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NORMAL STATE PROPERTIES OF CU-O SUPERCONDUCTORS

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## Special Sessions on High $T_c$ Superconductors

To deal with the rapid developments in the study of high  $T_c$  superconductors, three discussion sessions BP, DQ and ER were scheduled in addition to the plenary session BA and the four poster sessions on the same subject. These additional sessions consisting of short talks and comments took place on Aug. 21, 24 and 25 from 5 p.m. The short talks were given by the speakers invited by the program committee in advance of the conference. For the best use of the limited time available, those who wished to make a comment were requested to submit the resumé of their contributions on the first day of the conference. The chairmen and the co-chairmen of the sessions selected and organized these contributions. The detailed programs of the sessions, announced on Aug. 21, were as follows (T. Tsuneto):

### Material and Related Properties

August 21, 17:00–19:00

Chairmen: M. B. Maple and K. Kitazawa

#### *Short Talks*

J. R. CLEM (Ames)

Magnetization and Critical-Current Densities of the High-Temperature Superconductors

L. H. GREENE (Bellcore)

Plasma Oxidation and 3d Metal Doping of High  $T_c$  Superconductors

Jia-Qi ZHENG (Beijin)

Study of Y–Ba–Cu–O High Temperature Superconducting Thin Films

T. MURAKAMI (NTT)

Critical Current and Stability of Epitaxially Grown  $\text{Be}_2\text{YCu}_2\text{O}_{7-y}$  Thin Films

T. H. GEBALLE (Stanford)

Thin Film Research at Stanford University

D. DJUREK (Zagreb)

High Temperature Low Resistance States in  $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_4$

H. IHARA (Electrotech. Lab.)

Possible Superconductor at 65°C in Sr–Ba–Y–Cu–O System

#### *Comments*

J. ROSENBLATT (Rennes)

Penetration Depth and Meissner Effect in Sintered High- $T_c$  Superconductors

J. BOYCE (Xerox)

High  $T_c$  Ceramic Superconductors Studied by Extended X-Ray Absorption Fine Structure

Y. H. KAO (Stony Brook)

Temperature Dependence of Local Environment Surrounding Oxygen Atoms in Y–Ba–Cu–O

H. NAKAYAMA (Osaka)

Crystal Structure and Thermal Stability of Bulk and Single Phase Y–Ba–Cu–O–F Superconductors

P. VASSILEV (Sofia)

S-S Transitions in  $(\text{Y}_{1-x}\text{Sc}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{YBa}_2\text{Cu}_3\text{Co}_x\text{O}_{7-\delta}$  Compounds

R. VIJAYARAGHAVAN (Tata Inst.)

Anomalous Behaviour in High- $T_c$  Superconductors Based on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$

S. WOLF (Naval Res. Lab)

Possible Explanation of Resistance Anomalies in Non-Stoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

**Electronic Properties etc.**

August 24, 17:00–19:00

Chairmen: M. R. Beasley and T. Fujita

*Short Talks*

K. ASAYAMA (Osaka Univ.)

Antiferromagnetism and Superconductivity in  $(La_{1-x}Ba_x)_2CuO_4$

H. R. OTT (ETH)

Some Electronic Properties of  $Ba_2YCu_3O_{7-\epsilon}$

M. ISHIKAWA (Tokyo Univ.)

High and Low Temperature Specific Heat Results of  $Ba_2YCu_3O_{7-\delta}$

J. D. THOMPSON (Los Alamos)

Normal State Properties of Cu-O Superconductors

H. WÜHL (KfK)

Conclusions from Recent High- $T_c$  Activities at KfK, Karlsruhe.

C. C. TSUEI (IBM, Yorktown)

Anisotropy in  $Y_1Ba_2Cu_3O_7$

*Comments*

K. KUMAGAI (Hokkaido Univ.)

Pressure Effect on the Nuclear Relaxation Anomalies in  $La_{2-x}Ba_xCuO_4$

N. NISHIDA (Tokyo Inst. of Tech.)

First Observation of an Antiferromagnetic Phase in the  $Y_1Ba_2Cu_3O_x$  System

T. SHINJO (Kyoto Univ.)

Magnetism of Fe-Doped  $YBa_2Cu_3O_{7-x}$  from  $^{57}Fe$  Mössbauer Spectroscopy

T. FUJITA (Hiroshima Univ.)

Substitution for Cu and Mössbauer Effect of  $^{57}Fe$  in  $YBa_2Cu_3O_{7-\delta}$

H. ADRIAN (Universität Erlangen-Nurnberg)

Effect of Substituting Ni for Cu in  $Ba_2YCu_3O_7$  on  $T_c$

S. SUGAI (Osaka Univ.)

Characteristic Phonon Modes in High  $T_c$  Superconductors

S. MASE (Kyushu Univ.)

Phonon Dispersion Curves for  $YBa_2Cu_3O_7$ ,  $(La_{1-x}Sr_x)_2CuO_4$  and  $BaPb_{1-x}Bi_xO_3$  and Electron-phonon Interactions

G. THOMAS (AT & T Bell Labs.)

Observation of Nearly Drude Behavior and a Weak Energy Gap Structure in Single Crystal  $Ba_2YCu_3O_{7-\delta}$

N. E. ALEKSEEVSKII (Acad. Sci. Moscow)

Low Temperature Properties of Some High- $T_c$  Superconducting Systems

V. M. PAN (Inst. of Metal Phys.)

Electronic Properties of High  $T_c$  Metal Oxides  $La_{2-x}M_xCuO_{4-y}$  and Y-Ba-Cu-O

C. GOULD (Univ. of Southern California)

Normal State Magnetization of  $La_{2-x}Sr_xCuO_4$

G. W. CRABTREE (Argonne)

Enhanced Critical Current due to Fast Neutron Irradiation in Single Crystal  $YBa_2Cu_3O_7$

**Possible Mechanisms**

August 25, 17:00–18:30

Chairmen: T. M. Rice and H. Fukuyama

*Short Talks*

W. WEBER (KfK, AT & T Bell Labs.)

Electron-Phonon Interaction in the Oxide Superconductors

A. J. FREEMAN (Northwestern)

Charge Transfer Excitations and Superconductivity

C. M. VARMA (AT & T Bell Labs.)

What is the Right Model Hamiltonian for the New Oxide Superconductors?

G. BASKARAN (Princeton)

The Resonating Valence Bond State Theory of High Temperature Superconductivity

S. MAEKAWA (Tohoku)

A Theoretical Model of Superconductivity in Highly Correlated Systems

G. KOTLIAR (MIT)

Resonating Valence Bonds and D-Wave Superconductivity

M. IMADA (Saitama)

Superconducting Correlations and Pairing Mechanism in Two-Dimensional Cu-O<sub>2</sub> Lattice

V. L. GINZBURG (P. N. Lebedev Phys. Inst.)

On the  $\Psi$ -Theory of High Temperature Superconductivity

*Comments*

James P. SETHNA (Cornell)

2e or not 2e: Flux Quantization in the Resonating Valence Bond State

Daniel S. FISHER (AT & T Bell Labs.)

Zero-point Motion and Isotope Effect

D. NEWNS (IBM, Yorktown Heights)

Trends of  $T_c$  with Doping in Oxides Superconductivity

K. YAMAJI (Electrotechnical Lab.)

Exchange-Like Integrals Enhancing  $T_c$  in Cu Oxide Superconductors

J. ASHKENAZI (Technion)

Soft Plasmon Theory of the New Oxide Superconductors

E. ALLEN (Texas A & M)

LaO or BaO Excitons as the Mechanism of High Temperature Superconductivity

Shozo TAKENO (Kyoto Inst. of Tech.)

