NASA Conference Publication 10043

AMSAHTS '90
dvances in Materials Science and Applications of High Temperature Superconductors

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Advances in Materials Science and Applications of High Temperature Superconductors

Yury Flom, Editor

Goddard Space Flight Center
Greenbelt, Maryland

Abstracts for a Conference to be held at
Goddard Space Flight Center
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INTRODUCTION

Dear participants,

Welcome to AMSAHTS '90. This document contains the abstracts of the presentations (oral and poster) that will be given on April 2-6, 1990 at Goddard Space Flight Center.

The first conference on a similar subject in the metropolitan Washington area was held at the National Institute of Standards and Technology (formerly the National Bureau of Standards in Gaithersburg, Maryland) in October 1988. Its objective was to advance the understanding of High-Tc superconductivity and to discuss practical applications of bulk and thin film superconductors in space.

The objectives of the second conference are similar to the first, but with more emphasis on materials issues and applications. Again, we organized this meeting in such a way as to provide the best opportunity for the scientific and applications communities to interact with each other by discussions of technical problems as well as to establish fruitful ties and collaborations. This is a perfect time for you to ask questions and debate the issues.

The importance of High-Tc technology for NASA applications cannot be overemphasized. The utilization of superconducting instruments and components in space rests heavily on the progress in understanding of the materials science of High-Tc materials and also on willingness to commit some resources to the engineering of High-Tc devices using presently available superconducting materials and knowledge. To this end, we hope this conference will make an important contribution.

The Editors

"All things come to those who wait.

They come, but come too late."

--Madame Curie

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ORAL PRESENTATIONS

N90-27793

THE SUPERCONDUCTING STATE OF THE HIGH-TRANSITION TEMPERATURE SUPERCONDUCTORS: EXPERIMENTAL BASIS

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Abstract

Experiments on the high-T_c cuprate superconductors continue to narrow the possible theoretical explanations of the phenomenon. Experimental evidence to date points to a BCS-like state, with pairs in singlet s-states, the familiar gap in the excitation spectrum, Type II behavior in a magnetic field and a normal state with fermi liquid origins. Several other features of the superconducting state in the cuprates, however, appear to differ from those of conventional alloy superconductors - these relate to the detailed structure of the gap and to the nature of the coupling mechanism. Recent experiments have helped clarify what these differences are, and together with the earlier experiments, they now impose still stronger constraints on theories of these superconductors. These and other developments will be reviewed.

N90-27794

FLUX CREEP IN $Bi_2Sr_2CaCu_2O_{8+x}$ SINGLE CRYSTALS

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The results of a magnetic study on a $Bi_2Sr_2CaCu_2O_{8+x}$ single crystal are reported. Low field susceptibility (DC and AC), magnetization cycles and time dependent measurements have been performed.

With incresing the temperature the irreversible regime of the magnetization cycles is rapidly restricted to low fields, showing that the critical current J_c becomes strongly field dependent well below T_c. At 4.2 K the critical current in zero field, determined from the remanent magnetization by using the Bean formula for the critical state, is $J_c(//c) = 2\ 10^5\ Acm^{-2}$. The temperature dependence of J_c is satisfactorily described by the phenomenological law $J_c = J_c(0)(1 - T/T_c)^n$, with n=8.

The time decay of the zero field cooled magnetization and of the remanent magnetization has been studied at different temperatures for different magnetic fields. The time decay has been found to be logarithmic in both cases, at least at low temperatures.

At T=4.2 K for a field of 10 kOe applied parallel to the c axis, the average pinning energy, determined by using the flux creep model, is $U_o = 0.010$ eV.

N90-27795

Elliptical Flux Vortices in Polycrystalline $YBa_2Cu_3O_7$

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The formation of an Abrikosov flux vortex with its core axis perpendicular to an anisotropic ($a-c$ or $b-c$) plane in $YBa_2Cu_3O_7$ requires only 1/10 of the energy required by the formation of a vortex with its core axis perpendicular to an isotropic ($a-b$) plane. It is not unusual for 18 to 35 % of "shake and bake" bulk $YBa_2Cu_3O_7$ to consist of empty pockets or voids inside the material. Studies estimate that 75 % of the internal grain boundaries contain $a-b$ planes. If many of the $a-b$ planes are incident upon other grains, then many of the $a-c$ and/or $b-c$ planes must be incident on the voids. Evidently there are a large number of exposed anisotropic planes inside the bulk material. This condition is conducive to the formation of vortices that are perpendicular to the anisotropic planes. The magnetic flux density around such a vortex is constant along contour lines that are elliptical in shape, while the circulating supercurrent density must vary in magnitude along the same contour lines. The impact of this elliptical structure on the possibility of a Kosterlitz-Thouless type phase transition as the bulk material goes from superconducting to normal conducting is discussed. Implications with regard to the excess low frequency electrical noise that occurs at the temperature induced transition are also examined.

PINNING, FLOW AND PLASTIC DEFORMATION OF FLUX VORTICES IN HIGH T_C SUPERCONDUCTORS

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ABSTRACT

In HTSC-materials the vortexes are highly mobile and flexible. This has been reflected in different models of melt of a vortex lattice. I would like to stress another aspect of the problem: an easy nucleation and high mobility of dislocations in the vortex lattice. I consider some models of plastic deformation of vortex lattice as a result of its interaction with a real crystal structure. Depinning is interpreted as yield of plastic flow in vortex medium. Effect of macroscopic defects in crystal structures (pores, inclusions, grain and domain boundaries) is being considered in detail. Available experimental facts on magnetization and a critical current in HTSC and conventional superconductors are discussed from the points of view of depinning to vortexes vs. plastic flow of vortexes vs. plastic flow of vortexes medium.

N90-27797

FLUX FLOW AND FLUX DYNAMICS IN HIGH-T_c SUPERCONDUCTORS

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Because high temperature superconductors, including BYCO and BSCCO, are type II superconductors with relatively low H_{c1} values and high H_{c2} values, they will be in a critical state for many of their applications. In the critical state, with the applied field between H_{c1} and H_{c2}, flux lines have penetrated the material and can form a flux lattice and can be pinned by structural defects, chemical inhomogeneities, and impurities. A detailed knowledge of how flux penetrates the material and its behavior under the influence of applied fields and current flow, and the effect of material processing on these properties, is required in order to apply, and to improve the properties of, these superconductors. When the applied field is changed rapidly, the time dependence of flux change can be divided into three regions, an initial region which occurs very rapidly, a second region in which the magnetization has a ln(t) behavior, and a saturation region at very long times. We have defined a critical field for depinning, H_{cp}, as that field at which the hysteresis loop changes from irreversible to reversible. As a function of temperature we find that H_{cp} is well described by a power law with an exponent between 1.5 and 2.5. The behavior of H_{cp} for various materials and its relationship to flux flow and flux dynamics will be discussed.

N90-27798

MAGNETIC PROPERTIES OF HIGH-T_c SUPERCONDUCTORS: RIGID LEVITATION, FLUX PINNING, THERMAL DEPINNING, AND FLUCTUATION

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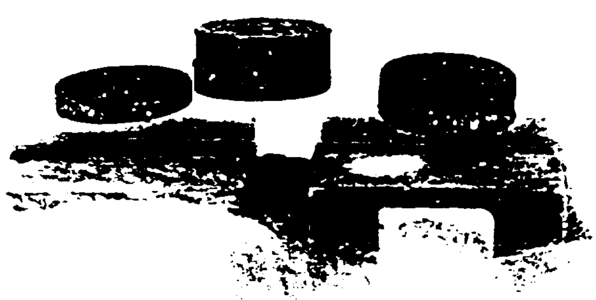
The levitation of high-T_c superconductors is quite conspicuous: Above magnets of low symmetry a disk of these ceramics floats motionless, without vibration or rotation; it has a continuous range of stable positions and orientations as if it were stuck in sand. Some specimens may even be suspended above or below the same magnet.

This fascinating stability, inherent to no other type of levitation, is caused by the pinning of magnetic flux lines by inhomogeneities inside these extreme type-II superconductors.

The talk deals with pinning of magnetic flux in these materials, with flux flow, flux creep, thermally activated depinning, and the thermal fluctuation of the vortex positions in the flux line lattice (often called "flux lattice melting"). Also discussed are the fluctuations of the (nearly periodic) magnetic field inside these superconductors which are caused by random pinning sites and by the finite temperature. These fluctuations broaden the van-Hove singularities observed in the density of the magnetic field by nuclear magnetic resonance and by muon spin rotation.



ORIGINAL PAGE IS OF POOR QUALITY

Disks of $YBa_2Cu_3O_7$ levitating motionless above a magnet

N90-27799

Magnetic Forces in High-T_c Superconducting Bearings

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In September 1987 researchers at Cornell levitated a small rotor on superconducting bearings at 10,000 RPM. In April 1989 a speed of 120,000 RPM was achieved in a passive bearing with no active control. The bearing material used was $YBa_2Cu_3O_7$. There is no evidence that the rotation speed has any significant effect on the lift force. We believe that the attainable rotation speeds in a vacuum will be over 300,000 RPM in the near future.

Magnetic force measurements between a permanent rare-earth magnet and high-T_c superconducting material versus vertical and lateral displacements have been made. A large hysteresis loop results for large displacements, while minor loops result for small displacements. These minor loops seem to give a slope proportional to the magnetic stiffness, and are probably indicative of flux pinning forces.

Experiments of rotary speed versus time show a linear decay in a vacuum. Measurements of magnetic drag forces of a magnetic dipole over a high-T_c superconducting disc of YBCO show that the drag force reaches a constant value, independent of the speed. Damping of lateral vibrations of levitated rotors have been measured which indicates that transverse flux motion in the superconductor will create dissipation.

As a result of these force measurements we have been able to design an optimum shape for the superconductor bearing pads which gives good lateral and axial stability. Recent force measurements on melt-quench processed superconductors indicate a substantial increase in levitation force and magnetic stiffness over free sintered materials. As a result, application of high-T_c supeconducting bearings are beginning to show great promise at this time.

F.C. Moon, M.M. Yanoviak, R. Ware, "Hysteretic Levitation Forces in Superconducting Ceramics," Appl. Phys. Lett., **52** (1988) 1534-1536.

N90-27800

Oxygen Stabilization Induced Enhancement in J_c and T_c of Superconducting Oxides

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In an attempt to enhance the electrical and mechanical properties of the high temperature superconducting oxides, we have prepared high T_c composites composed of the 123 compounds and AgO. The presence of extra oxygen due to the decomposition of AgO at high temperature is found to stabilize the superconducting 123 phase. Ag is found to serve as clean flux for grain growth and precipitates as pinning center. Consequently, almost two orders of magnitude enhancement in critical current densities has also been observed in these composites. In addition, these composites also show much improvement in workability and shape formation.

On the other hand, proper oxygen treatment of $Y_5Ba_6Cu_{11}O_y$ was found to possibly to stabilize superconducting phase with T_c near 250 K. I-V, ac susceptibility and electrical resistivity measurements indicate the existence of this ultra high T_c phase in this compound. Detailed structure, microstructure, electrical , magnetic and thermal studies of the superconducting composites and the ultra high T_c compound will be presented and discussed.

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N90-27801

NONLOGARITHMIC MAGNETIZATION RELAXATION AT THE INITIAL TIME INTERVALS AND MAGNETIC FIELD DEPENDENCE OF THE FLUX CREEP RATE IN $Bi_2Sr_2Ca_1Cu_2O_x$ SINGLE CRYSTALS.

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At the initial time intervals, preceding the thermally activated flux creep regime, fast nonlogarithmic relaxation is found. The full magnetic moment Pm(t) relaxation curve for T=77K, B∥c, B=8,92 mT is shown in Fig.I. The magnetic measurements were made using SQUID-magnetometer. Two different relaxation regimes exist. For $t<t_0\sim 10^2$s the relaxation is almost exponentional as it is illustrated by the insert in Fig.I. Moreover, the Pm(0) value is determined only by the external magnetic field. For large times $t>t_0$ the well known logarithmic dependence appears. It is shown by solid lines in the lower insert Fig.2, T=77K, B∥c, B=4,23 mT for the curve I and B=8,92 mT for the curve 2. The nonlogarithmic relaxation for the initial time intervals may be related to the viscous Abrikosov vortices flow with $j>j_c$ for high enough temperature T and magnetic field induction B. This assumption correlates with our Pm(t) measurements. The characteristic time t_0 separating two different relaxation regimes decreasesas temperature and magnetic field are

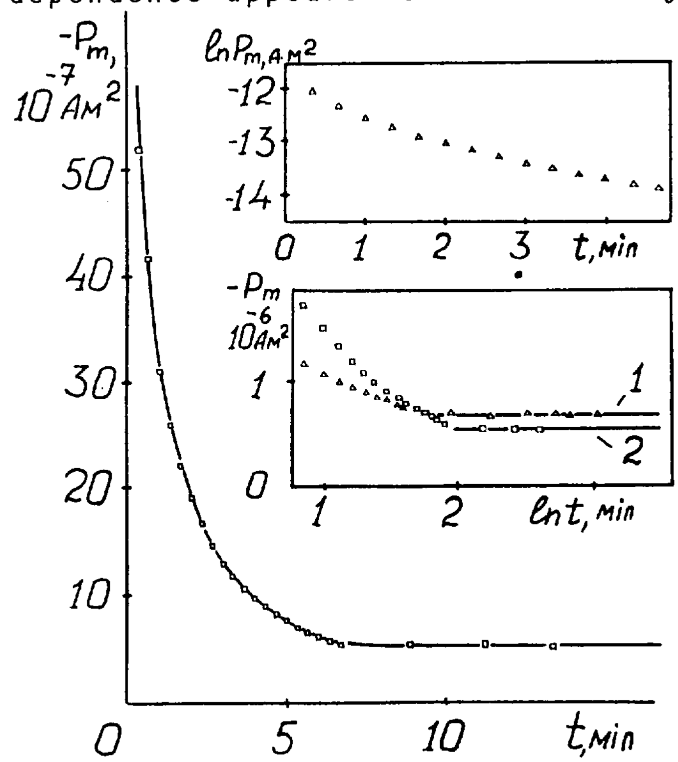

Fig.I

lowered. The logarithmic magnetization relaxation curves Pm(t) for fixed temperature T_0=50,0±0,IK and different external magnetic field inductions B are given in Fig.2. The B values are I–2,45 mT, 2 – 4,5I mT, 3–7,83 mT, 4–I3,84 mT, 5–I8,28 mT, 6–20,22 mT, 7–52 mT. The relaxation rate dependence on magnetic field, $R(B)=dPm(B,T_0)/d(\ln t)$ has a sharp maximum which is similar to that found for R(T) temperature dependences. The maximum shifts to lower fields as temperature goes up. The R(B) dependences for T_0=30K (curve I) and T_0=50K (curve 2) are shown in the insert in Fig.2. The observed sharp maximum is related to a topological transition in shielding critical current distribution and, consequently, in Abricosov vortices density. Taking into account the Anderson's thermally activated flux creep and the Abrikosov vortices distribution according to the Bean's model we have obtained curves shown in the insert in Fig.2 by solid lines.

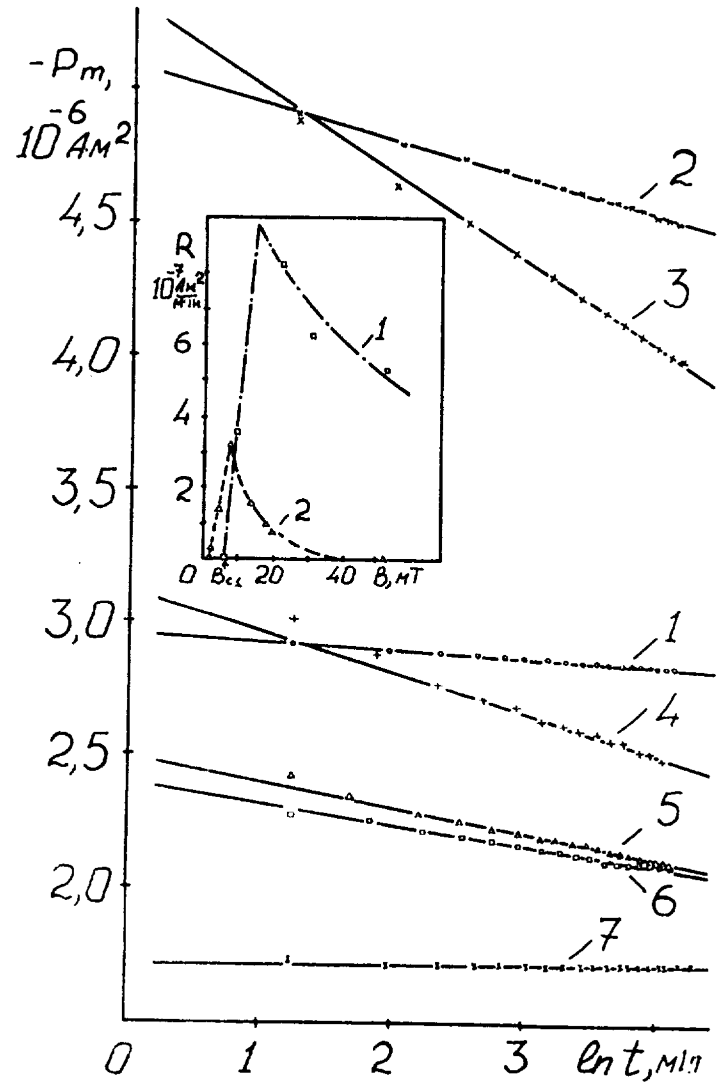

Fig.2

Summarizing, the nonlogarithmic magnetization relaxation for the initial time intervals is found. This fast relaxation has almost an exponentional character. The sharp relaxation rate R(B) maximum is observed. This maximum corresponds to a topological transition in Abrikosov vortices distribution.

N90-27802

SCALING BEHAVIOUR OF RELAXATION DEPENDENCIES IN METALOXIDE SUPERCONDUCTORS

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ABSTRACT

Superconducting glass state has been investigated in different types of metaloxide ceramics /Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, Ba-Pb-Bi-O/ using the highly sensitive SQUID magnetometer. The analysis of long-time relaxation processes of thermoremanent magnetization

$$M^{trm}(t) = M_O - S\ln t$$

displayed scaling depencence of the decay rate $S = -dM/d\ln t$ on quantity of trapped magnetic flux M_O: $\lg S = 3\lg M_O$ - observed universal dependence $S \sim M_O^3$ seems to one of the features of superconducting glass state in metal-oxide ceramics.

N90-27803

MICROSTRUCTURE AND MAGNETIZATION OF DOPED Y-Ba-Ca-O MATERIALS PREPARED BY THE MELT QUENCH AND POST ANNEALING METHOD

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Y-Ba-Cu-O bulk materials prepared using the melt quench and post annealing method have been shown to have very high maximum as well as remanent magnetization. Studies have been carried out on materials prepared using this method which deviate from the Y:Ba:Cu = 1:2:3 stoichiometry. In one series of materials, only the stoichiometry was changed, in particular by introducing an excess of yttrium. In other cases, dopants including several rare earths were introduced. Effects of variations in composition on microstructure and phase evolution are discussed, as well as effects on the magnetic susceptibility and on the magnetization. The results show that doped materials can exhibit improvements in magnetic properties. Furthermore, the use of dopants sheds light on the role of defect sites in flux pinning.

N90-27804

EFFECT OF SHOCK PRESSURE ON THE STRUCTURE AND SUPERCONDUCTING PROPERTIES OF Y-Ba-Cu-O IN EXPLOSIVELY FABRICATED BULK METAL-MATRIX COMPOSITES

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While it is now well established that copper-oxide-based powder, or virtually any other ceramic superconductor powder, can be consolidated and encapsulated within a metal matrix by explosive consolidation,[1,2] the erratic superconductivity following fabrication has posed a major problem for bulk applications. The nature of this behavior has been found to arise from microstructural damage created in the shock wave front, and the residual degradation in superconductivity has been demonstrated to be directly related to the peak shock pressure, as illustrated in Fig. 1a-d. The explosively fabricated or shock loaded $YBa_2Cu_3O_x$ ($x \cong 7$) examples exhibit drastically altered ρ (or R) - T curves (Fig. 1c-d). The normal state resistivity is increased by as much as 20 to 100 times after explosive (shock wave) processing and shows a negative temperature dependence having essentially the same slope; characteristic of semiconductor-like behavior. The superconducting transition is considerably broadened to lower temperatures with increasing shock pressure. Correspondingly, as shown in Fig. 1a, the range of order is reduced and the orthorhombic peak broadening is increased in proportion to increasing shock pressure (Fig. 1b).

The deterioration in superconductivity is even more noticeable in the measurement of a.c. magnetic susceptibility and flux exclusion or shielding fraction (χ/χ_0) which is also reduced in proportion to increasing peak shock pressure. The high-frequency surface resistance (in the GHz range) is also correspondingly compromised in explosively fabricated, bulk metal-matrix composites based on $YBa_2Cu_3O_7$.

The superconducting as well as the normal-state conducting behavior of $YBa_2Cu_3O_x$ is known to be sensitive to the value of x.[3] Since the oxygen atoms in the b chain are the most weakly bound, the loss of oxygen during shock loading or explosive fabrication was originally suspected to be the cause of the degradation observed in Fig. 1c-d. However, comparative thermogravimetric analysis of the samples subjected to the lower peak shock pressures indicated that while the shocked samples exhibited higher chemical reactivity, consistent with the peak broadening ($\Delta 2\Theta$) shown in Fig. 1a-b, there was no loss of oxygen,[4] and this was further supported by the fact that, as shown in Fig. 1e-f, the samples failed to recover T_c upon annealing and cooling in flowing oxygen until about 930°C. This difficulty in recovering the resistivity-temperature signature in shock-loaded, bulk $YBa_2Cu_3O_7$ is in marked contrast to the behavior of ion-beam irradiated thin films where the damage is easily annealed out and T_c restored even at room temperature.[5] Consequently, the nature of the damage (the microstructural defects generated) may be very different in each case. Furthermore, variations in oxygen stoichiometry (x) have been shown to shift the T_c onset (T_c decreasing with decreasing x)[3] while the onset remains at $T_c \cong 90K$ at low shock pressures (Fig. 1c).

Transmission electron microscopy (including lattice imaging techniques) is being applied in an effort to elucidate the fundamental (microstructural) nature of

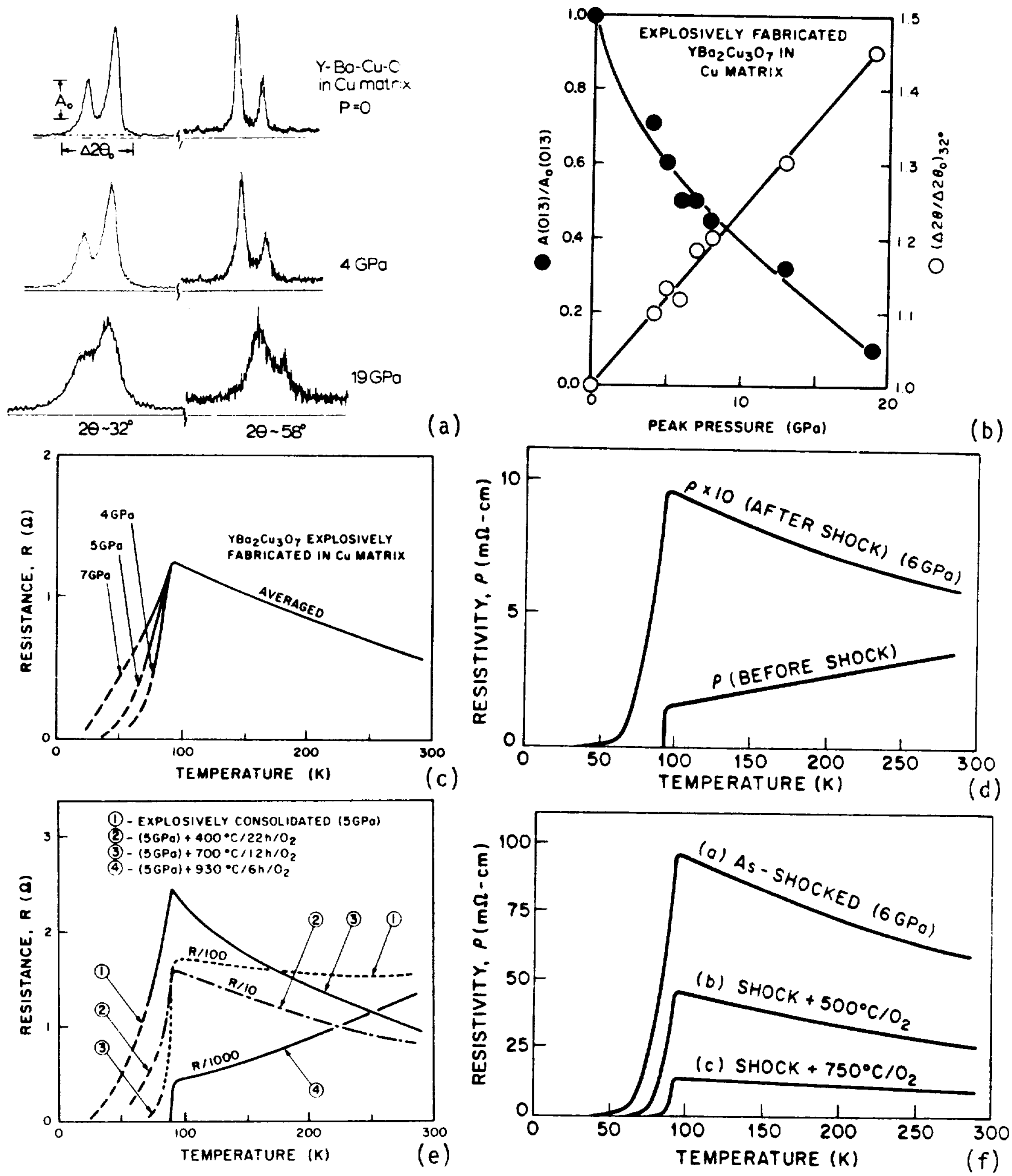

FIG. 1: X-ray (orthorhombic) split-peak signature variation for explosively fabricated $YBa_2Cu_3O_7$ powder (a) and quantitative variation with pressure (b). (c) and (d) show ρ (or R) - T curves for explosively fabricated (consolidated) $YBa_2Cu_3O_7$ powder extracted from a copper matrix and sintered bar of $YBa_2Cu_3O_7$ before and after plane-wave shock loading, respectively. (e) and (f) show corresponding annealing and T_c recovery of explosively fabricated and plane-wave shock loaded $YBa_2Cu_3O_7$ (data in (d) and (f) are reproduced from reference 4).

the shock-induced degradation of superconductivity and normal state conductivity. One "focus" of TEM observations has assumed that, as illustrated schematically in Fig. 2a-b, oxygen displaced from b-chains rather than oxygen-vacancy disorder in the basal plane of oxygen deficient $YBa_2Cu_3O_x$ (6.75 > x > 6.25) may be a prime mechanism. Shock-wave displaced oxygen may also be locked into new positions or interstitial clusters or chemically bound to displaced metal (possibly copper) atoms to form precipitates, or such displacements may cause the equivalent of local lattice cell changes as a result of stoichiometric changes. Some evidence for these phenomena are illustrated in the TEM images reproduced in Fig. 2c-d.

While the shock-induced suppression of T_c is not desirable in the explosive fabrication of bulk metal-matrix superconductors, we hope it may be turned into an advantage if the atomic-scale distortion can be understood and controlled as local flux pinning sites. The peak shock pressure cannot be lowered without compromising the cladding of the metal matrix assembly and some requisite density for the consolidated, encapsulated superconducting powder. Consequently, some adjustments must be made in other process or materials parameters.

This research is supported by the DARPA HTSC Program under Grant ONR-N00014-88-C-0684 and in part by NASA (Goddard)--SBIR Contract NAS5-30504 through Monolithic Superconductors, Inc.

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†Dr. L. H. Schoenlein is on leave from Battelle Pacific Northwest Laboratory, Richland, WA.

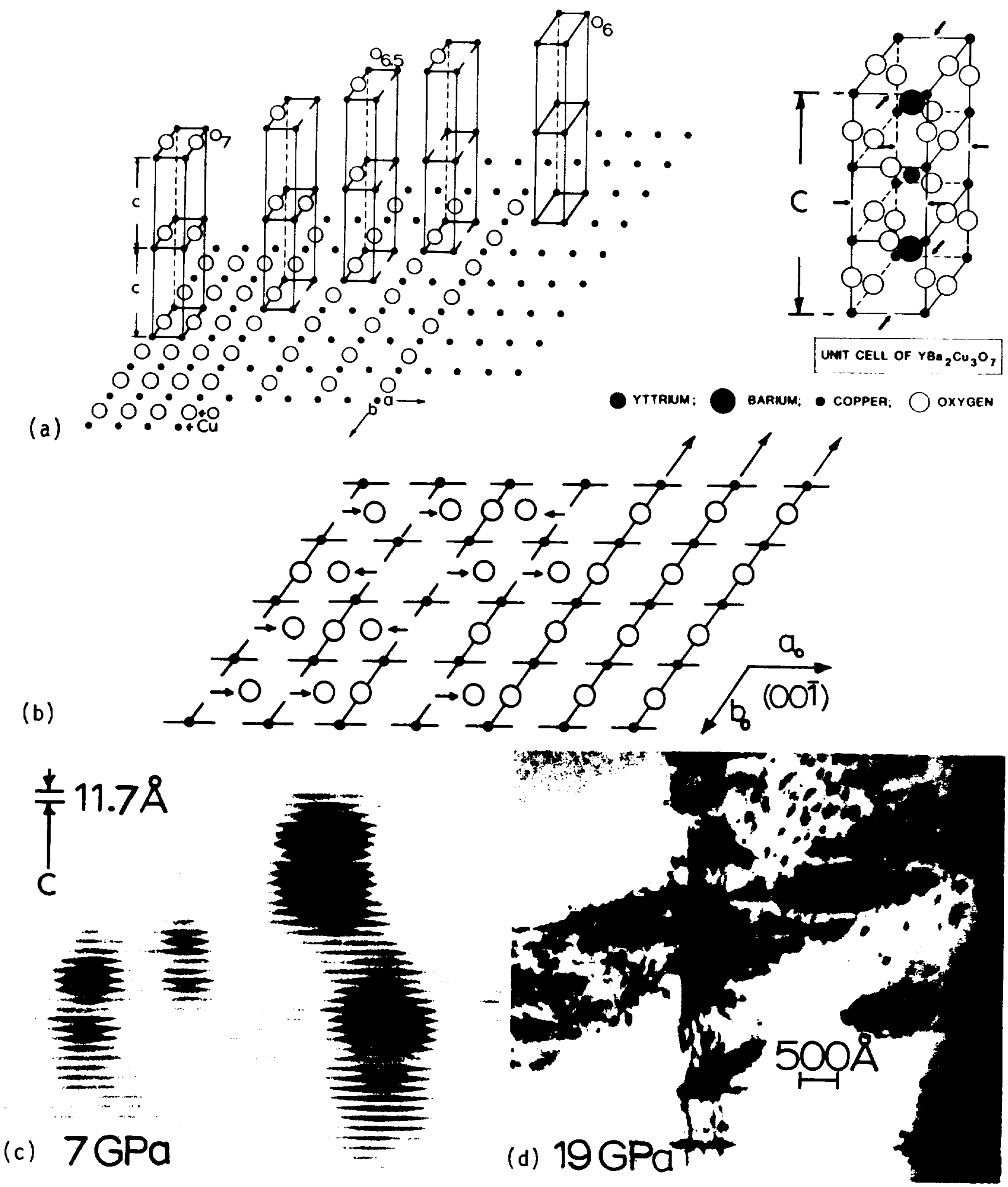

FIG. 2: Basal-plane oxygen (vacancy) order-disorder along b-chains with decreasing oxygen (a) and simple oxygen displacement creating interstitial defects in the shock front (b). (c) and (d) show TEM lattice and diffraction contrast images of atomic clusters, loops, and lattice strain in the explosively consolidated $YBa_2Cu_3O_7$.

