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Presented at the 1988 Applied Superconductivity Conference,
San Francisco, CA, August 21–25, 1988

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August 1988

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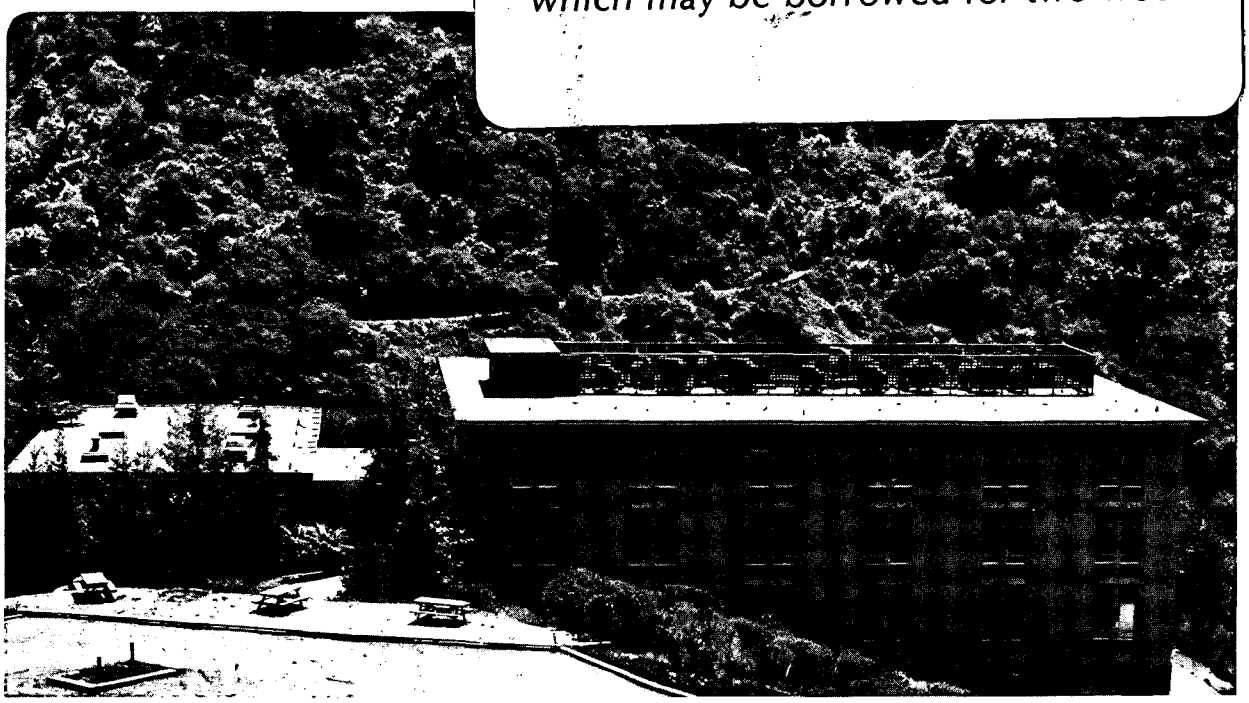

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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Bi-Ca-Sr-Cu-O SUPERCONDUCTORS : THE CONNECTIVITY ISSUE

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Summary

The connectivity problem in Bi-Ca-Sr-Cu-O superconductors is addressed in this paper. Our bulk samples always exhibit a step in the resitivity plot, consequent to which zero resistance is obtained around 75K, although the onset is above 110K. Magnetic measurements indicate the presence of almost equal fractions of two superconducting phases with transition temperatures of 110K and about 80K. The microstructure of these samples has been examined using several transmission electron microscopy techniques. The superconducting phases exhibit a polytypoid type structure with the general formula of $Bi_2 Sr_2 Ca_{n-1}Cu_nO_y$, where n takes on values of 1,2, 3 and in some infrequent cases 4. The c-parameter and T_c increase with n. In almost all the superconducting grains, the lower T_c (n =1or 2) polytypoid is observed at the grain boundaries. Thus, the 110K polytypoid in each grain is not "connected" to similar regions in other grains. The lower T_c polytypoid is observed at the grain boundaries due to a reduction of Ca and/or Cu. It is suggested that the controlled addition of PbO enables the formation of a Pb-rich liquid phase which makes the composition near the grain boundaries uniform. Consequently, the step in the resistivity plot disappears.