Fermion-Pairing in Real Space, Model Pseudo-Spin Hamiltonian, and Ginzburg-Landau Equation for High  $T_c$  Oxide Superconductors

## MATERIAL AND RELATED PROPERTIES

## Magnetization and Critical-Current Densities of the High-Temperature Superconductors

John R. CLEM

Ames Laboratory-USDOE and Department of Physics, Iowa State University, Ames, Iowa 50011, USA

Magnetization hysteresis measurements on bulk sintered specimens of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have been used to determine the critical-current density as a function of magnetic field and temperature. The observed exponential field dependence,  $J_c = J_1 e^{-H/H_0}$ , where  $H_0$  decreases with increasing temperature, can be understood in terms of the same pair-breaking description that is appropriate for superconducting-normal-superconducting structures. Magnetization studies also have been carried out on samples consisting of uniaxially aligned single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  embedded in epoxy. Strong anisotropy is found in the critical-current density,  $J_c$  being much

larger when the time-varying applied magnetic field is parallel to the  $c$  axis than when it is perpendicular to this axis. Near  $T_c$ , the nucleation field (upper critical field) parallel to the  $c$  axis is found to obey a square-root temperature dependence,  $H_{c2} = A(1 - T/T_c)^{1/2}$ . This result, combined with the observation of strong  $J_c$  anisotropy, suggests an interpretation in terms of  $T_c$  enhancement at twin boundaries, which are parallel to the  $c$  axis. Further studies of the superconducting properties as a function of the twin spacing are needed to check this hypothesis.

Plasma Oxidation and 3d Metal Doping of High  $T_c$  Superconductors

L. H. GREENE, J. M. TARASCON, B. G. BAGLEY, P. BARBOUX, W. R. MCKINNON and G. W. HULL

Bell Communications Research, 331 Newman Springs Road, Red Bank, New Jersey 07701 USA

Plasma oxidation replaces oxygen as the sole variable below  $80^\circ\text{C}^{1-2}$ , no  $T_c$  between 55K and 90K is observed<sup>2-4</sup> and bulk superconductivity in  $\text{La}_2\text{CuO}_4$  is induced.<sup>4-5</sup>

$\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_4$  with  $\text{M}=\text{Ni}$ ,  $\text{Zn}$  and  $0 \leq x \leq 0.3$ , relaxes the Jahn-Teller distortion. The magnetic moment from the Ni is greater than that induced by the Zn, but  $T_c$  falls faster with Zn-doping.<sup>6</sup> The Ni-doped forms over the entire range but the Zn-doped will not, suggesting a disorder effect.

1. J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull and E. M. Vogel, *Phys. Rev. B* **36**, 226 (1987).
2. B. G. Bagley, L. H. Greene, J. M. Tarascon, and G. W. Hull, *Appl. Phys. Lett.* **51**, 622 (1987).
3. J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W.

Hull, B. G. Bagley, E. M. Vogel and Y. LePage in High Temperature Superconductors, D. Gubser and M. Schluler, eds., (Mat. Res. Soc., Pittsburgh, PA, 1987). p65

4. J. M. Tarascon, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon and G. W. Hull in Chemistry of High Temperature Superconductors, D. L. Nelson, M. S. Whittingham and T. F. George, eds. (American Chemical Society, Washington, DC, 1987). p198

5. J. M. Tarascon, L. H. Greene, B. G. Bagley, W. R. McKinnon, P. Barboux and G. W. Hull, in Proceedings of the Intl. Workshop in Novel Mechanisms of Superconductivity, Berkeley, CA 22-26 June 1986. (in press)

6. J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Dellin, S. Foner and E. J. McNiff, Jr., *Phys. Rev. B*. (submitted)

## Study of Y-Ba-Cu-O High Temperature Superconducting Thin Films

J. Q. ZHENG, G. G. ZHENG, D. Q. LI, W. WANG, W. Y. GUAN, B. R. ZHAO, L. LI, H. S. WANG, Y. LU and Y. H. SHI  
Institute of Physics and Surface Physics Laboratory, Chinese Academy of Sciences, Beijing, China

$\text{YBaCuO}$  thin films were prepared by both e-beam evaporation and RF magnetron sputtering methods. The several kinds of substrates were used such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BaF}_2$ ,  $\text{ZrO}_2$  and  $\text{SrTiO}_3$  etc. For the electron beam evaporation method, the as-deposited films are taken in the form of multilayer. After the heat treatment at 850-890 °C for 1 hr the samples on  $\text{BaF}_2$  become uniform compositionally and show superconductivity with the midpoint  $T_c$  around 87 K and the zero resistance temperature at 77 K. With different heat treatment conditions the samples may display completely different resistance-temperature behaviors. For the RF magnetron sputtering method, the films deposited on  $\text{SrTiO}_3$  substrates

have the zero resistance temperature of 83 K with the critical current density of  $2.1 \times 10^3$  A/cm at 77 K. The X-ray diffraction results show that they are of single phase orthorhombic perovskites structure. We emphasize here that the substrate material is one of important factors for obtaining high- $T_c$  films with high critical current density. The composition and depth profile of these films have been studied by AES, XRFs and RBS. We find that during the annealing the reaction occurred between the films and substrates of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  which influences the superconducting properties of  $\text{YBaCuO}$  films.

Critical Current and Stability of Epitaxially Grown  $Ba_2YCu_3O_{7-y}$  Thin Films

Toshiaki MURAKAMI, Youichi ENOMOTO, Minoru SUZUKI, Kazuyuki MORIWAKI and Migaku ODA  
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Currently, there are serious problems with device applications in the following terms: (1)  $I_c$  value, (2) magnetic field dependence of  $I_c$ , (3) stability of superconducting properties. This describes the results of experiments focusing on solutions to these problems.

$Ba_2YCu_3O_{7-y}$  (BYCO) thin films were deposited on  $SrTiO_3$  (110) plates using magnetron sputtering method. The component of the target used was  $Ba_2YCu_{4.5}O_{8.5-y}$ . At substrate temperatures of about 700°C, the films grew epitaxially with the c-axis parallel to the substrate surfaces. Then, we measured anisotropy in the superconducting properties using line patterns parallel or perpendicular to the c-axis. It was found that

the films were undamaged in the etching process.

The I-V characteristics along the a-b plane were similar to conventional superconductors and the  $I_c$  value obtained from the curves was  $1.8 \times 10^6$  A/cm<sup>2</sup> at 77.3 K. This value is sufficiently large for device applications. The  $I_c$  decreased to about 40 % under a magnetic field of 4 T parallel to basal planes. However, this change is much smaller than that of the ceramic samples. Although the  $I_c$  value decreased by two orders after 75 days, this change can be reduced by preparing perfect single crystal films: The deterioration may be caused by chemical changes along dislocations in the films.

Thin Film Research at Stanford University

T. H. GEBALLE

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The Stanford program has concentrated on ways of preparing thin films of the cuprate perovskites. We have found that a polycrystalline film with a sharp  $T_c$  has a much higher  $J_c$  than do bulk ceramics (1). A surface current at 4.2K of  $3 \times 10^7$  /cm<sup>2</sup> which agrees with that expected for a thermodynamical critical field of 1T is found for oriented films (2). Studies of the critical field behavior, and of the paraconductivity above  $T_c$  including three-dimensional to two-dimensional crossover behavior determine in a self-consistent manner  $\xi_{\perp}(0)$  of the order of the CuO bond lengths 2A, while in the planes it is about 16A. The disc-shaped coherence volume fits nicely in each triade of CuO planes and accounts for the insensitivity of  $T_c$  to the actual rare earth of the  $ReBa_2Cu_3O_7$  compound.