N90-27805

PRODUCTION OF SUPERCONDUCTOR/CARBON BICOMPONENT FIBERS

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Certain materials are unable to be drawn or spun into fiber form due to their improper melting characteristics or brittleness. However, fibrous samples of such materials are often necessary for the fabrication of intricate shapes and composites. In response to this problem, researchers at Clemson University developed and patented a unique process, referred to as the "piggyback process", to prepare fibrous samples of a variety of nonspinnable ceramics.[1] In this technique, specially produced C-shaped carbon fibers serve as "micromolds" to hold the desired materials prior to sintering. Depending on the sintering atmosphere used, bicomponent or single component fibers result.

While much has been demonstrated worldwide concerning the $YBa_2Cu_3O_{7-x}$ superconductor, fabrication into unique forms has proven quite difficult. However, a variety of intricate shapes are necessary for rapid commercialization of the superconducting materials. Researchers at Clemson University are currently investigating the potential for producing fibrous samples of the $YBa_2Cu_3O_{7-x}$ compound by the piggyback process.

The carbon fibers employed for this research were melt spun in house from Amoco petroleum pitch, oxidized, and carbonized to produce high purity fibers with an approximate web distance of 30 microns and a length of 1-2 inches. The $YBa_2Cu_3O_{7-x}$ powders were prepared by combining stoichiometric amounts of Y_2O_3, $BaCO_3$, and CuO, calcining in air to ~900°C, and sintering in flowing oxygen to 950°C. Samples were analyzed for purity using X-ray diffraction and a standard four-probe electrical resistivity measurement. An average transition temperature of ~90K was obtained.

Various organic and acrylic materials were investigated to determine suspending ability, reactivity with the $YBa_2Cu_3O_{7-x}$ compound during long term storage, and burn out characteristics. It was found that several of the tested materials reacted with the copper ions present in the compound and sufficiently altered the stoichiometry such that superconductivity was lost. The best suspension was produced from a mixture of superconducting powder ($\leq 37\mu m$) with polyvinyl butyral in ethanol.

Carbon fibers coated with the various suspensions were subjected to low temperature firings (< 400°C) in air to burn out the organic radicals present. To retain the flexibility, strength, and protection of the carbon backbone, the composite fibers were subsequently fired to 950°C in an inert atmosphere to sinter the ceramic. During a series of thermogravimetric analyses of the $YBa_2Cu_3O_{7-x}$ compound in inert atmospheres, it was discovered that a significant amount of oxygen is released from the structure at high temperatures. A slightly smaller quantity of oxygen was found to be released during processing in oxidizing atmospheres. However, in the presence of flowing oxygen or air, the lost oxygen is easily regained during slow cooling. Results indicated that the majority of this oxygen was "picked up" in the temperature range of 650°C-300°C. As unprotected carbon can withstand up to 450°C in oxidizing atmospheres, a low temperature anneal in flowing oxygen was employed to restore oxygen to the superconducting structure after inert atmosphere processing.

However, the oxygen released from the $YBa_2Cu_3O_{7-x}$ compound at high temperatures reacted with the unprotected carbon fiber, resulting in the formation of a carbon monoxide atmosphere along the interfacial area. The presence of carbon monoxide served to further reduce the $YBa_2Cu_3O_{7-x}$ compound over time. Due to their unique valency configuration, the copper ions were found to reduce most readily, and patches of copper were visible on the fiber surface after the inert atmosphere processing. The low temperature oxygen anneal produced an insulating layer of CuO along the fiber surface. The formation of this black layer of CuO was indiscernable from the normal superconducting black layer on sight but was evident by resistivity measurements and energy dispersive X-ray analysis (EDAX).

To substantiate these results, bulk materials of high purity graphite and $YBa_2Cu_3O_{7-x}$ were placed in contact and heated to 950°C in an inert atmosphere. After holding two hours at the peak temperature, a significant layer of copper metal was present at the interface. EDAX results confirmed that the stoichiometric copper content of the material was incrementally changed throughout the bulk material. Superconductivity could not be restored in the sample, even after processing in flowing oxygen for 5 hours at 950°C.

To eliminate interfacial reactions, a number of potential barrier layers were proposed, including silicon carbide, gold, silver, copper, and nickel. At present, however, only the use of nickel has been studied in depth. For preliminary experiments, thin foils of nickel were placed between bulk superconductor and graphite materials, and the samples were heated in an inert atmosphere to 950°C. No visible copper migration occurred, suggesting the interfacial reaction was significantly impeded. The small amount of oxygen released from the superconductor was restored by a low temperature anneal in flowing oxygen. The resulting superconductor sample was found to exhibit the Meissner effect, and its composition was confirmed by X-ray diffraction.

To employ these results with fibrous samples, a thin, dense coating of nickel was applied to the carbon fiber surface using an electroless technique. Fibers treated with the electroless coating were filled with the superconductor suspension and heat treated in the same manner as before. No visible copper migration was present after inert atmosphere processing. Following a low temperature oxygen anneal, the fibers were examined using a Debye-Scherrer camera for small sample powder diffraction. Results indicated that the orthorhombic, superconducting phase of the compound was present (i.e. by the presence of a double peak at ~59°).

However, proper four point probe electrical measurements of the fibers have proven quite difficult and nonreproducible. Small microcracks have been discovered by electron microscopy, possibly resulting from a thermal expansion mismatch or an improper rate of heating or cooling. In addition, the resulting superconducting material is fairly porous, due to only short term soaks at the peak temperature and the burn out of the large amount of liquids required to produce the stable suspension. Both microcracking and porosity have been targeted to decrease overall critical current density in the superconducting materials. Therefore, the passing of very small currents through the fibers (i.e. ≤ 1 nA) may result in a reproducible measurement. At present, the smallest current passed through the samples has been on the order of 1mA. Nevertheless, for commercial applications, the bicomponent fibers must exhibit a much higher critical current density than this indicates.

While many questions have been answered with respect to the interfacial reactions between $YBa_2Cu_3O_{7-x}$ and carbon, much work is still necessary to improve the quality of the sintered material if the fibers produced are to be incorporated into useful composites or cables. Additional research is necessary to (1) evaluate the quality of the barrier layer during long soakings at the peak temperature; (2) adjust the firing schedule to avoid microcracking and improve densification; and (3) increase the solids loading in the superconductive suspension to decrease porosity.

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Acknowledgements

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All efforts in the production of carbon fibers were supported by Amoco and the Clemson Advanced Engineering Fibers Laboratory.

Figures

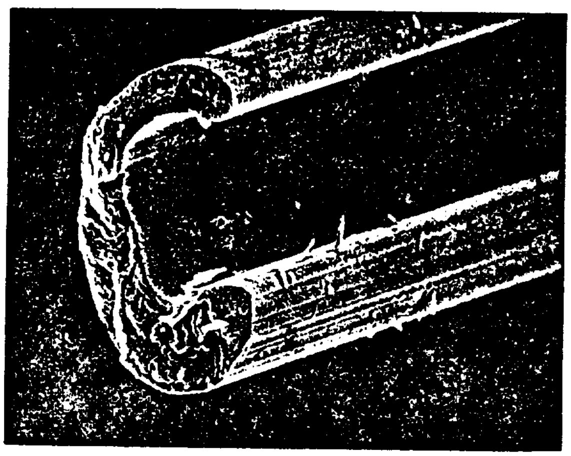

Figure 1. Electron micrograph of melt spun C-shaped carbon fiber

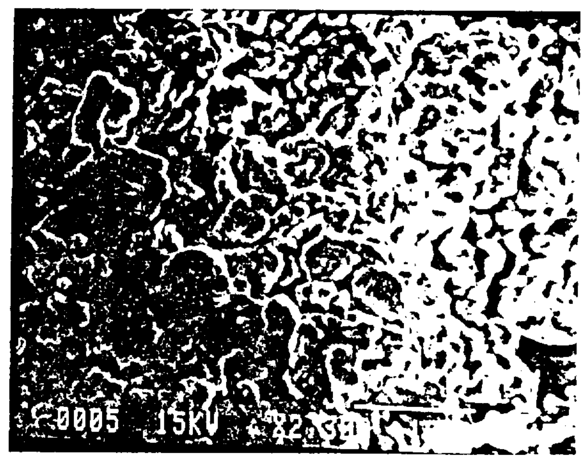

Figure 2. Electron micrograph of porous superconductor powder sintered inside the carbon fiber

N90-27806

HIGH-T_c SQUID APPLICATION IN MEDICINE AND GEOPHYSICS

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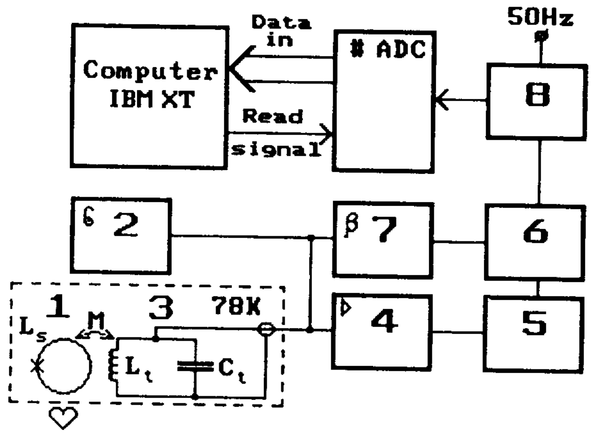
In our Laboratory a high-T_c one-hole squid was built from $Y_1Ba_2Cu_3O_{7-x}$ ceramics obtained by a standard procedure of solid state reaction. The ceramics with critical current density J_c>100 A/cm^2 was selected.

In the middle of 10×10×2mm ceramics pellet a 0.8mm hole was drilled in which superconducting loop of the squid was located. Between the hole and the edge of the pellet a cut was mechanically filed out with a bridge inside it connecting the superconducting ring. The bridge with characteristic size of 10μm must have the critical current $I_c \simeq 10\mu A$ for the squid hysteretic parameter $\beta=2\pi L_S I_C/\phi_o$ to be less than (5÷10). Here - L_S - quantum loop inductance, ϕ_o - magnetic flux quantum.

In fig.1 a scheme of the magnetometer is presented. The squid - 1 was pumped, as usual, at high frequency ($f_p \simeq 20$MHz) by the rf-generator - 2 and was tested by the tank circuit $L_T C_T$ - 3, inductively coupled with it which was tuned on resonant frequency - ω_p. In order to obtain the maximum response the coefficient of coupling is chosen by the relation $K^2 Q \simeq \pi/2$, where Q is the quality factor of the circuit. The circuit voltage is amplified by a low-noise rf-amplifier - 4 and is detected by an amplitude detector - 5. The detected signal is transformed by low frequency units - 6,7, which provide flux-locked regime to the magnetometer. All these units are completely identical to electronic units of low-temperature squids.



Main characteristics of the magnetometer

The squid inductance can be measured experimentally, by the method described before. The resonant frequency shift of the tank circuit, which arise influenced by the squid, the connection of the squid with this circuit and the squid inductance are evaluated:

$$L_S=I_o^2 C_T/\phi_o^2(\omega_{p1}^{-2}-\omega_{p2}^{-2}),$$

where I_o - current value through the L_T, changing the squid flux on ϕ_o;

C_T - tank circuit capacity;

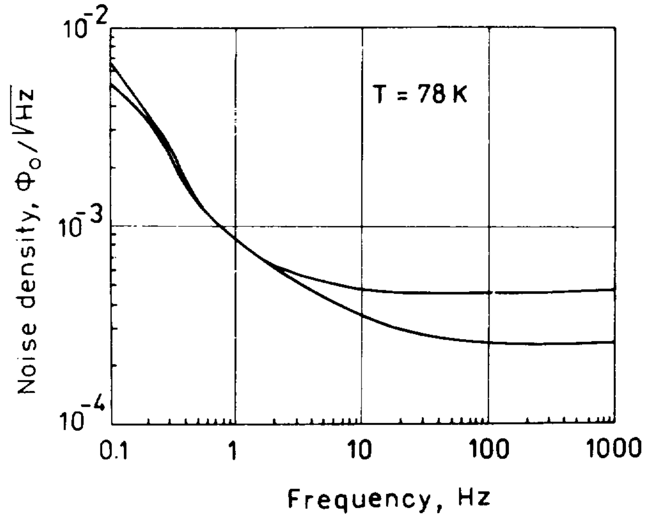
ω_{p1} -tank circuit resonant frequency measured at a low pumping level when the contact remains superconductive and dissipative processes in the squid are not observed;

ω_{p2} -tank circuit resonant frequency measured at a high pumping level when Josephson contact is not superconducting.

The measurements have shown that at superconducting ring diameter of 0.8mm $I_o \simeq (0.8\pm 0.1)\mu A$, $k \simeq (0.15\pm 0.01)$, $C_T \simeq (220\pm 10)pF$, $f_{p1}=(17.7\pm 0.1)MHz$, $f_{p2}=(17.35\pm 0.1)MHz$ and squid self inductance $L_S=(2.5\pm 0.1)\times 10^{-10}H$.

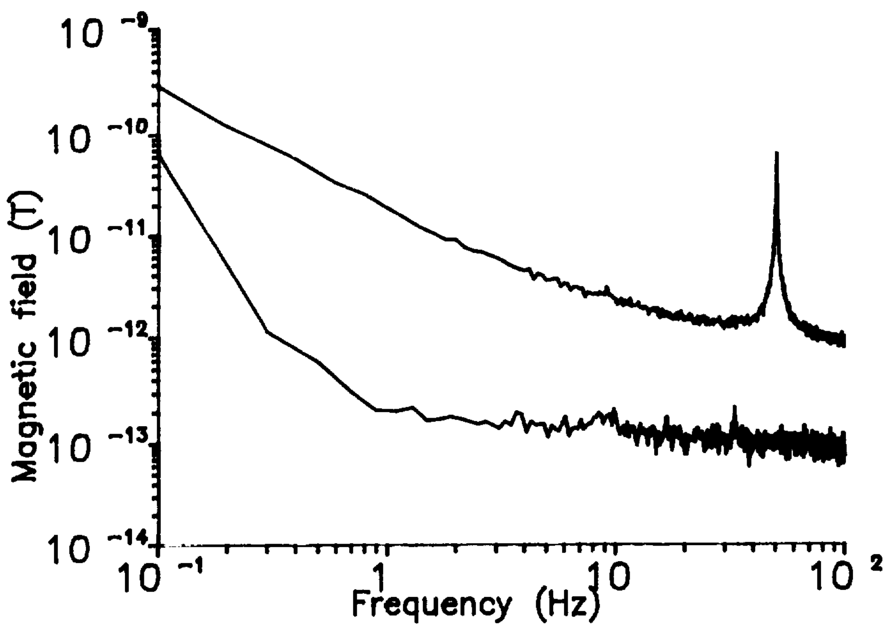
Spectral noise density dependence on magnetic flux ϕ_N is presented in fig.2. The calculations give us energy relation in the white noise region $\varepsilon=\phi_N^2/2L_S \simeq 9\times 10^{-28} J/Hz$.

The calibration in the Helmholtz rings has shown the volt-oersted field period to be $B_o=3.8\times 10^{-10}T$, knowing which one can



easily obtain the estimate of the squid field sensitivity: $\langle B_N \rangle = \langle \phi_N \rangle B_o/\phi_o$, where $\langle \phi_N \rangle$ - squid spectral noise density on magnetic flux.

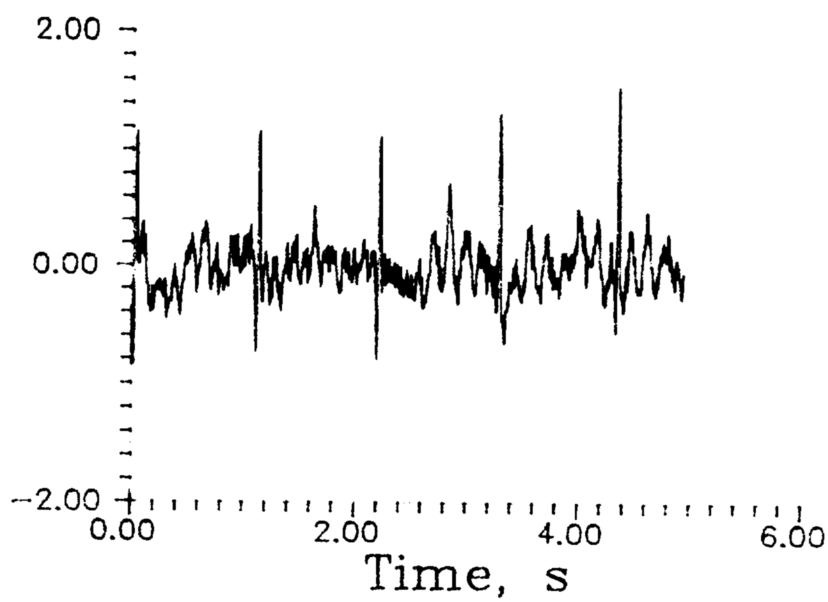
In fig.3 the spectral noise density on magnetic field of the magnetometer based on the high-T_c (T=77K) one-hole squid is shown (lower curve). It is evident that in the white noise region self field sensitivity is $\tilde{}10^{-13}T/Hz^{1/2}$. Thus, even today the high-T_c squids are inferior only to the best low-temperature squids at T=4.2K.



In fig.3 the ambient noise spectrum is depicted (upper curve), which was read at night at a distance of 20m from the nearest Laboratory building in Dubna. It is clearly seen, that the ambient noise is considerably higher than the squid self-noise. Thus, we can suppose that such a magnetometer can be used for geophysical investigations.

One of the most interesting fields of the squid-based magnetometer application is biomagnetism, particularly, the human heart magnetocardiogram measuring. The low-temperature squids for a long time have been used in this area and to the present moment many interesting and important scientific results have been obtained.

In fig.4 a magnetocardiogram is shown , which was recorded by the above described magnetometer in a bandwidth of 60Hz. The magnetocardiogram was taken in an aluminium box (~5mm wall) within 20m from the nearest Laboratory building.



As a sensitive element, as mentioned before, the one-hole squid was operating. The squid inside the sealed copper thinwall container was placed on the bottom of the biomagnetic nitrogen cryostat. The squid was placed ~25mm above the human chest.

The observations have show that the main noise contribution was not due to the squid but to the Earth's magnetic field variations,industrial inductions and mainly to the vibrations caused by liquid nitrogen boiling and by vibrations of the box. Further attempts in our work are needed in view to reduce the magnetic noise inductions. Nevertheless, the estimations promise us the maximum signal/noise relation of the high-T_c squid-magnetocardiometer to be (at the MkH amplitude - 20pT) not less than 10:1 in a bandwidth of 60Hz. Apparently, such resolution would be enough not only for steady cardiogram reading but even for thin structure investigation at average technique application.

OXIDE SUPERCONDUCTORS UNDER MAGNETIC FIELD

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One of the current most serious problems for the oxide superconductors from the standpoint of practical application is the various novel features derived mainly from their extremely short coherence. In particular, the coherence length so far observed in the cuprate superconductors is in the range of 0.1 nm perpendicular to the CuO_2 plane. This seems to be creating most of the difficulties in the device fabrication and in the performance under the magnetic field.

In this report, some of the superconducting properties under the magnetic field will be discussed in terms of the short coherence length. First of all, it is pointed out that the widely accepted criterion on the Meissner fraction to represent the quality of the specimen is baseless unless very special precautions are taken. The Meissner fraction has been systematically measured under various intensities of the magnetic field and for various morphologies of the samples, including powder, poly- and single-crystals of different superconducting oxides. It is strongly dependent on the field intensity and the size of the specimen. A model will be presented based on the gradual strengthening of the pinning force with decrease in temperature and the weak coupling at the grain boundaries.

Secondly, the broadening of the superconducting transition under the magnetic field is discussed. This is observed significantly only when the field is applied perpendicular to the basal plane and the relative orientation of the current to the field is insignificant in determining the extent of the broadening. Besides, the change in the strength of the pinning force does not affect the width of the broadening. From these observations discussions will be made on a model based on the "giant fluctuation". Based on this model, it is predicted that the coherence length along the c-axis will be the single most important material parameter to determine the performance of the superconductor under a strong magnetic field. It seems that BYCO is superior in this regard to Bi- or Tl-systems as far as the performance at 77K is considered, although another material with the coherence length slightly longer along the c-axis is still highly desired.

N90-27808

Laser Ablated High T_c Superconducting Thin $YBa_2Cu_3O_{7-x}$ Films on Substrates Suitable for Microwave Applications

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The development of high temperature superconducting $YBa_2Cu_3O_{7-x}$ thin films on substrates suitable for microwave applications is of great interest for evaluating their applications for space radar, communication, and sensor systems. Thin films of $YBa_2Cu_3O_{7-x}$ have been formed on $SrTiO_3$, ZrO_2, MgO, and $LaAlO_3$ substrates by laser ablation. The wavelength used was 248nm from a KrF excimer laser. During deposition the films were heated to 600° C in a flowing oxygen environment, and required no post annealing. The low substrate temperature during deposition with no post annealing gave films which were smooth, which had their c-axis allighned to the substrates, and which had grains ranging from 0.2 to 0.5 microns in size. The films being c-axis aligned gave excellent surface resistance at 35 GHz which was lower than that of copper at 77 K. At present, $LaAlO_3$ substrates with a dielectric constant of 22, appears suitable as a substrate for microwave and electronic applications. The films have been characterized by resistance-temperature measurements, scanning electron microscopy, and x-ray diffraction. The highest critical transition temperatures(T_c) are above 89K for films on $SrTiO_3$ and $LaAlO_3$, above 88K for ZrO_2, and above 86K for MgO. The critical current density(J_c) of the films on $SrTiO_3$ is above 2×10^6 amperes/cm^2 at 77K. The T_c and J_c are reported as a function of laser power, composition of the substrate, and temperature of the substrate during deposition.

Resistance versus temperature for a $YBa_2Cu_3O_{7-x}$ film on $LaAlO_3$ is shown in fig. 1. Its transition temperature is 89.6 K.

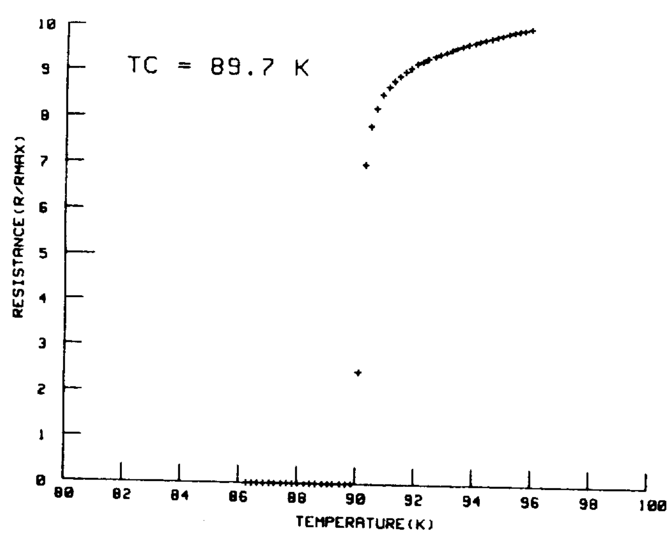

Fig. 1 Laser ablated $YBa_2Cu_3O_{7-x}$ Film on $LaAlO_3$.
Deposition temperature 610°C and oxygen pressure of 170 mtorr.

N90-27809

LASER SURFACE INTERACTIONS OF HIGH-T_c SUPERCONDUCTORS*

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During the past two years, one of the most exciting research fields in science has been the study of the newly discovered high-T_c metal oxide superconductors. Although many theoretical models were proposed, there has been no general agreement on any theory to explain these materials. One of the "peculiar" features of these high-T_c materials is the noninteger number of oxygen atoms. The oxygen content is extremely critical to the superconductive properties. Take $YBa_2Cu_3O_{7-x}$ as an example. Its superconductive properties disappear whenever x is larger than 0.5. The existence of Cu^{+3} has been considered to account for x less than 0.5. However, our results from mass spectroscopy of laser desorbed species indicate that significant quantities of oxygen molecules are trapped in the bulk of these high-T_c superconductors. It appears that these trapped oxygen molecules may play key roles in superconductive properties.

Preparation of superconductive thin films are considered very important for the applications of these new superconductors for the electronics industry. Fluorescence spectra and ion spectra following laser ablation of high-temperature superconductors were obtained. A real time monitor for preparation of superconductive thin films can possibly be developed.

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N90-27810

PERSPECTIVES ON HIGH TEMPERATURE SUPERCONDUCTING ELECTRONICS

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ABSTRACT

The major challenges in making HTSC electronics viable are predominantly materials problems. Unlike their predecessors the metal oxide-based superconductors are integratable with other advanced technologies such as opto- and micro-electronics. The materials problems to be addressed relate to the epitaxial growth of high quality films, highly oriented films on non-lattice matched substrates, heterostructures with atomically sharp interfaces for junctions and other novel devices, and the processing of these films with negligible deterioration of the superconducting properties. I will illustrate these issues with results based on films prepared in-situ by a pulsed laser deposition process. Films with zero-transition temperatures of 90 K and critical current densities of 5*10E6 A/cm^2 at 77 K have been prepared by this technique. Ultra-thin films, less than 100 A show Tc>80 K, supporting the idea of two-dimensional transport in these materials. By the use of appropriate buffer layers, films with Tc of 87 K and Jc of 6*10E4 A/cm^2 have been fabricated on silicon substrates. Sub-micron structures with Jc>2*10E7 at 10 K have been fabricated. Results on nonlinear switching elements, IR detectors and microwave studies will be briefly summarized.

N90-27811

UPCOMING PLANETARY MISSIONS AND THE APPLICABILITY OF HIGH TEMPERATURE SUPERCONDUCTOR BOLOMETERS

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Planetary missions to Mars and beyond can last 11 years and longer, making impractical the use of stored cryogens. Passive radiative coolers and single-stage mechanical coolers remain possibilities, although the power and mass of the mechanical cooler may prove problematical. Either option can provide about the same lower limit of temperature, which in the case of the Galileo mission to Jupiter is 75 K for a radiatively cooled focal plane.

For these temperatures far infrared (longer than 25 μm wavelength) observations are completely limited by detector performance. While high sensitivity InSb detectors may be used at 5 μm and somewhat lower sensitivity HgCdTe detectors may be used out to 20 μm or so, beyond 25 μm low sensitivity, essentially room-temperature thermal detectors must be used. These thermal detectors are no better than the Schwarz-type thermopile used on Voyager/IRIS, launched in 1977 to Jupiter, Saturn, Uranus and Neptune. No thermal detector currently takes advantage of operation at ~75 K, where the thermal noise is ~30 times lower than at 300 K.

CRAF and CASSINI, both using the newly developed Mariner Mark II spacecraft, will be the next outer planet missions after Galileo; they are intended to provide information on the origin and evolution of the solar system. CRAF is a cometary rendezvous mission slated for a 1994 launch. CASSINI has been chosen by ESA as its next science new start in the face of stiff competition, may be selected by NASA for a fiscal year (FY) 90 new start, and will be launched by a Titan IV/Centaur in 1996. It will fly by Jupiter in 2000, inject an ESA-supplied probe into Titan in 2002, and take data in Saturn orbit from 2002 to 2006.

NASA/Goddard is currently developing a prototype Fourier transform spectrometer (CIRS) under PIDDP funding (Planetary Instrument Definition and Development Program) that will be proposed for the CASSINI mission. The baseline infrared detectors for CIRS are HgCdTe to 16 μm and Schwarz-type thermopiles from 16 to 1000 μm. The far infrared focal plane could be switched from thermopiles to high temperature superconductor (HTS) bolometers between now and 1996.

An HTS bolometer could be built using the kinetic inductance effect, or the sharp resistance change at the transition. The transition-edge bolometer is more straightforward to implement and initial efforts at NASA/Goddard have been directed to that device. With internal funding (DDF, the Director's Discretionary Fund), Goddard has been collaborating with NIST/Boulder starting in FY 88 to develop an HTS bolometer. A working device was made and tested in early 1989- it is too slow to yet be useful. It also has somewhat elevated noise levels below 100 Hz. This effort will be continued beyond FY 89 using a second PIDDP grant.