Introduction

The recent discovery of a new family of Bi-Ca-Sr-Cu-O(BCSCO) superconducting oxides has further increased the worldwide interest in these oxide ceramics, which started with the discovery of superconductivity in La-Ba-Cu-O by Bednorz and Muller[1-4]. The original discovery of superconductivity in Bi-Sr-Cu-O in the temperature range of 7-20K by Michel et. al[2] was quickly improved upon by Maeda et. al[3] and Chu et. al[4] who

showed that the addition of Ca improves the T_c to 80K with resitive and magnetic anomalies occurring near 110K. These results were subsequently obtained by other groups working independently[5-8]. The structure and composition of the 80K superconducting phase has been elucidated by using high resolution transmission electron microscopy (TEM) combined with electron diffraction and xray microanalysis[9-11]. Our results on the 80K phase are in agreement with those reported by other workers. In addition we also carried out structural analysis of the phase thought to be responsible for the 110K transition and showed that it consists of two $Ca+CuO_2$ layers intercalated inside each unit cell of the 80K phase, thus increasing the c-parameter of the superconducting phase from 30.5Å to 37.2Å. This change in the periodicity with composition produces structures termed polytypoids, as distinct from polytypes, which involve no composition change. The stoichiometric composition changes from $Bi_2Sr_2Ca_1Cu_2O_y$ for the 80K polytypoid to $Bi_2Sr_2Ca_2Cu_3O_y$ for the 110K polytypoid. Homologous compounds with T_c of about 15K higher than the corresponding Bi- system have been synthesised using a Tl-Ba-Ca-Cu-O system[12-14]. One feature that characterizes the BCSCO system is the presence of steps in the resistivity plot. Consequently, the onset of the resistive drop is around 110K while zero resistance is obtained only around 75K. In an earlier paper we reported results of preliminary high resolution TEM examinations of the BCSCO samples which showed that the lower T_c polytypoid occurred at the boundaries of almost all the grains observed[15]. This suggested that the steps in the resistivity plot may be caused by a connectivity problem, i.e., the 110K regions in the grains of the samples are not in direct contact with one another. In this paper, results of further observations of the BCSCO samples through high resolution TEM are reported and the connectivity problem is discussed in the light of these observations. Results of microstructural observations of samples with controlled additions of PbO, through which the steps in the resistivity plot have been avoided, are also discussed.

Experimental

The samples were prepared by the solid state reaction technique described in ref. (16). The composition of the two samples (unleaded and leaded) is given in Figs.1&2. Figs.1&2 show the transport properties for the two samples. Samples for TEM were prepared by mechanically thinning a slice cut from bulk stock and finally Argon ion milling to electron transparency at liquid nitrogen temperature. High resolution TEM was carried out in a JEOL 200CX

at 200kV while analytical TEM was carried out in a JEOL 200CX at 200kV. The characteristic xrays from the region of interest were acquired using a Be window energy dispersive xray (EDX) detector. All standard precautions for xray microanalysis were taken.

Results and Discussion

Fig.3 shows a typical high resolution TEM image near a grain boundary of the unleaded sample. In this figure the c-planes are imaged. Near the grain boundary, the spacing of these planes decreases from the value inside the grains (37.2Å, corresponding to the 2-2-2-3 polytypoid), to 24.6Å (corresponding to the 2-2-0-1 polytypoid). In many cases, the c=30.6Å polytypoid (corresponding to the stoichiometry of 2-2-1-2) is observed near the grain boundaries. The thickness of this lower T_c region varies from a few unit cells to a few hundred Å. This lower c-parameter (and lower T_c) polytypoid at the long edges of the grains occurs due to the segregation of Bi to the grain boundaries and/or due to a deficiency of Cu+Ca at such grain boundaries. The excess Cu+Ca manifests as grains of $CaCu_2O_3$ and as Sr-Ca-Cu-oxide. The structure inside the grains is also not uniform. Dislocations and faults are frequently observed, the details of which are reported elsewhere. Due to these defects, the T_c should change locally inside the grain. Such defects can also be good sites for pinning or nucleation of fluxoids and can debilitate the current carrying capacity of the grains. The inherent tabular morphology of the grains, Fig.4, results in a certain degree of preferred orientation to the grains, although not perfect. As in the case of Y-Ba-Cu-O superconductors, mutual misorientation of the grains will play an important part in the evolution of the superconducting properties. In contrast to the unleaded samples, the leaded samples are characterized by the absence of the lower T_c polytypoid at the grain boundaries. Fig.5 shows a typical HREM image of the grain boundary region of the leaded sample and clearly the c-parameter is uniformly 37.2Å upto the grain boundary. Fewer stacking defects are observed inside the grains, unlike in the case of the unleaded samples, in which stacking faults are prevalent.