The tunneling data obtained early at Stanford still remain to be explained (2). The high gaps are of course inconsistent with the gapless superconductivity predicted by some versions of Anderson's RVB theory.

We have recently been able to do optical studies. As the film quality improves, the peak near 0.4 eV which has been attributed to excitons, disappears (3,4). We believe it is due to second phases or defects which have nothing to do with the intrinsic superconductivity.

The work is supported by AFOSR, NSF, and ONR.

1. B. Oh et al., submitted to APL.
2. A. Kapitulnik et al., Trieste Proceedings '87.
3. Bozovic et al., submitted to PRL.
4. M.R. Beasley, submitted to YCS'87.

Possible Superconductor at 65°C in Sr-Ba-Y-Cu-O System

Hideo IHARA, Norio TERADA, Masatoshi JO, Masayuki HIRABAYASHI, Madoka TOKUMOTO, Yoichi KIMURA,  
 Toshiya MATSUBARA and Ryoji SUGISE  
 Electrotechnical Laboratory, 1-1-4 Umezono, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

Transition to a zero-resistance state at 65°C (338 K) was observed in a Sr-Ba-Y-Cu-O system[1]. The resistivity changed from  $5 \times 10^{-4}$  Ω·cm to below a measurable limit between 71 and 65 °C. The zero-resistance state reminiscent of superconductivity was continued for ten days at room temperature in air. Magnetization drop observed below around 340 K corresponds to less than 0.01% volume fraction of the room temperature superconducting state, if any.

Samples were prepared by a powder method using  $SrCO_3$ ,  $BaCO_3$ ,  $Y_2O_3$  and  $CuO$  powders. The nominal composition was  $SrBaYCu_3O_y$ . The samples were sintered at 1000°C for 5 h in air and then cooled in a furnace. X-ray diffractogram of whole sample

showed almost a single phase of oxygen-deficient perovskite with a trace of unidentified phase.

The resistance at each temperature was determined by measuring the voltage against the applied current ranging from 1 to 100 mA. The I-V characteristics obeyed the Ohm law above 67°C, but showed nonlinearity at 65°C. The unmeasurably small resistance below 65°C was checked by changing the electrodes and lead lines as described in Ref. 1.

Similar results were also observed for another sample. The reproducibility and stability, however, are not sufficient at present stage.

- 1) H. Ihara et al. : Jpn. J. Appl. Phys. 26 (1987) L1413

Penetration Depth and Meissner Effect in Sintered High- $T_c$  Superconductors

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The low-frequency (1 KHz) magnetic response of Y-Ba-Cu-O cylindrical samples is astonishingly similar to that of granular arrays containing  $10^8$  weakly coupled Nb grains [1]: the response is linear only for very low ( $\lesssim 5$  mOe) and low but much higher ( $\gtrsim 8$  Oe) field amplitudes [2]. The system behaves as an extreme type II superconductor even if the individual grains are perfectly diamagnetic, displaying an overall penetration depth  $\lambda(T)$  due to the weak coupling between grains [1]. This analysis allows to extract  $\lambda(T)$  from the Y-Ba-Cu-O experimental data [2]. The weakness of the couplings results in macroscopic values,  $\lambda(0) \approx 0.8$  mm. The incomplete Meissner effect so frequently reported

would then be only trivially geometric due to samples' sizes being in the mm range. Critical exponents characterizing the transition to overall coherence in the grains result in a power-law for  $\lambda(T)$ . Indeed we find [2]  $\lambda(T) \propto (T_c - T)^{-0.7}$ , as expected.

[1] A. Raboutou, J. Rosenblatt and P. Peyral Phys. Rev. Lett. **45**, 1035 (1980).

[2] A. Raboutou, P. Peyral, J. Rosenblatt, C. Lebeau, O. Peña, A. Perrin, C. Perrin and M. Sergent, to be published.

High  $T_c$  Ceramic Superconductors Studied by Extended X-Ray Absorption Fine Structure

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The near neighbour environments of absorbing atoms in the high  $T_c$  ceramics  $YBa_2Cu_3O_{7-\delta}$ ,  $GdBa_2Cu_3O_{7-\delta}$ ,  $La_{1.8}Sr_{0.2}CuO_4$ ,  $La_{1.8}Ba_{0.2}CuO_4$ , and  $BaBi_{0.25}Pb_{0.75}O_3$  were studied by EXAFS. The results agreed with recent diffraction studies and no significant changes of the local environments or the absorption edge structures were seen in a temperature interval of 4-300K. An additional structure in the Cu-K absorption edge, that occurred when an YBaCuO sample was heated in a non-oxygen atmosphere, indicated an oxygen depletion of the Cu-O chains followed by a disappearance of superconductivity. The vibrational frequencies of the Cu-O

and the (Pb,Bi)-O bonds were estimated from the temperature dependence of the Debye-Waller type broadening of the pair distributions. The Einstein temperatures, characteristic of these vibrations, all fell in the range of 500-700K and no correlations were found between these local frequencies and the widely varying  $T_c$  for the three types of Perovskite compounds.

Temperature Dependence of Local Environment Surrounding Oxygen Atoms in Y-Ba-Cu-O

Y. H. KAO

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Measurements of the oxygen K edge extended x-ray absorption fine structure (EXAFS) were made to probe the local environment surrounding the oxygen atoms in the high- $T_c$  superconductor  $YBa_2Cu_3O_{7-\delta}$ . The EXAFS spectra were obtained by detecting the total electron yield at various temperatures between 77K and 300K. This technique allows a determination of the interatomic distance, coordination number, and local disorder about the oxygen atoms in the material.

An interesting change in the Debye-Waller factor  $\sigma$  was observed in the present study. As the sample was cooled from 300K to a transition temperature  $T_0$  near 160K,  $\sigma$  for both the O-Cu

and O-Ba bonds shows an abrupt increase. This suggests that a local structural instability may occur in the inhomogeneous material at  $T_0$ . One possibility is the existence of a local soft mode in the Ba-Cu-O substructure, which gives rise to enhanced bond length fluctuations near  $T_0$ .

The presence of such a local soft mode may be relevant to superconductivity below 93K. Also, electron tunneling through grains of the soft-mode compound may lead to an enhancement of the critical current.

This experiment was performed at NSLS. The present work is supported in part by DOE.

