INVESTIGATIONS OF SUPERCONDUCTING AND NON-SUPERCONDUCTING YBa2 Cu3 O7-x BY FIELD ION MICROSCOPY, ATOM-PROBE MASS SPECTROSCOPY AND FIELD ELECTRON EMISSION

G. Kellogg, S. Brenner

JOURNAL DE PHYSIQUE
Colloque C6, supplément au n°11, Tome 49, novembre 1988

INVESTIGATIONS OF SUPERCONDUCTING AND NON-SUPERCONDUCTING $YBa_2Cu_3O_{7-x}$ BY FIELD ION MICROSCOPY, ATOM-PROBE MASS SPECTROSCOPY AND FIELD ELECTRON EMISSION

G.L. KELLOGG and S.S. BRENNER[1]

Sandia National Laboratories, Division 1134, PO Box 5800, Albuquerque, NM 87185, U.S.A.

Abstract - The structure and composition of superconducting and non-superconducting samples of $YBa_2Cu_3O_{7-x}$ were examined by field ion microscopy, atom-probe mass spectroscopy and field-electron emission techniques. Field ion microscope images from both types of material exhibited ring structures associated with atomic or multiatomic layers and uniform, layer-by-layer field evaporation was possible. Atom-probe mass spectra contained signals corresponding to atomic and molecular oxygen, all three metals, and oxides of Cu and Y. Atom-probe mass spectra from the superconducting samples ($x \sim 0.35$) contained a much larger molecular oxygen signal than mass spectra from the non-superconducting samples ($x \sim 0.8$) indicating that oxygen in the CuO chains is field desorbed preferentially as molecular oxygen ions. Field electron emission from the superconducting samples exhibited normal Fowler-Nordheim characteristics above and below the superconducting transition temperature. Surface contaminates were found to decrease the work function of the material by as much as 39%. With the exception of one isolated experiment, no significant temperature effect on the field emission characteristics were observed.

I - INTRODUCTION

The recent discovery of bulk superconductivity at temperatures near 90 K has created considerable interest in the chemical, physical, and electronic properties of the ceramic oxide $YBa_2Cu_3O_{7-x}$ /1/. Of special importance is the relationship of these properties to the superconductivity of the material. During the past year it has been demonstrated that the techniques of field ion microscopy and atom-probe mass spectroscopy can contribute to the characterization of $YBa_2Cu_3O_{7-x}$ on a microscopic scale /2-7/. Atomic-resolution images showing layered structures have been obtained with the field ion microscope /2-4/, and mass spectra which are fairly consistent with the known stoichiometry of the material have been obtained with the atom-probe /5-7/. Having established the feasibility of analyzing these materials at the microscopic level, efforts are now underway to determine if any of the features observed in the field ion images or any of the species detected in the atom-probe are associated with the superconducting properties of the material. These investigations involve systematic studies of the differences between the tetragonal, non-superconducting phase and the orthorhombic, superconducting phase of $YBa_2Cu_3O_{7-x}$ /8/.

The ability to prepare field emission tips also suggests that it may be possible to gain information on the electronic properties of the material with field-electron-emission techniques. An especially exciting possibility is the examination of field electron energy distributions and how they vary above and below the transition temperature. These distributions are known to reflect the changes in the electronic density of states near the Fermi level /9/ and they may provide an important clue into the material's superconductivity As a first step in this direction, we have measured the Fowler-Nordheim characteristics of $YBa_2Cu_3O_{7-x}$ and how they change as a function of temperature and surface contamination.

In this paper we report the results of our field ion microscope, atom-probe, and field electron investigations of superconducting and non-superconducting $YBa_2Cu_3O_{7-x}$. Much of the field ion microscope and atom-probe work has been published in previous articles /2,4,5,8/ and only the major results are reviewed. The field emission investigations, however, have not been reported previously and are discussed in more detail.

[1] Associated Western Universities Visiting Summer Faculty from the Department of Metallurgical and Materials Engineering of the University of Pittsburgh

II - Sample Preparation

The superconducting and non-superconducting samples used in this investigation were obtained from the same starting material. Bulk samples of $YBa_2Cu_3O_{7-x}$ prepared by the hot-pressing technique /10/ were cut into square cross-section rods (0.4 mm cross-section, 1-2 cm long) on a low-speed diamond saw. Characterization of this as-received material indicated that its phase was tetragonal 1-2-3 with an oxygen content of approximately 6.2 /10/. Magnetization measurements indicated that this material was not superconducting. Some of the rods were subsequently annealed in oxygen at 900-950 C for 12 hours followed by a slow cool to room temperature. This oxygen anneal produced the orthorhombic 1-2-3 phase with measured oxygen contents of approximately 6.65. Magnetization and resistance measurements indicated that this material was superconducting with a transition temperature of 92 K. To produce sharply-pointed tips, both types of material were electropolished in a perchloric acid solution. Magnetization measurements indicated that even after this electrochemical etch, the annealed samples were still superconducting.