Another feature that characterizes the leaded samples is the presence of a thin amorphous grain boundary phase, especially at triple points. One typical example is shown in Fig.6. Xray microanalysis[17] reveals that this phase contains all the elements. Xray microanalysis of the BCSCO phase also revealed that Pb replaces Bi in the polytypoids to the extent of about 25% of the total Bi content. The amorphous nature of the grain boundary phase in the leaded sample and its presence at many of the grain boundaries suggests the

formation of a liquid phase during sintering. Since it is well known that liquid phase formation assists sintering and densification, the relatively uniform composition of the superconducting phase, especially near the grain boundaries, in the leaded samples may be attributed to solute redistribution near the boundaries.

The transport measurements, Figs.1&2 indicate that both the leaded and the unleaded samples are made up of the 80K and the 110K polytypoids. While the unleaded sample shows a step in the resistivity, the leaded sample does not. This difference in transport behaviour can be understood in terms of the microstructure of the samples, especially near the grain boundaries. The presence of the lower T_C polytypoid at the grain boundaries in the unleaded samples may be one of the main reasons for the lack of intergranular connectivity of the 110K regions. This, coupled with the strong effect of intergranular misorientations and the defect structure suggests a microstructural limitation on the attainment of zero resistance above 100K and more importantly on the attainment of a large value of critical current. It may be pointed out that the observed strong dependence of the critical current on the magnetic field and on the temperature[18] (if it is above 20K) additionally suggests that the presence of such regions of inhomogeneous composition (and lower T_C) may be the reason for the observed connectivity problem. This problem of connectivity is absent in the case of the Tl-based compounds and is probably related to the inherent formation of a liquid phase due to the decomposition of Tl oxide[19].

The role of Pb in raising the $T_{C,0}$ to above 100K may be more complex than just assisting in the formation of the liquid phase. However the differences in the microstructure of the two samples indicates that the formation of a liquid phase due to PbO addition and the consequent homogenization of the composition, may be one of the prime causes for the changes observed. The oxidation state of Pb (+2 or +4) in the superconducting polytypoids is not known. However, it is worthwhile noting that the ionic radius of Pb^{+2}(1.2Å) is about 25% larger than that of Bi^{+3}(0.96Å) while Pb^{+4} (0.84Å) is about 15% smaller than Bi^{+3}. These differences in the ionic radii may aid in the preferential stabilization of the n=3 polytypoid. In addition, the charge imbalance created due to the replacement of Bi(+3) by Pb(+2 or +4) will lead to changes in the oxygen (and vacancy) stoichiometry. A systematic study of the effect of Pb addition is in progress. Another aspect to consider is the phase equilibrium in this multi-component system. If the BCSCO polytypoids form after the formation of Ca-Cu-oxide and Sr-Ca-Cu- oxide, then there will be a deficiency especially of Ca and Cu, so that the 2-2-2-3 polytypoid is not easily formed. A detailed study of the phase stability and equilibria in

these multi-component systems is thus required in order to understand the evolution of the microstructure and its effect upon the electrical properties.

Acknowledgements

This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S.Department of Energy under contract No. DE-AC03-76SF00098. The work at UCSD is supported by the California MICRO program and by the Hughes Aircraft Co.

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FIGURE CAPTIONS

Fig. 1: Resistivity and susceptibility (FC= field cooled, Meissner) and (ZFC= zero field cooled, shielding) plots for the unleaded sample.

Fig. 2: Resistivity and susceptibility (FC=field cooled, Meissner) and (ZFC= zero field cooled , shielding) plots for the leaded sample.

Fig. 3: High resolution lattice fringe image of the Bi-Ca-Sr-Cu-O phase in the unleaded sample, showing the decrease in the c-parameter, due to polytypoid formation, near the grain boundary.

Fig. 4: Low magnification image showing the tabular morphology of the Bi-Ca-Sr-Cu-O phase.

Fig. 5: High resolution lattice fringe image of the leaded sample showing the uniform c-parameter of 37.2Å upto the grain boundary.

