be pinned within the superconductor to prevent heat generation by defects having physical dimensions smaller than the coherence lengths of the superconducting Cooper pair (b).

The conducting surface topology given in **Figure 1** is attractive in researching these new materials for a number of reasons. It allows the entire superconductor to be bathed completely in the thermal reservoir, thereby effecting more uniform control over the thermal load applied to, or generated within, the superconductor. If continuous ribbons of tape are used, this design reduces the potential need for spliced joints between segments of the coil. Spliced joints electrically connect superconducting segments of tape through the application of normal conductor material. They would certainly be needed if edge wound ribbon conductor coils are considered. When high currents are applied to these joints they can also generate heat sufficient to drive normal state transitions and *quench* the superconducting state along the entire coil.

Implicit to the successful design of a high- T_c superconducting magnet is the design of the conductor ribbon. A composite structure to these conductors is required. (See **Figure 3**). First, the superconductor needs to be intimately contacted to a metallic substrate material. This metal must have a high thermal conductivity so heat generated within the material can be quickly transported out of the superconducting medium. This thermal shunt is necessary to reduce the occurrence of normal state transitions and to avoid generating conditions which could precipitate a quenched coil. Secondly, the metal enveloping the superconductor must also be an excellent electrical conductor. In the event the coil does quench an electrical shunt is needed to drain the current in the system.

In addition to anticipating problems related to quenching the superconductor coil, the ribbon design must also anticipate the enormous pressures under which it is likely to be subject when incorporated into the design of a high field magnet. Differences in the field densities across a coil as it generates strong magnetic fields can exert enormous mechanical stress on the coil. Fields of 6 Tesla are known to exert mechanical pressures upon coils on the order of 140 atm, which is equivalent to pressures contained within gas cylinders. Magnetic fields approaching 10 Tesla can generate pressures equivalent to 520 atm, which approaches the yield strength of annealed copper. Therefore, it is imperative that a strong mechanical superstructure be

embedded within the ribbon. This can be accomplished by having a stainless steel base. Stainless steel has electrical and thermal properties which are not sufficient to accommodate shunt characteristics required in the structure. Finally, this entire structure should be encapsulated by a good electrical insulator to avoid high voltage arc discharges between various windings within the coil, or the coil and its confinement chamber.



Tape Cross-Section

Figure 3. Schematic design of the superconducting ribbon to be applied to the construction of a high field magnet.

III. FUNDAMENTAL PROPERTIES OF THE HIGH- T_c CERAMIC OXIDE SUPERCONDUCTORS.

The challenge presented to the materials engineer trying to overcome the natural difficulties posed by these materials systems is formidable. The difficulties involved can be appreciated by examining the "compositional windows" over which high- T_c superconductivity is observed to occur in these ceramics. High- T_c superconductivity is now known to occur in a number of ceramic materials systems with the perovskite crystal structure. Current understanding of the high- T_c ceramic oxides has been developed upon the observation that the superconducting compositions in these material systems are located over a compositional domain between adjacent semiconducting (insulating) and metallic manifestations of these *complex* metal oxides [Kitazawa, 1990]. (See **Figure 4**).

1. ELECTRONIC STRUCTURE OF THE CERAMIC SUPERCONDUCTORS.

The current focus in the scientific literature mainly emphasizes that the evolution of superconductivity, which is nestled in the vicinity of a semiconductor-to-metal compositional transition, is triggered by high-level carrier doping in a semiconductor (insulator) which has a nonconventional energy gap at the half-filled position of its conduction band. The energy gap involved in these systems has its origin in strongly correlated multi-body interactions: charge density waves (CDW) in the barium bismuthates ($BaBiO_3$) or electronic correlation in the case of the cuprates.

The electronic properties of the superconducting cuprates are fundamentally characterized by a two-dimensional network of covalent Cu-O bonds which form a CuO_2 square lattice in the a-b (basal) plane of the perovskite crystal structure. Cu-O bonding along the c-axis is believed to be ionic and electrical conduction is essentially two-dimensional along the a-b plane and can be modeled by assuming a pile of alternating ultra-thin metallic and insulating layers. (See **Figure 5**). The chemistry within the ionic layer controls the amount of charge carriers transferred into the superconducting sheets, which in turn, influences whether or not the superconductive phase will

form and at what temperature it occurs if it does [Cava *et al.*, Jorgensen]. As a result, these layers have come to be known as "electronic doping" regions. (See Figure 5).

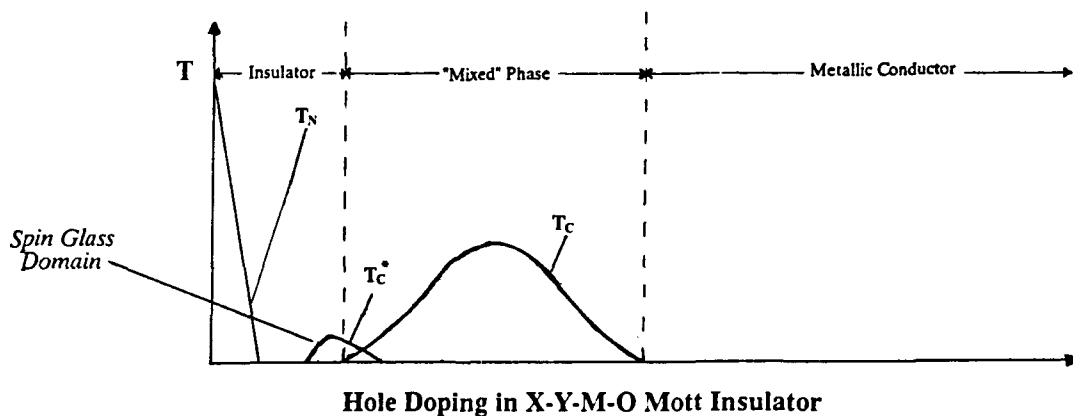


Figure 4. Compositional dependence on the electrical phase of high- T_c superconducting ceramic cuprates.