Some of the sample tips were imaged in a transmission electron microscope to determine their radius and morphology at the apex. Figure 1 shows examples of transmission electron micrographs from a superconducting and a non-superconducting sample. The TEM images indicate that the above electropolishing procedure produces smoothly-tapered tips with acceptable radii for field ion microscopy from both phases of the material. However, an obvious difference between the two materials can be seen in Fig. 1. Whereas the interior of the non-superconducting sample images with uniform contrast, the interior of the superconducting sample exhibits striking contrast variations. As discussed in our previous articles /2,8/, these contrast variations are due to the periodic twins which form in the material during the oxygen anneal /11/. The appearance of the twins in the superconducting samples and their absence in the non-superconducting samples provides supporting evidence that two different phases of the material exist at the tip apex.

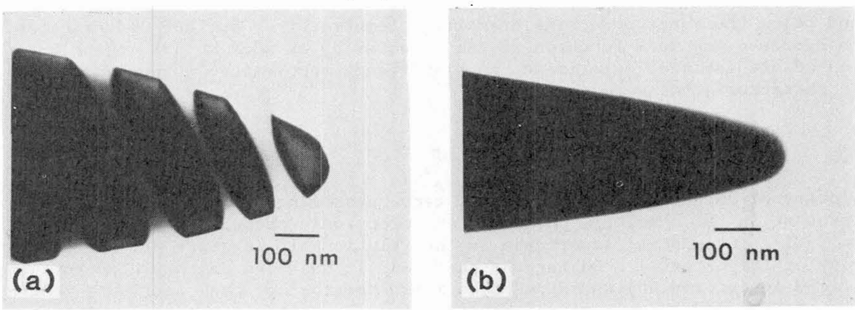

Fig. 1 - Transmission electron micrographs from (a) a superconducting and (b) a non-superconducting sample of $YBa_2Cu_3O_{7-x}$. Periodic twins are observed in the image from the superconducting sample. The images were obtained by T. J. Headley of Sandia National Laboratories.

III - Experimental Results and Discussion

A - Field Ion Microscopy

Field ion microscope images of $YBa_2Cu_3O_{7-x}$ were obtained with several different imaging gases. Neon and xenon imaging gases produced images with very little structure. Some structure could be observed with argon, but this required temperatures above 90 K to prevent the argon from condensing on the cold head. The best images were obtained with hydrogen. Fig. 2 shows hydrogen field ion micrographs taken from (a) a superconducting and (b) a non-superconducting sample of $YBa_2Cu_3O_{7-x}$. Ring structures indicative of atomic layers were observed in hydrogen field ion images from both types of samples. Computer simulations by Melmed et al. /3/ indicate that the imaged layers in superconducting samples are those perpendicular to the c-axis (long axis) of the orthorhombic unit cell, which is consistent with our earlier suggestions based on the symmetry of various field ion microscope patterns /2/. It is therefore reasonable to assume that the layers observed in the non-superconducting samples are those perpendicular to the c-axis of the tetragonal unit cell. Field evaporation of the tip surfaces proceeded in a uniform layer-by-layer fashion. However, as the topmost plane collapsed, it was possible to see residual atoms on the surface of the next layer. This observation suggests that the layer associated with each ring is not a single atomic layer, but two or more atomic layers which field evaporate together up to the final collapse of the plane.

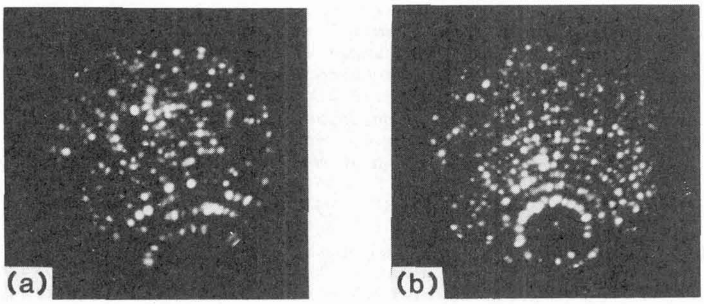

Fig. 2 Field ion microscope images from (a) a superconducting and (b) a non-superconducting sample of $YBa_2Cu_3O_{7-x}$. Ring structures indicative of atomic layers are observed.