Fig. 6: Low magnification lattice fringe image showing the presence of an amorphous grain boundary phase. This amorphous phase is observed at many of the grain boundaries and triple grain junctions.

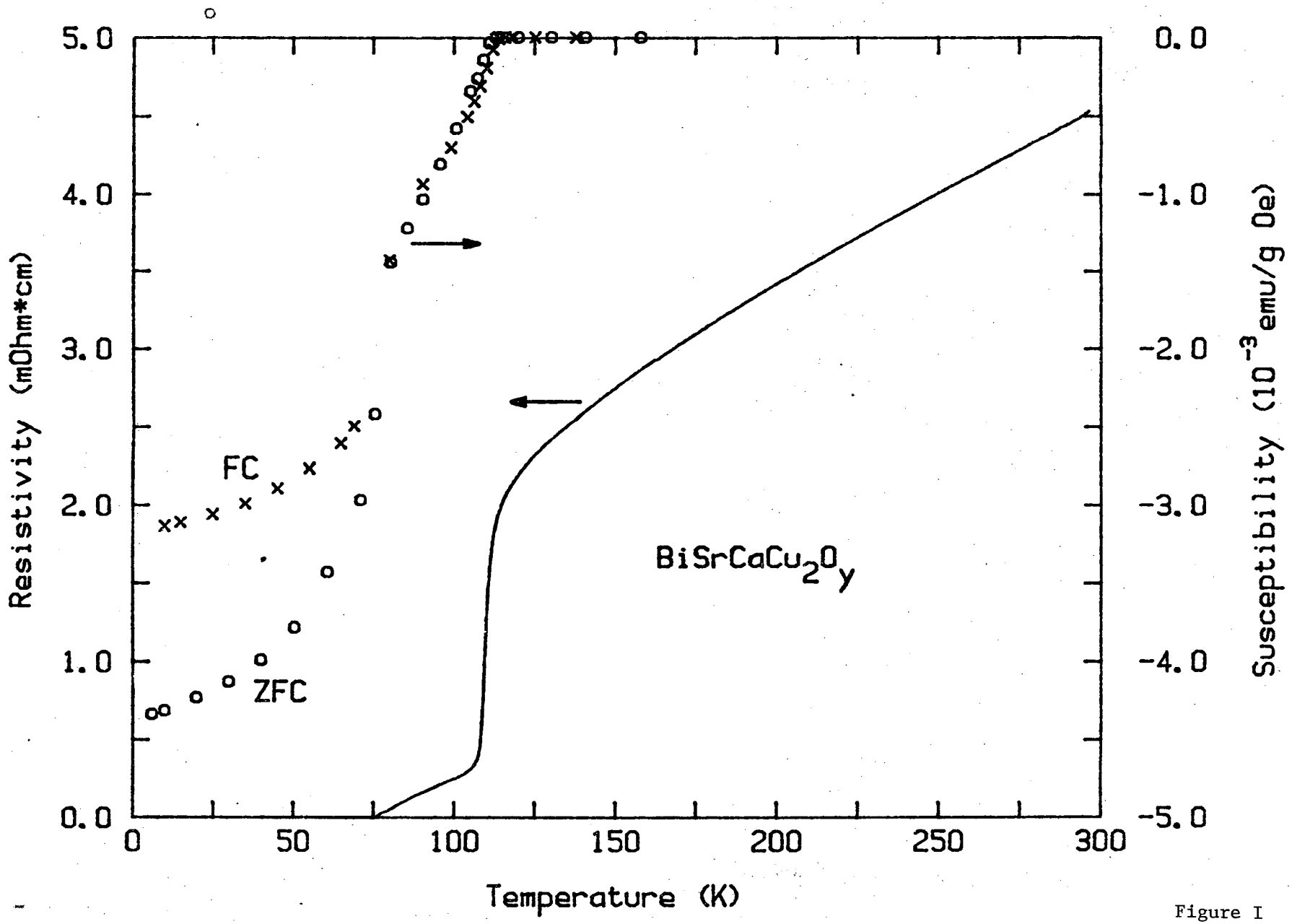
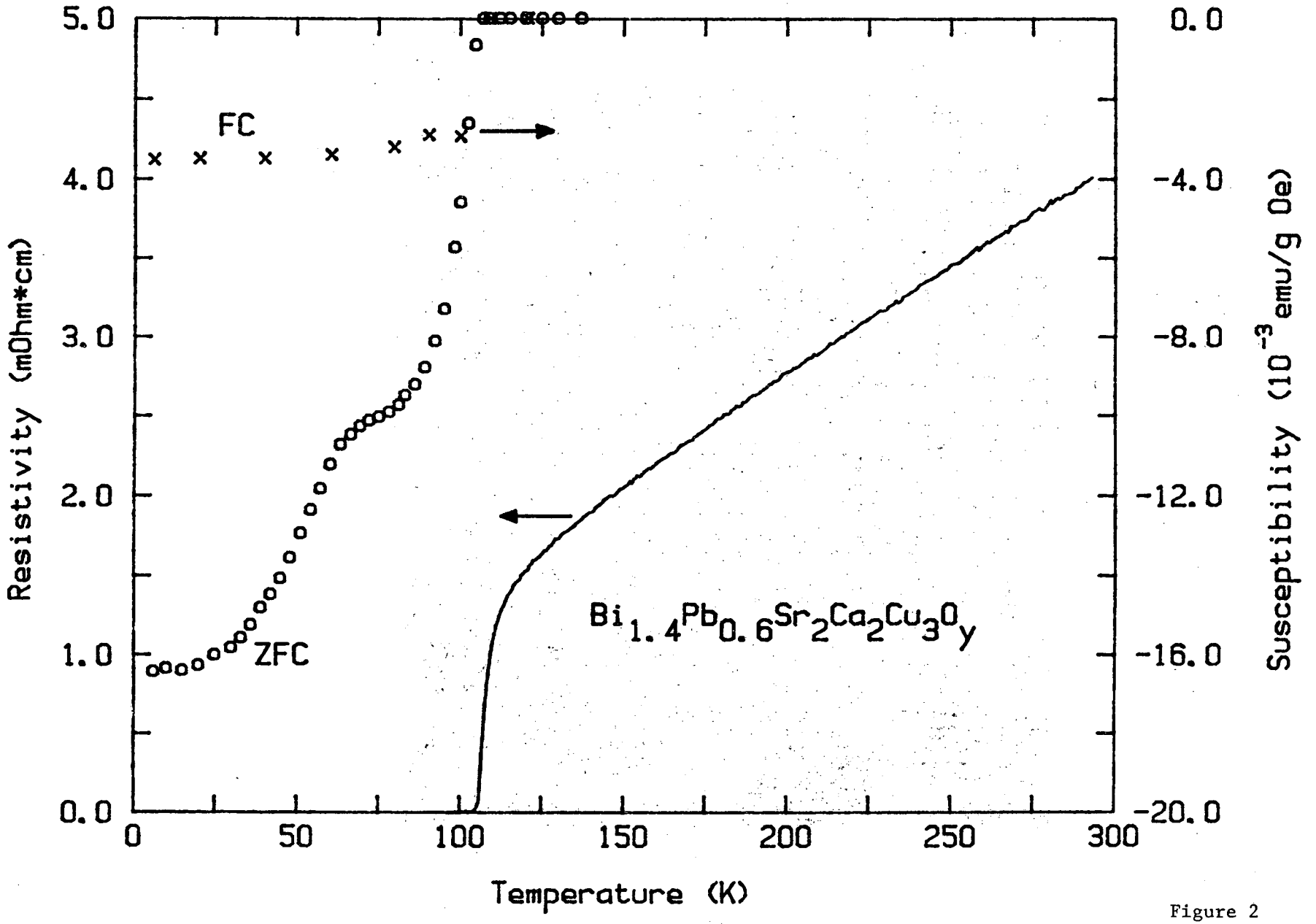

