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A NEW APPROACH TO UNDERSTANDING THE SEMICONDUCTOR SURFACE AND INTERFACES
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Report 1 November 1987 through 31 October 1988

a. Papers submitted to refereed Journals (and not yet published):

   Superconductivity up to 90 K in a cubic thallium-doped barium cuprate, Z. Iqbal, H. Eckhardt, B. L. Ramakrishna, J. C. Barry, D. C. Vier, S. Schultz, S. B. Oseroff, E. W. Ong, A. Bose, and F. Reidinger, submitted for publication to NATURE, August 1988. (Preprint attached.)

b. Papers published in refereed journals:


c. Books (and sections thereof) submitted for publication:

   None

d. Books (and sections thereof) published:

   None

e. Patents filed:

   None

f. Patents granted:

   None

g. Invited presentations at topical or scientific/technical society conferences:

   None

h. Contributed presentations at topical or scientific/technical society conferences:

   None

i. Honors, Awards/Prizes:

   None

j. Graduate students and postdoctorals supported under the crp for the year ending 31 October 1988:

   Joseph Anderberg, graduate student
   Dr. David C. Vier, postdoc
We have extended our application of electron spin resonance for the study of the silicon-metal interface to include Au, Al, and Ag overlayers. In Table 1 (below) we present representative data for the observed broadening of the ESR linewidth for each of these metals applied to the silicon surface. As can be seen from these data, whereas strong spin coupling was found for Au and Al (comparable to our earlier results for Cu), we found no evidence of coupling for Ag. We believe these differences illustrate the specificity of the Si-metal atom bond at the interface, whose quantitative measure is one of the goals of this research. We are now in the process of completing the dedicated UHV in-situ ESR system that will enable us to make the desired measurements of the Si-metal coupling at the submonolayer coverage level.

We have continued to search for ESR signals in the new high \( T_c \) superconductors, and also to apply the low field microwave absorption technique for the purposes of discovering new high \( T_c \) materials. In particular we have improved the sensitivity of our technique such that we are readily able to detect superconductivity in single crystals as small as \( 10^{-6} \) gm. Preprints of articles reporting this effort are enclosed.

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Enclosures:


Magnetization of the 120-K Ti-Ca-Ba-Cu-O superconductor

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dc magnetization measurements on the new Ti-Ca-Ba-Cu-O superconductor show superconductivity with an onset temperature as high as 118 K, 24 K higher than that of a high-quality Eu-Ba$_2$Cu$_3$O$_{7-\delta}$ sample. The resistive onsets of these new superconductors are near 140 K. The magnetic data show complete diamagnetic flux exclusion and 10–15% Meissner expulsion at 10 K.

Discoveries of 30-K superconductivity in the La-Ba-Cu-O system\(^1\) and 90-K superconductivity in the Y-Ba-Cu-O system\(^2\) have stimulated a worldwide race for higher-temperature superconductors. In spite of many efforts in the past year, stable and reproducible superconducting phases have been identified.\(^3\) Two superconducting glass state,\(^7\) discoveries of the 90-K TI-Ba-Cu-O system,\(^4\) recent made in rare-earth-free superconductors \(\text{TI-Ca-Ba-Cu-O,}^{11}\) and \(\text{Y-Ba-Cu-O,}^{12}\) have stimulated a worldwide race for higher-temperature superconductors. In spite of many efforts in the past year, stable and reproducible superconductivity has remained at the level of 90 K in the R-Ba-Cu-O system (\(R\) equals rare earth). Breakthroughs were recently made in rare-earth-free superconductors by the discoveries of the 90-K TI-Ba-Cu-O system,\(^3\) \(110\)-K Bi-Ca-Sr-Cu-O system,\(^5\) and \(120\)-K TI-Ca-Ba-Cu-O system.\(^6\)\(^7\)\(^8\)\(^9\) The TI-Ca-Ba-Cu-O superconducting samples have onset and zero-resistance temperatures much higher than those of the Bi-Ca-Sr-Cu-O system.\(^7\)\(^9\) Two superconducting phases have been identified.\(^9\) One has a composition of Ti$_2$Ca$_2$Ba$_2$Cu$_3$O$_{10+x}$ (2:2:2:3 phase), and another of Ti$_2$Ba$_2$Ca$_3$Cu$_4$O$_{8+x}$ (2:1:2:2 phase, which is similar to Bi$_2$CaSr$_2$Cu$_2$O$_{8+x}$). In this Brief Report we report magnetization and resistance data on the TI-Ca-Ba-Cu-O samples. The onset temperature of magnetization is 117–118 K, 23 K higher than that of a high-quality Eu-Ba$_2$Cu$_3$O$_{7-\delta}$ sample.