Crystal Structure and Thermal Stability of Bulk and Single Phase Y-Ba-Cu-O-F Superconductors

H. NAKAYAMA, H. FUJITA, T. NOGAMI\* and Y. SHIROTA\*  
 Department of Mat. Sci. and Eng., \*Department of Appl. Chem.  
 Faculty of Eng., Osaka Univ., Suita, Osaka 565, Japan

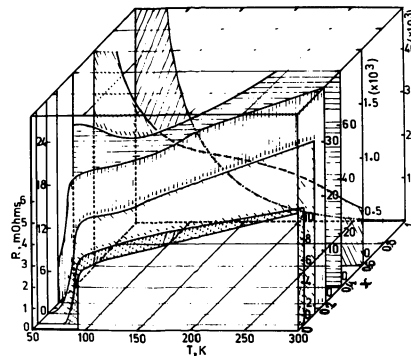
As was pointed out by ECD group, fluorine doping into Y-Ba-Cu-O materials is expected to cause drastic effects on the superconductivity properties. We have succeeded in synthesizing the bulk and single phase Y-Ba-Cu-O-F superconductors for the first time. The nominal composition of the materials is denoted by  $Y_{1-x}Ba_2Cu_3O_{6.5-\delta}F_{2y}$ , where  $\delta$  shows the oxygen content depending on the oxidation treatment after the high temperature sintering around 900°C. The lattice parameter  $b$  ( $a$ ) in the orthorhombic lattice increases (decreases) linearly with fluorine content up to around  $y=0.2$ . This shows that the solid solubility of fluorine lies around  $y=0.2$ . It was also found

by thermal annealing study that the orthorhombic phase is rather stable at high temperatures beyond 600°C, where fluorine-free  $Y_{1-x}Ba_2Cu_3O_{7-x}$  materials show the orthorhombic to tetragonal phase transition. Y-Ba-Cu-O-F samples with  $y=0.2$  show the highest room-temperature conductivity among the samples with fluorine concentration ranging from  $y=0$  to 1.0. Specimen with  $y=0.2$ , which was subjected to sintering at 900°C and subsequent oxidation at 280 to 400 °C, showed superconductivity transition temperature  $T_c(\text{onset})=89.0$  K and the  $T_c(\text{zero resistance})=77.4$  K. These value will be improved by optimizing the sintering/oxidation conditions.

S-S Transitions in  $(Y_{1-x}Sc_x)Ba_2Cu_3O_{7-\delta}$  and  $YBa_2Cu_3Co_xO_{7-\delta}$  Compounds

Petko Vassilev  
 Faculty of Physics, University of Sofia, 1126 Sofia, Bulgaria

Superconductor-semiconductor transitions are systematically studied in both systems, by rising  $x$  at constant sintering conditions. For  $0.1 < x < 0.5$ ,  $\rho_{120}(x) \approx A^x$ . As the resistivity, increase is larger at lower  $T$ ,  $dR/dT$  changes by  $x$ , becoming negative when the semiconducting behavior dominates. The results, including  $T_c$  shift and broadening of the superconductive transition, are surprisingly similar, despite of the expected strongly different role of the doped Sc- and Co-ions, which have to replace Y and Cu, respectively. It seems that the carrier's concentration and mobility are temperature dependent.  $R(T,x)$ -curves for the  $YBa_2Cu_3Co_xO_{7-\delta}$  compound, obtained at constant current density.  $J=1A/cm^2$



Anomalous Behaviour in High- $T_c$  Superconductors Based on  $YBa_2Cu_3O_{7-y}$

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 Tata Institute of Fundamental Research, Bombay 400 005, INDIA.

We have observed a number of anomalous but extremely interesting behaviour in some high- $T_c$  materials:

1. A 'single phase' sample of  $ErBa_2Cu_3O_{7-x}$  (as seen by the x-ray) material showed nearly zero resistance ( $R < 10^{-4} \Omega$ ) at as high temperature as 260K. This extra high- $T_c$  phase was unstable as it did not show up in subsequent coolings. The instability of the extra high- $T_c$  phase could be either due to aging, passage of current or thermal cycling.

2. A sample of  $Y(Ba_{1.6}K_{0.4})Cu_3O_{7-y}$  exhibited semiconducting resistive behaviour down to 8K in

the first cool-down. In the subsequent coolings, usual 90K-superconducting behaviour was observed.

3. Superconductivity ( $T_c \sim 90K$ ) in a sample  $YBa_{1.8}Pb_{0.2}Cu_3O_{7-y}$  was extremely short-lived as inferred from your ac- $\chi$  measurements. The diamagnetic response returned to normal response in a period of less than 30 minutes. The sample remained normal subsequently down to  $\sim 25K$ .

4. A reproducible magnetic response was observed just above the onset of superconductivity in  $(Y_{0.9}Ca_{0.1})Ba_2Cu_3O_{7-y}$  implying the possibility of a magnetic transition in this sample just below  $T_c$ . The magnetism could only be due to Cu-atoms.



Possible Explanation of Resistance Anomalies in Non-Stoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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The large resistance drops between 200 and 300 K seen in many nonstoichiometric samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are explained in terms of a tetragonal to orthorhombic transition in a thin layer at the surface of the grains. This surface layer is partially depleted of oxygen and therefore forms a semiconducting or insulating barrier between the grains at high temperatures. This region orders at lower temperatures forming the orthorhombic and therefore metallic phase which now couples the grains lowering the resistivity to a value comparable to the more stoichiometric material i.e., below  $10^{-3}$  ohm-cm. This model is based on the observation that in several samples showing

these resistance anomalies, the resistance above the transition is very voltage sensitive and the I-V characteristics are similar those for a diode, that is, the resistance decreases as the current is increased opposite to what is expected for superconductivity! In addition, the resistance below the anomaly is independent of current and voltage over several orders of magnitude of voltage, again opposite to that expected for a superconducting transition. Furthermore, recent data of A.T. Fiory et al. indicate that the orthorhombic to tetragonal transition temperature is dependent on the oxygen stoichiometry, decreasing linearly with  $\delta$ , the deviation from oxygen stoichiometry.

ELECTRONIC PROPERTIES ETC.

Antiferromagnetism and Superconductivity in  $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_4$

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$^{139}\text{La}$  NMR measurement has been performed in  $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_4$  to investigate the relation between antiferromagnetism and superconductivity. For  $x=0$  there appears a complicated structure in  $^{139}\text{La}$  NMR spectrum at 1.3K in zero external field. The spectrum is analyzed with a large electric quadrupole interaction and a small Zeeman term due to an internal field associated with the antiferromagnetic order. This internal field is a dipole field from Cu moments. The direction of the magnetic moment of Cu is concluded to be almost perpendicular to the principal axis of the electric field gradient with a small component parallel to the axis. The magnitude of the moment

is estimated to be  $0.44\mu_B$ . For  $x=0.1$  the magnetic moment at 1.3K has almost the same magnitude as for  $x=0$ . For  $x=0.25$ , the magnitude is considerably distributed, where the superconductivity appears below about 2K. Around this concentration magnetic order and superconductivity compete with each other.

More detailed report will be published in YCS '87 at Sendai by Kitaoka et. al..

High and Low Temperature Specific Heat Results of  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$

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The specific heat of the 90 K superconductor reported so far exhibits anomalous features such as a finite value of  $\gamma$  ( $\sim 8\sim 15$  mJ/mol-K<sup>2</sup>) in the superconducting state at  $T \ll T_c$ , a large upturn of  $C_p/T$  at low temperatures and a small discontinuity at  $T_c$ . In order to find causes of these anomalies, we have performed low and high temperature specific heat experiments on well characterized sintered samples of  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ . They are two samples of the 90 K superconducting phase, one sample of the 60 K superconducting phase and one non-superconducting tetragonal phase. We found that our hitherto best sample of 90 K phase exhibits the smallest upturn of  $C_p/T$  emerging only below 2 K and that the upturn grows with the oxygen deficiency,  $\delta$  in these phases. We attribute the upturn to localization resulting

from the randomness due to oxygen vacancies. On the other hand, the best quality sample revealed the largest jump at  $T_c$  of  $\Delta C_p/T_c = 53$  mJ/mol-K<sup>2</sup>, which conforms to the BCS prediction. We thus have an inverse correlation between the size of the jump at  $T_c$  and the upturn of  $C_p/T$  at low temperatures.