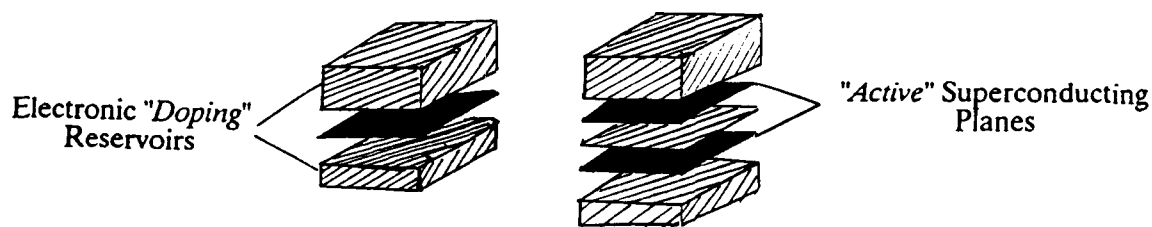


Figure 5. Electronic structure of the high- T_c superconducting cuprates.

The transfer probability from a metallic plane to the adjacent one across the intervening insulating layer(s) seems to be a very sensitive function of the nature of the ionic layer. As a result of these structural features, superconducting parameters in the cuprates are highly dependent upon interlayer coupling, and are consequently anisotropic. A fundamental consideration to making these systems work in high field magnet applications will be to maintain specific

crystallographic orientations *vis-à-vis* the applied magnetic field and the superconducting current path. This requires the entire ceramic to have a "textured" quality. That is, its c-axis must be oriented relative to the metallic substrate surface on a macroscopic scale.

T_c in these materials can depend sharply on composition, and the emergence of superconductivity is observed to be in a compositional domain located between insulating (semiconducting) and metallic manifestations of these material systems. The unit cell structures for these materials is indeed quite complex. **Figure 6** shows the unit cells for 6 of the superconducting phases which have been identified for the Tl-Ba-Ca-Cu-O superconducting system. The most interesting phases have the most complex structures. The primary task goal in manufacturing a single phase tape will be to replicate one of these atomic structures throughout a surface layer 20-50 μm thick, 1 cm wide, and 10-100 m long.

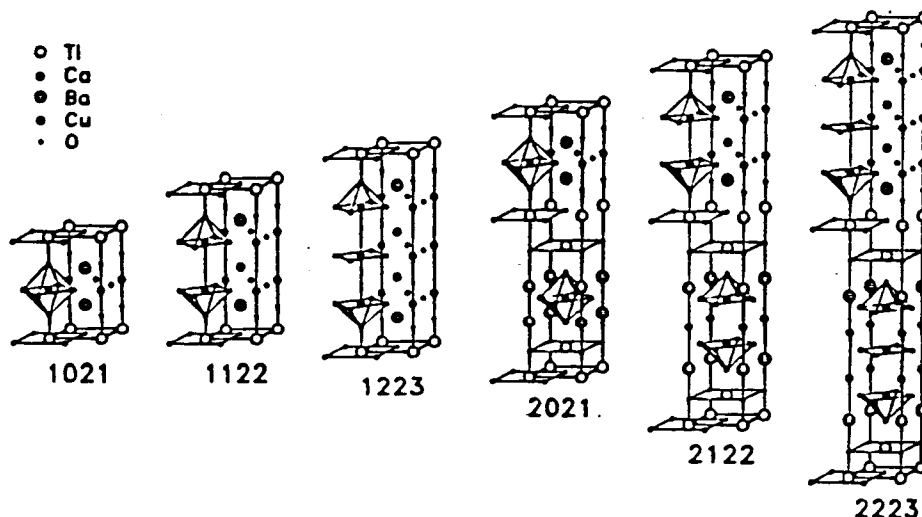


Figure 6. Six of the superconducting phases identified in the Tl-Ba-Ca-Cu-O system.

While depositing the proper stoichiometry in the film or coating is a necessary prerequisite, it will not assure the formation of the desired phase. During synthesis these materials have to be processed over wide temperature ranges. Over different thermal regimes various phases of the material will have stronger tendencies to form. For instance, if the 2223 stoichiometry is deposited but the material is processed at temperatures which favor the formation of the lower T_c 2021 phase, the material will phase separate into this phase and an equal stoichiometric blend of barium and copper oxides which can be insulating. As a general rule, it appears that the more interesting compositions have the narrowest synthesis windows to form phase stabilized solids and are the most difficult to form. Consequently, once phase separation has been initiated the coatings will have poor electrical properties and be of little use to fabricating a magnet.

2. INTRINSIC MAGNETIC PROPERTIES OF THE HIGH- T_c CERAMICS.

The truly magnificent property of these materials is their magnetic hardness. While actual values for the upper critical magnetic fields for these materials is still not yet known, for many of the different systems they are believed to be on the order of many hundreds, if not more than a thousand, of Tesla for many of the different compositional families [Kang *et al.*, Larbelestier]. Current impediments towards achieving an accurate appraisal for these properties has involved many complex issues related to defects. Defects in these materials can be both beneficial and detrimental to their ultimate performance. When point defects are arrayed into a structured lattice dramatic increases in transition temperature, upper critical field, and, most significantly, critical current density can be achieved. However, larger defects located in the path of the

superconducting currents can severely degrade their capacity to carry supercurrents as well as their performance in magnetic fields.

3. EXTRINSIC MAGNETIC PROPERTIES OF THE HIGH- T_c CERAMICS.

Many of the same "tricks" used to develop high quality low- T_c superconductors, such as the deliberate generation of defects to serve as flux pinning centers, can be adapted to the high- T_c superconducting ceramics. Flux pinning centers improve critical current densities by preventing the free motion of penetrating fluxoids, which dissipate their kinetic energies into the system through Lorentz force interactions with the supercurrents. Although this approach can be applied to high- T_c conductors, it must be done on a significantly different physical scale. The coherence length (ξ)--(nominally defined as the maximal separation of two electrons in a *Cooper pair*, beyond which they split and revert back to normally resistive charge conductors)--is anisotropic in the cuprates and are orders of magnitude shorter in the high- T_c materials. Typical values are found to be on the order of 2-4 Å for ξ parallel to the perovskite *c*-axis and $\xi = 16-30$ Å along the *a*-*b* plane. This compares unfavorably to coherence lengths of up to a couple microns for some of the low- T_c materials [Doss].