Two samples with nominal compositions Ti$_2$Ca$_2$Ba$_2$Cu$_3$O$_{7-\delta}$ and Ti$_2$Ca$_2$Ba$_3$Cu$_4$O$_{11+x}$ used in the present experiments were prepared using Ti$_2$O$_3$, CaO, and BaCu$_2$O$_4$ in the same batch.\(^8\) Both were heated at 900 °C for 3 min and furnace cooled. The resistance-temperature dependences of these two samples are shown in Fig. 1. The resistance was measured by the standard four-probe technique with silver-paste contacts. These two samples both have onset temperatures near 140 K (defined by the smallest curvature of the resistance-temperature curve\(^10\) ), midpoint of 127 K, and zero-resistance temperature at 121 K. Zero-resistance data correspond to resistivities less than \(10^{-6} \Omega \cdot \text{cm}\). The difference of calcium contents in these two samples does not seem to have significantly changed their superconducting behavior, which depends strongly on preparation conditions of the samples. Note that the Ti$_2$Ca$_2$BaCu$_2$O$_{7-\delta}$ sample consists of approximately 80% of the new 2:2:2:3 superconducting phase.\(^9\)

Magnetization measurements were performed utilizing a superconducting quantum interference device (SQUID) magnetometer manufactured by BTI Corp., San Diego, CA. Figures 2 and 3 show dc magnetization (field cooled and zero field cooled) as a function of temperature for an applied field of 1 mT for samples of Ti$_2$Ca$_2$Ba$_2$Cu$_3$O$_{7-\delta}$ and Ti$_2$Ca$_2$Ba$_3$Cu$_4$O$_{11+x}$, respectively, whose resistive behavior is shown in Fig. 1. The Meissner flux expulsion is 10–15% of the diamagnetic flux exclusion; the magnitude of the diamagnetic shielding is large and consistent with complete flux exclusion from the samples at 10 K. This behavior is similar to that observed in TI-Ba-Cu-O,\(^4\) La-Ba(Sr)-Cu-O,\(^11\) and Y-Ba-Cu-O samples.\(^12\) Explanations suggested to date include existence of a superconducting glass state,\(^11\) anisotropy effects,\(^13\) and superconductivity confined to thick shells around normal grains.\(^12\) At this stage, we hesitate to speculate on differentiation between these causes, and only note that our samples were...
In conclusion, the \( \text{Tl}_{2}\text{Ca}_{2}\text{Ba}_{3}\text{Cu}_{0.9+} \) samples show a complete diamagnetic exclusion, and 10–15% Meissner expulsion at 10 K. The onset temperature of magnetization drop for the \( \text{Tl}_{2}\text{Ca}_{2}\text{Ba}_{3}\text{Cu}_{0.9+} \) samples is 118 K, which is 23.5 K higher than that for a high-quality \( \text{EuBa}_{2}\text{Cu}_{3}\text{O}_{7-x} \) sample. This onset temperature is consistent with that observed from resistance-temperature variations.

The support of the National Science Foundation (Grant No. NSF-DMR-86-13858) and the U.S. Office of Naval Research (Grant No. ONR-N00014-87-K-0338) is gratefully acknowledged.

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BRIEF REPORTS

The layered tetragonal Bi-Sr-Ca-Cu\textsuperscript{1-3} and Tl-Ba-Ca-Cu\textsuperscript{4,5} oxides with bulk transition temperatures in the 80-125K range have been the centre of the recent excitement in the field of high $T_c$ superconductivity. Another important development has been the construction of a cubic, non-copper oxide superconductor of composition $\text{Ba}_4\text{K}_x\text{BiO}_3$,\textsuperscript{6,7} with a $T_c$ onset of 30K. Here we report the results of experiments in the Tl-Ba-Cu oxide precursor system with and without Ca, from which we were able to isolate a cubic phase with a superconducting transition onset which varies with thallium concentration from 30 to 90K. The cubic phase is a thallium-doped barium cuprate of typical composition $\text{Ba}_{0.9-x}\text{Tl}_x\text{CuO}_2$, where $x \approx 0.2$ as determined by the refinement of single crystal X-ray diffraction data. Superconductivity in this compound apparently occurs, as in $\text{Ba}_4\text{K}_x\text{BiO}_3$, within the framework of a 3-dimensionally linked array.

In the course of our investigation of the preparation conditions of the layered thallium-calcium-barium-copper oxide superconductors\textsuperscript{4,5}, we observed the formation of a metastable, superconducting cubic thallium doped barium cuprate phase under the particular synthesis conditions described here. The cubic phase was observed as the majority fraction (> 85% by volume via X-ray diffraction) in samples prepared from the starting nominal compositions of the metal atoms Tl$_3$Ba$_2$Ca - 1:2:3 and 1:2:4. The cubic phase is also formed as a 50% volume fraction from a precursor containing Ca in the ratio Tl$_4$Ba$_3$Ca$_x$Cu$_y$ = 2:2:2:3.