In the superconducting state, a small but finite value of  $\gamma$  of about 8.6 mJ/mol-K<sup>2</sup> was discerned for both 90 K samples of different quality. i.e. regardless of the size of the jump at  $T_c$ . The finite  $\gamma$ -value in the superconducting state may then be attributed to that of either the resonating valence bond state or normal conduction electrons in a two-band model. It would be clarified by examining other properties of a sample of further improved quality in future.

Normal State Properties of Cu-O Superconductors

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Using free-electron expressions, we analyze measurements of electrical resistance, thermoelectric power, Hall coefficient, magnetic susceptibility and upper critical field near  $T_c$  of  $YBa_2Cu_3O_x$  and  $GdBa_2Cu_3O_x$ . This simple analysis implies the presence of strong on-site Coulomb correlations in these materials that lead to an enhanced effective electronic mass at least one order of magnitude larger than the free electron mass. The Sommerfeld coefficient  $\gamma$  calculated from the susceptibility agrees with  $\gamma$  values derived from thermodynamic relations near  $T_c$ , indicating a Wilson ratio close to unity and a relatively small electron-phonon coupling

constant.

Conclusions from recent High- $T_c$  Activities at KfK, Karlsruhe.

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From resistive and inductive measurements on sintered bulk and powdered  $YBa_2Cu_3O_7$  a critical field anisotropy  $B_{c2}^{\parallel}/B_{c2}^{\perp} = 330 T/10 T \approx 30$  is derived neglecting Pauli paramagnetic limiting. Fast neutron irradiation of sintered  $YBa_2Cu_3O_7$  showed that the  $T_c$  degradation with fluence is slightly less than in  $PbMo_6S_8$  but larger than in A15 compounds. The irradiation induced increase of the normal state resistivity is accompanied by a remarkable decrease of the intergrain critical current and the superconducting volume fraction.

High-pressure x-ray investigations on  $YBa_2Cu_3O_7$  revealed a non-uniform decrease of the lattice parameters with increasing pressure. The bulk modulus  $B \approx 1800$  kbar (300 K) increases slightly on cooling to 15 K.

Additional phonon modes are observed at about 50 mV by neutron spectroscopy on  $YBa_2Cu_3O_7$  in comparison to the

phonon density of states of  $YBa_2Cu_3O_6$ . An obvious renormalization of oxygen vibrations, however, is not accompanied by a mode softening on cooling as observed in A15 superconductors.

Electron energy loss spectroscopy on  $YBa_2Cu_3O_7$  demonstrates an oxygen 2p hole character of the states at  $E_F$  which are filled up when the oxygen content is reduced ( $YBa_2Cu_3O_6$ ).

Single crystal x-ray diffraction studies on  $YBa_2Cu_3O_{6+\delta}$  showed a  $2\sqrt{2}a \times 2\sqrt{2}a$  superstructure. A model is proposed which relates the superstructure reflections to a 2 dimensional ordering of residual oxygen atoms on the 0(1) site.

Mössbauer spectroscopy on  $GdBa_2Cu_3O_7$  showed that the antiferromagnetic ordering of the Gd spins occurs within the Gd planes.

## Anisotropy in $Y_1Ba_2Cu_3O_7$

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From the consideration of atomic arrangement and electronic band structure, one expects that anisotropy plays an important role in determining the superconducting as well as the normal-state properties of high  $T_c$  superconductors such as  $Y_1Ba_2Cu_3O_7$ . Recent experiments have indeed demonstrated significant anisotropic effects in the magnitude and the temperature dependence of electrical resistivity<sup>1</sup>, lower and upper critical fields<sup>2</sup> ( $H_{c1}$  and  $H_{c2}$ ), critical currents, and the Hall coefficient<sup>1</sup>. In this talk, we present a study<sup>3</sup> of anisotropy and fluctuation-induced conductivity ( $\Delta\sigma$ ) of various  $Y_1Ba_2Cu_3O_7$  samples ranging from single-crystal epitaxial films to polycrystalline ceramics. A large  $\Delta\sigma$  above  $T_c$  in bulk samples has been observed previously<sup>4</sup> and is due to the effect of an extremely short coherence length  $\xi(0)$ . Our recent study shows: 1. Anisotropy manifests itself

in excess conductivity near and above  $T_c$ , 2. The anisotropic coherence lengths derived from the  $\Delta\sigma$  measurements are in good agreement with those from the  $H_{c2}$  results; 3. Based on the single crystal anisotropy data, one can predict properties such as  $dH_{c2}/dT$ , and  $\Delta\sigma$  for the ceramic samples if an angular averaging procedure is used. References: 1. S. W. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser and F. Holtzberg (preprint) 2. T. R. Dinger, T. K. Worthington, W. J. Gallagher, and R. L. Sandstrom, Phys. Rev. Lett. 58, 2687 (1987). 3. P. Freitas and C. C. Tsuei (to be published). 4. P. Freitas, C. C. Tsuei and T. S. Plaskett, Phys. Rev. B36, 833 (1987).

### Pressure Effect on the Nuclear Relaxation Anomalies in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$

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The magnetic properties of  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  have been investigated by  $^{139}\text{La}$  nuclear quadrupole resonance (NQR) between 1.5 and 250K. We have confirmed the antiferromagnetic order for  $x \leq 0.02$  by the analysis of the peak separations of the spectra which are originated from the internal fields due to Cu moments [1]. The unexpected enhancements of nuclear relaxation rates,  $1/T_1$  and  $1/T_2$ , in the low temperature region suggest the occurrence of the magnetic instability with Ba-doping. The magnetic transition of the spin re-orientation or a different type magnetic order from the antiferromagnetic alignment of Cu moments in  $\text{La}_2\text{CuO}_4$  are suggested as a possible origin for the anomalies at low temperatures [2]. We have also measured pressure effects on the NQR of  $^{139}\text{La}$  upto 8kbar. The

nuclear relaxation rates of  $^{139}\text{La}$  in the Ba doped compounds are enhanced by pressure in the "new" phase, although those are almost independent of pressure in the high temperature region. Interestingly,  $1/T_2$  under high pressure seems to increase with linear relation of temperature in the "new" phase. Detailed studies on the interplay of the superconducting and magnetic states are now in progress.

[1] I. Watanabe et al., J. Phys. Soc. Jpn. 56 (1987) No.9.

[2] K. Kumagai et al., to be published in Physica.

### First Observation of an Antiferromagnetic Phase in the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$ System

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In the  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$  system it is known that the physical properties change from a superconductor to an insulator, as we change its oxygen content. In the present study, magnetism of four distinct phases have been probed by positive muon spin relaxation method. Each phase was found to show a different magnetic behavior. In the orthorhombic superconductor ( $x \sim 6.9$ ,  $T_c \sim 90$  K), neither magnetic ordering nor magnetic fluctuation was observed down to 5 K. In another orthorhombic superconductor ( $x \sim 6.4$ ,  $T_c \sim 60$  K), magnetic fluctuation was seen below 10 K, though any magnetic ordering has not been

attained down to 2.4 K. The oxygen-rich tetragonal insulator ( $x > 7$ ) shows a similar magnetic behavior to the 60 K-superconductor. In the oxygen-poor tetragonal insulator ( $x \sim 6.2$ ), a new magnetically ordered phase, most likely an antiferromagnetic one, was discovered near room temperature. This is the first evidence for the presence of an antiferromagnetic phase in the  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$  system. A possible magnetic phase diagram of the  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$  system against the oxygen content was proposed.

### Magnetism of Fe-Doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ from $^{57}\text{Fe}$ Mössbauer Spectroscopy

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$^{57}\text{Fe}$  Mössbauer absorption spectroscopic measurements have been carried out for Fe-doped Y-Ba-Cu-O in the temperature range between 4.2K and 300K, with and without external field.