An very noticeable decrease in the field ion intensity was observed in the field ion microscope images of the superconducting samples when the sample temperature was increased through the superconducting transition temperature. Since field ion image formation involves an electron tunneling process, it is tempting to relate this change in field ion intensity to the superconducting properties of the tip. However, the possibility that the decreased intensity is the result of a decrease in the imaging gas supply cannot be ruled out. Examination of one of the non-superconducting samples in a system with accurate temperature control should provide the answer.

B - Atom-Probe Mass Spectroscopy

Uniform field evaporation of both phases of the material could be achieved with either a dc or a pulsed electric field. Pulsed field evaporation made it possible to analyze the material with a pulsed-voltage, atom-probe mass spectrometer. An atom-probe mass spectrum from one of the superconducting samples is shown in Fig. 3. The spectrum contains signals corresponding to both atomic and molecular oxygen, all three metals, and oxides of Y and Cu. The elemental concentrations calculated from approximately 12,000 was found to be fairly consistent with the known stoichiometry of the material /5/. Typically the Y concentration is a little high and the O concentration is a little low. The large compositional fluctuations observed by Nishikawa and Nagai /6/ in their pulsed-laser atom-probe analysis was not observed in our investigations.

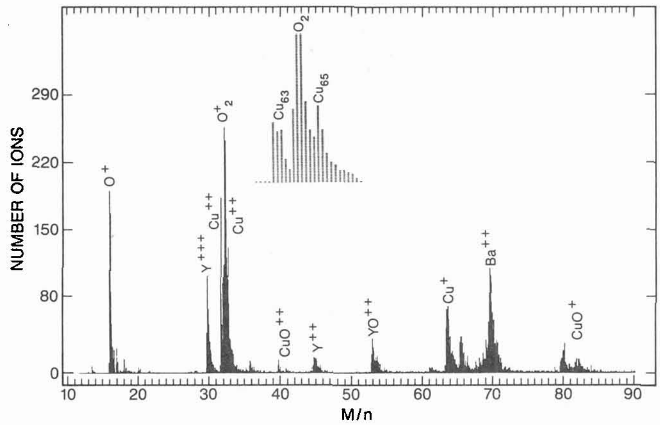

Fig. 3 - An atom-probe mass spectrum from a superconducting sample of $YBa_2Cu_3O_{7-x}$ obtained in 2×10^{-7} Torr neon. Insert shows peaks near m/n = 32. (From Ref. 5)

A qualitative comparison of mass spectra from superconducting and non-superconducting samples with an imaging atom-probe yields a very interesting result. Mass spectra from both phases of the material contain signals consistent with the above probe-hole atom-probe analysis. The major difference between the spectra is that the molecular oxygen signal is significantly larger in the mass spectra from superconducting samples, whereas the atomic oxygen and metal oxide signals are roughly the same. (Although we cannot distinguish between the molecular oxygen and the doubly-charged Cu signals in the imaging atom-probe, it is reasonable to assume that the predominant effect of an oxygen anneal would be to increase the molecular oxygen signal and not the copper signals.) This suggests that the oxygen introduced during the high-temperature anneal to make the samples superconducting goes into a site which field desorbs primarily as molecular oxygen. Past studies with neutron diffraction /12/ have identified this site as the (0, .5, 0) site in the copper oxide chains. Our observation suggests the possibility of monitoring the occupation of this site with the atom-probe. More quantitative studies with a higher mass resolution atom-probe are now in progress.

C - Field Electron Emission

Field electron emission experiments were conducted on the superconducting samples to determine if changes in the emission current occur as the temperature is varied through the superconducting transition temperature. The ultrahigh vacuum conditions required for field emission measurements (typically $< 1 \times 10^{-10}$ Torr) presents a problem for the analysis of the superconducting material. The standard procedure used to obtain ultrahigh vacuum involves a bakeout of the vacuum system at temperatures in excess of 200 C. At these temperatures, oxygen may be depleted from the ceramic material and cause the samples to become non-superconducting, particularly at the apex of a tip. To overcome this problem, we used a system with a vacuum interlock. The sample was first introduced into an entry chamber pumped by a turbomolecular pump. The entry chamber was evacuated until the pressure fell into the 10^{-9} Torr range. The sample was then transferred to an ion pumped chamber with a background pressure of 1-2 x 10^{-10} Torr.

To examine the temperature dependence of the field emission characteristics, the sample was first cooled to a base temperature of approximately 60 K by maintaining thermal contact with the cold head of a closed-cycle liquid helium refrigerator. Sample heating was accomplished by passing a dc current through the Pt wire loop onto which the sample was mounted. The temperature control electronics were isolated from ground potential so the tip could be heated while applying high voltages. To reduce the accumulation of surface contamination during the measurement, a computer controlled system was used to obtain the field emission data. In a typical experiment the tip was field evaporated and a set of current-voltage measurements was recorded in a period of approximately one minute.