Upcoming efforts will center on reducing the time constant of the HTS bolometer by attempting to deposit an HTS film on a diamond substrate, and by thinning $SrTiO_3$ substrates. Attempts will be made to improve the film quality to reduce the 1/f noise level, and to improve the thermal isolation to increase the bolometer sensitivity. If a sensitive HTS bolometer is produced attention will also have to be directed to long-term stability, radiation hardness, thermal cycling and vibration-induced damage. Simultaneously, Goddard is funding research through the SBIR program (Small Business Innovation Research) to attempt to deposit good-quality HTS films on diamond films using an MOCVD technique

N90-27812

THE EFFECT OF TEMPERATURE CYCLING TYPICAL OF LOW EARTH ORBIT SATELLITES ON THIN FILMS OF $YBa_2Cu_3O_{7-x}$

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The refrigeration of superconductors in space poses a challenging problem. The problem could be less severe if superconducting materials would not have to be cooled when not in use. Thin films of the $YBa_2Cu_3O_{7-x}$ (YBCO) superconductor were subjected to thermal cycling, which was carried out to simulate a large number of eclipses of a low earth orbit satellite. Electrical measurements were performed to find the effect of the temperature cycling.

Thin films of YBCO were formed by coevaporation of Y, BaF_2, and Cu and postannealing in wet oxygen at 850°C for 3.5 h. The substrates used were (100) $SrTiO_3$, polycrystalline alumina, and oxidized silicon; the last two have an evaporated zirconia layer. Processing and microstructure studies of these types of films have been published (1-4). The zero resistance transition temperatures of the samples used in this study were 91, 82, and 86 K, respectively. The samples were characterized by four point probe electrical measurements as a function of temperature. The parameters measured were: the zero resistance transition temperature (T_c), the 10 to 90% transition width (ΔT_c), and the room temperature resistance, normalized to that measured before temperature cycling (R_N).

The results for two samples are shown in Figures 1 and 2. Each sample had a cumulative exposure. The temperature cycling stages referred to in the figures are as follows:

1. Before temperature cycling.
2. After 5 cycles at $\pm$ 50°C in vacuum.
3. After an additional 200 cycles at $\pm$ 50°C in vacuum.
4. After an additional 200 cycles at $\pm$ 60°C in nitrogen.
5. After an additional 200 cycles at $\pm$ 80°C in nitrogen.

Cycling in atmospheric pressure nitrogen was performed at a rate of about 60 cycles per day, whereas in vacuum the rate was only about 10 cycles per day.

The results indicate only little or no changes in the parameters measured. T_c remains constant; R_N increases at first but seems to stabilize, indicating an ~ 10% increase in Fig. 1, and an ~ 20% increase in Fig. 2; ΔT_c is unchanged in Fig. 1, and increases by about one degree in Fig. 2.

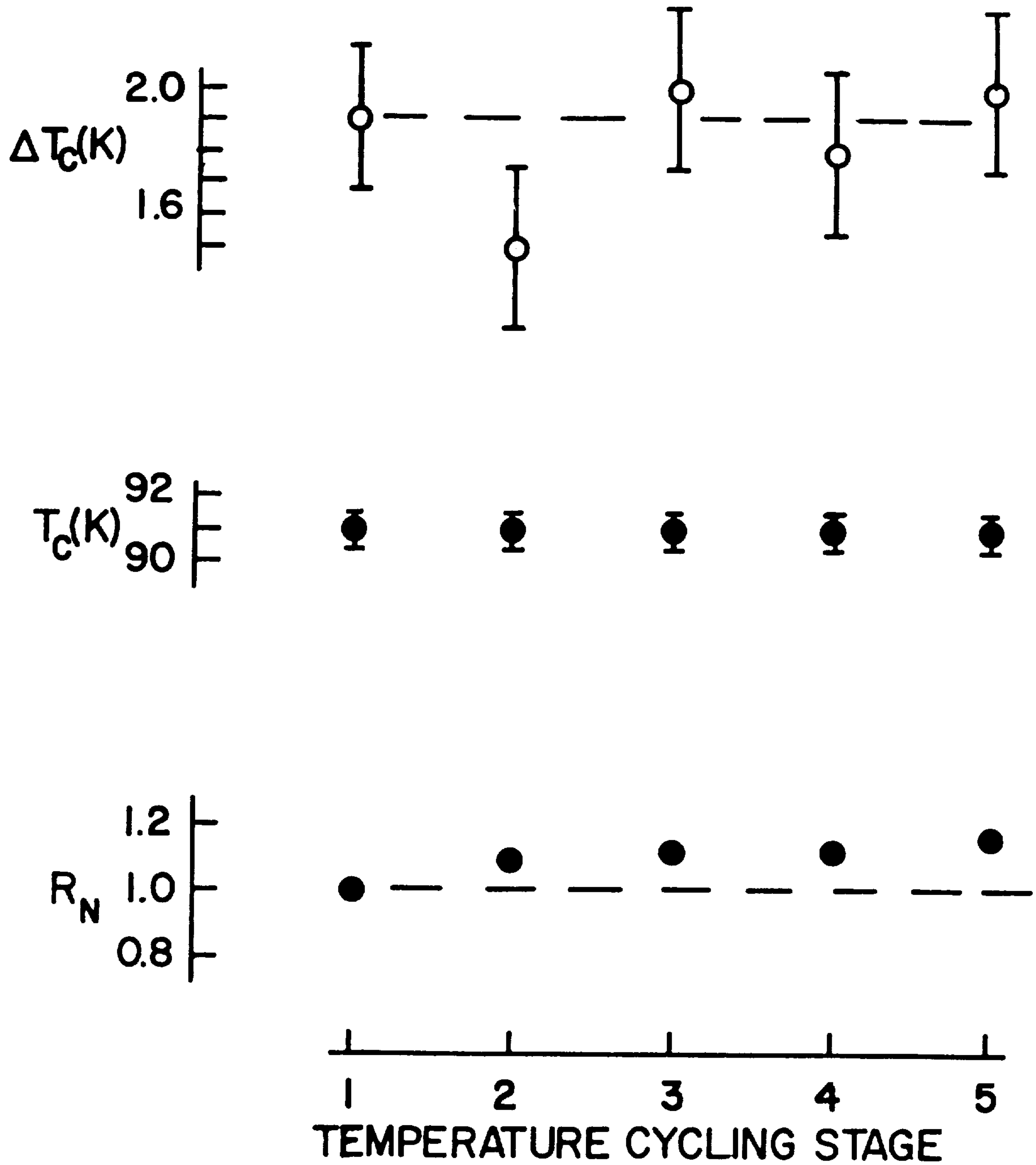

Figure 1. Electrical parameters measured after each cycling stage (defined in the text) for a YBCO thin film on (100) $SrTiO_3$

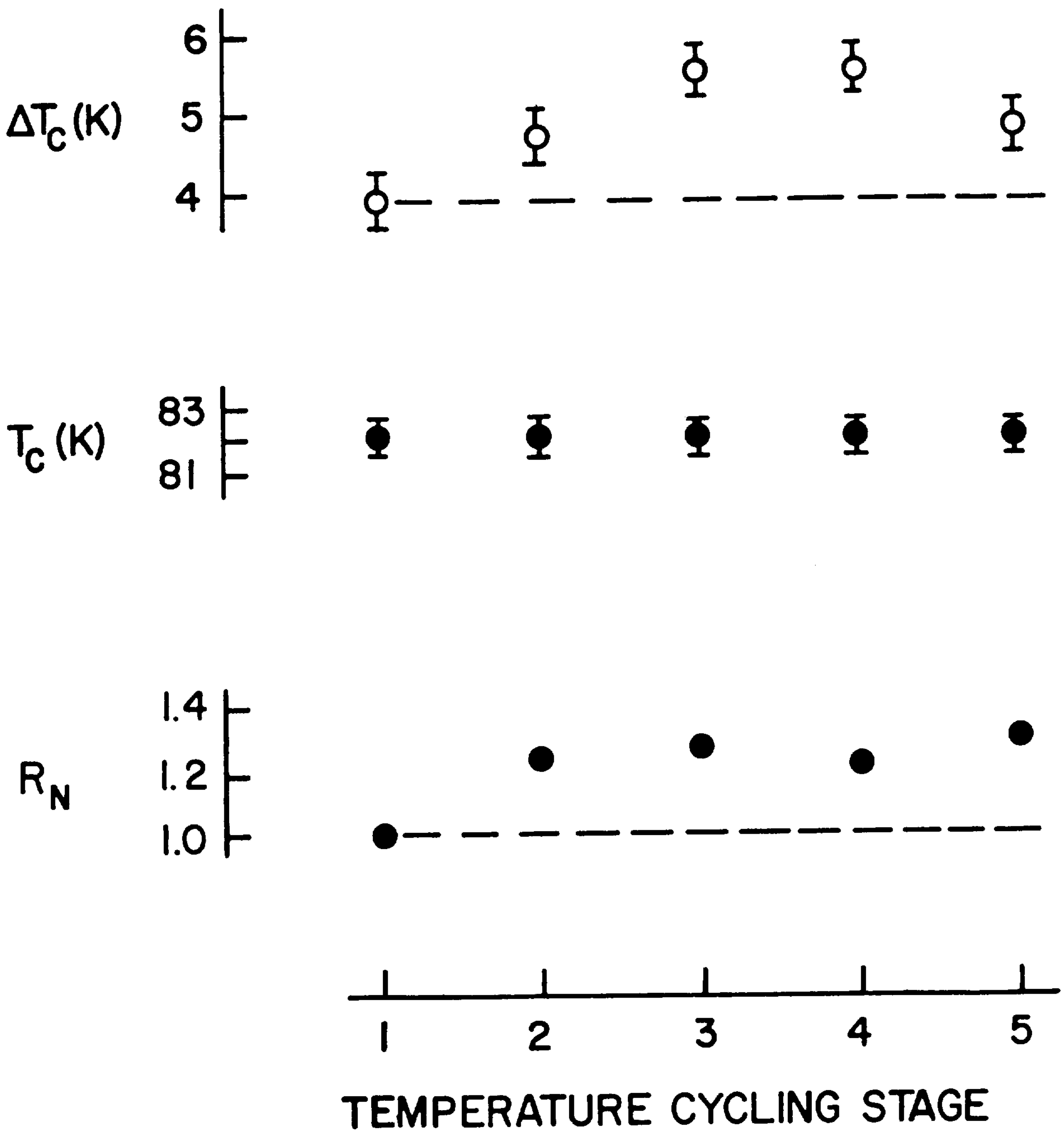

Figure 2. Electrical parameters measured after each cycling stage (defined in the text) for a YBCO thin film on polycrystalline alumina with a zirconia buffer layer.

Degradation of superconducting thin films of YBCO has been reported due to storage in nitrogen (5). We believe that the relatively good performance of our films after temperature cycling is related to the fact that BaF_2 was used as an evaporation source (6).

Our latest result on extended temperature cycling (3500 cycles at $\pm$ 80°C in nitrogen) indicates significant degradation. Further tests of extended cycling will be carried out to provide additional data and to clarify this preliminary finding.

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N90-27813

PREPARATION AND CHARACTERISTICS OF SUPERCONDUCTING CUPRATE THIN FILMS: $Nd_{2-x}Ce_xCuO_4$ AND SUBSTITUTED Bi-SYSTEM

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Characteristics of the electron-doped-type $Nd_{2-x}Ce_xCuO_4$ system and substituted $Bi_2(Sr,Ln)_3Cu_2O_y$ system have been systematically studied using the high quality thin-film samples.

The $Nd_{2-x}Ce_xCuO_4$ thin films with various Ce concentrations, x, have been prepared by rf magnetron sputtering on $SrTiO_3$ heated at around 500°C. After subsequent annealing at 1100°C in air, the films showed the c-axis orientation normal to the substrates. By means of the reducing treatment (annealing in a vacuum), superconductivity was induced for the films with $0.14 \leq x \leq 0.18$. The superconductivity and transport properties of the films were strongly affected by the reducing treatment. The x=0.15 film exhibited a sharp superconducting transition with zero resistivity at 22 K, in consistent with the diamagnetic properties. The resistivity of the films was fairly low with metallic characteristics, and the sigh of the Hall coefficient was negative in the normal state. On the other hand, the normal-state optical measurements showed that the undoped Nd_2CuO_4 is a semiconductor with a charge transfer gap of 1.3 eV, and that, when Ce ions were doped, a plasma reflection due to the free-carriers came to be seen with the plasma frequency of 1.07 eV for $0.14 \leq x \leq 0.18$. Moreover, x-ray photoemission study revealed that the Cu valence of the film decreased from 2+ for x=0 to 1+ for x=0.15. These physical properties are in contrast with those of hole-doped-type cuprate superconductors.

$Bi_2(Sr,Ln)_3Cu_2O_y$ thin films have also been prepared on MgO substrates heated at 600-700°C by similar methods. It was found that the growth conditions for Bi-system with two CuO_2 planes were different for each composition and species of lanthanoid in the films. Moreover, preparation of Bi-system with three CuO_2 planes was very difficult when lanthanoid atoms were doped in the system. Their electric transport properties and x-ray photoemission spectroscopy were investigated. Carrier concentration and Cu valence were discussed with regard to the superconductivity.

N90-27814

ENERGETICS AND CRYSTAL CHEMISTRY OF RUDDLESDEN-POPPER TYPE STRUCTURES IN HIGH T_c CERAMIC SUPERCONDUCTORS. Anurag Dwivedi and A. N. Cormack, Alfred University, Alfred, NY-14802

The formation of Ruddlesden-Popper type layers (alternating slabs of rocksalt and perovskite structures) is seen in these oxides which is similar in many respects to what is seen in the system Sr-Ti-O. However, we have observed that there are some significant differences, for example the rocksalt and perovskite blocks in new superconducting compounds are not necessarily electrically neutral, unlike in Sr-Ti-O system. This will certainly render an additional coulombic bonding energy between two different types of blocks and may well lead to significant differences in their structural chemistry.

In the higher order members of the various homologous series, additional Cu-O planes are inserted in the perovskite blocks. In order for the unit cell to be electrically neutral the net positive charge on rocksalt block (which remains constant throughout the homologous series) should be balanced by an equal negative charge on the perovskite block. It, thus, becomes necessary to create oxygen vacancies in the basic perovskite structure, when width of the perovskite slab changes on addition of extra Cu-O planes.

Results of our atomistic simulations suggest that these missing oxygen ions allow the Cu-O planes to buckle in these compounds. This is also supported by the absence of buckling in the first member of Bi-containing compounds in which there are no missing oxygen ions and the Sr-Ti-O series of compounds. We will present additional results on the phase stability of polytypoid structures in these crystal chemically complex systems. We will also focus our studies on (a) the determination of the location of Cu^{3+} in the structures of higher order members of the La-Cu-O system and (b) whether Cu^{3+} ions or oxygen vacancies are energetically more favorable charge compensating mechanism.

N90-27815

KINETICS AND THERMODYNAMICS OF CERAMIC/METAL INTERFACE REACTIONS RELATED TO HIGH T_c SUPERCONDUCTING APPLICATIONS

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Superconducting ceramic materials, no matter what their form, size or shape, must eventually make contact with non-superconducting materials in order to accomplish current transfer to other parts of a real operating system, or for testing and measurement of properties. Thus, whether the configuration is a clad wire, a bulk superconducting disc, tape, or a thick or thin superconducting film on a substrate, the physical and mechanical behavior of interface (interconnections, joints, etc.) between superconductors and normal conductor materials of all kinds is of extreme importance to the technological development of these systems. Fabrication heat treatments associated with the particular joining process allow possible reactions between the superconducting ceramic and the contact to occur, and consequently influence properties at the interface region. The nature of these reactions is therefore of great broad interest, as these may be a primary determinant for the real capability of these materials.

In this paper we describe our own research related both to fabrication of composite sheathed wire products, and the joining contacts for physical property measurements, as well as a review of other related literature in the field. Comparison will be made between "1-2-3," Bi-, and Tl-based ceramic superconductors joined to a variety of metals including Cu, Ni, Fe, Cr, Ag, Ag-Pd, Au, In and Ga. The morphology of reaction products and the nature of interface degradation as a function of time will be highlighted.

N90-27816

Thermal and electric properties of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$

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Electric resistivity, magnetic susceptibility, thermoelectric power, and Hall coefficient of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ whose onset temperature of the superconductivity are 24 K and 23 K were measured. Our experimental results show many interesting features. In particular, the Hall coefficients are negative and relatively flat as a function of temperature. However, the temperature dependence of the thermoelectric power (TEP) for these two samples shows the positive sign for both samples in contrast to the previous results. Moreover TEP for both samples remains flat in the normal state below 250 K, but decreases rapidly above 250 K. TEP of only $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ shows a peak near 50 K. Finally onset temperatures of sudden drop of TEP are higher than those of resistance drop.

We also measured the physical properties of these samples produced at different conditions such as different heat treatment temperatures, atmospheres. TEP and resistance measurement show that oxygen deficiency is essential to produce better superconducting samples. Correlation between TEP and superconductivity for these different samples will be discussed.

N90-27817

TERNARY AND QUATERNARY OXIDES OF Bi, Sr and Cu

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Before the discovery[1] of superconductivity in an oxide of Bi, Sr, and Cu, the system Bi-Sr-Cu-O had not been studied, although several solid phases had been identified in the two-component regions of the ternary system Bi_2O_3-SrO-CuO. The oxides Sr_2CuO_3, $SrCu_2O_2$, $SrCuO_2$, and Bi_2CuO_4 were then well known and characterized[2-10], and the phase diagram of the binary system Bi_2O_3-SrO had been established[11] in the temperature range 620-1000 °C. Besides nine solid solutions of compositions $Bi_{2-2x}Sr_xO_{3-2x}$ and different symmetries[12-15], this diagram includes three definite compounds of stoichiometries Bi_2SrO_4, $Bi_2Sr_2O_5$, and $Bi_2Sr_3O_6$ (x = 0.50, 0.67 and 0.75 respectively), only the second of which with known unit-cell of orthorhombic symmetry, dimensions (Å) **a** = 14.293(2), **b** = 7.651(2), **c** = 6.172(1), and Z = 4.

The first superconducting oxide in the system Bi-Sr-Cu-O was initially formulated[1] as $Bi_2Sr_2Cu_2O_{7+x}$, with an orthorhombic unit-cell of parameters (Å) **a** = 5.32, **b** = 26.6, **c** = 48.8. The superconducting transition at about 7 K was soon confirmed[16] for this oxide, that was described as showing a pseudo-tetragonal unit-cell, **a** = 5.38 Å, **c** = 24.6 Å, and signs of a weak superstructure with 5-fold periodicity along the **b**-axis. In a preliminary study some of the authors of the present paper formulated[17] the same oxide with half the copper content, $Bi_2Sr_2CuO_{6+x}$, and indexed its reflections assuming an orthorhombic unit-cell of dimensions (Å) **a** = 5.390(2), **b** = 26.973(8), **c** = 24.69(4). Subsequent studies[18-25] by diffraction techniques have confirmed the composition 2:2:1, proposing for this oxide the substructures included in table I.

Table I. Crystal structures proposed for superconducting $Bi_2Sr_2CuO_{6+x}$

Symmetry	S.G.	a/Å	b/Å	c/Å	β (°)	Z	Ref.
T	-	5.381(1)	-	24.65(1)	-	-	18
T	I4/mmm	3.8097(4)	-	24.607(3)	-	2	19
O	Amaa	5.392	5.394	24.537	-	4	20
O	-	10.8	53	24	-	-	21
T	I4/mmm	3.801(3)	-	24.61(9)	-	2	22
O	Amaa	5.362(3)	5.374(1)	24.622(6)	-	-	23
T	-	5.4	-	24.6	-	-	24
M	C2	26.856	5.380	26.908	113.55	4	25
M	-	5.4	26	28	116	-	26

T: tetragonal O: orthorhombic M: monoclinic

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The real structure is a modulated superstructure: for instance, the tetragonal substructure **a** = 5.4 Å, **c** = 24.6 Å of table I includes three kinds of long period superstructures that were observed[24] by electron diffraction: 1) base-centered monoclinic with parameters (Å): **a** = 5.4, **b** = 27, **c** = 26.9, α = 66.3° ; 2) simple monoclinic with **a** = 5.4, **b** = 27, **c** = 12.6, α = 77.6°; and 3) base-centered orthorhombic, with 5.4x22.6x24.6 $Å^3$. 'Single' crystals of $Bi_2Sr_2CuO_{6+x}$ often contain syntactic intergrowths of more than one phase, which are related to stacking faults along the **c** axis. These intergrowths are so abundant, that 'single' crystals are not neccesarily homogeneous with regard to either structure or composition.

Besides the phase with molar ratios Bi:Sr:Cu = 2:2:1, three quaternary oxides are known with ratios 4:8:5, 17:16:7, and 2:3:2. The crystal structure of $Bi_4Sr_8Cu_5O_{19+x}$ has been established[27]: the unit-cell is orthorhombic, S.G. Fmmm, with parameters (Å) **a** = 5.372(2), **b** = 33.907(6), **c** = 23.966(4). The unit-cell parameters (Å) of the other two oxides have been determined[28] in polycrystalline samples. Both are orthorhombic, with **a** = 5.425, **b** = 23.254, **c** = 24.427 for the phase 17:16:7, and **a** = 4.888, **b** = 5.396, **c** = 24.804 for the oxide 2:3:2.

The authors of the present paper have been able to characterize a new family of oxygen-deficient perovskites, $Sr(Sr_{0.5}Bi_{0.5-x}Cu_x)O_{2.75-1.5x}$ (0.2 > x > 0), after identifying by X-ray diffraction the phases present in the products of thermal treatments of about 150 mixtures of analytical grade Bi_2O_3, $Sr(OH)_2 \cdot 8H_2O$ and CuO at different molar ratios. The basic compound, $Sr(Sr_{0.5}Bi_{0.5})O_{2.75}$, was prepared from stoichiometric mixtures of the reagents, that were ground in an agate mortar, and then fired for 5 hours at 700 °C in alumina crucibles. The product was reground, fired again for 5 hours at 800 °C, reground, and heated for 5 hours at 900 °C. The mass changes, that were followed by weighing before and after each operation, showed that practically the whole Bi (III) oxidized to Bi (V) in the course of the thermal treatments.

The X-ray powder diffraction pattern for $Sr(Sr_{0.5}Bi_{0.5})O_{2.75}$ shows the reflexions of a cubic perovskite, **a** = 2$\mathbf{a}_o$ = 8.493(7) Å, with 1:1 order at the B-cations sublattice. This basic compound, which appears as not too crystalline, admits to substitute some Cu for Bi.

$Sr(Sr_{0.5}Bi_{0.3}Cu_{0.2})O_{2.45}$ was prepared from stoichiometric mixtures of the reagents, which were heated as indicated for the basic compound. Its unit-cell parameter, **a** = 8.465(14) Å, is slightly smaller than that for $Sr(Sr_{0.5}Bi_{0.5})O_{2.75}$. This could be expected considering the different size[29] of both cations, 0.76 Å for Bi^{5+} and 0.73 Å for Cu^{2+}, as well as the smaller oxygen content of the Cu compound.

Finally, the authors will present X-ray diffraction data for some other oxides of Bi and Sr, as well as for various quaternary oxides, among them a novel oxide of Bi, Sr, and Cu.

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EFFECT OF OXYGEN STOICHIOMETRY ON T_c OF Bi-BASED SUPERCONDUCTORS

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The role of oxygen stoichiometry on T_c is relatively well established on La_2CuO_{4+x} and the $YBa_2Cu_3O_{7-x}$ (123) superconductors[1,2], as compared to the Bi-based superconductors. In this paper we will present results of our investigations on the effects of oxygen stoichiometry on the transition temperature T_c of $Bi_2Sr_2CaCu_2O_{8+x}$ (2212 phase), and Pb-doped $Bi_2Sr_2Ca_2Cu_3O_{10+x}$ (2223 phase). We show that the effects of oxygen stoichiometry on T_c of these two phases are very different. These results might be helpful in understanding the mechanism of superconductivity in the Bi-based superconductors.

The 2212 and 2223 phases of Bi-based superconductors were synthesized using appropriate amounts of analytical grade Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO by the solid state reaction method. Some details of the method to produce the 2212 phase with excess oxygen has been recently reported[3]. Experiments on the thermal cycling of the annealed samples to affect change in oxygen stoichiometry are done using TGA (Thermogravimetric Analysis) technique which allows us to monitor weight changes of ~ 0.01%, followed by magnetic and resistivity studies to observe changes in T_c and superconductivity. In Fig.1, we present recent results on the change in T_c for the 2212 phase vs weight change produced by thermal cycling (heating in air to different temperatures up to 850 ^{o}C and cooling in air or Ar)[3]. An increase of T_c from 70 to 95 K for 2212 phase corresponding to weight loss of 0.16% is observed. This is opposite to the effect of oxygen stoichiometry on T_c for the La_2CuO_{4+x} and the 123 systems. In a $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_x$ sample, consisting of mainly 2223 phase with small amount of 2212 phase, it is observed that as T_c of the 2212 phase increases from 70 K to above 90 K with weight loss of ~0.2%, the T_c of the 2223 phase decreases from 110 K to 106 K. This leads us to infer that excess oxygen resides in different locations in the two phases, viz. Bi-O double layers in the 2212 phase, triple Cu-O layers in addition to Bi-O double layers in the 2223 phase.

In a recent paper, Hybertsen and Mattheiss[4] have used band structure calculations on the idealized (2212) structure to show that excess oxygen can reduce the metallic conductivity of the Bi-O layers, suppressing T_c. However the actual structure of the 2212 phase differs from the idealized structure and we have no proof that excess oxygen resides in the double Bi-O layers of the 2212 phase. Experiments planned for the near future may determine the location of excess oxygen in the Bi-based systems. These results will also be presented.

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PHENOMENOLOGICAL THEORY OF THE NORMAL AND SUPERCONDUCTIVE STATES OF Cu-O AND Bi-O METALS

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ABSTRACT

The universal normal state anomalies in the Cu-O metals follow from a marginal Fermi-liquid hypothesis: there exists a contribution to the polarizability over most of momentum space proportional to ϖ/T for $\varpi/T \ll 1$ and constant thereafter up to a cutoff ϖ_c. Using the same excitation spectrum, the properties of the superconductive state have been calculated. We can obtain the right order of T_c, the zero-temperature gap, $2\Delta(o)/T_c$ and the nuclear relaxation rate near T_c.

I will discuss the possible microscopic physics leading to the marginal Fermi-liquid hypothesis.

N90-27820

CHARGE TRANSFER POLARISATION WAVE AND CARRIER PAIRING
IN THE HIGH Tc COPPER OXIDES

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ABSTRACT

The High T_c oxides are highly polarisable materials and are charge transfer insulators. The charge transfer polarisation wave formalism is developed in these oxides. The dispersion relationships due to long range dipole-dipole interaction of a charge transfer dipole lattice are obtained in three and two dimensions. These are high frequency bosons and their coupling with carriers is weak and antiadiabatic in nature. As a result, the mass renormalisation of the carriers is negligible in complete contrast to conventional electron-phonon interaction, that give polarons and bi-polarons. Both bound and superconducting pairing is discussed for a model Hamiltonian valid in the antiadiabatic regime, both in three and two dimensions. The stability of the charge transfer dipole lattice has interesting consequences that will be discussed.

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N90-27821

Electronic Structure Fermi Liquid Theory of High T_c Superconductors; Comparison with Experiments*

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The most exciting issues in the microscopic theory of high T_c superconductivity are embodied in the questions: "What are the mechanisms of high T_c ?" and "What is the nature of the normal state of the Cu-oxide superconductors ?" In particular, a major issue in understanding of the normal state of these systems is how well a Fermi liquid picture (e.g., LDA energy band theory) works in describing their normal state properties.

For years, there has been controversy and confusion among theorists as well as experimentalists on whether the 'normal' state of the Cu-oxide superconductors is a Fermi liquid or some other exotic ground state. However, some experimentalists (including Arko *et al.*) are clarifying the nature of the normal state of the high T_c superconductors by surmounting the experimental difficulties in producing clean, well-characterized surfaces so as to obtain meaningful high-resolution angle-resolved photoemission data, which agrees with earlier positron-annihilation experiments by Smedskjaer *et al.* The experimental work on high-resolution angle-resolved photoemission by Campuzano *et al.* and positron-annihilation studies by Smedskjaer *et al.* has verified our calculated Fermi surfaces in $YBa_2Cu_3O_7$ superconductors and has provided evidence for the validity of our energy band approach. Similar good agreement has been found for $Bi_2Sr_2CaCu_2O_8$ by Olson et al.

In addition, LDA predictions on the normal state transport properties for $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ by Allen *et al.* are qualitatively in agreement with experiments on single crystals. Moreover, the measured Hall coefficient for the non-Cu based $Ba_{1-x}K_xBiO_3$ system was found to be negative, which agrees with our energy band calculation. Recently, for $Nd_{2-x}Ce_xCuO_4$ systems, we obtained (together wtih Hamada and Massidda) a positive Hall coefficient for the magnetic field oriented perpendicular to the Cu-O planes. This is to be compared with a negative experimental value found for $x < 0.18$ and recent experiments which show a change of sign of this Hall coefficient (from negative to positive with increasing x) for $x = 0.18$. These results on Hall coefficients indicate a trend (previously found for $La_{2-x}Sr_xCuO_4$) toward a regime where the conventional band theoretical description comes into better agreement with experiment.

As a Fermi liquid (metallic) nature of the 'normal' state of the high T_c superconductors becomes evident, these experimental observations have served to confirm the predictions of our local density functional calculations and hence the energy band approach as a valid natural starting point for further studies of their superconductivity.

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An explanation for the rise in T_c in the Tl- and Bi-based high temperature superconductors

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Using the plasmon exchange model for the high T_c superconductor, we show that the T_c rises with an increase in the number of CuO layers per unit cell, which is in agreement with recent observations in the Tl- and Bi-based compounds. Our calculation also suggests that the sample will become superconducting in successive stages and that there is a saturation effect, i.e. that T_c cannot be raised indefinitely by increasing the number of CuO layers.

N90-27823

CRITICAL CURRENTS AND HIGH TEMPERATURE SUPERCONDUCTORS

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ABSTRACT

In this talk I shall summarize the experimental information on critical currents and epitaxial thin films of high temperature superconductors. We also describe experiments carried out to measure critical currents across single grain boundaries. A variety of mechanisms responsible for limiting currents in films as well as across grain boundaries are presented and their predictions compared with experimental data.