5.0
4.0
3.0
2.0
1.0
0.0
Resistivity (mOhm*cm)
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
Susceptibility (10^{-3}emu/g Oe)
0
50
100
150
200
250
300
Temperature (K)
FC
ZFC
$BiSrCaCu_2O_y$

Figure I


5.0
4.0
3.0
2.0
1.0
0.0
Resistivity (mOhm*cm)
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-4.0
-8.0
-12.0
-16.0
-20.0
Susceptibility (10^{-3} emu/g Oe)
0
50
100
150
200
250
300
Temperature (K)
FC
ZFC
$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$

Figure 2

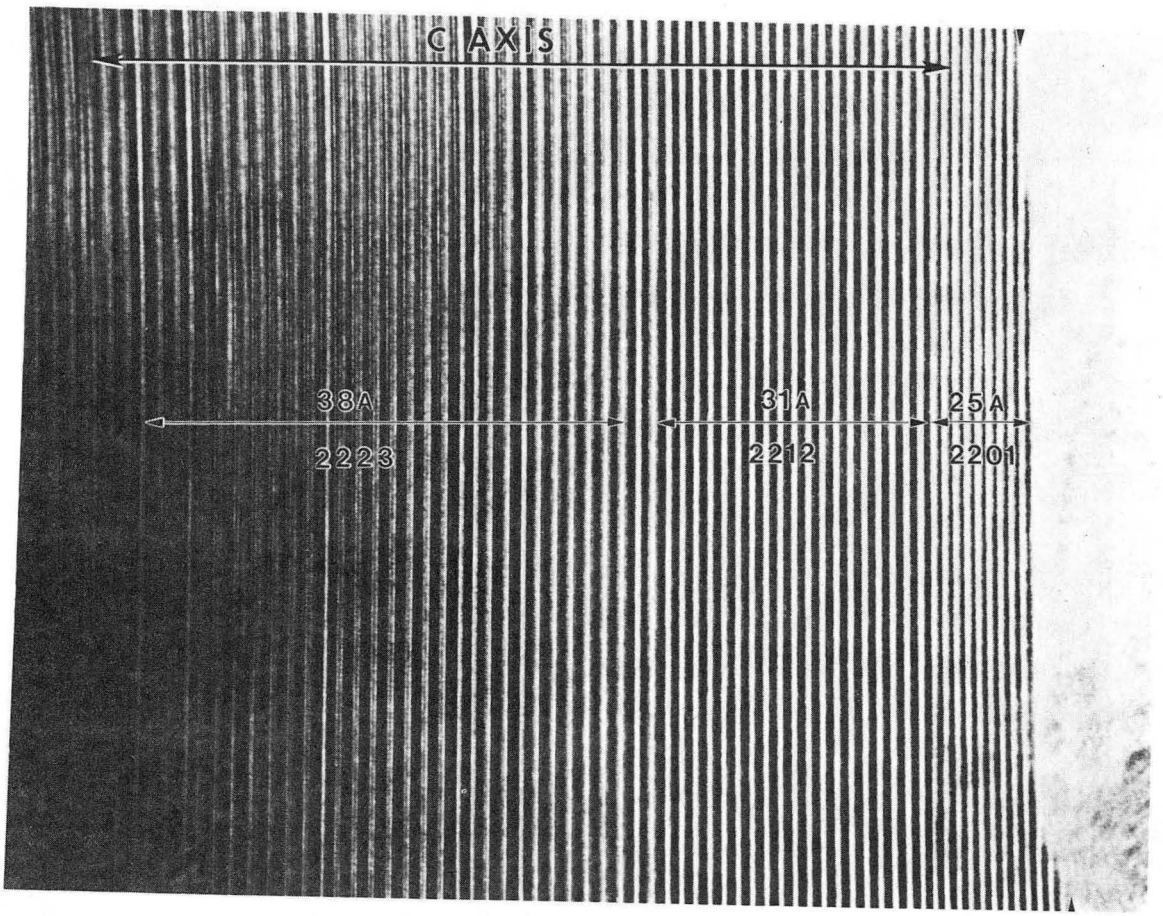

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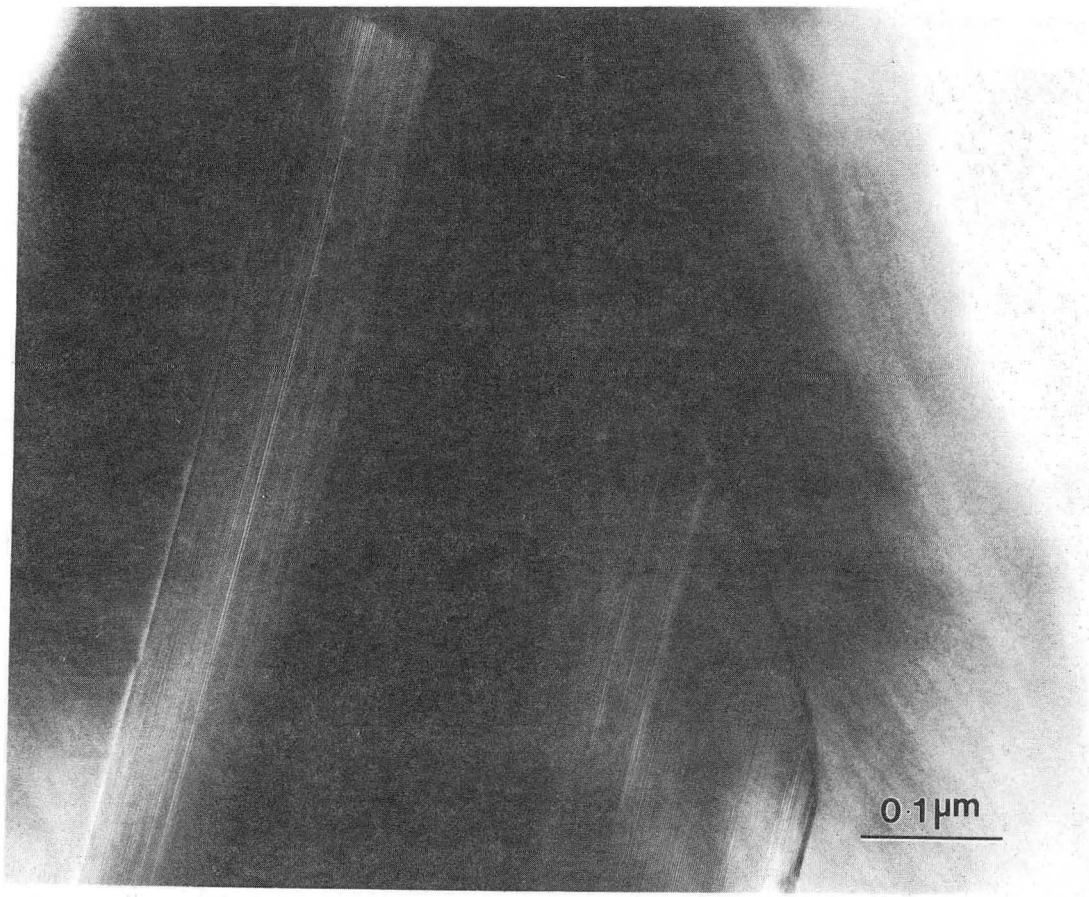
Figure 3



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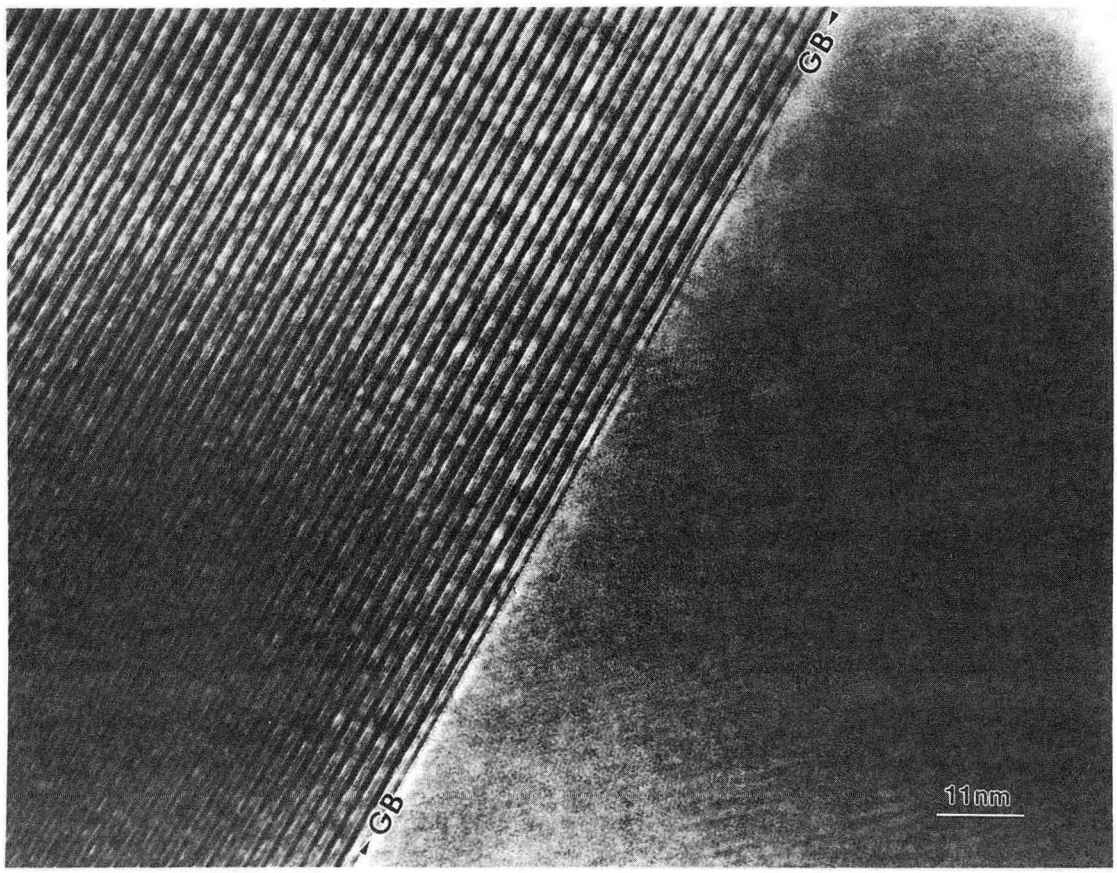