Conventional Fowler-Nordheim plots /13/ of $\ln(I/V^2)$ vs. 1/V, where I and V are the measured field electron current and applied voltage, respectively, were obtained from the superconducting samples. With only a few exceptions, these plots were straight lines indicating normal field emission characteristics. Moreover, with one notable exception, variation of the tip temperature from 60 K to over 200 K did not produce any change in the Fowler-Nordheim plots. Fig. 4 shows Fowler-Nordheim plots taken from a $YBa_2Cu_3O_{7-x}$ sample tip at 60 K and at 218 K, temperatures well below and above the superconducting transition temperature. As can be seen in the figure, the plots are identical. The results were the same for samples which were subsequently annealed in 1 atm. oxygen at 600 700 C overnight.

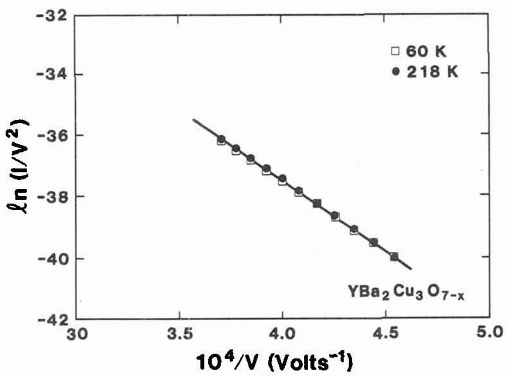

Fig. 4 - Fowler-Nordheim plots from a sample of $YBa_2Cu_3O_{7-x}$ recorded at temperatures of 60 K and 218 K. No differences in the field emission characteristics are observed.

The field emission characteristics were found to be very sensitive to surface contamination. A most vivid example of this is shown in Fig. 5. In this example the experiments were carried out in a vacuum chamber different from the one described above. Its background pressure was in the low 10^{-9} Torr range. The upper plot was taken after the sample has been cooled to a base temperature of 60 K without field evaporation. The lower curve was taken at the same temperature immediately after field evaporation. The removal of the surface contamination which condensed on the tip during cooling obviously produced a significant change in the work function of the surface. The reduction in work function due to the surface contamination calculated from the two slopes in Fig. 5 is 39%. In order to heat the sample tip in this chamber, the temperature of the entire cold head had to be raised This produced significant background contamination. As a result of this contamination, the slopes of Fowler-Nordheim plots recorded with increasing sample temperature decreased monotonically and approached the upper curve of Fig. 5. However, field evaporation would always cause the slope to return to that of the lower curve. These results indicate that care must be taken to avoid surface contamination when examining the field emission characteristics of ceramic superconductors.

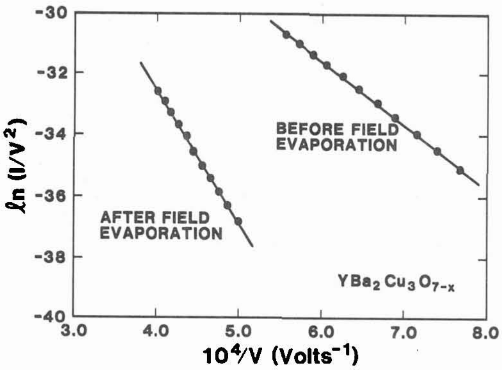

Fig. 5 - Fowler-Nordheim plots from a sample of $YBa_2Cu_3O_{7-x}$ recorded before and after field evaporation of the tip. Removal of surface contamination resulted in a significant increase in the work function.

As mentioned above, there was one exception to the observations that the Fowler-Nordheim characteristics were independent of temperature. In this particular case, the slope of the Fowler-Nordheim plots exhibited an abnormally large variation with temperature. Fig. 6 shows the plots. These results were obtained in the UHV transfer system and, unlike the above results in which contamination was responsible for lowering the work function, in this experiment the sample temperature could be switched back and forth between the higher temperatures and the base temperatures with reproducible plots. In those cases where contamination was involved, the plots at the base temperature could be reproduced only after field evaporation. Thus, it appears that the variations observed in Fig. 6 are a real temperature effect. Unfortunately, this effect could not be reproduced on any of the other samples which we examined. This was despite the fact that care was taken to reproduce the sample preparation and measurement conditions as close as possible. Thus, it is still not clear whether this result is some sort of experimental artifact or a real effect dependent on a variable not yet investigated, e.g., sample orientation, crystal grain size, etc.