N90-27824

STUDY OF LOCAL STRUCTURE AND MAGNETISM IN HIGH-Tc COPPER OXIDE SUPERCONDUCTORS

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ABSTRACT

This talk will focus on the muon-spin rotation (μSR) study of local magnetism of Sr-doped La_2CuO_4. Emphasis will be placed on magnetic order as detected by local and bulk probes with local atomic environments studied by x-ray absorption fine structure (XAFS). Correlations between the μSR study of local magnetic ordering and the bulk magnetization study will be presented along with a discussion of the dependence upon oxygen stoichiometry. Results will be presented for both superconducting phases and magnetic phases. Recent data which reveals the existence of local magnetic ordering in the hydrogen-doped $YBa_2Cu_3O_7$ system will also be discussed.

The work presented here is supported by the Department of Higher Education of the State of Connecticut. We also acknowledge the U.S. Department of Energy for support to the work carried out at Beam Line X-11 at the National Synchrotron Light Source under Contract No. DE-AS05-80-ER10742 and DE-AC02-76CH00016.

DYNAMICS OF THE IRON SPINS IN SUPERCONDUCTING $YBa_2(Cu_{1-x}Fe_x)O_7$

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ABSTRACT

The dynamics of the iron spins in $YBa_2(Cu_{1-x}Fe_x)_3O_7$ alloys ($0 \leqslant x \leqslant 0.12$) has been studied by the means of inelastic neutron scattering. Measurements were performed using the time of flight technique with an excellent resolution of 50 µeV, in a temperature range of 1.8 K to 300 K. The doped samples show an elastic and a quasielastic intensity strongly varying with temperature.

A spin glass like freezing is revealed at low temperature by a sudden decrease of the quasielastic intensity, an increase of the "elastic" or resolution limited intensity and a minimum in the quasielastic width. The freezing temperature ($T_f \sim 18$ K for x=0.06, $T_f \sim 35$ K for x=0.12) corresponds to the one already determinated by a magnetic splitting in Mössbauer experiments. Above T_f, the occurrence of superconductivity slightly modifies the characteristics of the spin relaxation in the paramagnetic state, as shown by measurements in two x=0.06 samples ($T_c \sim 65$ and 78 K). In the whole temperature range of measurement, the dependence of the quasielastic intensity with the scattering vector q, mainly reflects the variation of the Iron form factor, which shows that the spins are almost uncorrelated.

N90-27826

THE MECHANISM OF HIGH-T_c SUPERCONDUCTIVITY DUE TO BOUND HOLE MEDIATORS: RELATIONSHIP TO FERROELECTRICITY

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The mediation by bound-holes creating Cooper pairing in high-T_c superconductors has its origin in charge transfer excitations on the multivalence cation (virtual excitons) and in bound excitons or polarizations associated with the oxygen 2p electrons. These phenomena are produced and/or enhanced by a high internal electric field which is itself created by virtue of the unique crystal structures and polyhedral building blocks of high-T_c materials. The polarizations which can create oxygen holes (in addition to excitons) may be due to simply the internal electric field or to polaronic and electron-deficient bond behavior. This gives rise to two energy-dependent oxygen bands near the Fermi level. The magnitude and direction of the internal electric fields have been calculated for $Y_1Ba_2Cu_3O_{7-}$ (1-2-3) and show strong z-direction fields at the Cu(2), 02, and 03 sites and an even stronger -z direction field at the 04 site. The field calculations also show why electrical conductivity in the 1-2-3 material is essentially in the base plane of the CuO_5 pyramid (the CuO_2 plane). Empirical studies show that T_c scales with the number of bound holes associated with the pyramidal building block, and this scaling is refined by taking into account the lifetime and the degree of monopolar character of these holes. Recent work shows for both the 1-2-3 and the bismuth containing superconductors that the positive Hall (R_H) coefficient as a function of temperature undergoes reversible anomaly as temperature is decreased toward T_c indicating a decrease in the concentration of bound holes near the pre-onset temperature (where the resistance vs temperature data first begins to deviate from linearity). Experimental work also shows that the pre-onset temperature is associated with the inception of small oscillations in resistance vs time, the amplitude of which is strongly B field dependent up to 11T and saturates at higher B-field, the pre-onset temperature is also correlated with the spin and the magnetic moment associated with the paramagnetic rare earth which can substitute for Y^{3+}. It appears that Cooper-pairing of electrons is not stabilized until at least somewhere near the middle of the collapsing resistance transition, this being suggested by the B-field induced divergence of the R vs 1000/T data at $T<T_c$, and by a reverse in the sign of the slope of the $+R_H$ vs T data (and in the sign of R_H) at $T<T_c$. Strong relationship between high-Tc and ferroelectric materials suggests that T_c should be dependent on $(T^*-T_o)^n$ where T_o is the Curie Temperature, T^* is the temperature at which the dielectric constant peaks, and $n \simeq 3/2$. The value of T_c actually specifies the temperature at which the lifetime of the bound holes is sufficiently large to mediate the electron-electron Cooper pairing interaction ($\sim 10^{-13}$ sec). Superimposed on the bound hole mechanism there seems to be a conventional electron-phonon interaction, as well as the possibility of a contribution to T_c due to spin fluctuations from antiferro-magnetism.

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MAGNETIC CORRELATIONS IN $La_{2-x}Sr_xCuO_4$ FROM NQR RELAXATION AND SPECIFIC HEAT

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ABSTRACT

^{139}La and ^{63}Cu NQR relaxation measurements in $La_{2-x}Sr_xCuO_4$ for $0 \leq x \leq 0.3$ and in the temperature range 1.6 + 450 K are analyzed in terms of Cu^{++} magnetic correlations and spin dynamics. It is described how the magnetic correlations that would result from Cu-Cu exchange are reduced by mobile charge defects related to x-doping. A comprehensive picture is given which explains satisfactorily the x and T dependence of the correlation time, of the correlation length and of the Neél temperature $T_N(x)$ as well as being consistent with known electrical resistivity and magnetic susceptibility measurements. It is discussed how, in the superconducting samples, the mobile defects also cause the decrease, for $T \rightarrow T_c^+$, of the hyperfine Cu electron-nucleus effective interaction, leading to the coexistence of quasi-localized, reduced magnetic moments from 3d Cu electrons and mobile oxygen p-hole carriers. The temperature dependence of the effective hyperfine field around the superconducting transition yields an activation energy which could be related to the pairing energy. New specific heat measurements are also presented and discussed in terms of the above picture.

AN EPR METHODOLOGY FOR MEASURING THE LONDON PENETRATION DEPTH FOR THE CERAMIC SUPERCONDUTORS

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In this presentation we shall discuss the use of electron paramagnetic resonance (EPR) as a quick and easily accessible method for measuring the London penetration depth, λ, for the high-T_c superconductors. The method utilizes the broadening of the EPR signal, due to the emergence of the magnetic flux lattice, of a free radical adsorbed on the surface of the sample. The second moment, $<\Delta H^2>$, of the EPR signal below T_c is fitted to the Brandt equation for a simple triangular lattice: $<\Delta H^2> = 0.000371\lambda_0[1-(T/T_c)^4]^{-1/2}$. Application of this methodology yields $\lambda_0 = 2520 \pm 100$ Å with $T_c = 119$ K for the $Tl_2Ba_2Ca_2Cu_3O_x$, and $\lambda_0 = 2700 \pm 100$ Å with $T_c = 84$ K for $Bi_2Sr_2Ca_2Cu_2O_x$. The precision of this method (±100 Å or better) compares quite favorably with those of the more standard methods such as μ^+SR, Neutron scattering and magnetic susceptibility.

MAGNETISM AND SUPERCONDUCTIVITY OF SOME Tl-Cu OXIDES

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Many copper-oxide based "Thallium" compounds have now been discovered. Of these, the high temperature superconductors (HTSC) may be represented by the homologous series $(Tl_{1-x}A_xO)_m-(B_{1-v}C_y)_nCa_{p-1}Cu_pO_{2(p+1)+d}$; if A=Bi or Pb, B=Ba or Sr(5), C=Ce, Zr or Nd; n=2 and p=1-4. In comparison to the Bi-compounds, the Tl-system shows a richer diversity; viz., HTSC can be obtained with either one or two Tl-O layers (m=1,2); also, the triple-digit phases are easier to synthesize. The value of d, the oxygen stochiometry, is critical to achieving superconductivity. The Tl-system is robust to oxygen loss; Tl may be lost or incorporated by diffusion. We determine a diffusion coefficient equal to 10 m s at 900C. Both ortho-rhombic and tetragonal structures are evidenced, but HTSC behavior is indifferent to the crystal symmetry. This system has the highest Tc confirmed. Tc generally increases with p, the number of Cu-O layers, but tends to saturate at p=3. Zero resistance as high as 125K has been observed (1). Most of these HTSC's are hole type, but the Ce-doped specimens may be electronic.

The effort at USC has focused on the magnetic aspects; because in addition to defining the perfectly diamagnetic groundstate as in the conventional superconductors, magnetism of the copper oxides (1) show a surprising variety. This is true of both the normal and the superconducting states. Also, due to the large phonon contribution to the specific heat at the high Tc, accurate thermal measurement of important parameters such as the sp. heat jump, electronic density of states, D(Ef) and coherence length are uncertain, and thus, are estimated from the magnetic results.

We determine for single phases: (i) Tl-Ba; D(Ef)=2.0 states/ev.at. Cu, a BCS sp. ht. jump=6.2 mj/mol.Cu K; and (ii) Tl-(Ba,Ce); D(Ef)=2.2 and a BCS sp. ht. jump=6.8 (same units). For both, the Cu moment is about 0.1-0.4 Bohr mag. The Ce moment is 1.5, representing a charge state higher than 3+. This is indicative of electron doping and is evidence for n-type behavior. Paraconductivity and diamagnetic fluctuations are consistent with the expected two-dimensionality. Flux creep shows trapping potential somewhat stronger than those in Y-123. These and other results from the Tl-system Cu-O, LaBaCu-O,120 and the Bi-CuO compounds will be discussed. The emphasis will be on the role of magnetism in the Tl-CuO HTSC, but technological aspects will also be pointed out.

* In collaboration with A.M. Hermann (U. Colorado) and D.U. Gubser (Naval Research Lab.). Partially supported by USC and SDIO.

(1) Copper Oxide Superconductors, by C.P. Poole, T. Datta, and H.A. Farach, John Wiley & Sons, New York, NY, 1988.

N90-27830

THE COLOR OF POLARIZATION IN CUPRATE SUPERCONDUCTORS

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A technique for the identification of individual anisotropic grains in a heterogeneous and opaque material involves the observation of grain color in reflected light through crossed polarizers (color of polarization). Such colors are generally characteristic of particular phases. When grains of many members of the class of hole carrier cuprate superconductors are so viewed, using a xenon light source (6000 K color temperature), a characteristic color of polarization is observed. We have studied this color in many of these cuprate superconductors and found a strong correlation between color and the existence of superconductivity. We have also examined one of the members of the electron carrier cuprate superconductors ($Nd_{1.85}Ce_{.15}CuO_{4-x}$) and found that it possesses the same color of polarization as all the electron hole carrier cuprate superconductors so far examined. The commonality of the characteristic color in the cuprate superconductors indicates that the presence of this color is independent of the nature of charge carriers. The correlation of this color with the existence of superconductivity suggests that the origin of the color relates to the origin of superconductivity in the cuprate superconductors.

Using photometric techniques, we have quantified the color in the $RBa_2Cu_3O_7$-type superconductors by measuring reflectivity. The reflectivity measurements have been made with a xenon light source (6000 K color temperature), as used in viewing the color of polarization. The reflectivity data have been taken on a series of $ErBa_2Cu_3O_{7-x}$ samples, where $.1 \leq x \leq .7$, so as to include both tetragonal insulators and orthorhombic superconductors. These measurements have been iteratively fitted with smooth curves to represent the spectra throughout the visible. From these curves, we have calculated the chromaticity coordinates which can be located on a chromaticity diagram, where the color fields are denoted. The colors found compared well with those observed visually. Possible interpretations of the iterative fits to the reflectivity data by comparison with ellipsometry results available on this type of superconductor, including transmissivity, and noting the absorption characteristics of Cu^{+2} will be discussed.

N90-27831

A SYSTEMATIC STUDY OF SUPERCONDUCTIVITY IN Bi-Pb(Sn)-Sb-Sr-Ca-Cu-O SYSTEMS

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Abstract

Superconducting transition above 160K has been reported[1] in the Bi-Pb-Sb-Sr-Ca-Cu-O system. The results of a systematic study emphasizing the correlations between the type and amount of dopant, and superconducting transition will be presented. The effect of Sn (instead of Pb) substitution will also be highlighted.

[1]L. Hongbao et al., Univ. of Science & Technology, China, preprint.

N90-27832

STABILIZATION OF HIGH Tc PHASE IN BISMUTH CUPRATE SUPERCONDUCTOR BY LEAD DOPING

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ABSTRACT

It has widely been ascertained that doping of lead in Bi:Sr:Ca:Cu:0 systems promotes the growth of high Tc (110 K) phase, improves critical current density, and lowers processing temperature. A systematic investigation is undertaken in the present study to determine optimum lead content and processing conditions to achieve these.

A large number of samples with cationic compositions of $Bi_{2-x}Pb_xSr_2Ca_2Cu_3$ (x=0.2 to 2.0) were prepared by conventional solid-state reaction technique. Samples of all compositions were annealed together at a temperature and characterized through resistance-temperature (R-T) measurements and X-ray diffraction (XRD) to determine the zero resistance temperature, Tc(0) and to identify presence of phases, respectively. The annealing temperature was varied between 790°C and 880°C to optimize processing parameters.

For x value between 0.3 to 0.8, Tc(0) above 110 K is obtained when the samples were annealed at a temperature in the range of 855°C to 870°C for 40 hours. The best samples showed Tc(0)=113 K and critical current density of about 200A/cm^2. An optimum process yielded a large volume fraction of high Tc phase as determined from intensity peaks in XRD spectra. These results were supported through magnetic susceptibility measurements on samples having high Tc(0) values. The samples showed no change in R-T characteristics on repeated thermal cycling between 77 K and 300 K, even after a few weeks of their preparation.

In brief, we report an optimum process and composition of leaded bismuth cuprate superconductor which yields nearly a high Tc single phase with highly stable superconducting properties.

N90-27833

STRUCTURE AND SUPERCONDUCTING PROPERTIES OF $[(Ln_{1-x}Ln^{*}_{x})_{1/2}(Ba_{1-y}Sr_{y})_{1/3}Ce_{1/6}]_{8}Cu_{6}O_{z}$

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ABSTRACT

A variety of new oxide superconductors that can be represented by the formula, $[(Ln_{1-x}Ln^{*}_{x})_{1/2}(Ba_{1-y}Sr_{y})_{1/3}Ce_{1/6}]_{8}Cu_{6}O_{z}$ (Ln, Ln* = lanthanide elements), have been prepared. The crystallographic structures of the oxides were all tetragonal and of the $(Ln^{+},Ce)_{4}(Ln^{+},Ba)_{4}Cu_{6}O_{z}$ (Ln^{+} = Nd, Sm or Eu) type which had been previously discovered by Akimitsu et al. As the Sr content, y, increased when Ln=Ln*=Nd, the oxygen content, z, monotonically increased and the superconducting transition temperature, T_c, varied exhibiting a maximum. When z was controlled directly by means of high oxygen pressure sintering techniques, T_c was changed accordingly. T_c's of samples with different combinations of Ln and Ln* and different values of x and y were found to depend on the magnitude of the bond valence sum for a Cu atom located in the bottom plane of the $Cu\text{-}O_5$ pyramid. Transport and magnetization measurements were carried out to investigate the magnetic field dependence of superconducting properties and to determine the phenomenological parameters. The Hall coefficients were positive below room temperature and varied yielding a maximum with respect to temperature.

Phase compatibilities of $YBa_2Cu_3O_{9-\delta}$ type structure in quintenary systems Y—Ba—Cu—O—X (impurity)

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Electrical transport properties of the oxidic high Tc superconductors are significantly affected by the presence of minor amounts of various elements adventing as impurities, e.g., from the chemical environment during manufacturing. $YBa_2Cu_3O_{9-\delta}$ is prone to an extinction of the superconductivity on (partiall) substitution of all four elemental components. E.g., Pr (for Y), La (for Ba), Zn (for Cu) or peroxygroup (for O) substituents will alter some of the superconductivity preconditions, like mixed valence state in $[Cu_3O_{9-\delta}^{7-}]$ network or structural distortion of the network. Although various pseudoternary chemical equilibrium phase diagrams of the Y(O)—Ba(O)—Cu(O) system now are available [1-6], no consensus is generally shown, however, this is partly due to lack of compatible definitions of the equilibrium conditions. Less information is available about the phase compatibilities in the appropriate quaternary phase diagram (including oxygen) and virtually no information exists about any pentenary phase diagrams (including one impurity). Unfortunately, complexity of such systems, stemming both from number of (yet mostly uncharacterized and unknown) quaternary or pentenary compounds and from visualizing the five-component phase system, limits this presentation to more or less close surroundings of the $YBa_2Cu_3O_{9-\delta}$ type phase in appropriate pseudoquaternary or pseudopseudoternary diagrams, involving Y-Ba-Cu and O, $O{\cdot}CO_2$, alkaline metals, Mg and alkaline earths, and Sc and most of the 3-d and 4-f elements. The systems were investigated by means of X-ray diffraction, neutron diffraction and chemical analytical methods on samples prepared by sol-gel technique from citrates. The superconductivity was characterized by measuring the diamagnetic susceptibility by SQUID.

Substitution for oxygen. One of the most characteristic features of $YBa_2Cu_3O_{9-\delta}$ is the reversible oxygen uptake, driven by the gas partiall pressure. Formally, it can be considered as substitution of oxygen *by vacancies.* At high oxygen partial pressures (well above 1 atm) the structure is in principle preserved[4,9,10], but some of the O-sites apparently accommodate [11] peroxygroups (their presence in samples prepared even at ambient oxygen pressures is assumed in [12]). Low oxygen partial pressures will on the other hand lead to decomposition of $YBa_2Cu_3O_{5.91}$ into Cu_2O, Y_2BaCuO_5 and probably $Y_2Ba_3O_6$ (below $p_{O_2} = 5 \cdot 10^{-5}$ Pa at 770 °C). Below $p_{O_2} = 10^{-9}$ Pa, only Cu and yttrium-barium oxides are stable at 770 °C as follows from the appropriate phase diagrams in Fig. 1.

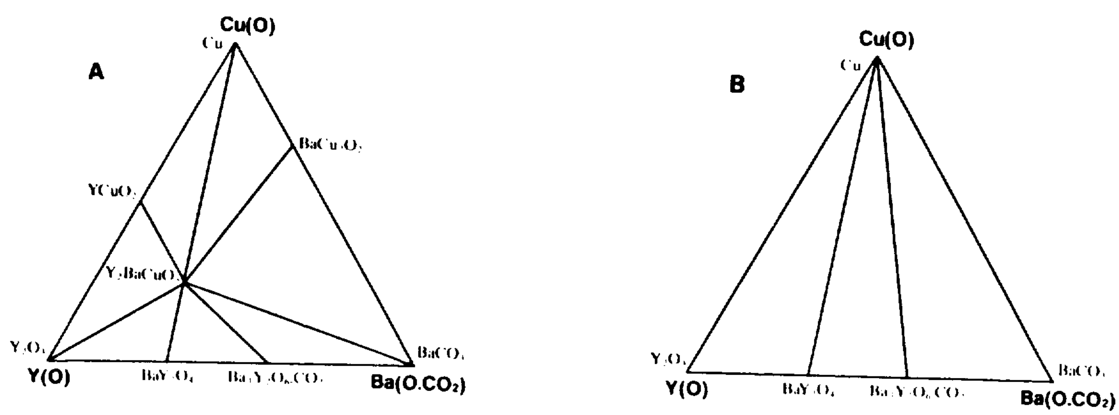

Figure 1. Phenomenological presentation of equilibrium pseudoternary phase diagram Y—Ba—Cu—O, projected on the plane of the metallic components at 770 °C for low oxygen partial pressures $p_{O_2} = 5 \cdot 10^{-5}$ Pa (A) and $p_{O_2} = 10^{-9}$ Pa (B).

Since it is an inherent property of Ba to form very stable peroxide and carbonate, the possibility of substitution for oxygen *by peroxide or carbonate anions* can hencefore be considered in the Ba rich region of the phase diagrams. In Fig. 2, Y—Ba—Cu—O(CO_2) phase diagrams are drawn including approximate (kinetic) stability regions of the appropriate carbonate-oxides for 10^5 Pa oxygen atmosphere (with $\leq$ 1 ppm of CO_2). Such phase diagrams apply if, e.g., a limited amount of CO_2 is introduced into the system via $BaCO_3$.

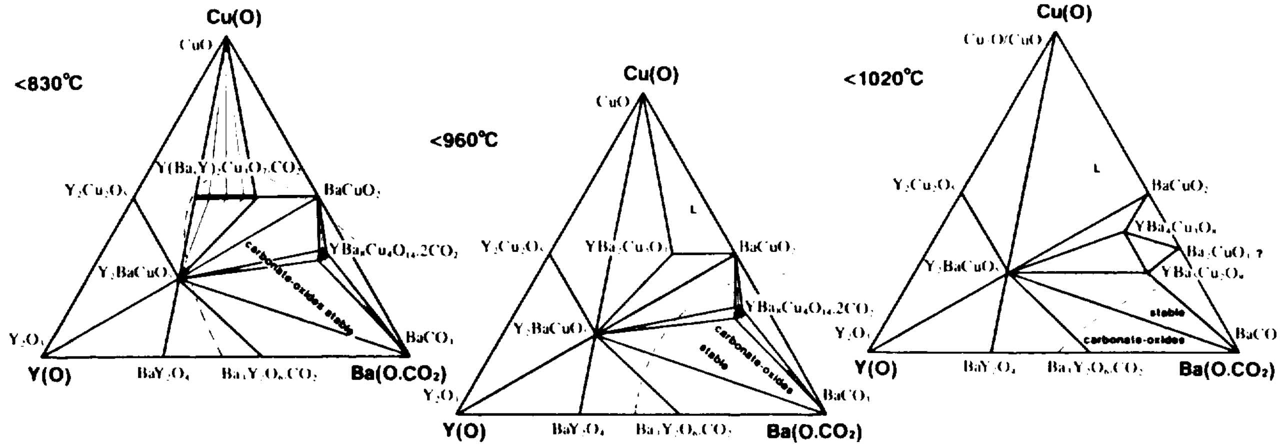

Figure 2. Equilibrium phase diagrams Y—Ba—Cu—O(CO_2) for various maximal firing temperatures of carbonates–containing starting materials in 10^5 Pa oxygen atmosphere with $\leq$ 1 ppm CO_2. Stability regions of the oxides–carbonates depicted (broken line).

As follows from the Fig. 2, the decompositon temperature of $YBa_2Cu_3O_{9-\delta}{\cdot}CO_2$ (tetragonal, nonsuperconducting) is rather low, 830 °C (formation at a temperature as low as 750 °C is observed). The Ba–richer phase $Ba_8Y_{1+x}Cu_{4+y}(CO_3)_2O_{10+\eta}$, with $x \leq 0.3$, $y \leq 0.5$ and $\eta \leq 3$, decomposes at 960 °C into $YBa_4Cu_3O_{8+\epsilon}$ (the phase is described in Ref. 5,. With even higher Ba–content, $Y_2Ba_3O_6{\cdot}CO_2$ (erroneously assigned as $Y_2Ba_2O_5$ in Ref. 13) decomposes at a temperature as high as 1080 °C.

Although of particular interest, no reliable data on substitution of oxygen *by peroxygroups* in the $YBa_2Cu_3O_{9-\delta}$ could yet be obtained since determination of O_2^{2-} in the structure is rather ambiguous [14]. A verified study using ^{18}O labeling is described in Ref. 15. Samples prepared from BaO_2 in closed pressurized systems showed contraction of c axis and no high T_c superconductivity. Rietveld refinements of the powder neutron diffraction data for such samples indicate coordination of oxygen–containing, cluster–like species around the Cu(1) atom. However, no clear distinction can be made between peroxygroups and carbonate groups which possibly originate from adventing carbon in the used BaO_2. Nevertheless, no reaction with permanganate, otherwise readily proceeding with BaO_2, was observed in the $YBa_2Cu_3O_{9-\delta}$ samples presumably containing the peroxygroups.

Substitution for Ba and Y by rare earths. A large variety of elements can, at least partially, be accommodated at the Y and Ba sites in the structure of $YBa_2Cu_3O_{9-\delta}$. Yttrium can be fully replaced by rare earths Yb–to–Dy and Gd, Eu and Sm. According to equilibrium firing experiments at 910 °C, followed by oxygen saturation at 340 °C, Lu and Tb replace Y up to 1/3. For Nd, Pr and La, an occupational equilibrium between the Y and Ba site exists, which means that the Ba site can accommodate the large rare earth. For Nd, the equilibrium favours occupation of the Y–site, whereas the Ba–site is preffered if La is involved. No substitution solely for Y can be reached using Nd and larger rare earths, neither can any substitution solely for Ba be obtained for Pr and smaller rere earths. If the former is attempted, the $BaCuO_{2+\nu}$ impurity phase bounds the simultaneously replaced Ba. If the latter is attempted, an Y_2BaCuO_5–type phase bounds the simultaneously replaced yttrium and emerges together with CuO. Only La is large enough as not to attack the Y–site unless it is present in the Ba–site in concentration higher than 35%. Then, Y is substituted by La as well and it emerges as $Y_2Cu_2O_5$. In Fig. 3., these situations are shown in psudoquaternary tetrahedral diagrams.

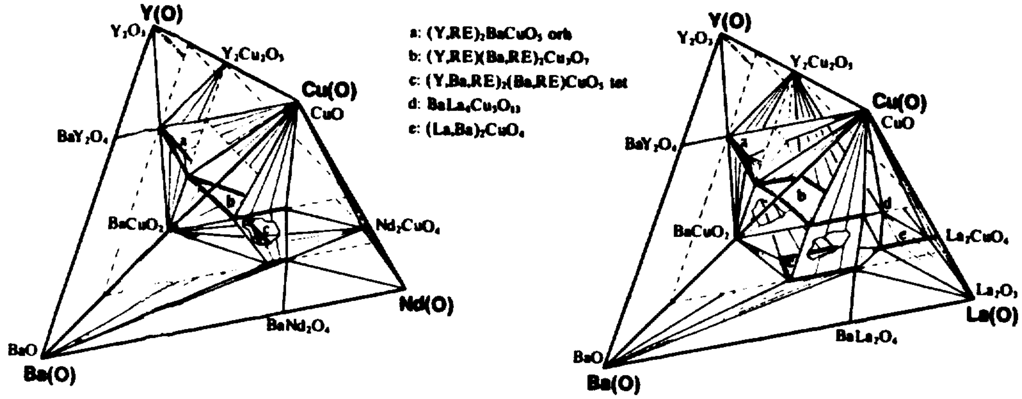

Figure 3. Relevant portions of the pseudoquaternary tetrahedral diagrams of the RE—Y—Ba—Cu—O phase system for RE = Nd and La after equilibrium firing at 910°C and oxygen saturation at 340°C. Note the surroundings of the $(Y,RE)(Ba,RE)_2Cu_3O_{9-\delta}$ solid solution regions in the pseudopseudoternary cut.

As for cerium, this element does not substitute either Y or Ba more than a few %. Excess of Ce is bound into $BaCeO_3$ (perovskite type; $(Ba(Tb,Cu)O_3$ in case of Tb) and a $(Ba,Ce,Y)_2CuO_4$ (T^*-type phase, Ref. 16) emerging together with $BaCuO_2$ in ratii depending on the elemental composition of the overall mixture.

Substitution for Ba and Y by alkaline earths. Of all possible combinations, only Ca for Y and Sr for Ba substitutions are significant, and replacements up to 25 % and 35 % respectively can be reached. Above these limits, Y_2BaCuO_5 together with another yet unidentified phases in case of Ca and Y_2BaCuO_5 with $Sr_{14}Cu_{24}O_{41}$ (Ref. 17) in case of Sr emerge as impurity phases. If substitution of Ca for Ba is attempted, no substitution for Ba takes place, but a portion of Y is replaced instead and Y_2BaCuO_5 together with unindentified Ca poly-nary oxides appear as impurities. If substitution of Sr for Y is attempted, virtually no replacement, (4 ± 4)%, is achieved, a portion of Ba is substituted instead, and $BaCuO_2$ appears as impurity. The situation is depicted in Fig. 4.

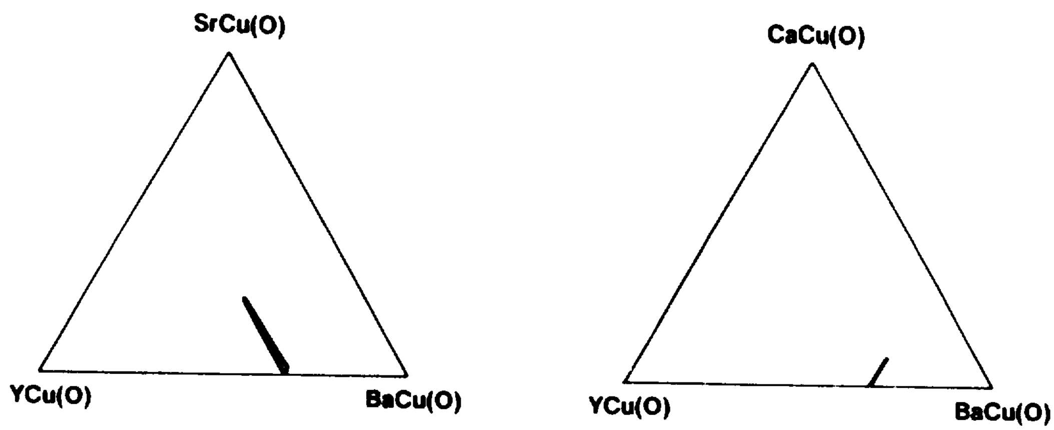

Figure 4. Pseudopseudoternary diagrams of the M—Y—Ba—Cu—O system, M = Ca and Sr, at 910°C equilibrium firing and oxygen saturation at 340°C; MCu(O)—BaCu(O)—YCu(O) cuts.