The spectrum at 4.2K for  $\text{YBa}_2\text{Cu}_2.94\text{Fe}_0.06\text{O}_{7-x}$  is non-magnetic but by applying an external field of 4.5T, a fairly large hyperfine field (c.a.20T in the average) has been induced. This fact means that Fe impurities in this superconducting compound ( $T_c=76\text{K}$ ) have significantly large magnetic moments.

In the case of  $\text{YBa}_2\text{Cu}_2.76\text{Fe}_0.24\text{O}_{7-x}$ , whose  $T_c$  is 34K, a magnetic hyperfine splitting has been

observed at 4.2K without an external field. Therefore the existence of magnetic order is confirmed. The average hyperfine field at 4.2K is about 25T. From the temperature dependence, the Neel temperature is found to be 16K.

Substitution for Cu and Mössbauer Effect of  $^{57}\text{Fe}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 

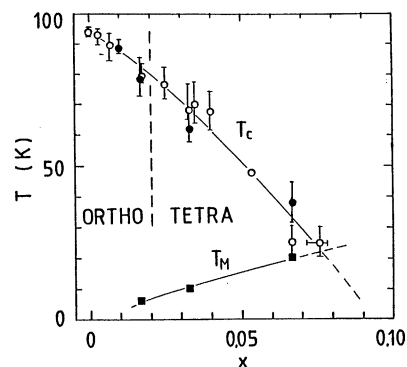
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Structural, superconducting and magnetic properties of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$  were investigated as a function of both temperature  $T$  and Fe-concentration  $x$ . Doping with Fe induces an orthorhombic to tetragonal phase transition at  $x_c \approx 0.02$ . The nearly  $T$ -independent value of  $x_c$  suggests that the transition is distinguished from that induced by releasing oxygen around 900 K. With increasing  $x$  across  $x_c$ , the superconducting transition temperature  $T_c$  of the samples decrease gradually without any appreciable anomaly. Susceptibility measurements indicate that the superconductivity in the Fe-induced tetragonal phase is of bulk nature. Mössbauer experiments show that Fe atoms are substituted for both Cu1 and Cu2 sites. The hyperfine field is observed for  $x > 0.01$  at low temperatures. The coexistence of superconductivity and some "magnetic order" is suggested below  $T_M$ . See Fig. in the right.

Characteristic Phonon Modes in High  $T_c$  Superconductors

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Two kinds of characteristic modes observed in the infrared spectra of  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is commented in comparison with nonsuperconducting  $\text{La}_2\text{NiO}_4$ . The first is the  $248\text{ cm}^{-1}$  mode which gives a large peak in the imaginary part of the dielectric constant, when La is substituted by Sr in  $\text{La}_2\text{CuO}_4$ . This mode is not a normal lattice vibration, because usual phonon peak decreases by doping due to the screening by free carriers. This mode is assigned to a localized mode of Cu atomic vibration parallel to the  $c$ -axis with a localized charge as in the case of a charged soliton in polyacetylene. For the vibration perpendicular to the  $c$ -axis charge is delocalized and Drude

spectra of plasma oscillation is presented. In  $\text{YBa}_2\text{Cu}_3\text{O}_7$  the corresponding peak is missing. It suggests that the charge is delocalized even in the vibration parallel to the  $c$ -axis.

The second characteristic modes are side bands which appear at  $249 \pm 61$ ,  $249 \pm 80$  and  $249 \pm 100\text{ cm}^{-1}$  at 80 K in  $\text{La}_2\text{CuO}_4$  and at  $236 \pm 42$  and  $234 \pm 80\text{ cm}^{-1}$  at 65 K in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The intensity ratio of the peaks on both sides shows that these side bands are not due to the two phonon process but intrinsic. These side bands do not appear in  $\text{La}_2\text{NiO}_4$ . The mechanism of appearance of the side bands probably related to the high  $T_c$  superconductivity mechanism.

Phonon Dispersion Curves for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  and Electron-phonon Interactions

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We have calculated the phonon dispersion curves of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ . First, the normal modes are derived and then the eigenvalue equations are set up. The force constants were determined so as to be in agreement with our data on the ultrasonic attenuation coefficients  $\alpha(T)$  and the sound velocities  $V(T)$  as a function of  $T$ . Based on a previous work on BPBO, the peaks of  $\alpha(T)$  vs.  $T$  were ascribed to some optic phonons. Following some theories, we supposed that the optic phonon modes due to Cu-O or Pb(Bi)-O bonds play the most important role in these high  $T_c$  superconductors. Equalizing these energies of the optic phonons at  $\Gamma$ -point,  $\omega_{M-O} = 26.7$ ,  $21.2$  and  $20.6\text{ meV}$  for YBCO,

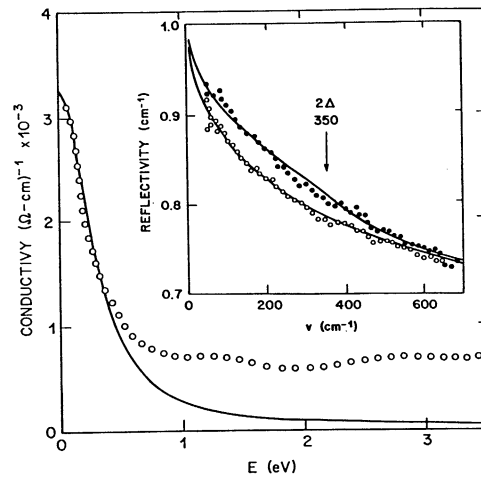
LSCO and BPBO, respectively, to  $\langle \omega^2 \rangle^{1/2}$ , we evaluated the McMillan parameter  $\lambda$  from the Allen-Dynes curve: the values of  $\langle \omega^2 \rangle^{1/2}$  are rather similar to each other. The results are  $\lambda = 4.6$ ,  $2.0$  and  $0.86$  for YBCO, LSCO and BPBO, respectively. The large difference of  $\lambda$  in LSCO and BPBO must come from a large difference in the magnitudes of the electron density of states, while the large difference of  $\lambda$  in YBCO and LSCO may come from the existence of the linear Cu-O chain with a short Cu-O side bond and an associated larger electron-phonon interaction constant in YBCO. However, the large value of  $\lambda$  might exceed the limit for the lattice to be kept in a stable state.

Observation of Nearly Drude Behavior and a Weak Energy Gap Structure in Single Crystal  $Ba_2YCu_3O_{7-\delta}$

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The figure shows preliminary results from a K-K transformation of reflectivity normal to  $\langle a-b \rangle$  vs. photon energy, as compared to a Drude spectrum (solid line). The results differ from the apparent peak at .5 eV in polycrystalline material<sup>1</sup> if the anisotropy is not taken into account. The inset shows reflectivity at  $T=95K$  (open circles) and at  $20K$  (solid circles) compared to a Drude curve (lower) and the curve (upper) for 87% Drude and 13% Mattis-Bardeen with  $2\Delta = 350cm^{-1} = 5.5kT_c$  ( $T_c = 89K$ ), with a large uncertainty.