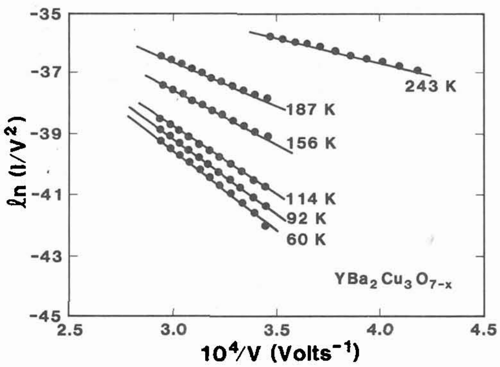

Fig. 6 - Fowler-Nordheim plots from a sample of $YBa_2Cu_3O_{7-x}$ which show a large temperature effect on the field emission characteristics. This result could not be reproduced on similar samples.

IV - Summary

The examination of $YBa_2Cu_3O_{7-x}$ samples by various high-field techniques was reported. Smoothly-tapered tips from both phases of the material were prepared by electrochemical etching in a perchloric acid solution. Transmission electron micrographs from the superconducting tips showed the twinned structure of the orthorhombic phase with remarkable contrast. Field ion microscope images from both the superconducting and non-superconducting phases were found to exhibit ring structures associated with multi-atomic layers. Atom-probe mass spectra from the superconducting phase exhibited an enhanced molecular oxygen signal compared to the non-superconducting phase indicating that the oxygen introduced during the high-temperature anneal goes into a site which field desorbs primarily as molecular oxygen. Field electron emission experiments indicated that for the superconducting samples examined in this study the Fowler-Nordheim characteristics are the same above and below the superconducting transition temperature. Surface contamination was found to significantly decrease the field emission work function.

V - Acknowledgments

The authors gratefully acknowledge E. L. Venturini of Sandia National Laboratories for many helpful discussions and the magnetization measurements. The following researchers at Sandia National Labs are also acknowledged for their contributions to this work: R. E. Loehman for supplying the hot-presses samples; D. S. Ginley and M. Mitchell for oxygen treatment of the sample rods; J. F. Kwak for the resistance measurements; and T. J. Headley for the Transmission Electron Microscope analysis. S. S. Brenner's summer visit was supported, in part, by Associated Western Universities, Inc. This work was supported by the U. S. Department of Energy under Contract # AC04-76DP00789.

REFERENCES

/1/ M. K. Wu, J. R. Ashburn, C. T. Torn, P. H. Hor, R. L. Meng, L. Gao, J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. 58, 908 (1987).

/2/ G. L. Kellogg and S. S. Brenner, Appl. Phys. Lett. 51, 1851 (1987).

/3/ A. J. Melmed, R. D. Shull, C. K. Chiang, and H. A. Fowler, Science 239, 176 (1988).

/4/ G. L. Kellogg and S. S. Brenner, AIP Conference Proceedings No. 165, eds. J. M. E. Harper, R. J. Colton, and L. C. Feldman (American Institute of Physics, New York, 1988), p. 421.

/5/ S. S. Brenner and G. L. Kellogg, Mat. Res. Soc. Proc., 99, 947 (1988).

/6/ O. Nishikawa and M. Nagai, Phys. Rev. B 37, 3685 (1988).

/7/ A. Cerezo, C. R. M. Grovenor, R. M. Hoyle, and G. D. W. Smith, Appl. Phys. Lett. 52, 1020 (1988).

/8/ G. L. Kellogg and S. S. Brenner (submitted for publication).

/9/ J. W. Gadzuk and E. W. Plummer, Rev. Mod. Phys. 45, 487 (1973).

/10/ R. E. Loehman, W. F. Hammeter, E. L. Venturini, R. H. Moore, and F. P. Gerstle, Jr., J. Am. Ceramic Soc. (submitted for publication).

/11/ R. Beyers, G. Lim, E. M. Engler, R. S. Savoy, T. M. Shaw, T. R. Dinger, W. J. Gallagher, and R. L. Sandstrom, Appl. Phys. Lett. 51, 367 (1987).

/12/ D. W. Murphy, S. A. Sunshine, P. K. Gallagher, H. M. O'Bryan, R. J. Cava, B. Batlogg, R. B. van Dover, L. F. Schneemeyer, and S. M. Zahurak, Proc. Symp. on High-T_c Superconductors, 193rd American Chemical Society National Meeting, Denver, CO, 1987 (in press).

/13/ R. Gomer, Field Emission and Field Ionization (Harvard University Press, Cambridge, 1961) and references therein.