Deliberately induced defects will only serve as flux-pinning centers if they have a spatial extent less than the coherence length of the *Cooper pair*, (see Figure 2), otherwise they will stimulate pair transitions to the normal state. Flux pinning point defects can be generated in these films using high-energy particle irradiations. This treatment will form defects by slightly perturbing the location of an ion from its equilibrium position in the lattice. It can raise the critical current density in films from 10^5 to 10^7 A/cm² [Venturini *et. al.*, van Dover, *et al.*, 1989, 1990]. Unfortunately, these techniques are only useful in samples exhibiting good *texture*, for instance, single crystals or high quality epitaxial films. A materials synthesis process, like spray pyrolysis, capable of producing large area films will produce inherently polycrystalline films which could conceivably be dominated by weak link intergranular connections. The ultimate success of any large area deposition process will be strongly influenced by its ability to control the orientation of these individual grain granules.

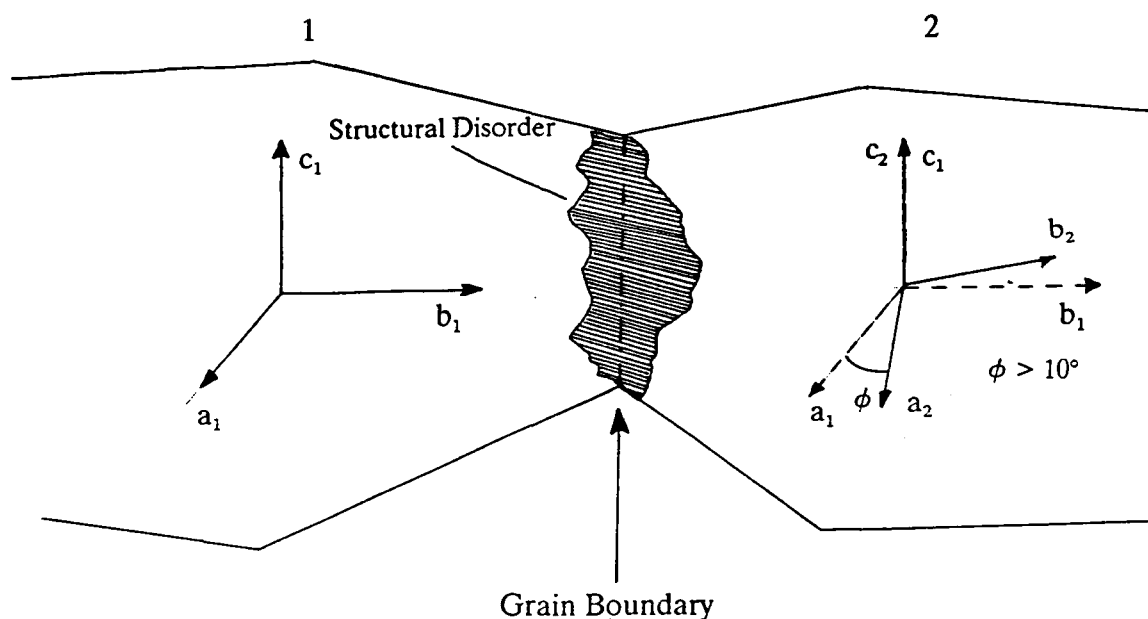


Figure 7. Superconducting-Insulating-Superconducting (SIS) junctions at the boundaries between grains limit critical current densities in *c*-axis aligned polycrystalline ceramics.

In view of the strong anisotropy and poor conductivity of the cuprate superconductors in directions parallel to the perovskite *c*-axis, a necessary, but not sufficient requirement, will be to orient all the individual grains with their *c*-axes perpendicular to the current paths in the conductor, i.e., in the plane of the substrate. It has been shown that the relative orientation of the basal (*a*-*b*) planes in *c*-axis aligned bicrystals can greatly influence the critical current densities transported across the grain boundary [Dimos *et al.*, 1988]. Grain boundaries in which the *c*-axes are perfectly aligned but have the orientation of their basal planes skewed by a screw rotation of more than 10° behave as Josephson junctions and will have relatively low and highly magnetic field dependent critical current densities. (See **Figure 7**). This occurrence can greatly inhibit the performance of the superconductor in magnetic applications.

The formation of these superconductor-insulator-superconductor (SIS) junctions is believed to be the result of structural disorder at the grain boundary which occurs as a natural consequence of the need to accommodate the lattice mismatch at the boundary plane [Dimos *et al.*, 1990]. One would expect that this region of *insulating structural disorder* to be on the order of 10's of angstroms, and that tunneling current densities through these effective Josephson junctions will depend directly on the degree of coupling between the superconducting regions. Polycrystalline films loaded with these superconductor-insulator-superconductor (SIS) junctions will have relatively low and highly magnetic field dependent critical current densities which cannot be improved through the generation of radiation induced defects. This occurrence can greatly inhibit the performance of the superconductor in high field magnet applications.

Consequently, the suitability of using high- T_c superconducting ceramics in high field magnet applications will likely depend upon the selection of a materials system based on a number of intrinsic properties. As a result of the sensitivity of these grain boundaries to magnetic fields, intrinsic parameters other than transition temperature will likely play a more determinant role in selecting the materials systems for a high field magnetic component. Since charge transport through the insulator is a tunneling process, higher critical current densities across the grain boundary are likely to be obtained using a materials system exhibiting longer coherence lengths. If one of the electrons in a Cooper pair has tunneled through the barrier, but its coherence length is long enough to remain bound to the other electron in the superconducting paired state across the insulating region, the probability for supercurrent transport across the junction is greatly enhanced. (See **Figure 8**). In general, coherence lengths seem to follow an inverse relationship to the T_c of the material.

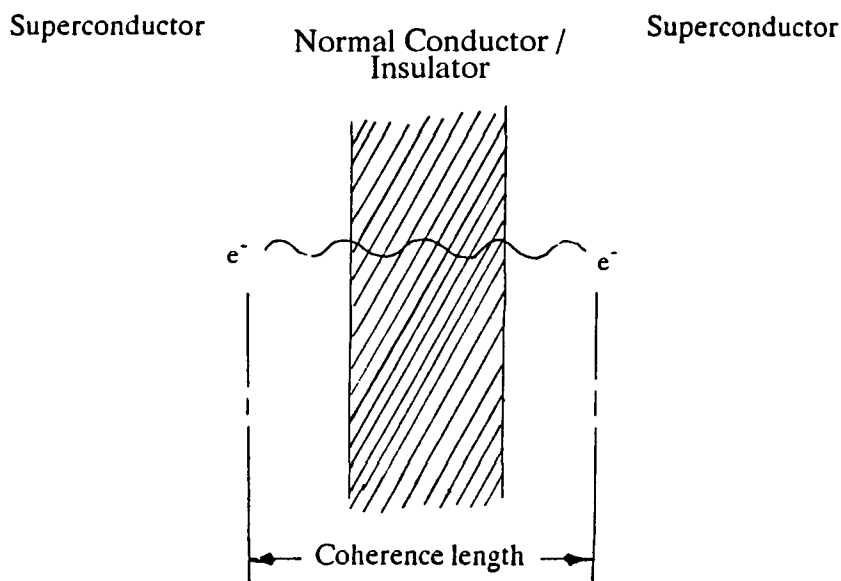


Figure 8. Tunneling of a paired electron state through an insulating barrier.