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Low Temperature Properties of Some High- $T_c$  Superconducting Systems

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We have prepared and investigated some of the high  $T_c$  superconductors  $La-Sr-Cu-O$ ,  $Y-Ba-Cu-O$  and  $RE-Ba-Cu-O$ , where RE denotes all RE metals excepting  $La_{1.8}Sr_{0.2}CuO_{4-z}$ . All these systems have  $T_c$  value in the region of 80-95K. For  $Y-Ba-Cu-O$  system we measured  $H_{c2}(T)$  dependence in the fields up to  $H \approx 40T$  in steady and pulse fields and estimated  $H_{c2}(0) \approx 150T$ . For the specimens of  $La-Sr-Cu-O$  and  $Y-Ba-Cu-O$  the I-V characteristics of tunneling junctions (superconductor-normal metal), are measured. The ratio  $2\Delta/kT \approx 3.5 \pm 0.3$ . For  $La_{1.8}Sr_{0.2}CuO_{4.7}$ ,  $Y-Ba-Cu-O$  and  $(RE)-Ba-Cu-O$  magnetic properties in superconducting and normal states are investigated. For many systems the value of magnetic

susceptibility at 4.2K in low fields  $\chi \approx 0.8 \times (-1/4\pi)$ . The temperature dependence of the susceptibility for  $T > T_c$  for RE compounds corresponds to  $\chi = \chi_0 + C/(T-\theta)$ . The value of  $\theta$  is relatively low. It means that the magnetic interactions are weak. For  $La_{1.8}Sr_{0.2}CuO_{4-z}$  for temperatures in the region of 40-200K,  $\chi$  is independent upon temperature  $\chi = 10.8 \times 10^{-6} cm^3/g$ . For the  $Lu-Ba-Cu-O$ ,  $\chi = \chi_0 + C/(T-\theta)$ ,  $\chi_0 = 1.73 \times 10^{-7} cm^3/g$ . It can be supposed that  $\chi_0$  is a Pauli susceptibility, then  $\gamma = 5.6 mJ/mol \cdot K^2$ .

Electronic Properties of High  $T_c$  Metal Oxides  $La_{2-x}M_xCuO_{4-y}$  and  $Y-Ba-Cu-O$

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Electrical and magnetic properties (susceptibility, ESR) as well as electron-positron annihilation spectra of high  $T_c$  ceramics have been studied.

It was shown that ESR signals of  $Cu^{2+}$  and temperature dependent paramagnetic part of susceptibility for  $LaMxCuO$  and  $YBaCuO$  ceramics are not connected with superconducting phase, which has no paramagnetism of localized spins of  $Cu^{2+}$  and  $Cu^{3+}$ .

ESR Spectra and susceptibility data show the presence of antiferromagnetic

(up to  $T \approx 700K$ ) phase, it's quantity depending on oxygen content. Antiferromagnetic inclusions show effects like superparamagnetism, being possibly canted antiferromagnetics themselves.

Parabolic component of positron annihilation spectra due to free electrons was not observed. Spectra could be described by two Gaussians.

The insulator-metal transition in  $LaMxCuO$  takes place with increasing  $x$  due to Anderson localization because of oxygen vacancy disorder.

Normal State Magnetization of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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The magnetization of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (studied here in the range  $0.125 \leq x \leq 0.25$ ) is composed of two terms, only one of which is linear in magnetic field. The linear term's magnitude agrees well with published values when they are taken at high fields.

The second term is linear in field only at the lowest fields, saturating at a characteristic field of 1 kOe. This characteristic field is independent of temperature and Sr concentration. The amplitude of the saturable magnetization is temperature independent but it does depend on Sr concentration, increasing monotonically from a negligibly small value at  $x = 0.25$  to become as large as the linear term at  $x = 0.125$ .

A number of tests have been performed to ensure that this result is not of instrumental origin. First, the magnetic fields used in the analysis are not the fields indicated by the SHE susceptometer, but are measured fields. The two quantities can differ by as much as 50 Oe. Second, the field dependence is inconsistent with a simple model of paramagnetic impurities or of ferromagnetic inclusions. Finally, the results are reproducible in different samples. All samples were prepared identically by Peter Morgan at the Rockwell International Science Center.

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POSSIBLE MECHANISMS

Charge Transfer Excitations and Superconductivity\*

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Detailed high resolution local density energy band results<sup>1-3</sup> for the  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (with  $\delta = 0, 0.5$  and  $1.0$ ) superconductors are invoked which serve (i) to demonstrate the close relation of the physics (band structure), and chemistry (bonds and valences) to the structural arrangements of the constituent atoms and (ii) to provide possible insights and understanding of the basic mechanism of their superconductivity. Particular attention is addressed to the role of charge transfer excitations (CTE) from localized Cu-O d<sub>π</sub> states to itinerant Cu-O d<sub>σ</sub> states. These "local" CTE (especially in the chains) may lead to significant charge polarization. Incorporating the interactions with the 2D

Cu-O conduction electrons and the CTE (excitons) produces pairing interactions, via an exchange of excitons, which enhances  $T_c$ .

\*Supported by the U.S. Natl. Science Foundation

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A Theoretical Model of Superconductivity in Highly Correlated Systems

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We examine the resonating valence bond (RVB) superconductors proposed by P. W. Anderson and discuss various properties of the superconductors. Electron operators with spin  $\sigma$  at site  $i$ ,  $c_{i\sigma}$ , are transformed by atomic operators as  $c_{i\sigma} = b_i^\dagger a_{i\sigma} + \sigma a_{i-\sigma}^\dagger d_i$ , where  $b_i$  and  $d_i$  are boson operators and represent the empty (hole) and doubly occupied sites, respectively, and  $a_{i\sigma}$ 's are fermion (spinon) operators and represent the sites with an electron of spin  $\sigma$ . Then, the local charge and the spin at site  $i$  are given by  $Q_i = -b_i^\dagger b_i + d_i^\dagger d_i$  and  $S_i = (1/2) a_{i\sigma}^\dagger \sigma_{\sigma\sigma'} a_{i\sigma'}$ , respectively. This transformation was first proposed by Y. Isawa

in 1979. In the system with strong on-site correlation, the superconductivity requires both the RVB condensation and the Bose condensation of holes. 1) We calculate the specific heat at low temperatures, the electrical resistivity in the normal states, and their dependences on magnetic fields. The recent experimental data in high  $T_c$  oxides are discussed in the light of the present theory.

- 1) Y. Isawa, S. Maekawa, and H. Ebisawa: to be published in Proc. of Yamada Conf. XVIII on Superconductivity in Highly Correlated Fermion Systems.

Resonating Valence Bonds and D-Wave Superconductivity

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We review the slave Boson-Hartree Fock approach to the Anderson model in the framework of Bascowen, et al., and Ruckenstein, et al. We examine the different possible pairing states. A coherent mixture of anisotropic s and d wave superconducting order parameter has the lowest energy and opens up a full gap in the quasi-particle spectrum. We then outline the procedure for going beyond mean field theory in the treatment of the constraint eliminating the doubly occupied sites.

Superconducting Correlations and Pairing Mechanism in Two-Dimensional Cu-O<sub>2</sub> Lattice

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The mechanism of high- $T_c$  superconductivity is discussed from the point of strong electron correlation. Finite temperature properties of the single band Hubbard model and two-band Cu-O<sub>2</sub> lattice are investigated by a hybrid-type quantum simulation technique. The structure factor and the susceptibility of superconducting pairings are measured.

In the case of the single band model on a squared lattice, temperature and system size dependences up to  $16 \times 16$  show neither precursor for superconductivity nor enhancement of the superconducting correlation.

The two-band Cu-O<sub>2</sub> lattice is the model, where the role of oxygen p-orbit connecting neighboring

two Cu d-orbits is taken into account explicitly. The levels are chosen so that holes mainly occupy d-orbits in the half filled case, while excess holes beyond the half filling mainly go into p-orbits due to strong on-site Coulomb repulsion on Cu sites. Simulation data for the superconducting structure factor and susceptibility show enhancement as compared to the single band case.