The best synthesis conditions consisted of firing BaCO$_3$ and CuO in the 2:3 or 2:4 atomic proportions for 25 hrs. near 930°C (or close to the melting point of the starting composition) in air with one intermediate grinding. The pre-formed barium copper oxide was then mixed carefully with the appropriate amount of Tl$_3$O$_2$, and pressed into pellets at ~5kbar pressure. The pellets were placed in an alumina boat lined with gold foil, which was placed in the cold part of a tube furnace under flowing O$_2$. The reaction zone of the furnace was heated to between 860°C and 865°C, the boat was then pushed into the reaction zone and the temperature stabilized within 3 minutes. The heat treatment was carried out typically for 5 min. followed by removal of
the boat to the cold zone of the furnace where it is allowed to cool down within 5 minutes to at least 400°C under flowing O₂. The powder X-ray diffraction pattern of a sample prepared from a 1:2:3 initial composition is shown in Fig. 1(a). The same X-ray pattern was obtained for a sample prepared from a 1:2:4 precursor. Peaks associated with the minority thallium-rich phase in the sample are indicated by asterisks. Because of the better match of the ionic size of Tl⁺ with Ba²⁺, we prepared a few samples of the Tl-doped barium cuprate phase from a 2:2:3 precursor under flowing Ar with thallous carbonate or nitrate instead of Tl₂O₃ in the precursor composition. This was followed by annealing under flowing oxygen at 450°C for 1 hr. The X-ray diffraction pattern of a sample prepared from a 2:2:3 initial composition containing Tl₂CO₃ is shown in Fig. 1(b). The volume fraction of the minority phase indicated by asterisks is somewhat smaller than in the sample prepared from a 1:2:3 nominal composition containing Tl₂O₃. Our experiments with a variety of starting stoichiometries and temperatures suggest a need for excess thallium in the starting precursor and processing above 800°C where both Tl₂O₃ and Tl₂CO₃ decomposes and liquid phase formation can occur, thus allowing rapid chemical doping of the barium cuprate phase. In addition, control of the oxygen content of the barium cuprate phase precursor appears necessary via flux formation and/or an annealing step under Ar.

Electron microprobe analyses in the focused mode (1 μm) in a scanning electron microscope were carried out for typical preparations from precursor compositions mentioned above. The microprobe analyses of the doped phase showed a Cu:Ba atomic ratio that was consistently near 1.4. The Cu:Ti atomic ratio in the doped phase was found to range from 5.5 to 7.0.

The samples described above were examined extensively in the high resolution transmission electron microscope at Arizona State University. The micro-crystals were consistently found to be cubic in the imaging and diffraction modes. Typical (100) and (111) images and the corresponding diffraction patterns are shown in Fig. 2. We have also recorded the structure image of the undoped phase and found the intensity distribution of the dark spots (which represent the atomic positions) and the electron diffraction pattern to be different from that of the thallium-doped structure. The minority component in the samples investigated consisted of a fine grained material which did not correspond to any of the known superconducting layered thallium-barium-copper oxide phases, both from the images (which were difficult to obtain because of disorder in this phase) and the electron diffraction patterns. Electron microprobe analyses of the minority phase showed that it is thallium-rich, but there is no unique thallium-barium-copper composition.

Single crystal X-ray diffraction analyses were carried out on a number of microcrystals isolated from a partially melted pellet prepared from a Tl:Ba:Ca:Cu = 2:2:2:3 composition. These crystals and those obtained from a CaO-free precursor contained no Ca as shown by electron microprobe analyses (to a 300 parts per million level as determined by calibration scans). The results indicate a cubic structure similar to that reported for BaCuO₂ but with important differences. In the doped structure, Ba atoms are missing from the 0,0,0 and 1/2,1/2,1/2 positions, and there is substitutional doping by thallium at three Ba positions. The structure is cubic with a lattice constant of 18.277 Å and belongs to the space group Im3m. The fractional coordinates, thermal factors and occupancies at R = 0.05 are listed in Table 1. A model of the structure which shows hexagonal Cu₄O₁₂ rings involving the Cu(1) and O(2 and 3) sites capped by Ti occurrences and sitting astride the body diagonals, is shown in Fig. 3. The Cu atoms in this position are four-coordinated. This local structure may provide the key to the observed superconductivity in this material. The formula unit derived from the structure determination is Ba₁₀·₉·₄Ti₄Cu₁₄O₃₆ with x = 0.2. There is disorder involving the Cu (4) and O(6) locations. Hence the oxygen and copper concentrations are not uniquely determined from the single crystal X-ray diffraction data. The electron microprobe data, however, fixes the Cu:Ba atomic ratio close to a value of 1.4.