4. CHEMICAL SENSITIVITIES OF HIGH- T_c SUPERCONDUCTING CERAMICS.

All of the high- T_c superconducting ceramics are known to participate in thermodynamically unstable reactions with carbon dioxide (CO_2) and water (H_2O) [Sleight]. They generally have favorable chemical reactivities with oxygen. As a result of the unstable reactions, a finished film with a nice sharp high- T_c transition will degrade over time as lower T_c knees grow into the transition region, and insulating regions metamorphose within the grain boundaries to pinch-off critical current densities (J_c). Water is known to attack the Y-Ba-Cu-O superconductor by preferentially dissolving barium, so the use of organic solvents is now preferred in solution bulk processes [Trolrier *et al.*]. However, the use of organic solvents will increase the likelihood that CO_2 remains trapped in the lattice and corrodes the lattice through other reaction paths. CO_2 is created in the lattice during the initial firing of these organic laden ceramic formulations.

It has recently been confirmed that the presence of either H_2O or CO_2 will deteriorate critical current densities in these films by altering the surface properties of individual grains, thereby degrading current transport across their boundaries. The formation of BaCO_3 , insulating Y_2BaCuO_5 , Y_2O_3 , and CuO have been observed to occur at various temperatures and pressures as the Y-Ba-Cu-O ceramic oxides react with CO_2 which evolves during firing [Poeppele *et al.*, 1990a]. However, substantial improvements in J_c and thermodynamic phase stabilization can be achieved if CO_2 is efficiently removed from the lattice. It has been confirmed that the kinetics of CO_2 removal from these ceramics is strongly influenced by the partial pressure of CO_2 gas over the solid. Low-pressure high oxygen (O_2) flow rate treatments or low pressure annealing in ozone (O_3) have produced large, multilayer Y-Ba-Cu-O coils with acceptable critical current densities [Poeppele *et al.*, 1990a, 1990b].

IV. CHEMICAL SPRAY PYROLYSIS AND CERAMIC MATERIALS PROCESSING.

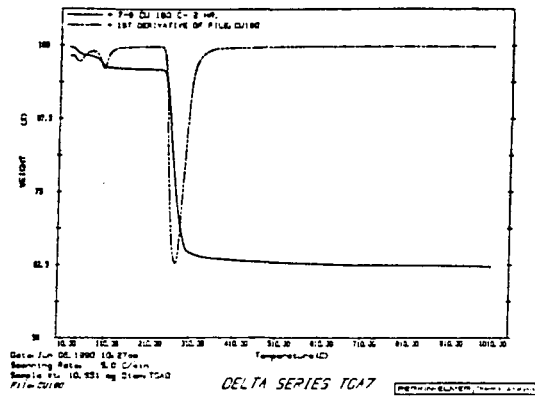
This research program will focus on adapting chemical spray pyrolysis to the manufacture of superconducting ribbons. Spray pyrolysis is a process where soluble precursor salts are dissolved in a solution which is then sprayed on to a hot surface. The cationic salts then precipitate out of solution and react together to form a coating of the desired compound, as the solvent, used to transport the reactants to the substrate, is evaporated from the surface. The high- T_c superconductors comprise a fairly complex materials system, not yet fully understood, and have very unique chemical properties (sensitivities) which must be respected if good quality films are to be produced. The entire synthesis process is composed of three basic steps: deposition, calcination, (where the precursor by-products are broken down and driven out of the film), and sintering, (where the stoichiometric mix is annealed to drive local atomic displacements to form a stabilized superconductive phase).

1. Strategies Towards Achieving Stoichiometric Control at the Molecular Level.

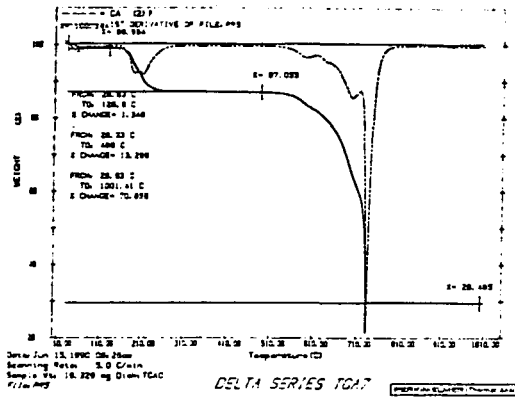
As is evident upon inspecting the electronic-structure properties of the high- T_c superconducting crystal structure, any bulk process capable of producing good quality films or coating must exert stoichiometric control at the molecular level. Although solution processes are attractive for the homogeneous mixing they can provide, not all of the precursor salts exhibit good or similar solubility in the solvent. Therefore, the likelihood for single species agglomerations to form as the salts precipitate out of solution and into the films near the hot substrate surface is real.

In the first phase of this development we countered the possibility for single phase agglomeration by preparing stoichiometric solutions which used an organic (glycerol) as a chemical binder. The objective was to find ways to "gel" all the different precursors together though an organic chain(s). This approach greatly enhanced the chemical uniformity of the sprayed films, as determined by backscattered scanning electron microscopy. On the basis of thermal analysis it appears as though we are forming derivatized salt complexes. **Figure 9** shows individual thermogravimetric (TGA) spectra of the various precursors used in our process. TGA measures the percentage weight changes in a compound residue versus temperature and allows the experimentalist to determine at which temperature regimes the material is likely to outgas and to infer what chemical decomposition species are forming on the basis of molar percentage weight changes.