A possible mechanism of such enhancement is discussed from the point that neighboring p-holes may form a Cooper pair. The origin of the attractive interaction of two p-holes is ascribed to the attraction of two Cu-O singlet pairs.

On the  $\Psi$ - Theory of High Temperature Superconductivity

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$\Psi$  - theory of superconductivity is good for ordinary superconductors because correlation length  $\xi$  is long in this case. (Fluctuations near  $T_c$  are proportional to  $\xi^{-6}$  and are small.) In high temperature superconductors (HTS)  $\xi$  is possibly short and in this case fluctuation region must be relatively wide. In such a situation the generalized Landau theory of phase transitions can be used (see Ginzburg and Sobyenin [Invited paper BF1 at LT18]). For HTS this mean to use for the free energy density the expression

$$F = F_0(T, p) + \sum_j \frac{1}{2m_j} \left\{ (-i\hbar \nabla_j - \frac{e^*}{c} A_j) \Psi \right\}^2 + A |\Psi|^2 + \frac{B}{2} |\Psi|^4 + \frac{C}{3} |\Psi|^6, \quad (1)$$

with (in the simplest case)  $A = -A_0 \tau |d|^{1/3}$ ,  $B = B_0 |\tau|^{2/3}$ ,  $C = C_0$ ;  $\tau = (T_c - T/T_c)$ . Due to pairing  $|e^*| = 2|e|$ , where  $e$  is the electronic charge. The  $\Psi$ - theory for HTS based on these principles is not developed yet. Large fluctuations in HTS near  $T_c$  can manifest themselves in different way. The precursor thermoelectric effect in HTS observed by A. Mawdsley et al. [Nature 328, 233 (1987)] can in principle be connected with fluctuations. Observations of thermoelectric effects (See, J. Low Temp. Phys. 56 195 (1984), and literatures cited there) in HTS are interesting from several points of view.

Exchange-Like Integrals Enhancing  $T_c$  in Cu Oxide Superconductors

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We have developed a two-band model of superconductivity including the usual intraband BCS interactions, the on-site Coulomb energy  $U$  and the interband BCS-form matrix elements originating in the exchange-like integral  $K$  at each atomic site pointed out by J. Kondo in 1963. The mean field treatment in a few typical cases discloses that  $K$  reduces  $\mu^*$  by partly canceling the effect of  $U$  in Morel-Anderson's expression of  $T_c$  and that  $T_c$  is substantially enhanced by the present mechanism in the Cu oxide superconductors having multiple bands with typical values of  $K \sim 1$  eV, if  $U \leq 2$  eV; the possibility of the latter was recently suggested by optical data etc. Further when there are two quasi 1D bands, due to

the interband Fermi surface nesting the ladder and bubble diagrams prove to divergently enhance the effect of  $K$  in reducing  $\mu^*$ , even possibly leading to its negative value, in a reasonable range of parameter values. In the Y compounds having two quasi 1D bands along the CuO chains this effect is claimed to elevate  $T_c$  up to 94 K and to sharply decrease  $T_c$  with decrease of the oxygen content due to submergence of one of the two 1D bands below the Fermi energy or its disappearance. Also the super high  $T_c$  in metastable states looks tractable in the present framework.

References: K. Yamaji and S. Abe, submitted to J. Phys. Soc. Jpn.; K. Yamaji, to be published in Solid State Commun.

Soft Plasmon Theory of the New Oxide Superconductors

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The new high- $T_c$  oxide superconductors are close to a Mott metal-insulator transition. The incipient transition reflects a tendency towards formation of an electronically-driven CDW (charge density wave), whose wave vector is appropriate for Fermi-surface (FS) nesting. When this CDW is commensurate with the lattice ( $La_2CuO_4$ ), a structural transition to a non-metallic state can occur. In other cases, the incipient instability can drastically soften the plasma modes at these wave vectors. Although their frequency is much lower than "bare" plasmons, these soft plasmons are still well above the Debye phonon cut off. There is experimental evidence for their existence. The soft plasmons couple fairly strongly to the conduction electrons, and induce an

attraction. (To achieve this, rather than just a screened Coulomb repulsion, a relatively slow electronic mode is needed. Our soft plasmons meet this criterion.) The soft-plasmon wave vectors are just those needed for Cooper pairing, since the CDW connects points on the FS. The Debye-energy prefactor of BCS is replaced by the order-of-magnitude-larger plasmon energy. Also the interaction is strong enough to ensure that the exponential factor is not small. We suggest that Ba or La f-orbitals play a role in both the plasma softening and the coupling strength; this possibly explains the observation that one of these elements is present in high- $T_c$  systems. *Prima facie*, there is no isotope effect, but plasmon - phonon hybridization can give a non-zero effect.

*LaO* or *BaO* Excitons as the Mechanism of High Temperature Superconductivity

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Varma et al. and others have discussed *CuO* excitonic resonances as a possible mechanism of high  $T_c$  superconductivity. Here we suggest an alternative possibility — charge transfer excitations associated with the out-of-plane oxygen and metal atoms. The mechanism that we are proposing is a specific version of the excitonic superconductivity originally envisioned in the work of Little, Ginzburg, and Allender, Bray, and Bardeen: The excitons, in the *LaO* or *BaO* layers, are spatially separated from the charge carriers, in the *CuO<sub>2</sub>* planes or *CuO* chains, rather than coexisting with them. The excitons proposed here are suggested by our calculations of the electronic energy bands, local densities of states, and valences within a one-electron,

semiempirical tight-binding model. We find that the *LaO* system in  $La_{1.85}Sr_{0.15}CuO_4$  and the *BaO* system in  $YBa_2Cu_3O_7$  are very ionic and insulator-like. Excitons, with the electron transferred from the occupied *O(p)* to the unoccupied *La(d)* or *Ba(d)* states, are strong and unscreened. They may therefore yield a high  $T_c$  even though their energies are large — several eV even with the binding energy included. If the mechanism proposed here is correct, higher  $T_c$ 's will result from larger matrix elements, which may in turn result from phases with shorter oxygen metal bond lengths.



Fermion-Pairing in Real Space, Model Pseudo-Spin Hamiltonian, and Ginzburg-Landau Equation for High  $T_c$  Oxide Superconductors

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In view of a possible new mechanism involving antiferromagnetism for high  $T_c$  superconducting oxides, Fermion pairing in real space is studied by employing a pseudo-spin Hamiltonian. By identifying the coherent-state representation of pseudo-spin raising operators with order parameter function, the Ginzburg-Landau (GL) equation is derived. The pseudo-spin parameters are related to superconducting parameters. The present pairing model gives: (1) short coherence length  $\xi(0) \simeq 10 \sim 20 \text{ \AA}$ , (2) large value of the GL parameter  $\kappa \simeq 100 \sim 150$ , (3) reasonable fitting of the numerical value of  $T_c$  for

the Y-Ba-Cu-O system to  $T_c \simeq 90 \text{ K}$  for the pseudo-spin parameters deduced from the Meissner effect measurement, (4) sensitivity of  $T_c$  to carrier concentration, (5) similarity of excitation spectrum to the case of liquid  $\text{He}^4$ , and so on. Pairing mechanism by bipolarons proposed by Chakraverty and others is unlikely to exist here, since it yields much smaller value of  $T_c$ . The difference of the present pairing mechanism from the BCS pairing mechanism is clearly seen by studying, for example, the temperature dependence of specific heat.