Substitution for Ba and Y by alkali metals. Contrary to some reports, rather limited substitution by alkali metals into $YBa_2Cu_3O_{9-\delta}$ is found, although various precautions were made to prevent evaporation of the alkali metal peroxides, which are readily formed in the system. At 850 °C, in saturated vapour of an extra added peroxide, no more than cca 8 % of Ba is replaced by Na, while possibly up to 4 % of Y being replaced simultaneously.

No substitution of Ba with elements similar in size, K–to–Cs, was accomplished for levels above 5–10 %.

Substitution for Cu by Li, Mg and 3–d elements. Contrary to some other quaternary cuprates, a rather low solid solublity, up to some 3 % is found for Li at the Cu–sites of $YBa_2Cu_3O_{9-\delta}$. Similar observations are done for Mg. Extended solid solubility is shown only by Fe and Co (20 % and 30 %, respectively), and Ni and Zn (5–10 %). For the other 3d–elements the extent of the solid solubility coincides with the detection limits of the X–ray method (Guinier–Hägg focusing camera). It is estimated to be lower than 3 % for Sc, Cr and Mn and below 1 % for Ti and V. In the copper poor region of the corresponding phase diagrams, the neighbouring phases to $YBa_2(Cu,M)_3O_{9-\delta}$ are poly–nary oxides rich in the metal M, like $BaSc_2O_4$, $Ba(Ti,Y)_4O_9$ + TiO_2, etc.

Superconducting properties. The existence of 3–d homogeneity spaces adjacent to a $YBa_2Cu_3O_{9-\delta}$ line in five component (one impurity) equilibrium phase diagrams allows T_c to change with up to three degrees of freedom in the compositional paremeters (considering fixed field H and current I). For an oxygen content defined by saturation at 10^5 Pa, T_c is a strongly decreasing function of any substitution for Cu, e.g., 14 K/% of substitution by Zn or Mg, and for Fe and Co above a 5% substitution level. 3.2 K/% Ni and 2 K/% Li. The same trend is found on partial replacing of Ba with a smaller element, e.g., 0.26 K/% of substitution by Sr. If substitution for Y takes place, it affects the T_c only in case where the substituting element alters the charge balance. T_c is especially prone to higher–valent substituents of Y which will lower the hole concentration in the copper–oxygen network. Thus Ca for Y substitution lowers T_c at a rate of $\sim$ 0.5 K/% Ca, whereas Pr at a rate of at least 1 K/% Pr. Similar results are observed for Tb.

The preparations of the variously substituted samples learn that the presence of some impurities, either in form of solid solutions or as phase admixtures, improves the sintering characteristics and resulting mechanical properties of the $YBa_2Cu_3O_{9-\delta}$ based products, leaving the T_c– and I_c–detrimential effects negligible. It seems therefore feasible to optimize the mechanical properties of the superconducting cuprate materials by substituting them with various elements, even if these eventually produce impurity phases.

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PROGRESS OF RESEARCH OF HIGH-Tc SUPERCONDUCTORS

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ABSTRACT

The research of high-Tc superconductors has made big progress in these last few years. New materials were found and the systematic investigations of these materials must contribute to understanding the mechanism of high-Tc superconductivity.

The critical currents in thin films, bulks and tapes increased drastically, and the origin of flux pinning will be clarified in the near future.

These progressions give us a view of a bright future of high-Tc superconductivity in both the basic and application research areas.

Recent activities in research of high-Tc superconductivity and superconductors in Japan will be overviewed.

N90-27836

THE NASA HIGH TEMPERATURE SUPERCONDUCTIVITY PROGRAM

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ABSTRACT

It has been recognized from the onset that high temperature superconductivity held great promise for major advances across a broad range of NASA interests. The current effort is organized around four key areas: communications and data, sensors and cryogenics, propulsion and power, and space materials technology. Recently, laser ablated $YBa_2Cu_3O_{7-x}$ films on LaAIO produced far superior RF characteristics when compared to metallic films on the same substrate. This achievement has enabled a number of unique microwave device applications, such as low insertion loss phase shifters and high-Q filters. Melt texturing and melt-quenched techniques are being used to produce bulk material with optimized magnetic properties. These Yttrium-enriched materials possess enhanced flux pinning characteristics and will lead to prototype cryocooler bearings. Significant progress has also occurred in bolometer and current lead technology. Studies are being conducted to evaluate the effect of high temperature superconducting materials on the performance and life of high power magneto-plasma-dynamic thrusters. Extended studies have also been performed to evaluate the benefit of superconducting magnetic energy storage for LEO space station, lunar and Mars mission applications. The projected direction and level of effort of the program are also described.

Navy Superconductivity Efforts

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Both the new high temperature superconductors (HTS) and the low temperature superconductors (LTS) are important components of the Navy's total plan to integrate superconductivity into field operational systems. Fundamental research is an important component of the total Navy program and focuses on the HTS materials. Power applications (ship propulsion, etc.) use LTS materials while space applications (MMW electronics, etc.) use HTS materials. The Space Experiment being conducted at NRL will involve space flight testing of HTS devices built by industry and will demonstrate the ability to engineer and space qualify these devices for systems use. Another important component of the Navy's effort is the development of Superconducting Quantum Interference Device (SQUID) magnetometers. This program will use LTS materials initially, but plans to implement HTS materials as soon as possible. Hybrid HTS/LTS systems are probable in many applications. In this presentation, a review of the status of the Navy's HTS materials research will be given as well as an update on the Navy's development efforts in superconductivity, with particular emphasis on the related SDIO-sponsored program on HTS applications.

AMSAHTS '90

POSTER PRESENTATIONS

N90-27838

PLASTIC SUPERCONDUCTOR BEARINGS
ANY SIZE - ANY SHAPE
77 k AND UP

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ABSTRACT

"Friction free" bearings at 77 k or higher are possible using the high Tc copper oxide ceramic superconductors. (1), (2)

The conventional method for making such bearings is to use a sintered ceramic monolith. This puts great restraints on size, shape and post-forming machining. The material is hard and abrasive.

It's possible to grind up ceramic superconductors and suspend the granules in a suitable matrix. Mechanical properties improve and are largely dependent on the binder. The Meissner effect is confined to individual grains containing electron vortices. (3)

Tracks, rails, levitation areas and bearings can be made this way with conventional plastic molding and extruding machines or by painting. The parts are easily machined. The sacrifice is in bulk electrical conductivity.

A percolating wick feel for LN2 can be used to cool remote superconductors and large areas quite effectively. A hollow spheroid or cylinder of superconductor material can be molded with the internal surfaces shielded by the Meissner effect. It might be thought of as the DC magnetic analogue of the Faraday cage and the inside can be called the Meissner space."

It's selective. AC fields are transmitted with minor attenuation. Particle size and distribution have a profound effect on final magnetic and electrical characteristics.

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N90-27839

THERMAL RESPONSE OF LARGE AREA HIGH TEMPERATURE SUPERCONDUCTING YBaCuO INFRARED BOLOMETER

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ABSTRACT:

Thermal analysis of large area high temperature superconducting infrared detector operating in the equilibrium mode (bolometer) was performed. An expression for the temperature coefficient $\beta=1/R(dR/dT)$ in terms of the thermal conductance and the thermal time constant of the detector were derived. A superconducting transition edge bolometer is a thermistor consisting of a thin film superconducting YBaCuO evaporated into a suitable thermally isolated substrate. The operating temperature of the bolometer is maintained close to the midpoint of the superconducting transition region where the resistance R has a maximum dynamic range. Measurements on the electrical response of YBaCuO thin films to a fast optical laser pulses (100Ps long) was recently reported[1]. It was found that although the magnitude of the signal corresponds to radiation heating, nonequilibrium energy transport have played a part in distributing the heat through the thickness of the film. A thermal diffusion model was developed to explain the experimental observations and to describe the overall thermal response of large area detector to external excitations. The results of these simulations agree reasonably well with the reported measurements. In this approach a detector with a strip configuration (see Fig.1) was analyzed and an expression for the temperature rise ΔT above the ambient due to a uniform illumination with a source of power density P_i was calculated to be,

$$T=(P_i t_h/C\Gamma)(1-\exp(-t/t_h)) \qquad (1)$$

where t_h is the thermal time constant of the detector, C is the volume specific heat, and Γ is the mass density of the thin film. the temperature rise in equation (1) was converted into voltages using R aganist T data provided in Ref.1 and the bias current of the thin film. The results of these calculations together with the measurements of Ref.1 are shown in Fig.2. On the other hand an expression for the thermal responsivity of the detector was derived using the above thermal diffusion analysis with appropriate boundary conditions. It was found that the thermal

responsivity depends upon the spatial modulation frequency and the angular frequency of the incoming radiation. For a given material with its characteristic diffusivity value, higher chopping frequencies will result in higher spatial frequencies to produce the same thermal response while quadrupling the chopping frequencies requires doubling the spatial frequency. The response of the HTS detector will ultimately be determined by tradding off the electrical-thermal gain bandwidth and the noise bandwidth. the bandwidth limits are determined by the thermal time constant t_h and the electrical time constant t_e and the signal rise time will be affected by the thermal coupling between the film and the insulator substrate.

The problem of the thermal cross talk between different detector elements was addressed. In the case of monolithic HTS detector array with a row of square elements of dimensions 2a and CCD or CID readout electronics the thermal spread function was derived for different spacing between elements. It was found that the thermal cross talk decreases rapidly with increasing the spacing between elements in the array. This analysis can be critical for future design and applications of large area focal plane arrays as broad band optical detectors made of granular thin films HTS YBaCuO.

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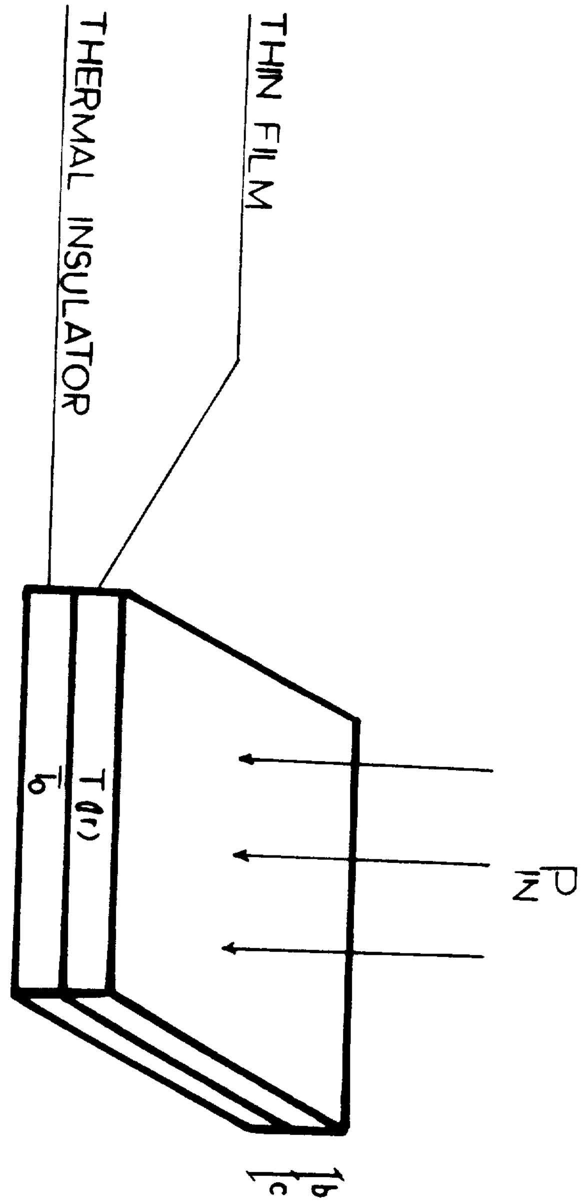

FIG. 1

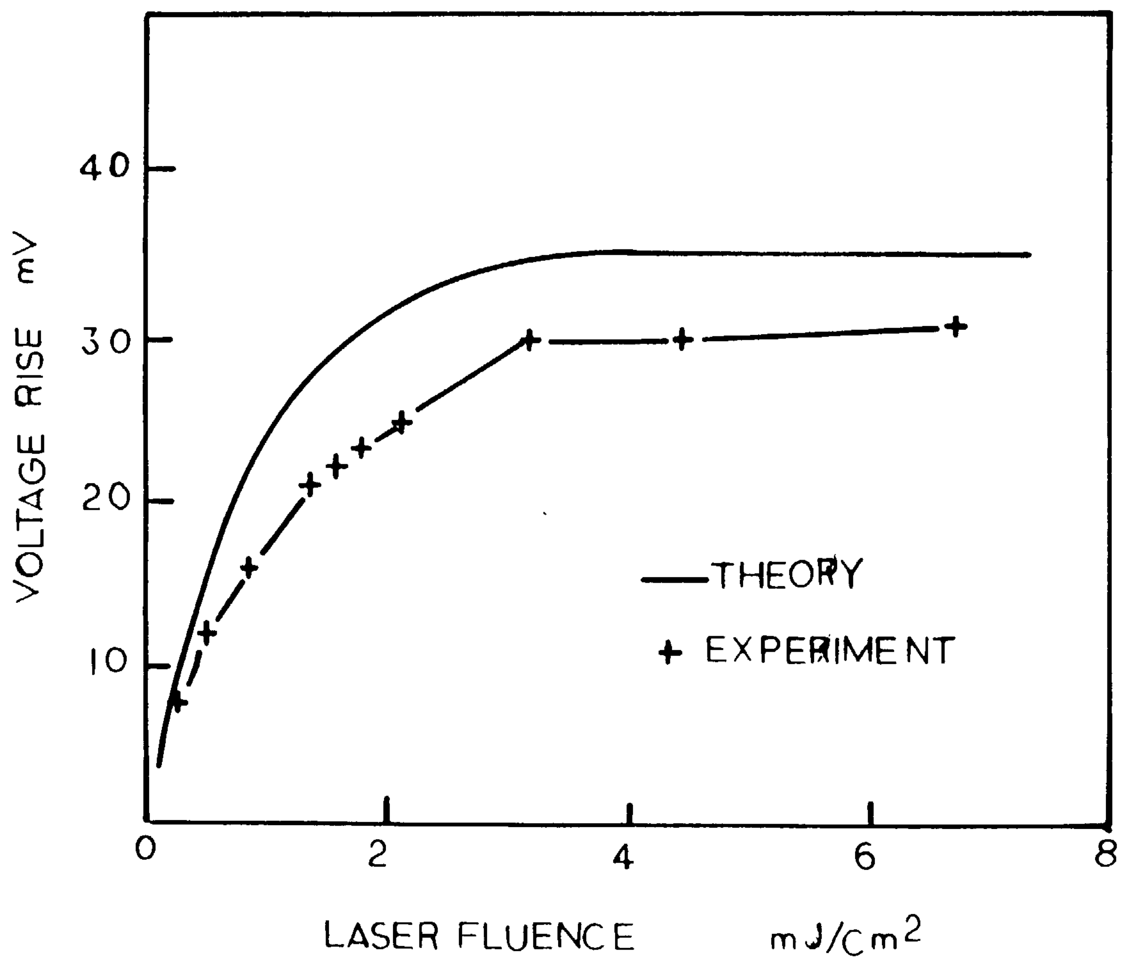
VOLTAGE RISE mV
40
30
20
10
0
2
4
6
8
THEORY
EXPERIMENT
LASER FLUENCE mJ/Cm2

FIG. 2

N90-27840

SUPERCONDUCTING FILM ON METALLIC WIRE

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Abstract

For technological applications of high-T_c superconductors, it will be necessary to overcome the inherent problem of brittleness, to develop materials with high current carrying capacity, and to devise ways of joining superconductors with other materials. These issues will be addressed in the context of superconducting films on metallic wires. These composite systems are expected to produce flexible wires with desirable properties.

N90-27841

Low Frequency Electrical Noise Across Contacts Between a Normal Conductor and Superconducting Bulk $YBa_2Cu_3O_7$

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Virtually every practical device that makes use of the new ceramic superconductors will need normal conductor to superconductor contacts. The current-voltage and electrical noise characteristics of these contacts could become important design considerations. This paper presents I-V and low frequency electrical noise measurements on contacts between a normal conductor and superconducting polycrystalline $YBa_2Cu_3O_7$. The contacts were formed by first sputtering gold palladium pads onto the surface of the bulk superconductor and then using silver epoxy to attach a wire(s) to each pad. For small current densities, voltage across the contacts was found to be proportional to $I^{.71}$. The voltage spectral density, $S_V(f)$, a quanity often used to characterize electrical noise, very closely followed an empirical relationship given by,

$$S_V(f) = \frac{C(VR)^2}{f},$$

where V is the DC voltage across the contact, R is the contact resistance, f is frequency, and C is a constant found to be $2 \times 10^{-10}/\Omega^2$ at 78° K. This relationship was found to be independent of contact area, contact geometry, sample fabrication technique, and sample density.

N90-27842

ELECTRONIC STATE AND SUPERCONDUCTIVITY OF $YBa_2Cu_{3-x}M_xO_{7-y}$ (M=Al, Zn and Sn) SYSTEMS

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A series of $YBa_2Cu_{3-x}M_xO_{7-y}$ (M=Al, Zn and Sn) single-phase samples are prepared, and the measurements of the crystal structure, oxygen content, electric resistivity, thermoelectric power, Mössbauer spectrum, XPS and superconductivity have been performed. The experimental results of X-ray powder diffraction, Mössbauer spectrum and oxygen content show that the Zn^{2+} and the Al^{3+} occupy the Cu(2) site in Cu-O planes and the Cu(1) site in Cu-O chains respectively, but the Sn^{4+} occupies both the Cu(1) and Cu(2) sites. As regards the properties in superconducting state, both the Zn^{2+} and the Al^{3+} depress T_c strongly, but the Sn^{4+} does not. As for the electronic transport properties in normal state, the system doped by Al^{3+} displays a rapid increase of resistivity and some electron-localization-like effects, and the thermoelectric power enhances obviously; the series contained Zn^{2+} almost shows no changes of electric resistivity but the sign of the thermoelectric power is reversed. The experimental results also reveal that, although both the replacements for Cu(1) and for Cu(2) can suppress T_c and modify the electronic structure, the mechanism in these two kinds of replacements is not the same. The substitution of Al^{3+} for Cu(1) waekens the coupling intensity between the Cu-O planes, making the electron energy band narrow and the electrons localized; the replacement for Cu(2) with Zn^{2+} mainly influences the Cu-O plane itself, changing the structure of the Fermi surface. The simultaneous substitution of Sn^{4+} for Cu(1) and Cu(2) make the electronic structure vary complexly: sometimes it makes T_c high, sometimes low, depending on the preparation conditions. In additions, another noticeable phenomenon in this substitution study is the appearance of the Cu^{3+} oxidation state. Our XPS study shows when the Cu(1) was replaced by Al^{3+} or by Sn^{4+}, a peak corresponding to the Cu^{3+} oxidation state appears in the core level spectrum Cu_{2p}, but this phenomenon can not be observed in Zn-doped system. As we all know, it was believed that the presence of the Cu^{3+} plays a predominat role on high-T_c superconductivity, and the most probable candidate of the Cu^{3+} is at the Cu(1) site. The XPS data show that the Cu^{3+} do exist in the Cu(1) site. Unfortunately, our experimental results also reveal that there is no intrinsic relationship between the Cu^{3+} oxidation state and the high-T_c superconductivity. Observing and studying all our results noted above, at least one conclusion can be drawn as the following: intact Cu-O planes and strong coupling between these planes are two absolutely necessary conditions for the high-T_c superconductivity in 1:2:3 compounds.

N90-27843

EFFECTS OF GRAIN SIZE AND GRAINBOUNDARY ON CRITICAL CURRENT DENSITY OF HIGH-T_c SUPERCONDUCTING OXIDES

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By means of adding impurity elements in high-T_c oxides, we have studied the effects of grain size and grainboundary on the critical current density of the following systems: $YBa_2Cu_3O_{7-y}$ and Bi-Pb-Sr-Ca-Cu-O. In order to only change the microstructure instead of the superconductivity of the grains in the samples, the impurity elements were added into the systems in terms of the methods like this: 1) substituting Y with the lanthanide except Pr, Ce and Tb in $YBa_2Cu_3O_{7-y}$ system to finning down grains in the samples, therefore, we can investigate the effect of the grain size on the critical current density of 1:2:3 compounds; 2) mixing the high-T_c oxides with the metal elements, such as Ag, according to the comsition of (high-T_c oxide)$_{1-x}$Ag$_x$ to metallize the grainboundaries in the samples, studying the effect of the electric conductivity of the grainboundaries on the critical current density; 3) adding SiO_2, PbO_2 and SnO_2 into the high-T_c oxide to form impurity phases in the grainboundaries, trying to find out the effects of the impurity phases or metalloid grainboundaries on the critical current density of the high-T_c superconductors. The experimental results indicate that in the case of the presence of the metalloid grainboundaries finning down grains fails to enhance the j_c, but restrains it strongly, the granular high-T_c superconductors with the small size grains coupled weakly is always the low j_c system. On the contrary, the systems with the grainboundaries metallized display striking improvment in the superconducting current-carrying properties. Mixing SiO_2, PbO_2 or SnO_2 with high-T_c oxides can clean the brainboundaries, making the j_c increase. The optimal method of improving the practical properties of the oxide superconductors is discussed.

N90-27844

Microwave Conductivity of Laser Ablated YBaCuO Superconducting Films and Its Relation to Microstrip Transmission Line Performance

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The discovery of high temperature superconductor oxides has raised the possibility of a new class of millimeter and microwave devices operating at temperatures considerably higher than liquid helium temperatures. Therefore, materials properties such as conductivity, current density, and sheet resistance as a function of temperature and frequency, possible anisotropies, moisture absorption, thermal expansion, and others, have to be well characterized and understood. In order to evaluate the suitability of such devices, and in an attempt to understand the nature of superconductivity in these new high Tc superconductors, the millimeter wave response of these new oxides has been investigated.

In this paper, we have studied the millimeter wave response of laser ablated $YBa_2Cu_3O_{7-x}/LaAlO_3$ thin films as a function of temperature and frequency. In particular, we have concentrated our efforts in the evaluation of their microwave conductivity, since knowledge of this parameter provides a basis for the derivation of other relevant properties of these superconducting oxides, and for using them in the fabrication of actual passive circuits. The microwave conductivity for these films has been measured at frequencies from 26.5 to 40.0 GHz, in the temperature range from 20 to 300 K. The values of the conductivity are obtained from the millimeter wave power transmitted through the films, using a two fluid model. The behavior of the real and imaginary parts of the complex conductivity, σ_1 and σ_2 respectively, at temperatures below T_c, is consistent with the predictions of carrier pairing mechanisms, as is shown in figures 1 and 2.

Values of the order of $1.8x10^7$ and $4.9x10^3$ S/M, for the imaginary and real parts of the microwave conductivity respectively, have been obtained at temperatures around 20 K. Values for the surface resistance, magnetic penetration depth, superconducting carrier density, and an effective energy gap (assuming BCS theory applicability), derived using σ_1 and σ_2, are reported.

A microstrip ring resonator was produced on 10 mil lanthanum aluminate by patterning a laser ablated film in a liquid bromine/ethanol etch, and evaporating 1 micron of gold for a ground plane (Fig.3). The resonator operated at a frequency of 35 GHz. The quality factor "Q" of resonators made entirely of evaporated gold on lanthanum aluminate (both strip and ground plane). Around 20 K, the "Q" of the hybrid was approximately twice that of the gold circuit, while closer to the transition temperature T_c of the HTS film, the improvement in Q was less. The improvement in "Q" implies a reduction in the surface resistance and losses in the HTS as compared to gold.

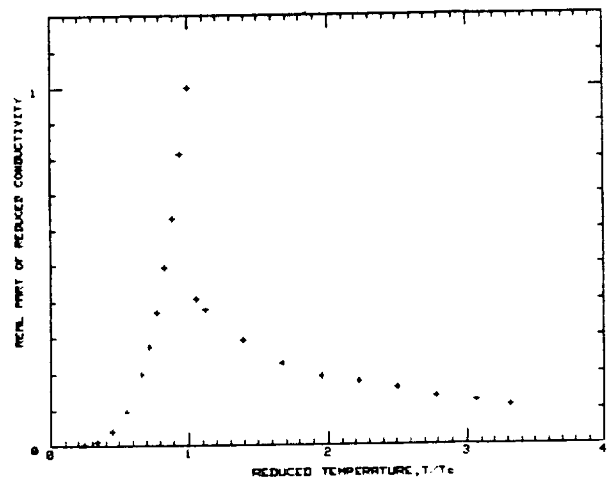

Figure 1: Real part of the microwave conductivity for a Laser Ablated $YBa_2Cu_3O_{7-x}/LaAlO_3$ thin film (.7 microns, T_c=89.7K) at 38.0 GHz.

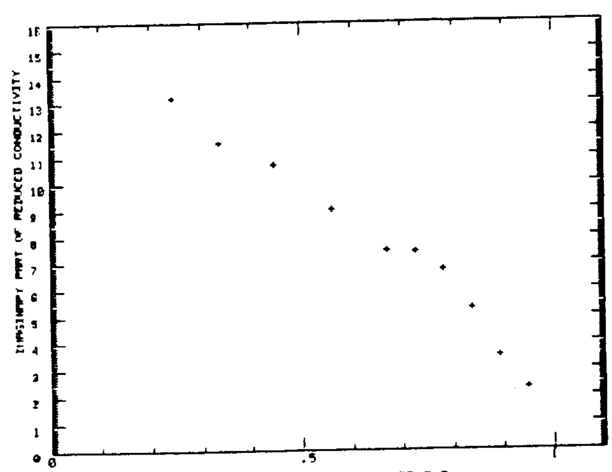

Figure 2: Imaginary part of the microwave conductivity for a Laser Ablated $YBa_2Cu_3O_{7-x}/LaAlO_3$ thin Film (.7 microns, T_c=89.7K) at 38.0 GHz.

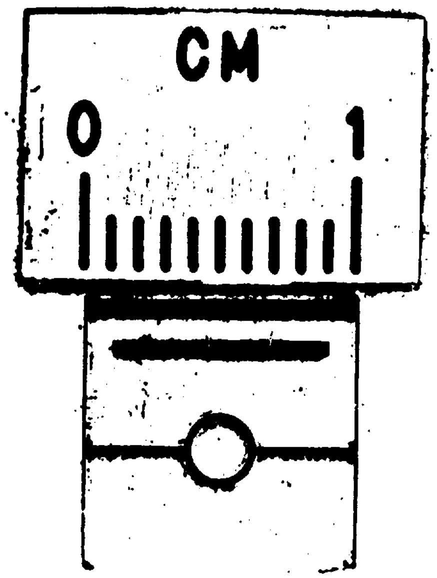

Figure 3: 35 GHz Ring Resonator circuit on $LaAlO_3$ substrate

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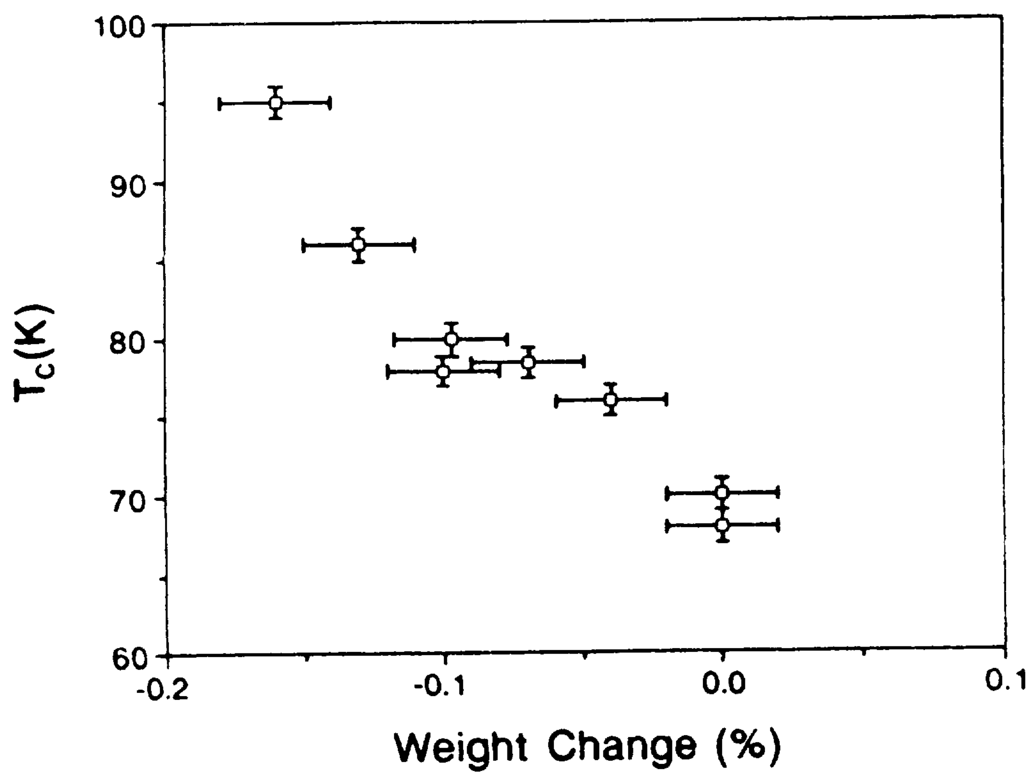

Fig.1 Superconductor transitions T_c verses weight change for 2211 phase

N90-27845

THE EFFECTS OF SPACE RADIATION ON THIN FILMS OF $YBa_2Cu_3O_{7-x}$

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High temperature superconducting materials are expected to offer significant improvements in the performance of spacecraft components. Specifically, low surface resistance at high frequencies is expected to result in reduced RF losses in superconducting waveguides, bandpass filters, and antennas. The broader bandwidth response of these materials may lead to improved and more sensitive IR detectors. The ability to exclude outside magnetic fields will result in high quality EMI-shielded enclosures, and the absence of resistive losses may lead to superconducting batteries with improved energy density and round-trip efficiencies.