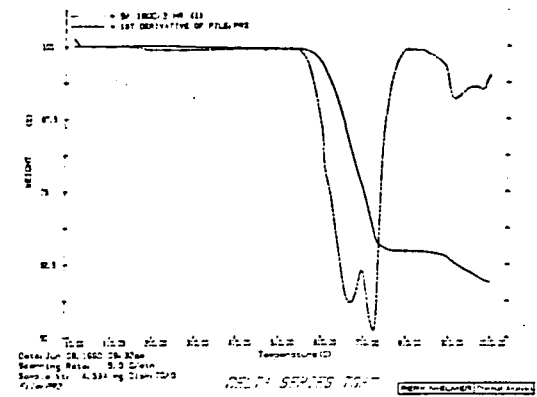
As is clearly evident in the figure the decomposition spectra is seen to change from the



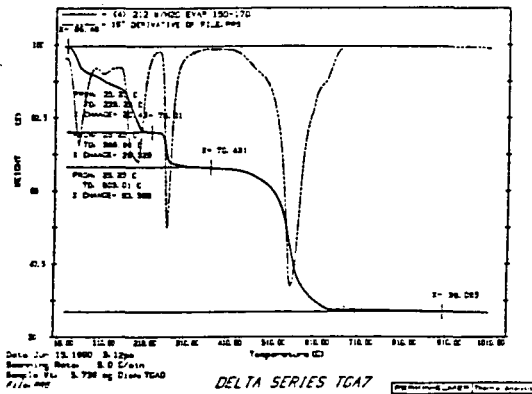
Cu₂(OH)₃ - (NO₃)



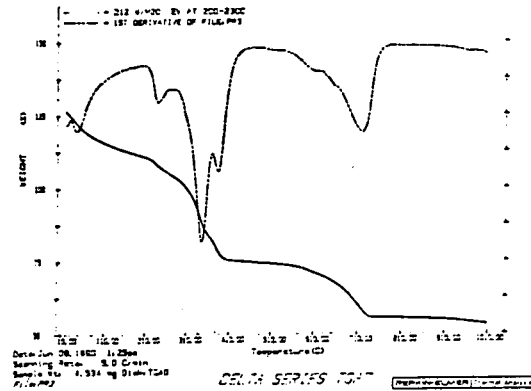
Ca(NO₃)₂



Ba(NO₃)₂



212 Ba-Ca-Cu-(NO₃)₂ in H₂O only



212 Ba-Ca-Cu-(NO₃)₂ in H₂O with 20% Glycerol Binder by volume

Figure 9. Thermal decomposition spectra of residues dried from aqueous salt solutions containing Ba(NO₃)₂, Ca(NO₃)₂, Cu(NO₃)₂, only, and solution mixtures of the three salts with and without an organic binder.

single species cases. In aqueous solution both $\text{Ba}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ appear to have an affinity for each other and complex together. This is verified through the loss of their individual spectra, and by percentage weight changes which indicate that they are decomposing simultaneously. However, the $\text{Cu}(\text{NO}_3)_2$ aqueous salt derivative decomposes independently in the case of aqueous only, and aqueous/20%-ethanol by volume solutions. When the glycerol is added the spectra for the $\text{Cu}(\text{NO}_3)_2$ aqueous salt derivative is observed to shift to higher temperatures as the $\text{Ca}(\text{NO}_3)_2/\text{Ba}(\text{NO}_3)_2$ complex shifts to lower temperatures.

Our objective in performing this work is to identify the conditions which derivatize all of the salts into a "single complex" which decomposes simultaneously at an intermediate temperature. This eventuality would allow all of the metal oxide components in superconductor to form together and to be located physically close to one another to facilitate the sintering process.

Figure 10 shows the R-T curve for films prepared in the first phase of the research effort. In this instance Ba-Ca-Cu-O precursor films were spray pyrolyzed using a nitrate salt aqueous solution which contained 20% glycerol as a chemical binder. Tl_2O_3 was diffused into the film to form the superconducting Tl-Ba-Ca-Cu-O phase. While these results represent, to our knowledge, the highest zero resistance temperatures for films prepared using this process, the films were phase unstable. Over time lower- T_c knees grew into the transition to zero resistance. We attribute this phase instability to the likely presence of water and CO_2 , formed in the material during processing, which are naturally abundant as a result of our aqueous/organic solution chemistry.

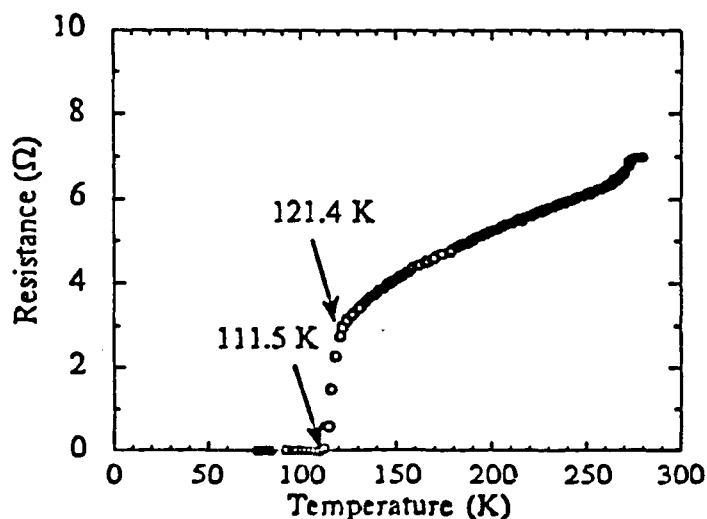


Figure 10. R-T curve of a film prepared by spray pyrolyzing Ba-Ca-Cu-O and diffusing Tl_2O_3 to form superconducting Tl-Ba-Ca-Cu-O.

A current objective of our work is to reduce the amount of water used in the process. While investigating other nonaqueous solvents we have found that formamide, (H_3CCN), is an excellent solvent for non-transition metal salt precursors. It should be noted that extreme care must be exercised when mixing $\text{Cu}(\text{NO}_3)_2$ with organics. The redox active copper atom can catalyze the formation of some very explosive compounds. However, these reaction pathways appear to be shunted when the less reactive salts are mixed into the organic prior to the introduction of $\text{Cu}(\text{NO}_3)_2$.

2. CALCINATION--FORMING THE SUPERCONDUCTING CERAMIC.

The sprayed films are not initially superconducting. Solution stoichiometries could be maintained in the precipitated surface residue by spraying at surface temperatures which did not

pyrolyze the salt compounds into their respective oxides, even though these films had been dried of most of their solvents. Once the appropriate stoichiometry had been deposited on to the surface it could then be converted into its oxide form through calcination.