Superconducting transitions were established with onset near 90K in two isolated crystals about 50 μm x 50 μm 100 μm of the thallium-doped barium cuprate phase that had been first examined in an X-ray diffractometer and found to be a pure cubic single crystal. The tech-
nique used to detect superconductivity in such small samples is the onset of field-modulated microwave absorption in the superconducting state due to inter-domain Josephson junctions. The temperature dependence of the absorption for the crystals is shown in Fig. 4. This phenomenon has now been widely investigated in the new high $T_c$ oxide superconductors. Although a relatively strong microwave absorption signal relative to the mass of the sample was observed there may not be a direct relationship between absorption and the amount of superconducting phase present. We have also performed the microwave experiment on the undoped barium cuprate precursor and found no evidence of non-resonant microwave absorption at low temperatures. DC magnetometry measurements using both a SQUID and a force magnetometer were performed on samples prepared from Tl:Ba:Cu = 1:2:3 and 1:2:4 precursors, which showed majority thallium-doped barium cuprate fractions via powder X-ray diffraction. The results at different magnetic fields for these samples are shown in Fig. 5. The flux expulsion and exclusion approaches 50 to 60% of ideal diamagnetism at 5K indicating that bulk superconductivity occurs in these samples. From the data in Fig. 5 it is also evident that superconductivity in the doped phase is very sensitive to the magnetic field. From a magnetization versus field curve we estimate the lower critical field to be ~100 G. The above results suggest that the superconducting state in this phase has spin glass-like character. In addition, the $T_c$ onset temperature decreases from 60K to 70K for the 1:2:3 sample to 30K for the 1:2:4 sample. Comparison of the Ti content distribution by electron microprobe analyses shows that the Ti content is lower in the 1:2:4 sample. However, the differences are small and quantitative numbers cannot be quoted at this time. We also found that Ti loss occurs (depressing $T_c$ and decreasing the superconducting fraction) on aging of the samples in air.

AC and DC four-probe transport measurements were attempted on as-prepared pellets from the 1:2:3 and 1:2:4 precursors. Both samples showed strong metallic behavior down to our measurement limit of ~10K. Zero resistance was not achieved but kinks in the data at 70 and 30K in the 1:2:3 and 1:2:4 precursor prepared sample respectively, were observed. It is possible that the percolative pathway in these samples is blocked by excess thallium much in the same way as excess potassium blocks the transport path in K-doped BaBiO$_3$. Future work should determine the conditions of re-annealing the as-prepared pellets so that transport properties of the thallium-doped barium cuprate phase can be measured.

We believe at this time that thallium doping results in the closure of the semiconducting gap in BaCuO$_2$ and concomitant suppression of its known ferromagnetic interactions, to give a glass-like superconductor. Some remnant ferromagnetic character may, however, be still present as evident from the presence of reproducible oscillations near 40K in the susceptibility data (indicated by arrows in Fig. 5a).

We would like to thank Dr. J. Ferraro of the Molecular Structure Corporation for performing the crystal structure analyses and Dr. R. Antrim of Allied-Signal for obtaining the extensive microprobe data on these samples. The research at the University of California, San Diego, was partially supported by grants from NSF-DMR-13588 and ONR-N00014-87-0338.
REFERENCES

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TABLE I
Atomic coordinates, thermal factors (B) and occupancies for the cubic thallium doped barium cuprate phase at R = 0.05.
Figure Captions

Fig. 1 Powder X-ray diffraction of pellets prepared from precursors:
(a) Ti:Ba:Cu = 1:2:3 using Ti₂O₃, and (b) 2:2:3 using Ti₂CO₃.
Asterisks indicate peaks associated with the minority thallium-rich phase.

Fig. 2 Unit cell of thallium doped barium cuprate showing the
Cu(i), 0(2) and 3) thallium atoms along the body diagonal.

Fig. 3 (100) and (111) structure images and corresponding electron
diffraction patterns (marked a and b respectively) of a
crystal of the thallium-doped barium cuprate phase.

Fig. 4 Plots of the microwave absorption signal versus temperature
for two single crystals of the thallium-doped barium cuprate
phase. A background scan is also shown. The data was taken
while warming the sample, which typically results in the
sample temperature being approximately 5K cooler than the
temperature indicated in the plot. Note that the temperature
scales are different for each plot and non-linear.

Fig. 5 (a) Zero-field cooled DC magnetization data taken in a force
magnetometer at fields of 3 and 6 Oe for two separate
preparations from a Ti:Ba:Cu = 1:2:3 precursor.
(b) Zero-field cooled and field-cooled (Meissner) DC
magnetization SQUID magnetometer data for a Ti:Ba:Cu = 1:2:4
precursor-prepared sample measured in fields of 1.0 and 0.1
Oe.