It is attractive to provide passive cooling to superconductors by locating them on the shaded side of a space vehicle, radiating directly into space. Unfortunately, the technique results in exposure to high radiation dose levels due to trapped electrons and protons in the space environment. The high energy electrons and the protons will lose most of their energy in the first few microns inside the surface. For example, a typical surface dose for a 5-year mission in low earth atmospheric remote sensing orbit is 10^{15} electron/cm^2 which deposits 10 Megarads (10^9 ergs/gram) of energy in surface material. This is two or three orders of magnitude higher than the dose to most satellite electronics, which are shielded by at least several millimeters of material. The effects of space radiation on superconducting properties of YBCO materials are therefore critically important in incorporating these materials into spacecraft systems. The effects of charged particle irradiation on surface morphology of superconducting thin films has been published (1-3).

This investigation had two objectives: (1) to determine the effects of space radiation on superconductor parameters that are most important in space applications and (2) to determine whether this effect can be simulated with Co-60 gamma rays, the standard test method for space materials.

Thin films of YBCO were formed by coevaporation of Y, BaF_2, and Cu and post-annealing in wet oxygen at 850°C for 3.5 h. The substrate used was (100) silicon with an evaporated zirconia buffer layer. Processing and microstructure studies of these types of films have been published (4-7). The zero-resistance transition temperatures of the samples used in this study were 84 to 86K. The samples were characterized by four point probe electrical measurements as a function of temperature. The parameters measured were: the zero resistance transition temperature (T_c) and the room temperature resistance. The samples were then exposed to Co-60 gamma-rays in air and in pure nitrogen, and to 780-keV electrons, in air. The parameters were then remeasured. The results are summarized in Tables 1 and 2.

The results indicate little or no degradation in the parameters measured for samples exposed up to 10 Mrads of gamma-rays in nitrogen. However, complete degradation of samples exposed to 10-Mrad in air was observed. This degradation is preliminarily attributed to the high level of ozone generated in the chamber by the gamma-ray interaction with air. Furthermore, no degradation in superconducting properties of samples exposed to 10^{15} electrons at 780 kev in air was observed. Apparently these samples are more radiation resistant than the bulk materials which were degraded by exposure to 6.5 x 10" electrons/cm^2 at 1 Mev (Ref. 8).

It can be concluded that (1) the electron component of space radiation does not degrade the critical temperature of the YBCO films described herein, at least for energies around 800 KeV and doses similar to those received by surface materials on spacecraft in typical remote sensing missions; (2) for qualifying this and other superconducting materials against the space-radiation threat the standard test method in the aerospace industry, namely, exposure to Co-60 gamma rays in air, may require some further investigation. As a minimum, the sample must be either in vacuum or in positive nitrogen pressure.

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TABLE 1. SUMMARY OF GAMMA-RAY EXPOSURES ON SUPERCONDUCTING MATERIALS

SAMPLE DESCRIPTION	AMBIENT ENVIRONMENT	GAMMA-RAY DOSE (Mrad)	TRANSITION TEMPERATURE(K) BEFORE EXPOSURE	TRANSITION TEMPERATURE(K) AFTER EXPOSURE	COMMENTS
1a) YBaCuO on Si	Air	10	86	-	Catastrophic Failure
1b) YBaCuO on Si	Air	100	85	-	Complete erosion of superconducting film
2a) YBaCuO on Si	Nitrogen	10	85	84	Slight degradation in Tc
2b) YBaCu on Si	Nitrogen	10	86	82	Slight degradation in T_c
3) YBaCuO on Si (Control Sample)*	Air	--	85	85	No degradation in Tc (after 21 days)

* The control sample was placed outside of the Co-60 source and its superconducting properties were compared to the exposed samples.

TABLE 2. SUMMARY OF ELECTRON EXPOSURES ON SUPERCONDUCTING MATERIALS

SAMPLE TYPE	AMBIENT ENVIRONMENT	ELECTRON DOSE	TRANSITION TEMPERATURE(K)		COMMENTS
			BEFORE EXPOSURE	AFTER EXPOSURE	
1) YBaCuO on Si	Air	10^{15} electron/cm^2 at 780 kev	84	84	No degradation in Tc
2) YBaCuO on Si (Control Sample)*	Air	-	85	85	No degradation in Tc

* The control sample was placed outside of the electron generator and its superconducting properties were compared to the exposed samples.

A TECHNIQUE TO MEASURE THE THERMAL DIFFUSIVITY OF HIGH T_c SUPERCONDUCTORS

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High T_c superconducting electrical current leads and ground straps will be used in cryogenic coolers in future NASA Goddard Space Flight Center missions. These superconducting samples will be long, thin leads with a typical diameter of two millimeters. A longitudinal method is being developed to measure the thermal diffusivity of candidate materials for this application. This technique will use a peltier junction to supply an oscillatory heat wave into one end of a sample and will use low mass thermocouples to follow the heat wave along the sample. The thermal diffusivity will be calculated using both the exponential decay of the heat wave and the phase shift of the wave. Measurements will be done in a cryostat between 10 K and room temperature.

N90-27847

SUPERCONDUCTIVITY IN 2-2-3 $Y_2Ba_2Cu_3O_{8+\delta}$

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ABSTRACT

We have synthesized a new high Tc 2-2-3 superconductor $Y_2Ba_2Cu_3O_{8+\delta}$ by a special preparation technique and have characterized it by ac-susceptibility measurements. Diamagnetism and Meissner effect sets in at low fields and superconducting transition onsets at 90 K. The systematic investigation of the real and imaginary components of ac-susceptibility as a function of temperature and applied ac magnetic field reveals that the magnetic behaviour is that of a granular type superconductor.

N90-27848

Microstructures and properties of superconducting Y-Er-BaCu-O thin films obtained from disordered Y-Er-BaF_2-Cu films

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Since the first reports on superconducting thin films obtained by evaporating BaF_2, Cu and Y [1], or Yb or Er [2] several others have followed. To our knownledge, however, all these reports describe thin films prepared by means of molecular beam cells or electron guns. Here we show that films with similar properties can be obtained by R.F. sputtering of a single mosaic target composed by Y-Er, BaF_2 and Cu. We have prepared first a precursor film that is characterized by an almost unstructured x-ray spectra; indeed we observed only a peak at $2\theta = 25\,°$ that is due to the reflection from the 111 plane of the BaF_2. Its intensity is strongly dependent on the humidity of the atmosphere to which the sample is exposed, its decrease can be correlated with the appearance of two small bumps in the positions of the 111 and 200 lines of the copper fcc. After the post-annealing process the sample grown on zaffire and $SrTiO_3$ are superconductors. In particular the latters have an onset temperature of 92.5 K and an offset temperature of 86.8. K and results to be constituted by randomly oriented plaquettes whose c axis has a tendence to orient along the plane of the substrates. The critical temperature, and more in general the properties, of these samples are strongly correlated with their annealing temperature and with the composition of the fluxing gas. We will show that there exist a strict correlation between the intensity of the BaF_2 111 line observed after the annealing, the proportion of the cristallites that have geminated, the critical temperature and the composition of the gas mixture. Distilled water is essential because helps in trasforming the BaF_2 in BaO, while the use of ozone by itself seems to be, at least for this class of films, more detrimental than useful. Resistive and magnetic characterizations will be also discussed in all the details.

In conclusion we have shown that (Y-Er)-Ba-Cu-O thin films can be obtained using (Y-Er)-BaF_2-Cu precursors, not only by means of molecular beam cells or electron guns but also with much less inexpensive R.F. sputtering.

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Spatial Conductivity Measurements on High T_c Superconducting Films

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High T_c superconducting thin and thick films have potential applications in future NASA flight projects. In anticipation of film use, the Materials Branch is developing a nondestructive, non-contact method of measuring the spatial variation of conductivity across a film sample. This method uses a computer-controlled, X-Y positioning table to scan a conventional eddy current probe across the surface of a film. The induced changes in impedance caused by variations in film conductivity are recorded during the scanning process. Ultimately the two-dimensional data set is displayed using imaging equipment on a personal computer.

N90-27850

COMPOSITE SUPERCONDUCTING WIRES OBTAINED BY HIGH-RATE TINNING IN MOLTEN Bi-Pb-Sr-Ca-Cu-O SYSTEM

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In the given communication we report on the principle possibility of the preparation of high-T_c superconducting long composite wires by short-time tinning of the metal wires in a molten Bi-Pb-Sr-Ca-Cu-O compound. As far as we know the application of this method to the high-T_c materials is tested for the first time.

The initial materials used for this experiment were ceramic samples with nominal composition $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ and T_c= 80 K (fig.1, curve 1) prepared by the ordinary solid-state reaction, and industrial copper wires from 100 to 400 μm in diameter d and from 0.5 to 1 m long. The continuous moving wires were let through a small molten zone (~100 mm^3). The Bi-based high-T_c ceramics in a molten state is a viscous liquid and it has a strongly pronounced ability to spread on metal wire surfases. The maximum draw rate of the Cu-wire, at which a dense covering was still possible, corresponds to the time of direct contact of wire surfaces and liquid ceramics for less than 0.1 s. A high-rate draw of the wire permits to decrease essentially the reaction of the oxide melt and Cu-wire. The realisation of the given method by simple technical means allowed to make the cylindrical composite wires, consisting of the copper core in a dense covering with uniform thickness of about h≈ 5-50 μm. Composite wires with h≈ 10 μm (h/d≈ 0.1) sustained bending on a 15 mm radius frame without flexs cracking.

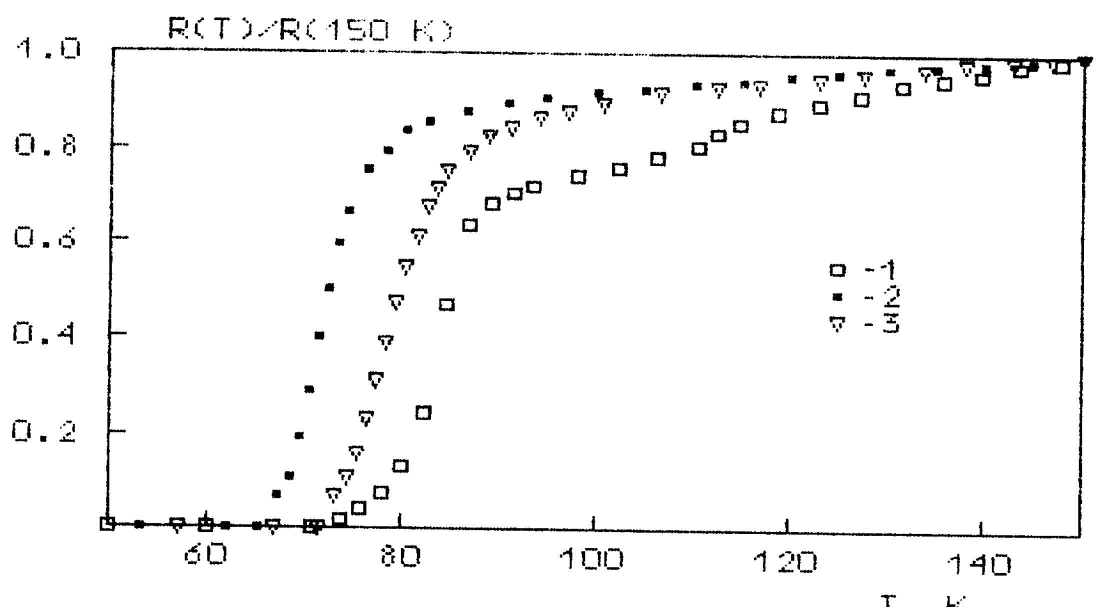

Figure 1

The microstructure and electrical resistivity R of the covering depend in a complicated manner on the covering process parameters. For example, the covering obtained at the draw rate of about 100 mm/s has a strongly marked axial texture consisting of thin plate-like crystals (the axis of the texture is parallel to the wire axis). As-obtained covering has no superconductivity properties. To restore the superconductivity the pieces of composite wires about 5 cm long were subjected to heat treatment at 800°C in air. Figure 1 shows the temperature dependence of the resistivities of the composite wires annealed for 20 (curve 1) and 41 min (curve 2). The electrical resistivity R was measured by a standard dc four-probe method with silver paste contacts using a constant current of 10 μA. According to the resistivity curves the superconductivity transitions started at $T_{co} \approx$ 90-95 K and ended at $T_{ce} \approx$ 68-71 K. These values practically coincided with the values of critical resistivity points obtained on the initial multiphase ceramic bar (curve 1).

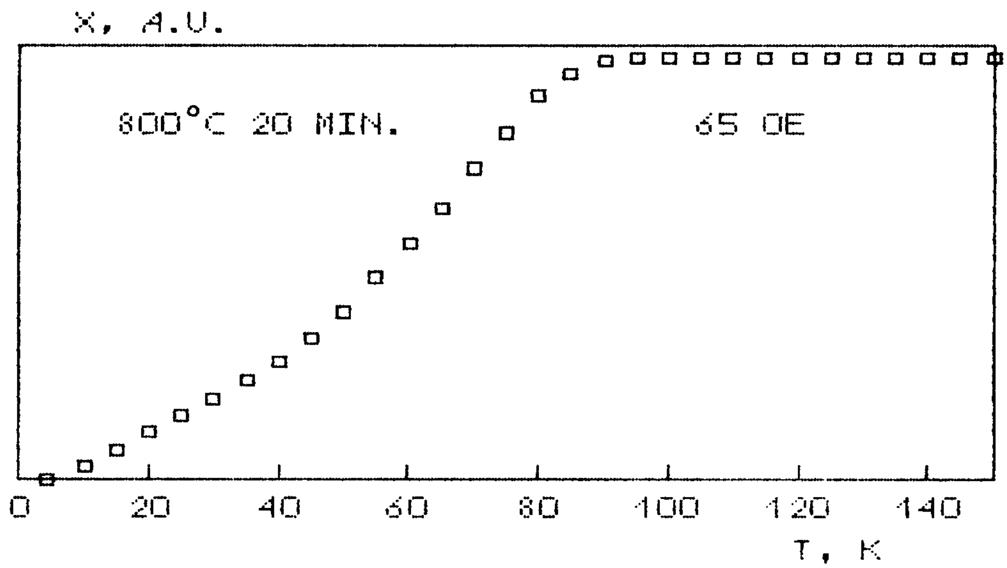

Figure 2

The direct evidence of composite wires supeconductivity followed from their magnetic properties. Figure 2 shows the typical curve of susceptibility vs temperature for composite wires annealed at 800°C for 20 min. These measurements where performed using a SQUID magnetometer. The X-T curve, similar to R(T), has only one bend at 90 K. It is supposed that annealing at 800°C results in the predominant formation of only one superconductive ($T_c \approx$ 80 K) phase. This concords with the data on the bulk Bi-Pb-Sr-Ca-Cu-O glass-ceramics, produced by the liquid quenching method and subsequently annealed at 750-800°C. Recently, as a result of improving the annealing conditions, we succeeded in preparation of composite wires with the higher zero-resistance temperature.

In summary, long high-T_c composite wires where prepared by high-rate draw of flexible bare conductor through molten Bi-based metal-oxide system.

IN-SITU INTEGRATED PROCESSING AND CHARACTERIZATION OF THIN FILMS OF HIGH TEMPERATURE SUPERCONDUCTORS, DIELECTRICS AND SEMICONDUCTORS BY MOCVD

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Low temperature deposition, high throughput, sharp interfaces, selective deposition with direct ion, electron, and photon beam controlled techniques, and deposition in conventional as well as atomic layer epitaxy mode are some of the attractive features of MOCVD. In addition to the well established role in semiconductor and optoelectronics industry, MOCVD is expected to play a significant role in high temperature superconductor industry. High temperature superconducting thin films as well as semiconductors and/or dielectrics are essentially required for the fabrication of superconductor and hybrid superconductor/semiconductor devices. From materials compatibility point of view, the interface between two disimilar materials (e.g.superconductor/dielectric, semiconductor/dielectric, etc.) should have chemical, physical, and thermal integrity during and after the processing of materials. In our strategity of depositing the basic building blocks of superconductors, semiconductors, and dielectric having common elements, we have deposited superconducting films of Y–Ba–Cu–O, semiconductor films of Cu_2O, and dielectric films of BaF_2 and Y_2O_3 by MOCVD. By switching source materials entering the chamber, and by using direct writting capability complex device structure like three terminal hybrid semiconductors/superconductors transistors can be fabricated. The Y–Ba–Cu–O superconducting thin films on BaF_2/YSZ substrates show a T_c of 80K and are textured with most of the grains having their $c - axis$ or $a - axis$ perpendicular to the substrate. In this paper, we will report electrical characteristics as well as structural characteristics of superconductors and related materials obtained by X-ray deffraction, SEM, TEM, and energy dispersive X-ray analysis.

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N90-27852

GRAIN ORIENTATION STUDIES IN SUPERCONDUCTORS

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Abstract

Grain oriented fabrication of ceramics utilizes the presence of some form of anisotropy in the particles of the starting material to obtain textured microstructures. Molten salt or the flux method has been a popular technique for growing crystals and particles with anisotropic morphology and is utilized in this study. The formation of $Ba_2YCu_3O_{7-x}$ in the presence of molten salts of Na, K, Li belonging to chloride and Sulfate systems does not appear feasible in the temperature range upto 900° C. We will also present the results of our studies in using BaY_2CuO_5 as seed crystals in the formation of $Ba_2YCu_3O_{7-x}$ wherein BaY_2CuO_5 has been observed to have better stability in water and against most of the salts as compared to $Ba_2YCu_3O_{7-x}$. Additional results of Molten salt processing of Bismuth systems will also be presented.

N90-27853

LOCALIZATION EFFECTS IN RADIATIONALLY DISORDERED HIGH-TEMPERATURE SUPERCONDUCTORS: THEORETICAL INTERPRETATION

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Theoretical interpretation of recent experiments on radiationally disordered high-temperature superconductors is presented, based on the concepts of mutual interplay of Anderson localization and superconductivity.

Microscopic derivation of Ginzburg-Landau coefficients for the quasi-two-dimensional system in the vicinity of localization transition is given in the framework of self-consistent theory of localization. The "minimal metallic conductivity" for the quasi -two-dimensional case is enhanced due to a small overlap of electronic states on the nearest neigbour conducting planes. This leads to much more strong influence of localization effects than in ordinary (three-dimensional) superconductors. From this point of view even the initial samples of high-temperature superconductors are already very close to Anderson transition.

Anomalies of H_{c2} are also analyzed, explaining the upward curvature of $H_{c2}(T)$ and apparent independence of dH_{c2}/dT $(T=T_c)$ on the degree of disorder as due to localization effects.

We discuss the possible reasons of fast T_c degradation due to the enhanced Coulomb effects caused by the disorder induced decrease of localization length. The appearance and growth of localized magnetic moments is also discussed. The disorder dependence of localization length calculated from the experimental data on conductivity correlates reasonably with the theoretical criterion for suppression of superconductivity in the system with localized electronic states.

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CUOPLED BIPOLARONS AND OPTICAL PHONONS AS A MODEL FOR HIGH-T_c SUPERCONDUCTORS

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1. INTRODUCTION.

All known up-to-date high-temperature superconductors are oxides (mainly copper oxides although compounds without copper were obtained, e.g. $BaKBiO_3$). On the other hand, more than 95 % of all ferroelectric compounds are also oxides or contain oxygen ion [1] . Therefore, the problem of mutual relation between ferroelectricity and superconductivity is of great theoretical interest.

The electron-phonon interaction is important in both phenomena. In ferroelectrics a cubic electron-phonon and/or a quartic electron-two-phonon interactions play an essential role [1] . In classical superconductors (of the BCS type) a cubic electron-one-phonon interaction leads to the formation of Cooper pairs of two electrons with opposite momenta and spins . The average distance (in real space) between the two electrons is of order of the so-called coherence length ξ which is much greater than lattice constant of such a classical superconductor. However, the coherence length of the new high-temperature superconductors reaches very small value which is comparable to the dimensions of unit cell of these compounds [3] . This means that a pair consists of two holes occupying the same site or two adjacent sites . Such a situation seems to be described by a model of the local-pairs (bipolarons) [2,3].

The origin of local-pair may come not only from strong enough electron or hole-phonon interaction but also from other interactions . Independently of a specific nature of such local-pairs, they can undergo a Bose-like condensation to the superconducting state at a critical temperature which is usually much lower than the temperature of the pair formation.

In this paper an interplay of ferroelectric and superconducting properties is considered within the model of hole-like local-pairs interacting with optical phonons . Therefore, we extend the usual local-pair Hamiltonian [2] by including an direct interaction between the local-pairs and the optical phonons. These optical phonons are known to play an important role in the ferroelectric transition if any and they transform into an additional pseudo-acoustic branch at the ferroelectric critical temperature [1] (this is associated with arising of nonzero electric polarization due to existence of two separate lattices composed of negative and positive ions, respectively).

2. HAMILTONIAN OF INTERACTING LOCAL-PAIRS AND OPTICAL PHONONS.

The Hamiltonian of our system is as follows

$$H = - w_o \sum_i \sum_j (N_i N_j - A_i^+ A_j) + \sum_i (h\nu_o b_i^+ b_i - \mu N_i - \lambda N_i (b_i^+ + b_i)), \text{ where}$$

$A_i^+(A_i), b_i^+(b_i)$ are creation (annihilation) operators for the local-pair and the optical phonon (with frequency ν_o) at the i-th site, respectively, $N_i = A_i^+ A_i$, w_o is a local-pair bandwidth and μ denotes the chemical potential. An analysis of the above Hamiltonian can be carried out on the ground of the Bogolyubov's inequality [4] for the free energy $F \le F_t = F_0 + \langle H \rangle_0 - \langle H_t \rangle_0$, with the trial Hamiltonian in which the local-pairs and the phonons are decoupled

$$H_t = \sum_i (- W_i A_i^+ - W_i^* A_i - Q_i N_i + h\nu_o B_i^+ B_i) = H_{pair} + H_{ph}$$

where W_i , W_i^* and Q_i stand for variational parameters and B_i^+ (B_i) are new creation (annihilation) operators for phonon at the i-th site . The thermal averages of the $\langle \ \ \rangle_0$ type are defined as usual, e.g., $\langle H \rangle_0 = \mathrm{Tr} (\varrho_0 H)$, $\varrho_0 = \exp(-\beta H_t) / \mathrm{Tr}(\exp (-\beta H_t))$, $\beta = (k_B T)^{-1}$, k_B - the Boltzmann's constant . Within the single site approximation which is equivalent to the mean-field approximation (MFA)

$F_0 = - \beta^{-1} \sum_i \ln Z_0$ with the single-site partition function

$$Z_0 = (\exp(-\beta\varepsilon_1) + \exp(-\beta\varepsilon_2) / (1 - \exp(-\beta h\nu_o))) ,$$

where ε_1 and ε_2 are the eigenvalues of the Hamiltonian H_{pair} calculated in the basis of states consisting of two single-site states : φ_o and φ_1 which describe a given site occupied (φ_1) or unoccupied (φ_o) by a local-pair . A straightforward diagonalization of the H_{pair} matrix $\begin{pmatrix} 0 & -W^* \\ -W & Q \end{pmatrix}$ leads to the following eigen-energies

$$\varepsilon_1 = (- Q - (- Q^2 + 4| W |^2)^{1/2}) / 2$$

$$\varepsilon_2 = (- Q + (- Q^2 + 4| W |^2)^{1/2}) / 2$$

The variational parameters Q, W and W^* should be calculated by minimizing the trial free energy F_t . One obtains the mean-field Hamiltonian H_{MFA} by means of the following decouplings

$$\sum_i\sum_j A_i^+ A_j \Rightarrow \sum_i\sum_j \langle A_i^+ \rangle A_j + \sum_i\sum_j A_i^+ \langle A_j \rangle = \sum_i z (\alpha A^+ + \alpha^* A)$$

$$\sum_i\sum_j N_i N_j \Rightarrow \sum_i\sum_j \langle N_i \rangle N_j + \sum_i\sum_j N_i \langle N_j \rangle = 2z\nu \sum_i N_i$$

where $\alpha = \alpha_i = \langle A_i \rangle = \langle A \rangle$ is the superconducting order parameter, $\nu = \nu_i = \langle N_i \rangle = \langle N \rangle$ is the concentration of the local-pairs per one site and z denotes a coordination number (a number of the nearest neighbours of a given site). In the result

$$H_{MFA} = \sum_i (- w (\alpha A^+ - \alpha^* A) + 2w\nu N + h\nu_o b^+ b - \mu N - \lambda N (b^+ + b))$$

with the parameter $w = zw_o$.

3. FREE ENERGY AND COUPLING EQUATIONS.

In this section we determine the trial free energy according to the above Hamiltonian. The trial energy per one site $f_t = F_t / \sum_j 1$ takes the form

$$f_t = -\beta^{-1}\ln(\exp(-\beta\varepsilon_1) + \exp(-\beta\varepsilon_2)) + \beta^{-1}\ln(1-\exp(-\beta h\nu_0)) + W\alpha^* + W^*\alpha -$$
$$-2w|\alpha|^2 + 2w\nu^2 + (Q-\mu)\nu + h\nu_0 (\langle b^+b\rangle_0 - \langle B^+B\rangle_0) - \lambda \langle N (b^+ +b)\rangle_0$$

In order to calculate the necessary averages let us introduce the new states

$$\Phi_1 = c_{10}\varphi_0 + c_{11}\varphi_1 \qquad \Phi_2 = c_{20}\varphi_0 + c_{21}\varphi_1 \quad .$$

for which the matrix of H_{pair} has a diagonal form. The coefficients c_{kl} can be obtained from the equation : $H_{pair}\Phi_i = \varepsilon_i \Phi_i$,i.e.

$$\begin{pmatrix} -\varepsilon_i & -W^* \\ -W & Q-\varepsilon_i \end{pmatrix} \begin{pmatrix} c_{i0} \\ c_{i1} \end{pmatrix} = 0 .$$

Taking into account the normalization condition for eigenfunctions Φ_1 and Φ_2 one obtains in the result :

$$c_{i0} = (1 + |\varepsilon_i/W^*|^2)^{-1/2} = (W/(Q-\varepsilon_i)) (1 + |W^*/(Q-\varepsilon_i)|^2)^{-1/2}$$
$$c_{i1} = (1 + |W^*/(Q-\varepsilon_i)|^2)^{-1/2} = (-\varepsilon_i/W^*) (1 + |-\varepsilon_i/W^*|^2)^{-1/2}$$

Consider the quantities $\xi_k = \langle\Psi_k|b-B|\Psi_k\rangle$, where Ψ_k are the phonon eigenfunctions i.e. $H_{ph}\Psi_k = kh\nu_0 \Psi_k$ ($k = 0,1,2,\dots$) . Let us assume for simplicity that $\xi_k = \xi$ and $\langle\Psi_{k-1}|b-B|\Psi_k\rangle = 0$ for all values of k. The parameter ξ can be treated as a non-variational quantity which is proportional to a lattice deformation . This deformation can be associated with arising a nonzero dipole electric moment, i.e. with a ferroelectric phase transition. After some algebra one comes to the following :

$$\langle b^+b\rangle_0 - \langle B^+B\rangle_0 = \xi^*\xi .$$

Using the calculated coefficients c_{i1} one obtains :

$$\langle N b \rangle_0 = \xi/2 + \xi Q(Q^2+4|W|^2)^{-1/2}\left[2-\tanh(\beta(Q^2+4|W|^2)^{1/2})\right]/2$$

The trial reduced free energy is then readily written as

$$f_t = -\beta^{-1}\ln(\exp(-\beta\varepsilon_1) + \exp(-\beta\varepsilon_2)) + \beta^{-1}\ln(1-\exp(-\beta h\nu_0)) + W\alpha^* + W^*\alpha - 2w|\alpha|^2 +$$
$$2w\nu^2 + (Q-\mu)\nu + h\nu_0\xi^*\xi - \lambda(\xi^*+\xi)\left[1 + Q (Q^2+4|W|^2)^{-1/2}\left[2-\tanh(\beta(Q^2+4|W|^2)^{1/2})\right]\right]/2$$

A minimization of the above thermodynamic potential with respect to W, W^*, α, α^*, Q and ν leads to the following coupling equations

$$(2w)^{-1} = (Q^2+4|W|^2)^{-1/2}\tanh(\beta(Q^2+4|W|^2)^{1/2}) - \lambda(\xi^*+\xi)Q(Q^2+4|W|^2)^{-3/2}$$
$$\tanh(\beta(Q^2+4|W|^2)^{1/2}) + \lambda(\xi^*+\xi)\beta Q(Q^2+4|W|^2)^{-1}\left[\cosh(\beta(Q^2+4|W|^2)^{1/2})\right]^{-2}/2$$
$$2\nu-1 = Q(Q^2+4|W|^2)^{-1/2}\tanh(\beta(Q^2+4|W|^2)^{1/2}) + 4\lambda(\xi^*+\xi)|W|^2(Q^2+4|W|^2)^{-3/2}$$
$$\tanh(\beta(Q^2+4|W|^2)^{1/2}) + \lambda(\xi^*+\xi)\beta Q^2(Q^2+4|W|^2)^{-1}\left[\cosh(\beta(Q^2+4|W|^2)^{1/2})\right]^{-2}/2$$
$$W = 2w\alpha \qquad Q = -4w\nu + \mu \qquad + \text{c.c.}$$

It is easily seen that $W=W^*$ and $\alpha=\alpha^*$. The above set of equation should be self-consistently solved.

4. GROUND STATE .

By taking the limit $T \to 0$, the energy of a ground state per one site is given by

$$E = \langle H\rangle_o / \sum_i 1 = -2w\alpha^2 + 2w\nu^2 - \mu\nu + h\nu_o\xi^2 + \lambda\xi(1+Q/(Q^2+4W^2)^{1/2})$$

Let us consider the purely superconducting ground state for which the ferroelectric order parameter ξ disappears ($\xi=0$) . The superconducting order parameter strongly depends on the local-pair concentration , i.e. $\alpha^2 = \nu(1-\nu)$. The energy of the superconducting ground state is as follows

$$E_{sc} = -2w\alpha^2 + 2w\nu^2 = 2w(2\nu-1)\nu$$

For the purely ferroelectric ground state the superconducting order parameter disappears ($\alpha=W=0$) and the energy is given by

$$E_{fe} = 2w\nu^2 + h\nu_o\xi^2 - \lambda\xi(1+Q/(Q^2)^{1/2})$$

The normal state , i.e. non-superconducting and paraelectric ($\alpha=0$ and $\xi=0$), has the energy $E_n = 2w\nu^2$. It is clearly seen that normal state cannot be realized because of the lower energy of the superconducting state , at least ($E_{sc} < E_n$). Nevertheless, an competition is possible between superconducting and ferroelectric ground states. The superconducting state is prefered if $2\nu(1-\nu) > (2\lambda\xi - h\nu_o\xi^2)/w$.