Over the course of the next year this development will focus on how gas pressure and atmosphere flow rates can be optimized during the calcination process to efficiently remove CO_2 from the lattice. It has been confirmed that the kinetics of CO_2 removal from these ceramics is strongly influenced by the partial pressure of CO_2 gas over the solid. Low-pressure high oxygen (O_2) flow rate treatments or low pressure annealing in ozone (O_3) have produced large, multilayer Y-Ba-Cu-O coils with acceptable critical current densities [Poeppel *et al.*, 1990a, 1990b].

Once optimal solution chemistries have been identified, studies into the calcination process will be performed at Argonne National Laboratories, Argonne, IL. ANL, through the Superconductivity Pilot Center Program, will examine outgassing products during the thermal conversion processing step to determine optimal gas atmosphere and pressure parameters for this stage of the process. This work will involve *in situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic and gas chromatographic investigations to probe the chemical transformations that take place when the spray pyrolyzed high- T_c superconducting ceramic formulations are calcined and converted to superconducting films and coatings. The dried salt-complex residues obtained from the spray pyrolysis process will be placed in a controlled environment DRIFT cell (CEDC), (see Figure 11), and the thermal treatment schedule will be monitored by recording the infrared spectra of the solid residue and the gases evolving from the residue. The outgassing species will also be monitored downstream of the DRIFT cell using on-line gas chromatography. Thermal treatment parameters, such as heating rate and gas atmosphere, will be varied in a systematic manner designed to optimize product properties. The useable range of the DRIFT technique is normally limited to $\leq 550^\circ\text{C}$ and total pressures near atmospheric; however, ANL will attempt (on a best effort basis) to perform DRIFT studies of the thermal treatment process under reduced pressure conditions.

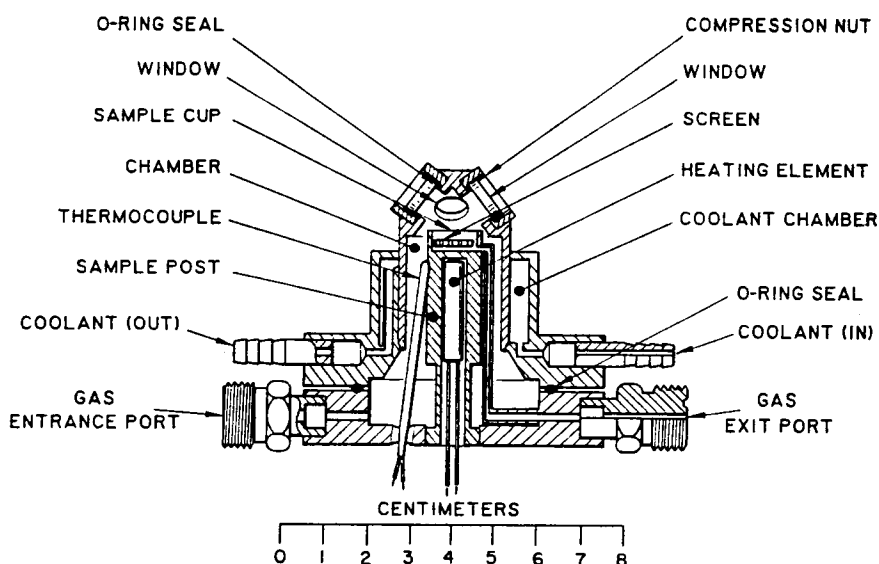


Figure 11. Schematic of the Argonne National Laboratory, DRIFT cell to be used to study the calcination process of the high- T_c superconducting ceramics.

3. TEXTURING THE CERAMIC.

Films prepared via solution processes are inherently porous and in fact need to have a spongy texture in order to allow the outgassed products a pathway to efficiently escape the lattice.

It is therefore necessary to densify the film after calcining. This can be accomplished by cold pressing the ceramic under pressures which densify the film to roughly 10% of its initial thickness. This process is essential to obtaining good c-axis alignment and texture in these ceramics. (See **Figure 12**). Texture can be loosely defined as c-axis alignment and excellent grain boundary alignment.

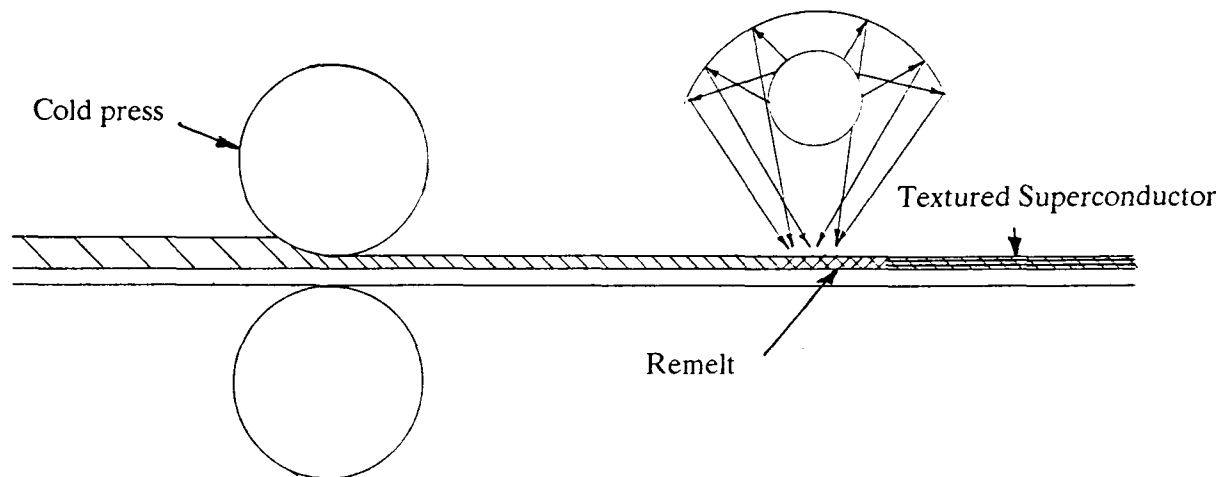


Figure 12. Densification and melt processing leads to films with improved texture.

Once the films have been pressed they should be subject to partial remelt. The purpose of this remelt is to locally rearrange atomic configurations into a phase-stabilized superconducting crystalline phase. A key objective to this aspect of the process is to improve supercurrent transport across the grain boundary.