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Figure 5

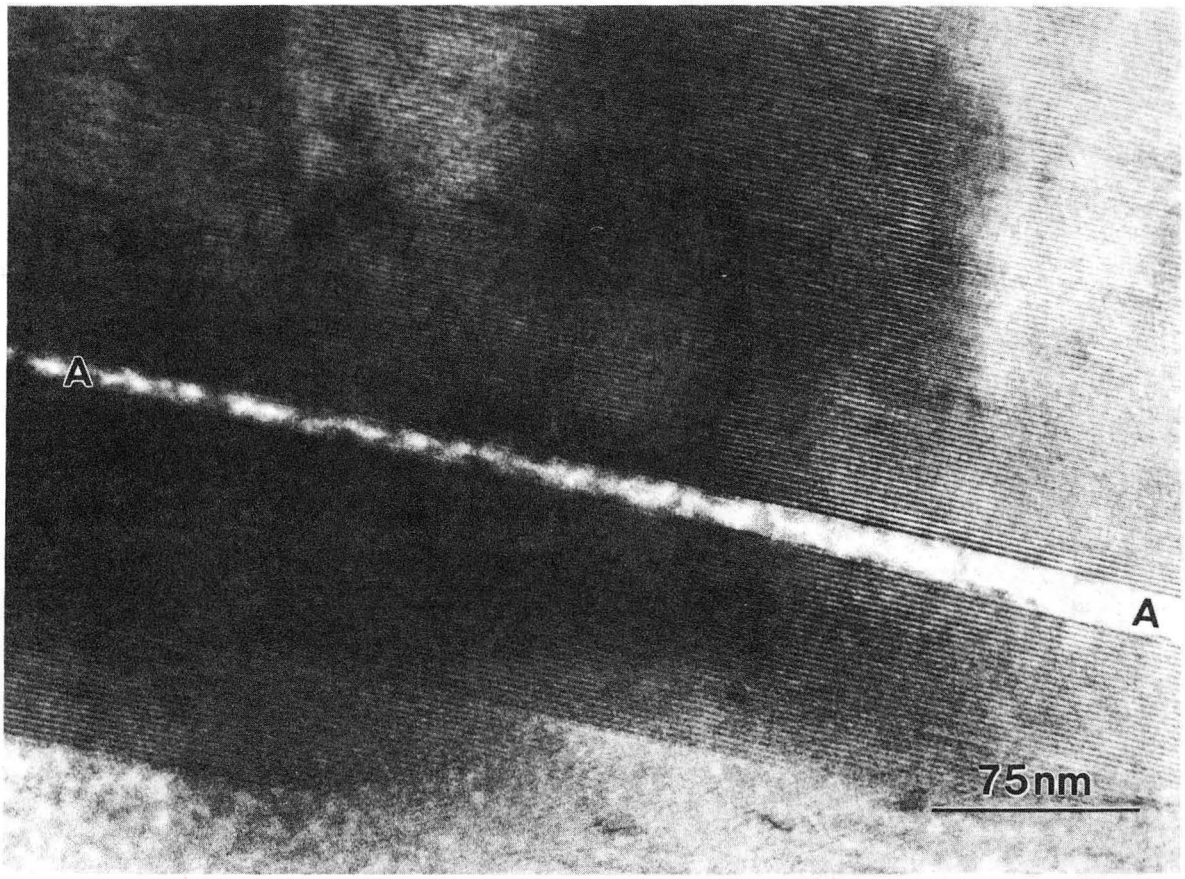

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Figure 6

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