5. SUPERCONDUCTING TRANSITION

Let us return to finite temperatures. To get the superconducting critical temperature T_c we assume that superconducting order parameter disappears ($\alpha=\langle A\rangle=0$). The reduced critical temperature is thus given by

$$t_c = k_B T_c/w = q / \ln((1+Z)/(1-Z)),$$

where $q = Q/w = 2\nu-1+((2\nu-1)^2-4pZ)^{1/2}$, $p = \lambda\xi/w$ and the quantity Z can be numerically calculated from the additional condition

$$0 = q^2/2 - (q-2p)Z - p(1-Z^2)\ln((1+Z)/(1-Z))$$

It can be shown that maximum critical temperature is strongly enhanced due to the rather moderate interaction up to $p \cong 0.3$. However, a nonzero value of ξ , i.e. temperature below ferroelectric transition temperature, is necessary. For stronger coupling and/or smaller bandwidth w , this effect weakens . On the other hand , the high-temperature superconductivity is rather restricted to the regions far from half-filling ($\nu \neq 1/2$).

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SYNTHESIS OF $Y_1Ba_2Cu_3O_x$ SUPERCONDUCTING POWDERS BY INTERMEDIATE PHASE REACTION.

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One of the more stricking problems for the synthesis of the $Y_1Ba_2Cu_3O_x$ compound is the high-temperature decomposition of the $BaCO_3$. This compound is present as raw material or as an intermediate compound in chemical processes such as amorphous citrate, coprecipitation oxalate, sol-gel process, acetate pyrolisis, etc. This fact difficults the total formation reaction of the $Y_1Ba_2Cu_3O_x$ phase and leads to the presence of undesirable phases such as the $BaCuO_2$ phase, the "green phase", Y_2BaCuO_5 and others.

In the present work a new procedure to overcome this difficulty is estudied. The barium cation is previously combined with yttrium and/or copper to form intermediate compounds which can react between them to give $Y_1Ba_2Cu_3O_x$.

BaY_2O_4 and $BaCu_2O_3$ react according to the following equation

$$BaY_2O_4+3BaCu_2O_3 \longrightarrow 2Y_1Ba_2Cu_3O_x$$

BaY_2O_4 is a stable compound of the Y_2O_3-BaO system, $BaCu_2O_3$ is an intimate mixture of $BaCuO_2$ and uncombined CuO.

The reaction kinetics of these phases have been established between 860 and 920ºC. The phase evolution has been determined. The crystal structure of the $Y_1Ba_2Cu_3O_x$ obtained powder was studied by means of XRD. According to the results obtained from the kinetics study the $Y_1Ba_2Cu_3O_x$ the synthesis was performed at temperatures of 910–920ºC for short treatment times (1-2 hours). Pure $Y_1Ba_2Cu_3O_x$ was prepared, which developes orthorombic type I structure despite of the cooling cycle. Superconducting transition took place at 91 K.

The sintering behaviour and the superconducting properties of sintered samples were studied. Density, microstructure and electrical conductivity were measured. Sintering densities higher than 95% D_{th} were attained at temperatures below 940º. Relatively fine grained microstructure wer observed, and little or no-liquid phase was detected.

N90-27856

SPIN BIPOLARON IN THE FRAMEWORK OF EMERY MODEL FOR HIGH-Tc COPPER OXIDE SUPERCONDUCTORS.

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The high-Tc oxide compounds discovered recently exhibit a number of interesting physical properties. Two-dimensional antiferromagnetic spin order has been observed in these materials at the oxygen deficiency. This fact can be explained by strong correlation of the spins, situated on Cu sites in the conducting planes of the oxide superconductors. The doping or the oxygen deficiency lead to the occurence of holes, occupying the oxygen p-orbitals according to Emery model. At the small hole concentration they can move along the antiferromagnetic lattice of spins, localized on Cu sites.

We consider two holes situation and describe in what way their behaviour depends on the antiferromagnetic exchange interaction J. It is known that in the framework of Hubbard model with strong on-site Coulomb repulsion a single hole can form spin polaron of the large radius [1]. It is reasonable to admit that two holes with parallel spins (triplet) form the spin bipolaron complex owing to the hole excitations' capability to polarize Cu spin surrounding. Such an excitation was considered in the fenomenological way in [2].

Here the problem is discussed on the basis of the microscopic approach in the framework of the variational principle. The special kind of wave function is used for such a purpose. The wave function is constructed by generalizing the trial functions proposed in [3,4] over two holes excitation situation (triplet) and then the region of spin bipolaron existance in the framework of Emery model is studied.

In this model the Hamiltonian [3,4] can be easily rewritten by forming the oxygen states transforming as the irreducible representations of the group D_4. This transformation can be performed by using the matrix B:

$$B = \frac{1}{2}\begin{pmatrix} 1 & 1 & -\sqrt{2} & 0 \\ 1 & -1 & 0 & \sqrt{2} \\ 1 & 1 & \sqrt{2} & 0 \\ 1 & -1 & 0 & -\sqrt{2} \end{pmatrix} \qquad (1)$$

where every column determines the basis of the representations A_1, B_1, E of the group D_4.

Finally, the Hamiltonian has the following form:

$$H = H_t + H_J \quad ; \quad H_J = J \sum_{\langle i_1 i_2 \rangle} \vec{S}_{i_1} \vec{S}_{i_2}$$

$$H_t = 2t \sum_{j \in A} a^{+(1)}_{j\sigma} \left(1 + 2\vec{S}_j \vec{\sigma}\right) a^{(1)}_{j\sigma'} + \frac{t}{2} \sum_{\substack{\gamma\gamma' \\ \alpha\alpha'}} \sum_{j \in A} a^{+(\alpha)}_{j\sigma} \times \tag{2}$$

$$\times \left(1 + 2\vec{S}_{j+2\hat{x}-\tau_\gamma} \vec{\sigma}\right) a^{(\alpha')}_{j+\tau_{\gamma'}-\tau_\gamma} B_{\gamma\alpha} B_{\gamma'\alpha'}$$

where σ_λ are Pauli matrices, $\vec{S}_j$ is a spin operator on Cu site

$$a^{+(\delta)}_{j\sigma} = \sum_\alpha B_{\alpha\delta} \hat{p}^{+(\alpha)}_{j\sigma} \quad ; \quad \hat{p}^{+}_{j\sigma} = \left(p^+_{j+\hat{y}}, p^+_{j-\hat{x}}, p^+_{j-\hat{y}}, p^+_{j+\hat{x}}\right) \tag{3}$$

$$\tau_1 = 2\hat{x} - 2\hat{y} \quad ; \quad \tau_2 = 4\hat{x} \quad ; \quad \tau_3 = 2\hat{x} + 2\hat{y} \quad ; \quad \tau_4 = 0$$

the translation τ is expressed in a units(a is a distance between Cu and O sites), J is an antiferromagnetic exchange interaction, $p^+_{j\sigma}$'s describe $p_{x,y}$ oxygen states.

The representation of the Hamiltonian in the form (2) is rather convenient, because the summation is taken only over the sublattice A (the lattice parameter is equal to $2\sqrt{2}\, a$) and $a^{(\alpha)}_{j\sigma}$'s satisfy commutation relations for fermion operators. It is worth mentioning that only spin operators $\vec{S}_{j+2\hat{x}-\tau_\gamma}$ are connected with the sites of another sublattice B.

The trial function is chosen in the following form:

$$|\psi^+\rangle = \frac{A}{N_R} \sum_{\substack{i \le N_R \\ \tau}} \varphi^+_i \varphi^+_{i+\tau} \exp\left[- \frac{x|\tau|}{R} \right] \text{[illegible]} \tag{4}$$

where N_R -the number of atoms inside the circle with radius R, [illegible] is a variational parameter, the constant A is determined by the normalizing condition $\langle\psi|\psi^+\rangle = 1$. The summation is taken over the sublattice A (i is expressed in the lattice parameter units). $|G\rangle$ describes the spin state of the copper sublattice(the ferromagnetic one at $i \le N_R$ and the antiferromagnetic one otherwise).

$$\varphi^+_i = a^{+(1)}_{i\uparrow} \sqrt{1-z} - \sqrt{\frac{z}{2}}\, a^{+(1)}_{i\downarrow} b^+_i - \frac{1}{2}\sqrt{\frac{z}{2}} \sum_{\gamma\lambda} B_{\gamma\lambda}\, a^{+(\lambda)}_{i\downarrow} b^+_{i+2\hat{x}-\tau_\gamma}$$

$$f(\tau) = -f(-\tau) \quad ; \quad f(\tau_1) f(\tau_2) = \frac{(\vec{\tau}_1, \vec{\tau}_2)}{|\vec{\tau}_1| \cdot |\vec{\tau}_2|} \tag{5}$$

$$b^+_i = S^+_i \quad ; \quad b^+_{i+2\hat{x}} = \begin{cases} S^+_{i+2\hat{x}} & ; \ i \le N_R \\ S^-_{i+2\hat{x}} & ; \ i > N_R \end{cases}$$

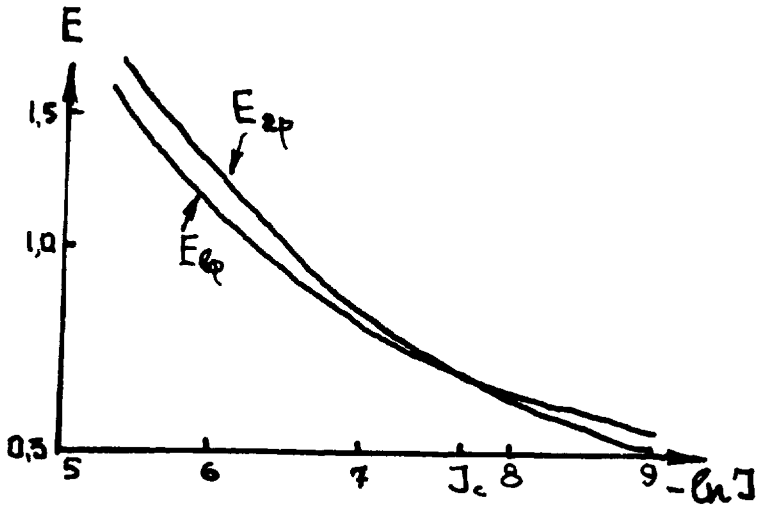
The results obtained below show that the region of the spin bipolaron existance corresponds to the small value of the exchange interaction J .Therefore,one can choose $z = 0.46$ (this value is obtained in $J \to 0$ limit in [3,4]) and consider only two variational parameters (α , N_R).Using the trial function (4)-(5) ,the energy of the system is calculated:

$$E_{bp} = -10.36 + 6.05 \frac{\alpha \exp(-\alpha)}{(1-\exp(-\alpha))} \cdot \frac{1}{\sqrt{N_R}} + \frac{\alpha}{N_R}\left(2.87 + 0.11 \ln \frac{N_R}{\alpha}\right) + 4 N_R J \quad (6)$$

The calculation for two separate polarons can be performed in the analogous way:

$$E_{2p} = -10.36 + 7.98 \frac{\alpha \exp(-\alpha)}{(1-\exp(-\alpha))} \cdot \frac{1}{\sqrt{N_R}} + 4.45 \frac{\alpha}{N_R} + 8 N_R J \quad (7)$$

Minimizing E_{bp} E_{2p} with respect to α and N_R ,one finds that the region of the spin bipolaron existance-as it follows from the plot-is determined by the following condition: $J > J_c = 4.42 \cdot 10^{-4} t$



The energy versus exchange coupling (all the quantities are expressed in t units,the energy origin is -10.36)

It is worth mentioning that in $J \to 0$ limit the extended state($\alpha \to 0$ $\psi(z) \sim 1/\sqrt{N_R}$ in(4)) is the most advantageous one,providing the energy minimum.Therefore,the localized state is absent in this limit.

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ELECTRON ENERGY SPECTRUM AND MAGNETIC INTERACTIONS IN HIGH-T_c SUPERCONDUCTORS

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The character of magnetic interactions in La-Sr-Cu-O and Y-Ba-Cu-O systems is of primary importance for analysis of high-T_c superconductivity in these compounds. Neutron diffraction experiments showed the antiferromagnetic ground state for nonsuperconducting La_2CuO_4 and $YBa_2Cu_3O_6$ with the strongest antiferromagnetic superexchange being in the ab plane [1,2]. Nonsuperconducting "1-2-3" system has even two Neel temperatures T_{N1} and T_{N2}. The first one corresponds to the ordering of Cu atoms in the CuO_2 planes, T_{N2} reflects the antiferromagnetic ordering of magnetic moments in CuO chains relatively to the moments in the planes T_{N1} and T_{N2} depend strongly on the oxygen content [3] (T_{N1}=450 K for x=0.1 and T_{N2}=80 K, but T_{N1}=230 K and T_{N2}=10 K for x=0.35).

We have tried to describe magnetic interactions in high-T_c superconductors basing on the LMTO band structure calculations. Exchange interaction parameters can be defined from the effective Heisenberg hamiltonian:

$$H_{eff} = -1/2 \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j \tag{1}$$

When the magnetic moments are not too large, as copper magnetic moments in superconducting oxides, J_{ij} parameters can be defined through the non-local magnetic susceptibility of spin-restricted solution for the crystal [4,5]:

$$J_{ij} = \frac{1}{2} \frac{I_i \cdot I_j}{S_i \cdot S_j} \sum_{LL'} \chi^{ij}_{LL'}, \tag{2}$$

where
$$\chi^{ij}_{LL'} = 1/\pi \int^{E_F} \mathrm{Im}\, G^{ij}_{LL'}(E) \cdot G^{ji}_{L'L}(E)\, dE \quad , \tag{3}$$

$$G^{ij}_{LL'} = 1/\Omega_{BZ} \int_{BZ} d\vec{k} \sum_n \frac{\psi_{nL}(\vec{k})\psi^*_{nL'}(\vec{k})}{E - E_n(\vec{k})} e^{i\vec{k}\cdot\vec{R}_{ij}} \tag{4}$$

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– is the nondiagonal Green function which can be calculated through the energy spectrum $E_n(\vec{k})$ and $\psi_{nL}(\vec{k})$ of the LMTO-hamiltonian. I_i in formulae (2) is interatomic exchange parameters of atom i. Due to the sharp dependence of nondiagonal Green function $G_{LL'}^{ij}(E)$ on the E the integral (3) should be calculated as contour integral in complex plane.

The results of nonlocal magnetic susceptibility calculations and the values of exchange interaction parameters for La CuO and $YBa_2Cu_3O_7$ systems are given in the Table.

Strong anisotropy of exchange interactions in the ab plane and along the c axis in La_2CuO_4 is obviously seen. The value of Neel temperature found agrees well with the experimental data available. In the $YBa_2Cu_3O_7$ system there is strong antiferromagnetic Cu-O-Cu interaction in the CuO_2 plane, which results in antiferromagnetic ground state of $YBa_2Cu_3O_6$. Superexchange of Cu1-O4-Cu2 type is antiferromagnetic also, in accordance with the experiment. Using the simplest mean field approximation $T_N = \frac{1}{3}|J|zS(S+1)$, where z is the number of the nearest magnetic neighbours, it is possible to estimate Neel temperature values. They are T_{N1} = 265-314 K, T_{N2} = 61 K agree well with the experimental data. Large ferromagnetic moment exchange in Cu1-O4-Cu1 chains (which follows from NMR experiments [6] also) does not influence antiferromagnetic ordering, as when δ = 1 all the chaines are broken.

In the planes of "1-2-3"system there are quite strong antiferromagnetic Cu-O and O-O interaction which appear due to holes in oxigen subbands. These results are in line with the magnetic model of oxigen holes pairing in high-T_c superconductors suggested in [7].

We have performed also a number of LMTO spin-polarised calculations for $GdBa_2Cu_3O_6$ and $GdBa_2Cu_3O_7$ both for ferromagnetic and antiferromagnetic ordering of magnetic moments. For antiferromagnetic state the energy gap of 0,04 ev is formed at the Fermi level. Spin splitting of Gd f-states equals to 5 ev, and magnetic moment of Gd atoms is 6.5 μ_B. The estimation of stability parameters [8] leads to the conclusion of more stable antiferromagnetic ordering: the difference of J_0 parameters is 230 K (O_6) and 180 K (O_7). The value of s-f integral in antiferromagnetic phase of $GdBa_2Cu_3O_7$ appears to be about 20 K, and correspond to small changes of T_c when Gd atoms enter the crystal lattice.

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Table. Exchange interaction parameters for $YBa_2Cu_3O_7$ and La_2CuO_4 (for $s=1/2$ and $I_{Cu}=0,07$ Ry, $I_O=0,11$ Ry)

pair	$\vec{R}_{ij}$	$\gamma^{ij}_{dd(p)}$ (mRy^{-1})	J^{ij} (K)
$YBa_2Cu_3O_7$			
Cu2-O2-Cu2	(0 1 0)	-50,8	-157
Cu2-O3-Cu2	(1 0 0)	-42,8	-132
Cu1-O4-Cu2	(0 0 1)	-9,9	-31
Cu1-O1-Cu1	(0 1 0)	72,5	225
Cu2-O2	(0,5 0 0)	112,3	545
O2-O2	(0,5 0,5 0)	35,5	270
La_2CuO_4			
Cu-O1-Cu	(1 0 0)	73,5	227
Cu-O2-Cu	(0 0 1)	-0,45	1,4

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CRYSTAL CHEMICAL AND QUANTUM CHEMICAL STUDIES OF Ba(Sr)-Nb OXIDE COMPOUNDS

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The information available on the BaO(SrO)-NbO-NbO_2 system with the niobium atom in the lower oxidation degree is very limited. Very few compounds have been found previously in this system. They are $BaNbO_3$, Sr_xNbO_3 ($0,7 \leq x \leq 1$), $Ba_2Nb_2O_9$, $SrNb_8O_{14}$ and some suggestions on the $BaNb_8O_{14}$ existence have been made also. At the same time Nb-based oxide compounds could be quite interesting in the search of new noncopper high T_c superconductors (see, for example, [1,2]).

In the present paper we have studied Ba(Sr)-Nb_xO_{2x-2} (I) and $Ba_2(Sr_2)$-Nb_xO_{2x-1} (II) compositions in the phase diagram of BaO(SrO)-NbO-NbO_2 system. The synthesis of the materials has been carried out in vacuum at the temperatures of 1000-1500 C. Barium carbonate and niobium pentoxide have been used as initial components. X-ray analysis has been carried out at DRON-UM1 CuK_α radiation.

In the subsystem (I) the following individual compounds have been obtained: $BaNb_4O_6$ (x=4), $BaNb_5O_8$ and $SrNb_5O_8$ (x=5), $BaNb_8O_{14}$ and $SrNb_8O_{14}$ (x=8). In the subsystem (II) $Ba_2Nb_5O_9$ and $Sr_2Nb_5O_9$ (x=5) have been separated only. The crystal structure of the compounds obtained has been studied dy the neutron difraction experiments with the use of Rietveld analysis. The crystal lattice of $BaNb_4O_6$, $Ba_2Nb_5O_9$ and $Sr_2Nb_5O_9$ appears to have P4mmm, z=1 space group and they represent the series of n·($BaNbO_3$)·3(NbO) compounds with $a_T \approx a(NbO)$, $c_T \approx (n+1) \cdot a(BaNbO_3)$, where n is the thickness of perovskite layer. All of the compounds obtained have typical perovskite layered structure with two-dimensional perovskite layers and niobium monoxide layers perpendicular to c axis. $BaNb_5O_8$ contians one-dimentional cluster of niobium monoxide, which is parallel to c axis. This compound possesses the P4/m, z=1 space group lattice. Crystal lattice parameters are closely related with niobium monoxide block size: $a_T=6,608A \approx \sqrt{5/2}\, a(NbO)$, $c_T=4,107A \approx$ $\approx a(NbO)$. $BaNb_8O_{14}$ and $SrNb_8O_{14}$ are isostructural (of Pbam, z=2 space group) and contain chains of isolated niobium monoxide clusters.

The study of electrophysical properties carried out reveals the compounds with one-dimentionalniobium monoxide clusters - $BaNb_5O_8$ and two-dimentionalclusters - $BaNb_4O_6$, $Ba_2Nb_5O_9$, $Sr_2Nb_5O_9$ are paramagnetics of the Curie-Weiss type and reveal the metallic character of $\rho(T)$ dependence ($\rho_{293} \approx 10^{-4}$ om·cm). At the same time the compounds with isolated clusters - $BaNb_8O_{14}$ and $SrNb_8O_{14}$ are weak diamagnetics at the room temperature and have metal-semiconductor phase transition at $T_t \approx 270K$. Isomorphic substitution of Ba(Sr) for La results in the shift of phase transition to the low temperature region (1% of La - $T_t \approx 80K$, 2% of La - $T_t \approx 10K$).

The next peculiarity of $BaNb_8O_{14}$ and $SrNb_8O_{14}$ compounds is their tendency to oxygen absoprtion, their mass is increased by 1% under the yeat treatment (T 250 C) in the air.

The results obtained show that all the Sr and Ba niobium oxides with the niobium in the lower oxydation states form the lattices containing niobium monoxide clusters which could be isolated, one- or two-dimentional. Compound with isolated clusters satisfay the superconductivity criterion by Sleight [3]. The metal-semiconductor phase transition appear to realize at electron concentration in the clusters equal to 14 instead of 22 as in Shevrel phases.

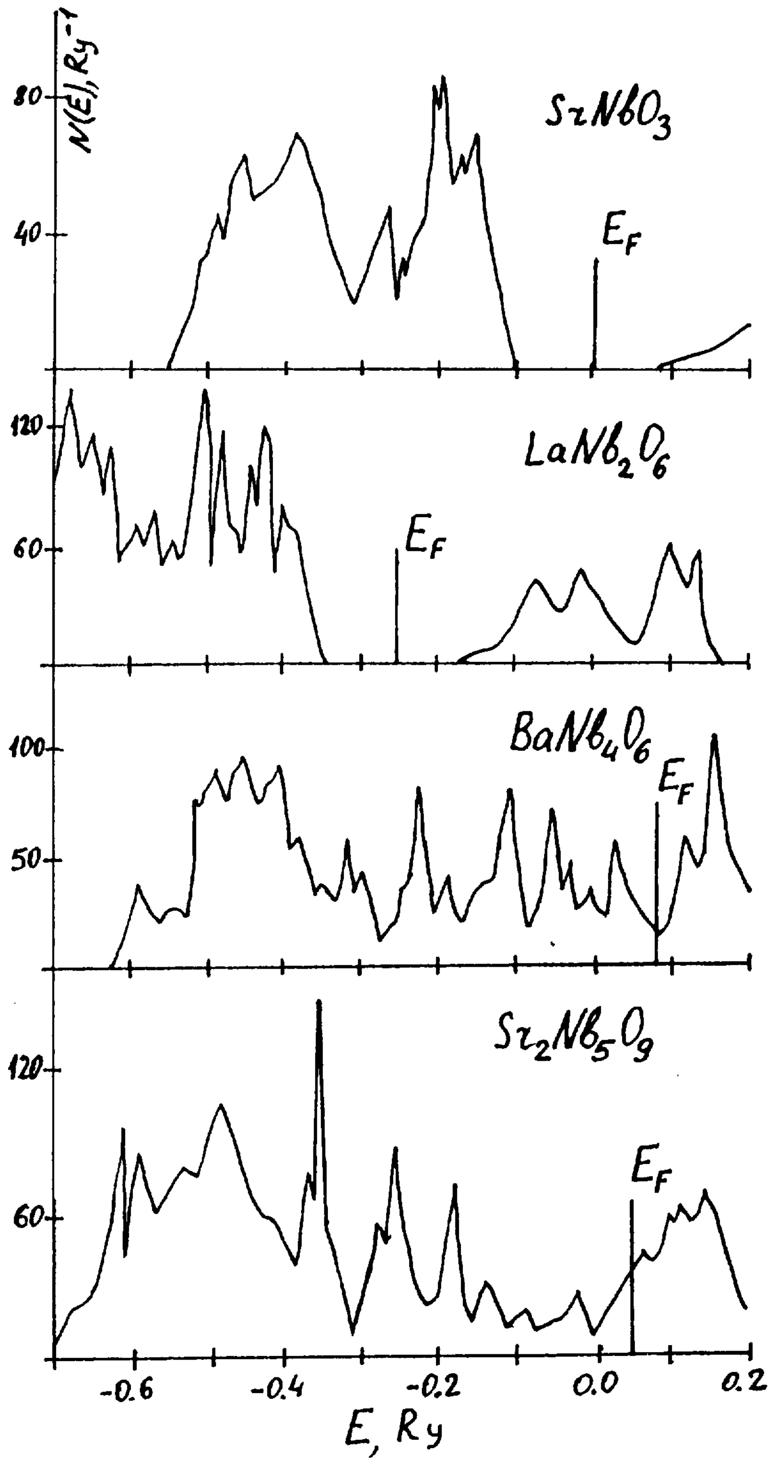

Fig.1. The total density of states

In order to estimate of some of the compounds obtained possess similar pecualiritiеs in electronic structure as copper high-T_c superconductors, we carried out the LMTO band structure calculations for the following niobium compounds: $SrNbO_3$, $La_{0,66}Nb_2O_6$,

$BaNb_4O_6$, $Sr_2Nb_5O_9$. The calculations performed showed that for the $SrNbO_3$ and $La_{0,66}Nb_2O_6$ compounds Nb4d and O2p bands are completely separated and the Fermi level is situated between them.

In the $BaNb_4O_6$ and $Sr_2Nb_5O_9$ partial hibridization of Nb4d and O2p states at the energies lower then E_F takes place and the common Nb4d-O2p band is formed (Fig.1). For $BaNb_4O_6$ O2p contributions at the Fermi energy (which are typical for high-T_c copper superconductors) are missing, but for $Sr_2Nb_5O_9$ quite essential oxygen atoms contributions at the E_F appear. Their value could be significantly increased when the Fermi level is shifted, for example, when doping the crystal lattice by atoms of another valence or changing the oxygen stehiometry ratio. In some cases, probably, the characteristic picture of high-T_c superconductor electronic structure could appear together, hopefully, with superconductivity properties.

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XES STUDIES OF DENSITY OF STATES OF HIGH TEMPERATURE SUPERCONDUCTORS

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ABSTRACT

X-ray emission spectroscopic studies concerning the superconducting crystals, thin films and ceramics of the Y-Ba-Cu-O, Tm-Ba-Cu-O, Bi-Sr-Ca-Cu-O, Bi-Pb-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O types are presented. The contributions of the $|3d^9L\rangle$, $|3d^{10}L\rangle$, $|3d^{10}LL\rangle$ and $|3d^{10}L^2\rangle$ configurations, where L denotes a ligand hole at the oxygen orbitals, in the spectroscopic pattern of these superconductors is discussed. An attempt to connect the X-ray "as registered" Cu $L\alpha$ emission spectra with the density of states close to the Fermi level, considering an influence of the CuL_3 absorption edge, is presented. The corrected intensity distributions below the Fermi level are found to correspond to the theoretical density of states.

Furthermore, an approach to the average valence of copper basing on the account of the self-absorption and fluorescence effects and on the configurations listed above is shown. The average valence of copper in the materials investigated is estimated to lie in the range of +2.10-2.32 when the formal trivalent copper is considered as this characterized by the $|3d^9L\rangle$ configuration. The density of states at the Fermi level was estimated to be 2.4 states/eV-cell for a Bi-Sr-Ca-Cu-O crystal and 3.6 states/eV-cell for a Tl-Ba-Ca-Cu-O ceramic.

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PROCESSING Bi-Pb-Sr-Ca-Cu-O SUPERCONDUCTORS FROM AMORPHOUS STATE,

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We produced superconducting ceramics of the Bi-Pb-Sr-Ca-Cu-O system started from a glass. To form the glass, the mixed oxide powder was melted at 1200 °C in air. The liquid was quenched rapidly by pouring it onto an aluminum plate and rapidly pressing with another plate. The quenched compound was in the form of black amorphous solid, whose x-ray powder pattern has no crystalline peaks. After heat treatment at high temperatures, the glass crystallized into a superconductor. The crystalline phases in the superconductor identified using x-ray diffraction patterns. These phases were that associated with the superconducting phases of T_c = 80 K ($Bi_2Ca_1Sr_2Cu_2O_x$) and of T_c = 110K ($Bi_2Ca_2Sr_2Cu_3O_x$). The dc resistivity and the ac susceptibility of these superconductors were studied.

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THE RELATION BETWEEN FERROELASTICITY AND SUPERCONDUCTIVITY

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ABSTRACT

The high-temperature superconductivity is explained widely by the layered crystallic structure. The one- and two-dimensional subsystems and their interaction are investigated in this work. It is assumed that the high-Tc superconductivity takes place in the two-dimensional subsystem [1] and the increase of the phase transition temperature from 60 K up to 90 K is the consequence of turning on the influence of one-dimensional chains. The interaction between the two subsystems is transferred along the c axe by the phonons of breathing mode, what causes the hybridization of the electronic bonds between these subsystems [2].

The experimental works indicate that the existence of both the chains Cu(1)-O [3] and their interaction with the superconducting plane of Cu(2)-O modify the temperature of the transition to the superconducting state. It is seen from the neutron scattering data that the rates of the interatomic distance dependencies on temperature are changed around 240 K and 90 K [4]. The "zig-zag" order in Cu(1)-O chains has been postulated [4], but, on the other hand, the vibrations with a large amplitude only were reported [5].

The bi-stabilized situation of the oxygen ions can be caused by the change of distance between these ions and the Ba ions [4]. It leads to the appearance of a two-well potential [6]. Its parameters depend on temperature and the determine the dynamics of the oxygen ions' movement. They can induce the antipolar order, which can be, however, more or less chaotic.