V. FLUX PINNING IN HIGH- T_c SUPERCONDUCTORS

The generation of flux pinning centers is a critical aspect of high- T_c superconducting magnet technology. Flux pinning centers are deliberately induced defects embedded within the superconductor which have physical dimensions shorter than the coherence length(s) of superconducting Cooper pairs. If they were to have dimensions larger than the coherence length they would induce transitions to the normal state. Fluxoids pinned at a defect center will be prevented from dissipating their kinetic energy through the generation of heat in the system. A difficulty of working with the high- T_c ceramics is that their coherence lengths are very short. However, flux pinning centers can be introduced in these systems using ionizing radiation to randomly introduce point defects throughout the medium.

Researchers at Oak Ridge National Laboratory, Oak Ridge, TN, have recently shown that high energy, heavy-ion ($Z \approx 30$) irradiations can increase intragranular critical current densities to magnitudes of 10^8 A/cm^2 in 5-10 Tesla fields [Christian]. The orientation of the incident irradiation must be aligned parallel to the orientation of the penetrating magnetic flux lines. This irradiation is capable of producing a line (or lattice) of correlated point defects in the crystal roughly 3 to 5 microns in length. (See **Figure 13**). This kind of flux pinning can be likened to a seamstress' hem. A hem made with a greater number of stitches is more resistant to tearing than one made with a single stitch. Analogously, a fluxoid pinned by a single point defect will be more responsive to stress imposed by Lorentz forces than a fluxoid pinned along a line of defects. Increases in the flux pinning potentials appear to be independent upon the crystallographic orientation and are solely dependent on the relative orientation of the line defect to the orientation of penetrating lines of flux.

While this technology represents some major breakthrough, both in terms of assessing the quality of these new materials and focusing attention on how strong a role correlated forces play in these systems, they may not be useful at all in films lacking any kind of texture. The susceptibility of polycrystalline films to magnetic fields at grain boundaries is a far greater problem which does not appear to be remedied through the generation of defects with improved flux pinning potentials.

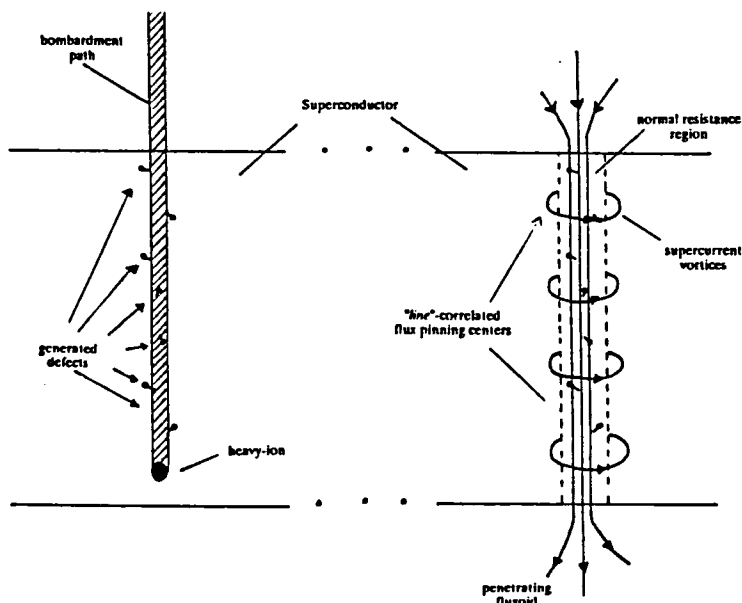


Figure 13. Heavy-ions accelerated to high energy leave a trail of point defects within the crystal along their bombardment path. Enhanced flux pinning will result when the penetrating flux lines are oriented parallel to this defect string.

VI. COMMENTS ON THE SELECTION OF WHICH MATERIALS SYSTEMS

At present there are a number of different compositions in the perovskite crystal family which exhibit high- T_c superconductivity. Each family has been observed to have intrinsic properties unique to its compositional domain. Some are observed to have higher transition temperatures, others have lower anisotropy, and yet others, those with the lower T_c 's have longer coherence lengths. Table I lists these various properties for some of the more well known and technologically important oxide superconductors. All of these factors come into play when considering the practical design and construction of a high field, high- T_c magnet. There is not one single property which can be used to evaluate the relative merits of one materials system over another. The timing of the development of a magnetic coil using various materials systems should immediately take into account the volume of data available on materials processing. Delivery of a coil or component can be severely hampered in cases where insufficient data is available of the temperature-compositional phase relationships and chemical sensitivities of the materials system. Most significantly, more pragmatic development may result if the current focus of development were to shift from transition temperature and more towards coherence lengths and relative isotropy as the alluring intrinsic properties.

VII. COMMENTS ON WHERE TO FOCUS SYSTEM DESIGNS TO TAKE ADVANTAGE OF THESE MATERIALS.

Even though the high- T_c superconductors may still be many years from widespread application in systems the engineering community should start taking a good look now on how to take advantage of these systems. At this stage, and perhaps on into the future, the concept of liquid nitrogen-cooled **high field** superconducting magnets does not appear relevant to any of the materials systems under study. **Figure 14** shows data collected by researchers at Oak Ridge

Table 1

Material System	Tc(K)	Coherence Length (Å)	Known Synthesis Properties
<i>Isotropic</i>			
(Ba,K)BiO ₃	20-30	43	Difficult, (Hygroscopic)
YBa ₂ Cu ₃ O _x	60-90	31	Most well Known
Tl/A/Cu/O	90-120	16-30	Toxic, Not Well Known
(Nd,Ce) ₂ CuO _{4+x}	22-30	70	Not Well Known
Bi-Sr-Pb-Ca-Cu-O	88-110	30-40	Relatively Well Known
Bi-Sr-Sb-Ca-Cu-O	90-132	-----	Unknown
<i>Most Anisotropic</i>			

National Laboratory and the General Electric Research Laboratory, Schenectady, NY, on the magnetic dependence of c-axis oriented Tl-Ba-Ca-Cu-O films prepared by diffusing Tl_2O_3 in spray pyrolyzed Ba-Ca-Cu-O. It is clear that even though this system has one of the highest T_c superconducting phases, and on the basis of its single crystal properties is one of the hardest magnetic materials of this new class of crystals, it is not capable of sustaining a magnetic load until it is cooled to lower temperature. This plot does not describe the upper critical fields which this material system can sustain, rather it diagrams the irreversibility field conditions provoked by defect structures which are extrinsic to the material system itself.

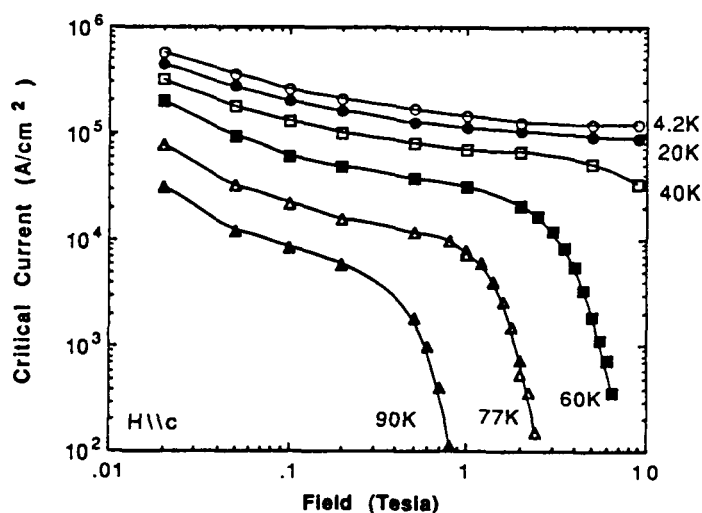


Figure 14. Critical current density versus magnetic load in c-axis aligned polycrystalline Tl-Ba-Ca-Cu-O films. (After Tkaczyk et al.)

Similar behavior has been observed in the Bi-Sr-Pb-Ca-Cu-O family of oxide superconductors which also have T_c 's greater than 100 K. This family of superconductor is generally considered to be the most anisotropic. The anisotropy of these materials is a matter of serious concern to high field magnet design engineers. However, again at lower temperature the anisotropy of this system appears to be lifted and the relative orientation of the crystal *vis-à-vis* the application of thermodynamic stress on the system is less of a problem. (See **Figure 15**).

The points at which these recently discovered materials really come into their own is in the niche of low temperature, very high field applications. By low temperature we include temperatures up to 25-30 K. **Figure 16** compares the magnetic load performance of Bi-Sr-Ca-Cu-O (BiSCCO) superconductors to niobium-titanium (Nb-Ti) and niobium-tin (Nb_3Sn) at 77 K and 4.2 K. Even though the low- T_c superconductors do not operate at liquid nitrogen temperatures, critical current densities in this high- T_c superconductor drop very rapidly with increasing load. However, at liquid helium temperatures the BiSCCO systems can sustain 10^5 A/cm² critical current densities to fields well beyond the operating potential of the conventional superconductors. This mapping should define the design parameters for systems which take advantage of the advances in technology which can be exploited by these new materials systems. As it is now possible to purchase cryostats capable of reaching ≈ 10 K at reasonable cost, the attraction of the high- T_c superconducting ceramics should not emphasize liquid nitrogen operation as much as high magnetic load capability.

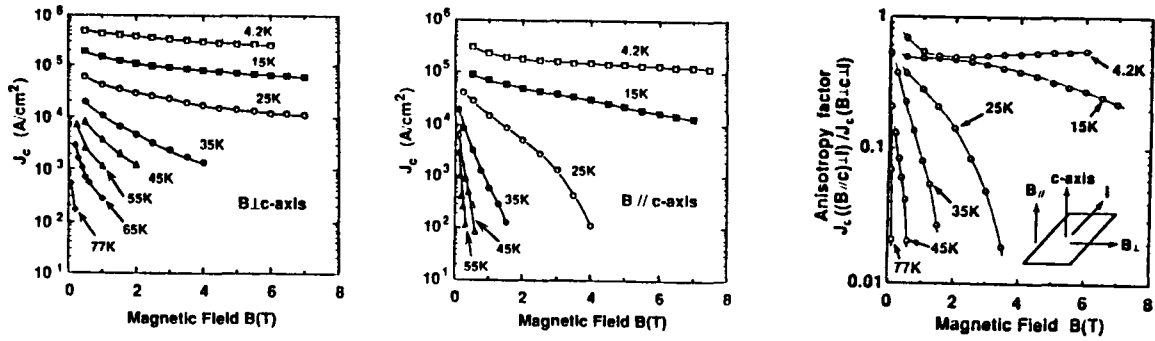


Figure 15. Temperature dependence of the critical current density anisotropy factor for textured 2212 BiSCCO tape [After Kumakura *et al.*].

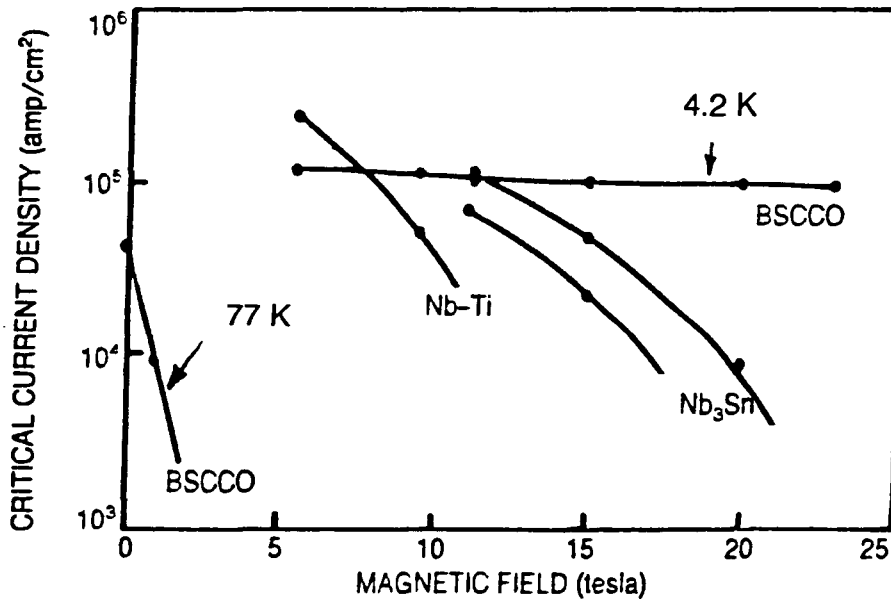


Figure 16. Critical current density versus magnetic load in BiSCCO wires. [After Larbalestier]

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