The investigation of the ferroelastic properties of Y-Ba-Cu-O samples lead to the conclusion that they are related to jumps of ions inside the given chain and not to a diffusion between different sites in the ab plane [7]. We deduce thus that the fluctuating oxygen ions from these chains create dipols in the ab plane. They can be described with the pseudo-spin formalism / - Pauli matrices/. The system can be described with Ising model:

$$H_s' = -\frac{1}{2} J \sum_{ij} \sigma_{3i} \sigma_{3j} \qquad (1)$$

The pseudo-spins interact with phonons and influence the superconductivity in the second subsystem:

$$H_{sI} = \sum_q \sum_i \gamma_i(q)\, \sigma_3 \left(b_{q,3} + b_{-q,3} \right) \qquad (2)$$

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The Ising model in the molecular field approximation / though fully correct in the one-dimensional case/ gives the phase transition for the anti-polar order parameter:

$$\langle \sigma_{3i} \rangle = (-1)^{i} \eta \neq 0 \tag{3}$$

The effective field conjugated to the pseudo-spin interacts with the ferroelastic order like an external magnetic field with a real spin system:

$$H' = B_z \sigma_3 \tag{4}$$

$$B_z = 2 \xi_o \gamma(o) = A' u \tag{5}$$

where u denotes condensation of phonons of breathing mode /deformation of pyramids/:

$$u = (h/2M)^{1/2} \{ \xi_o + \xi_o^{+} \} \tag{6}$$

We obtain the description of the relation between the superconductivity and ferroelasticity in such a way.

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NOVEL SUPERCONDUCTING PHASES OF Tl-BASED COMPOUNDS

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ABSTRACT

Several new superconducting phases of the Tl-based compounds were prepared. Structural studies revealed cell lengths of 31.9 Å and longer. Properties of Ce-containing compounds are also discussed.

N90-27863

SUPERCONDUCTIVITY IN THE Sn-Ba-Sr-Y-Cu-O SYSTEM

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Since Bednorz and Müller /1/ discovered high-T_c superconductivity in the La-Ba-Cu-O compound, several families of superconducting oxides have been synthesized /2/. In this paper we report the results of search for superconductivity in the compounds based on tin which has a lone electron pair like Bi, Tl, Pb.

The following compounds were synthesized: $Sn_1Ba_1Sr_1Cu_3O_x$, $Sn_1Ba_1Ca_1Cu_3O_x$, $Sn_1Ba_1Mg_1Cu_3O_x$, $Sn_1Sr_1Ca_1Cu_3O_x$, $Sn_1Sr_1Mg_1Cu_3O_x$, $Sn_1Ca_1Mg_1Cu_3O_x$. The initial components were oxides and carbonates of the appropriate elements. Standard firing-grinding procedure was used. Final heating was carried out at 960°C during 12 hours. Then the samples were cooled inside the furnace. All the synthesis cycles were carried out in air atmosphere.

Among the synthesized compounds only $Sn_1Ba_1Sr_1Cu_3O_x$ showed remarkable conductivity ($\rho \sim 10$ Ohm·cm). Other compounds were practically dielectrics ($\rho > 1000$ Ohm·cm). Presence of a possible superconductivity in $Sn_1Ba_1Sr_1Cu_3O_x$ was defined by using the Meissner effect. At low temperature a deviation from paramagnetic behaviour is observed. The hysteresis loops obtained at lower temperatures undoubtly testify to the presence of a superconductive phase in the sample. However, the part of the superconductive phase in the $Sn_1Ba_1Sr_1Cu_3O_x$ ceramic turned out to be small, less than 2%, which agrees with the estimation from magnetic data. In order to increase the content of the superconductive phase two-valent cations Ba, Sr were partially substituted by univalent (K) and three-valent ones (Y). Two samples were obtained: $Sn_1Ba_{0.7}Sr_{0.7}K_{0.7}Cu_3O_x$ and $Sn_1Ba_{0.7}Sr_{0.7}Y_{0.7}Cu_3O_x$. The former is a typical paramagnet without any anomaly down to 4.2K. The latter has shown the magnetic and electric properties undoubtly indicating the presence of a superconductivity phase with the onset temperature $T_c \simeq 55$K. The superconductive properties of the sample do not seem to be caused by the phase $YBaSrCu_3O_7$ /3/. This conclusion follows from the study of the $Sn_2Sr_2Ba_{0.5}Y_{0.5}Cu_3O_x$ and $Sn_2Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$ samples that were synthesized by analogy with the recent communications on superconductivity in $Pb_2Sr_2(Y,Ca)_1Cu_3O_8$ /4,5/. One may expect equal probability of the $YBaSrCu_3O_7$ content for both samples, however their electrical properties are quite different. The compound $Sn_2Sr_2Ba_{0.5}Y_{0.5}Cu_3O_x$ is a good dielectric while $Sn_2Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$ has clearly expressed superconductive properties /6/. The magnetic moment was measured in an external field H = = 100 Oe. At T < 86K the sample exhibits a clearly defined diamagnetic behaviour characteristic of superconductors. At these temperatures the hysteresis loop has the form typical of high-T_c superconductors. The amount of the superconductive phase in this sample, as a magnetic estimation in powder, is ~15% of the volume of the sample.

A comparative analysis of the X-ray powder diagrams leads us to believe that the main motive of the $Y_1Ba_2Cu_3O_7$ structure is preserved in the structure of $Sn_2Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$. The unit cell parameters are: a = 4.1 Å, c = 12.4 Å (or multiple).

We have also used the same procedure for $Sn_1Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$. The sample is a typical paramagnet without any anomaly down to 4.2 K.

The presence of superconductivity in the system based on tin allows us to suggest that other cations, besides the well-known Bi, Tl, Pb, having the lone electron pair effect, should also form superconductive compounds. If we limit ourselves to consideration of copper-containing oxides, we may suppose that definite alkali-earth ions (or their combination) would suit for each of the ions: Hg,Sb,In,... in order to form a superconductive phase.

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MEASUREMENT OF H_{C1} IN A SINGLE CRYSTAL OF $YBa_2Cu_3O_7$ WITH LOW PINNING

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The measurement of H_{c1} in BYCO is often ambiguous because the presence of large pinning fcrces makes it difficult to discern exactly where the first deviation from linearity occurs. In addition there are complications because demagnetizing factors are often not well known. By utilizing a single crystal of YBCO with a nearly cubic shape, the uncertainty in the demagnetizing factor was minimized. In addition, the crystal used exhibited a very small amount of pinning with H applied perpendicular to the c axis, and a sharp break in the initial magnetization vs. field curve could be observed over a wide range of temperature. This allowed a precise determination of H_{c1}. The measured values of H_{c1} could be well described by the Abrikosov relation[1] with a Ginzburg-Landau parameter which varied linearly with temperature.

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N90-27865

STUDIES OF IRON IMPURITIES IN $Y_xPr_{1-x}Ba_2Cu_3O_{7-\delta}$

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Pr is the only rare earth which, when substituted for Y in $YBa_2Cu_3O_7$, significantly alters the superconducting transition temperature, T_c, without changing the crystal structure. For $Y_xPr_{1-x}Ba_2Cu_3O_{7-\delta}$ with $\delta \simeq 0$, T_c is reduced rapidly as x is increased, reaching zero for x about 0.5. For x above 0.5 the compound is antiferromagnetic with a Neel temperature that increases with increasing x, rising to above room temperature for x near 1. A similar behavior is observed when the oxygen deficit δ is increased from zero to 1 with x=0. For the case of Pr substitution, the drop in T_c is believed due to magnetic interactions. For the case of varying δ with x=0, the drop can be attributed to a combination of magnetic interactions, band filling, and changes in crystal structure. To study these effects, the Mossbauer effect of ^{57}Fe atoms substituted for the Cu atoms has been observed as a function of δ, x, and temperature. The observed spectra are all well described by a two quadrupole-split pairs, a central singlet, and a six-line magnetic hyperfine field pattern. For several Pr compositions both δ and temperature were varied, and the results support the hypothesis that a magnetic interaction exists between the Fe in the Cu lattice and the substitutional Pr atoms.

STUDY OF THE SUPERCONDUCTING PROPERTIES OF THE Bi-Ca-Sr-Cu-O SYSTEM

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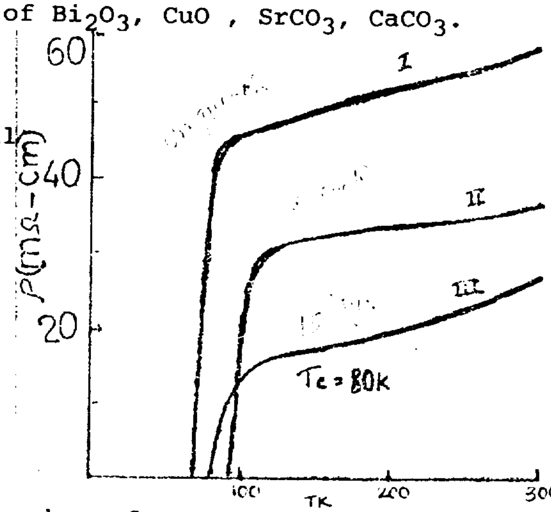
INTRODUCTION

High Temperature Superconductivity in the Bi-Ca-Sr-Cu-O System has been observed and has attracted considerable attention in the year 1988 (103). The 80 K superconductivity phase has been identified to have a composition of $Bi_2Ca\ Sr_2Cu_2O_x$ while 110 K phase as reported in the literature has a possible composition of $Bi_2Ca_2Sr_2Cu_3O_x$.

We present here a study of the electrical properties of bulk samples of slowly cooled and rapidly quenched 2:1:2:2 system. The samples used in this study were prepared from appropriate amounts of Bi_2O_3, CuO , $SrCO_3$, $CaCO_3$.

ADDITIONAL INFORMATION



Resistivity vs. temperature curves for typical unquenched and quenched specimens are shown in Fig. (a). The resistivity of the unquenched sample (curve I) shows metallic temperature behaviour down to the superconducting onset at Tc onset 90 K while zero resistance Tc is observed at 72 K. The resistivity of the rapidly quenched sample (curve II) showed a Tc onset around 105 K while zero resistance was found at 90.5 K. Neither sample shows any evidence of a second onset at 105-110 K. The electrical resistivity curve for a sample similar to curve II but exposed to atmosphere for 15 days is shown in curve III. This behaviour is in agreement with the work reported in Ref. (4). However, it has been suggested that the improved behaviour of quenched materials is caused by an oxygen deficiency (5) and this decay could then result from the uptake of atmospheric oxygen. The X-ray crystallographic studies showed that most of the samples were of single phase.

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N90-27867

A YBCO RF-SQUID MAGNETOMETER AND ITS APPLICATIONS.* Luwei Zhou, Jingwu Qiu, Xianfeng Zhang, Zhiming Tang, and Yongjia Qian. Physics Dept., Fudan Univ., Shanghai, China. -- An applicable RF-SQUID magnetometer has been made using a bulk sintered YBCO. The temperature range of the magnetometer is 77-300K and the field range 0-0.1T. At 77K, the equivalent flux noise of the SQUID is $5X10^{-4}$ $\Phi_0/\sqrt{Hz}$ at frequency range of 20-200 Hz. The experiments show that the SQUID noise at low-frequency end is mainly from 1/f noise. A coil test shows that the magnetic moment sensitivity Δm is 10^{-6}emu. The RF-SQUID is shielded in a YBCO cylinder with a shielding ability B_{in}/B_{ex} of about 10^{-5} when external dc magnetic field is about a few Oe. The magnetometer is successfully used in characterizing superconducting thin films.

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N90-27868

Magnetic properties of the 110K superconducting phase in Pb-doped Bi-Sr-Ca-Cu-O thin films

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Abstract

The relaxation of the remnant moment induced in a nearly single phase high Tc thin film of Pb-doped Bi-Sr-Ca-Cu-O has been investigated. Measurements reveal that the relaxation obeys a logarithmic time dependence for observation times up to 2000 seconds. The temperature dependence of the initial magnetization of the film and its decay rate are obtained. The initial magnetization monotonically decreases, however, the decay rate normalized by initial magnetization has a peak at approximately 14 K for an applied field of 500 gauss. The peak shifts to lower temperature for stronger magnetic field. These data are compared with existing data on other high Tc superconducting materials.

Introduction

The recent report of large flux creep in a single crystal of $YBa_2Cu_3O_7$ (YBCO)[1] has prompted investigation into the time dependence of remnant magnetization in that system and in other high Tc superconductors[2,3,4]. However, thin films of the oxide superconductors, particularly in the Bi system, have received relatively little attention. As the first applications of high Tc oxides will likely be in the form of thin films, it is important to examine the nature of magnetic relaxation in films. In this report the results of magnetic relaxation experiments on highly oriented, polycrystalline films of the high Tc phase in the Bi system are presented.

Sample preparation

The Bi-Sr-Ca-Cu-O (BSCCO) films were prepared on (100) MgO substrates by rf magnetron sputtering from a composite target and Pb was doped by means of an additional PbO target. The details of the sample synthesis have been reported elsewhere[5]. X-ray diffraction (XRD) results showed the film possessed a high degree of c-axis orientation perpendicular to the substrate surface and also indicated that the film was nearly single phase high Tc material. Very weak signals corresponding to the low Tc phase were observed in the XRD spectra. The thickness of the film used for this study was 0.85 microns. SEM photographs indicated that thin plate like crystals were stacked each other. The Tc (R = 0) was 106.2 K.

Experiment

The magnetic measurements were performed by means of a *Quantum Design* squid magnetometer in which the sample was cooled from room temperature in a field of approximately 2 gauss. A magnetic field was then applied parallel to the c-axis, maintained for ten minutes, and then removed. The time dependence of the resulting remnant moment was measured at several temperatures. Fields of 0.5 kgauss and 1 kgauss were used in this investigation.

Results and discussion

The relaxation of the moment was measured at several temperatures. The decay was linear in ln time during observation intervals of 2000 seconds. Some deviation from logarithmic dependence was observed after longer times. For magnetic relaxation observed over a period of 2000 seconds, a linear least squares fit to the data was made and the decay rate and initial (t = 1 second extrapolation) value of the magnetic moment (Mo) was calculated. Fig. 1 shows the initial value of the magnetic moment as a function of temperature for applied fields of 0.5 kgauss and 1 kgauss. It is seen that at temperatures between 3 and 14 K the temperature dependence of the initial magnetization Mo(T) is sensitive to the magnitude of the applied field. It is nearly linear when a 1 kgauss field is applied but exhibits a rollover when the measurements are performed after the removal of a 0.5 kgauss field. At temperatures above 14K the two curves become very similar.

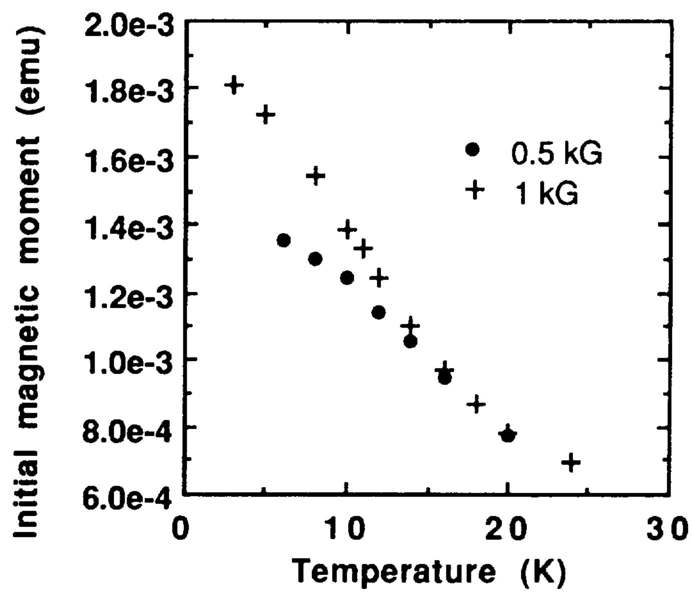

Fig. 1. Temperature dependence of the initial magnetization after a field of 1 kgauss (plus signs) and .5 kgauss (filled circles) was applied perpendicular to the substrate for ten minutes and then removed.

The average temperature-dependent pinning potential U(T) was estimated from the Anderson-Kim relation: $1/Mo(T)\ \{\partial M(T,t)/\partial \ln(t)\} = k_bT/U(T)$, where k_b is the Boltzmann constant and Mo(T) is the value of the initial magnetic moment at fixed temperature. The value of the pinning potential exhibited a nearly constant value of approximately 40 meV in the temperature range of 8 to 14 K. Above 14K, the pinning potential increased rapidly.

Fig. 2 shows the temperature dependence of the normalized decay rate $1/Mo\{dM(T)/d\ln(t)\}$ obtained at .5 kgauss and 1 kgauss. Both plots exhibit a pronounced peak and subsequent rapid drop. This behavior has been observed in bulk polycrystals of $YBa_2Cu_3O_7$ [6] after field cooling in 500 gauss. The temperature at which the maximum normalized rate occurs is observed to shift from 14K to 12K as the field is increased from .5 kgauss to 1 kgauss. While there is a qualitative similarity to the YBCO result, it should be noted that the temperature at which the maximum normalized rate occurs is roughly 15K lower in the Bi film than in the YBCO sample for the same applied field.

Recently, several theoretical models within the framework of thermally activated flux creep have been proposed to explain the origin of the peak in the temperature dependence of the normalized rate. In one such model[7], based on a theory of the elastic moduli of the vortex lattice, the pinning potential is related to critical current (Jc), the effective radius of pinning (d) and the average volume of flux bundles (V_b). This model, however, was not able to simultaneously reproduce the structure and position of the peak for the data presented here. Another model [8] involving a distribution of activation energies $\rho(U_0)$ has also been proposed. Relaxation results similar to ours have been reported for thin films of $ErBa_2Cu_3O_{7-\delta}$ and have been analyzed using the energy distribution model.[9] The distribution function obtained from an inversion of that data yields a peak in the distribution function at roughly 40 meV. This is similar to our estimated value of the pinning potential in the temperature range of 8-14K.

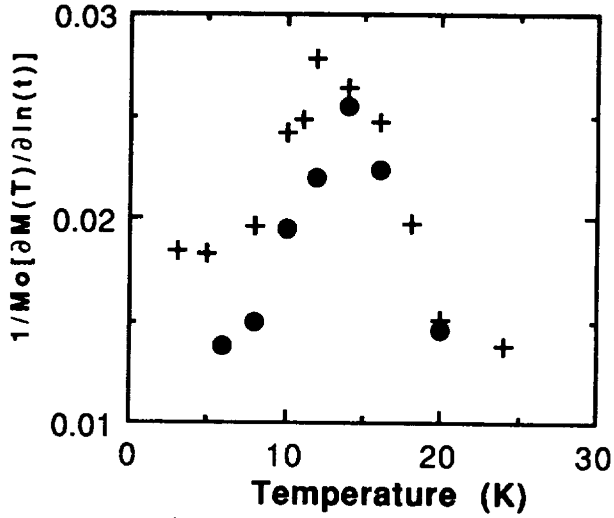

Fig. 2. Temperature dependence of the normalized relaxation rate 1/Mo{dM(T)/d(lnt)} after a field of 1 kgauss (plus signs) and .5 kgauss (filled circles) was applied perpendicular to the c-axis of the film for ten minutes and then removed.

Summary and conclusions

We have observed logarithmic decay of remnant magnetization in thin films of the high Tc phase in the Bi superconducting system and we report the first observation in this material of a peak in the temperature dependence of the normalized rate. The peak was found at a lower temperature and was sharper than that of YBCO for relaxation measured from the same field. Of the present theoretical attempts to explain the origin of the peak, we find the model of a distribution of activation energies most satisfactory.

It should be noted that a peak has not yet been observed in either Sr-La-Cu-O or Ba-La-Cu-O[10] at least for temperature less than 10 K. Therefore, further investigation is required in order to determine whether such a peak is a general feature of high Tc cuprate materials or is particular to those having several Cu-O planes in a unit cell.

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N90-27869

COMPARATIVE STUDY OF FLUX PINNING, FLUX CREEP AND CRITICAL CURRENTS BETWEEN YBaCuO CRYSTALS WITH AND WITHOUT Y_2BaCuO_5 INCLUSIONS

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In the Y-Ba-Cu-O system $YBa_2Cu_3O_x$ phase is produced by the following peritectic reaction: Y_2BaCuO_5 + liquid $\rightarrow$ $2YBa_2Cu_3O_x$. Through the control of processing conditions and starting compositions it becomes possible to fabricate large crystals containing fine Y_2BaCuO_5(211) inclusions. Such crystals exhibit Jc values exceeding 10000 A/cm^2 at 77K and 1T.

Recently, we have developed a novel process which can control the volume fraction of 211 inclusions. Elimination of 211 inclusions is also possible. In this study, we prepared YBaCuO crystals with and without 211 inclusions using the novel process and compared flux pinning, flux creep and critical currents. Figure 1 shows magnetic field dependence of Jc for YBaCuO crystals with and without 211 inclusions. It is clear that fine 211 inclusions can contribute to flux pinning. It was also found that flux creep rate could be reduced by increasing flux pinning force. Critical current densities estimated based on the conventional flux pinning theory were in good agreement with experimental results.

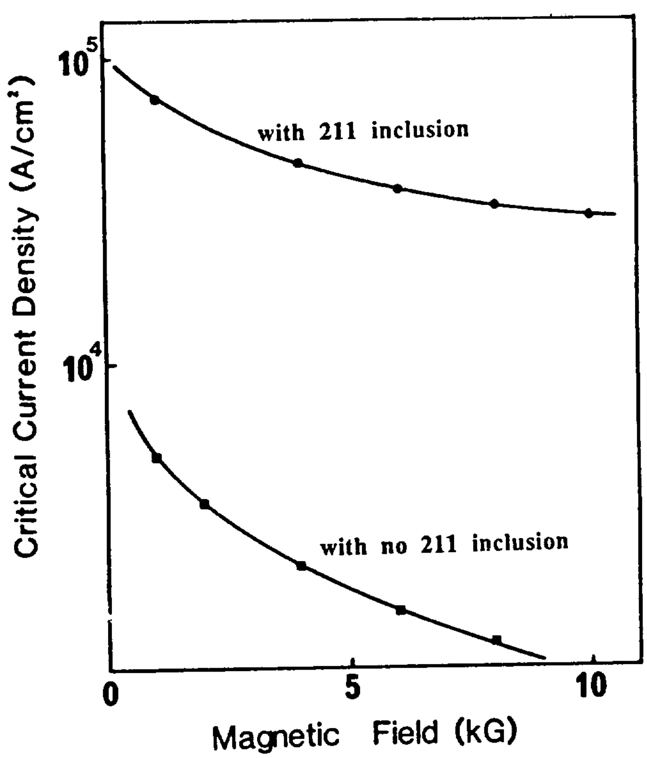

Fig. 1. Magnetic field dependence of YBaCuO crystals with and without 211 inclusions at 77K.

N90-27870

OPTICAL AND MICROWAVE DETECTION USING Bi-Sr-Ca-Cu-O THIN FILMS

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Recent progress at the Johns Hopkins University Applied Physics Laboratory (JHU/APL) in the development of optical and microwave detectors using high temperature superconducting thin films will be described. Several objectives of this work have been accomplished, including: deposition of Bi-Sr-Ca-Cu-O thin films by laser abation processing (LAP), development of thin film patterning techniques, including in-situ masking, wet chemical etching and laser patterning, measurements of bolometric and non-bolometric signatures in patterned Bi-Sr-Ca-Cu-O films using optical and microwave sources, respectively, analysis and design of an optimized bolometer through computer simulation, and investigation of its use in a Fourier transform spectrometer. This paper will focus primarily on results from the measurement of the bolometric and non-bolometric response.

Typical samples are deposited on single crystal MgO substrates at 300 °C in the LAP cell. They are shadow-masked during deposition and annealed after deposition at 880 °C for 10 minutes, preceded and followed by a 75 minute ramp-up and a 3 hour ramp-down relative to room temperature. Silver epoxy contacts are placed on the sample and annealed-in during film annealing, a procedure that almost always eliminates contact resistance problems. In addition, we find that the samples can be thermally recycled many times with little degradation of the contacts or the intrinsic film properties, and they can be reused after a long shelf-life.

For optical detection, a 4 mW helium-neon (HeNe) laser (633 nm wavelength) beam was chopped at 26 Hz and focused onto the center of the sample. For microwave detection, a 9 GHz microwave signal was generated with a microwave oscillator and square wave modulated at 40 Hz with a PIN diode modulator. The signal was then amplified and fed into an X-band horn positioned directly in front of the sample. In both cases the induced output voltage from the sample was synchronously detected with a lockin amplifier.

Results for the optical detection experiment indicate a response peak located at the center of the transition region. From standard bolometric theory, it is known that the bolometric response is proportional to the derivative of the resistance curve. Calculated derivatives of the resistance curves correlate well with the measurements. Thus we believe that the optical response is primarily bolometric. In addition, measurements of the lockin response versus chopper frequency indicate a response time consistent with a thermal response mechanism.

The measured voltage response for various microwave power levels indicates that the peak of the response varies linearly with microwave power until saturation is reached. Unlike the optical response, the peak in the microwave response is located (in temperature) in the region of the resistive tail well-below T_c and clearly separated from the optical bolometric response peak. This implies that the microwave response is non-bolometric. As expected, the width of the resistive tail increases with increasing microwave power. More interestingly, several characteristics of the microwave response change as a function of increasing bias current; not only does the response height increase, but both its position decreases (with temperature) and its width increases as current increases. In addition, lockin response to microwaves does not rolloff with chopper frequency as does the optical response, implying the response mechanism is not thermal.

Noise voltage measurements were also taken with an equivalent noise bandwidth of 1 Hz. Even with no illumination the sample has a response in the resistive tail region. In addition, peak excursions of the noise voltage in the region of the peak were much higher than the RMS noise voltage levels. This behavior would be expected if individual transient fluctuations occur in the film over very short time intervals, perhaps associated with flux motion and dissipation. With increasing bias current, the characteristics of the noise peak resembled the behavior of the microwave response peaks. We also determined that there is a decrease in the noise level versus temperature just above the non-bolometric peak, which probably corresponds to a drop in thermal noise associated with the resistive transition.

Several hypotheses could be put forward to explain the microwave response peak, and they are currently under study. A detailed theoretical and experimental study of the microwave response, however, is required to resolve the question of the non-bolometric mechanism and is currently underway. Some of the efforts and their results will be described. Eventually we hope to exploit this phenomenon as a faster, more sensitive technique for microwave detection than the bolometric optical response.

N90-27871

In-Situ Deposition Of YBCO High-Tc Superconducting Thin Films By MOCVD and PE-MOCVD

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Metalorganic Chemical Vapor Deposition (MOCVD) offers the advantages of a high degree of compositional control, adaptability for large scale production, and the potential for low temperature fabrication. The capability of operating at high oxygen partial pressure is particularly suitable for in-situ formation of HTSC films. YBCO thin films having a sharp zero-resistance transition with T_c > 90K and $J_c \sim 10^4$Å on YSZ have been prepared, in-situ, at a substrate temperature of about 800°C. Moreover, the ability to form oxide films at low temperature is very desirable for device applications of HTSC materials. Such a process would permit the deposition of high quality HTSC films with a smooth surface on a variety of substrates. Highly c-axis oriented, dense, scratch resistant, superconducting YBCO thin films with mirror-like surfaces have been prepared, in-situ, at a reduced substrate temperature as low as 570°C by a remote microwave-plasma enhanced metalorganic chemical vapor deposition (PE-MOCVD) process. Nitrous oxide was used as a reactant gas to generate active oxidizing species. This process, for the first time, allows the formation of YBCO thin films with the orthorhombic superconducting phase in the as-deposited state, as shown in Fig.1 by the filled circle. Fig.1 plots oxygen partial pressure vs. temperature showing the phase transition lines of $YBa_2Cu_3O_{7-y}$ and parameters from the literature for successful in-situ growth.[1] The as-deposited films grown by PE-MOCVD show attainment of zero resistance at 72K with a transition width of about 5K. MOCVD was carried out in a commercial production scale reactor with the capability of uniform deposition over 100 cm^2 per growth run. Our preliminary results indicate that PE-MOCVD is a very attractive thin film deposition process for superconducting device technology.

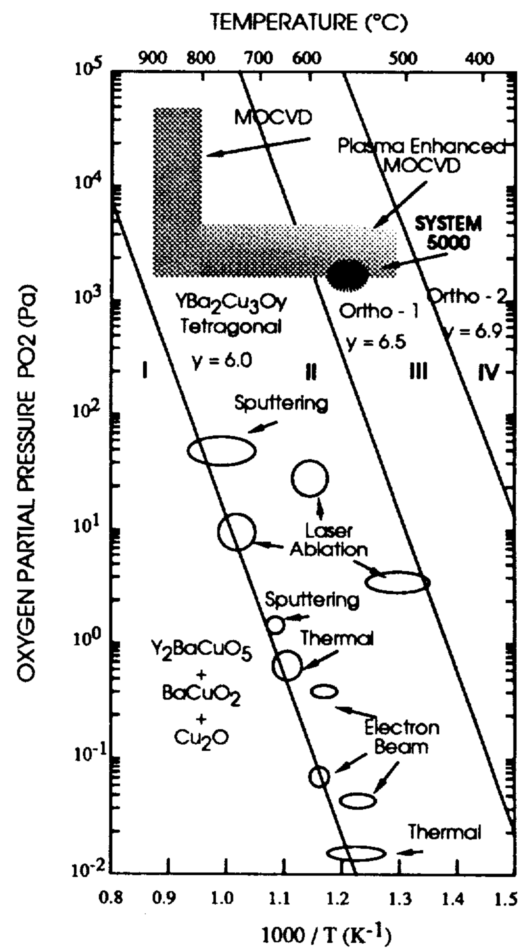

Fig.1. Oxygen partial pressure vs. temperature plot showing the critical stability line for YBCO at y = 6.0 together with parameters from the literature for successful in-situ growth. In addition, the tetragonal-orthorhomic transition line at y = 6.5 and the stability line for y = 6.9 are given.

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16. Abstract

This publication is comprised of abstracts for oral and poster presentations scheduled for AMSAHTS '90, to be held at NASA-Goddard Space Flight Center April 2-6, 1990. The conference will focus on understanding High-Temperature superconductivity with special emphases on materials issues and applications. AMSAHTS '90 will highlight the state of the art in our fundamental understanding of the nature of High-Tc superconductivity (HTSC) as well as the chemistry, structure, properties, processing and stability of HTSC oxides. As a special feature of the conference, space applications of HTSC will be discussed by NASA and Navy specialists.

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