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THE EFFECTS OF OXYGEN AND STRONTUM VACANCIES ON THE SUPERCONDUCTIVITY OF SINGLE CRYSTALS OF $Bi_2Sr_{2-x}CuO_{6-y}$

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ABSTRACT

Single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$ were grown from CuO-rich melts. The Sr content in the crystals was varied from $x=0.1$ to $x=0.5$ by varying the starting composition of the melt and the oxygen content was adjusted using an appropriate heat treatment of the crystals in a thermogravimetric system. With decreasing Sr content the superconducting transition temperature ,T_c, of the crystals decreased rapidly from 10 K to below 4.2 K and the resistivity in the **a-b** plane changed from metallic (linear in T from 30 to 300 K) to semiconducting. Reducing the oxygen content in the crystals had a similar effect on the resistivity. Only crystals with close to the maximum oxygen content ($y=0$) were superconducting, and removal of oxygen from previously superconducting crystals resulted in a rapid decrease of T_c , and the eventual loss of superconductivity ($T_c < 4.2$ K). Although crystals of $Bi_2Sr_{2-x}CuO_{6-y}$ could be made sequentially superconducting-semiconducting-superconducting by the addition-removal-addition of oxygen, the process was not totally reversible. After only one such cyclic heat treatment x-ray diffraction indicated that for some compositions such cycling resulted in the appearance of CuO and an another layered structure that has been identified previously and is slightly deficient in CuO. The new layered structure is semiconducting and has a layer-stacking repeat distance that is 1 Å smaller than the superconducting "221" phase.

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INTRODUCTION

The compound $Bi_2Sr_2CuO_6$ (2201 phase) was the first and "simplest" phase discovered [1] in a large family of superconducting compounds. The ideal stochiometry, $Bi_2Sr_2CuO_6$, is based on crystal structure analysis [2]. Previous work on ceramics with the 2201 structure [3,4] , demonstrated that the "ideal" 2201 phase is deficient in Sr and is actually a solid solution tolerating a range of Sr deficiency ($x=0.1-0.5$). We also showed that with decreasing Sr content the ceramics exhibited a metal to semiconducting transition at nominal values of x between 0.25 and 0.5 [3]. The oxygen content of these materials can also be altered [5] which results in a transition from the superconducting to the semiconducting state with decreasing oxygen content. To further complicate matters, the "simple" 2201 materials also exhibit a variable superstructure that depends on the Sr composition but is essentially unaffected by the O content of the crystals [6]. The superlattice structure is therefore not directly related to superconductivity in the 2201 materials and it most likely reflects the mismatch between the Bi_2O_2 and CuO layers along the **b** direction and the ordering of Sr vacancies along **c**.

The present work focuses on the growth of single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$, and the effects of variable Sr and O vacancies on the resistivity, ac susceptibility, lattice constants and superconducting transition temperature.

EFFECTS OF VARIABLE STRONTIUM CONTENT

Crystals with variable Sr content were grown by slowly cooling (2-10 °C/h) melts of $Bi_2Sr_{2-x}CuO_{6-y}$ + 0.5 CuO from about 950 °C in either air or flowing oxygen. A detailed description of the crystal growth process has been reported elsewhere [5]. The as-grown crystals were micaeous and typically 5x5x0.02 mm in size. The maximum Sr concentration that was incorporated into any of the 2201 crystals was

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about 1.9 Sr per formula unit. Attempts to grow crystals with higher Sr contents resulted in the formation of the true 2:2:1 phase, a related layered structure with a somewhat smaller stacking repeat distance. This phase is semiconducting and has been investigated previously [3,4,7].

A deficiency of Sr in these crystals is deduced from : 1) Energy dispersive x-ray analysis of the crystals (EDAX) 2) The variation of the **c** dimension of the unit cell with Sr content [3] and 3) The systematic variation of the superstructure modulation with Sr content [6]. In fact we have shown that the position of the superstructure sattelite peaks around the (00l) reflections recorded in θ–2θ x-ray diffraction scans provides a sensitive, yet quick and simple measure of the Sr content of the crystal (Fig 1).

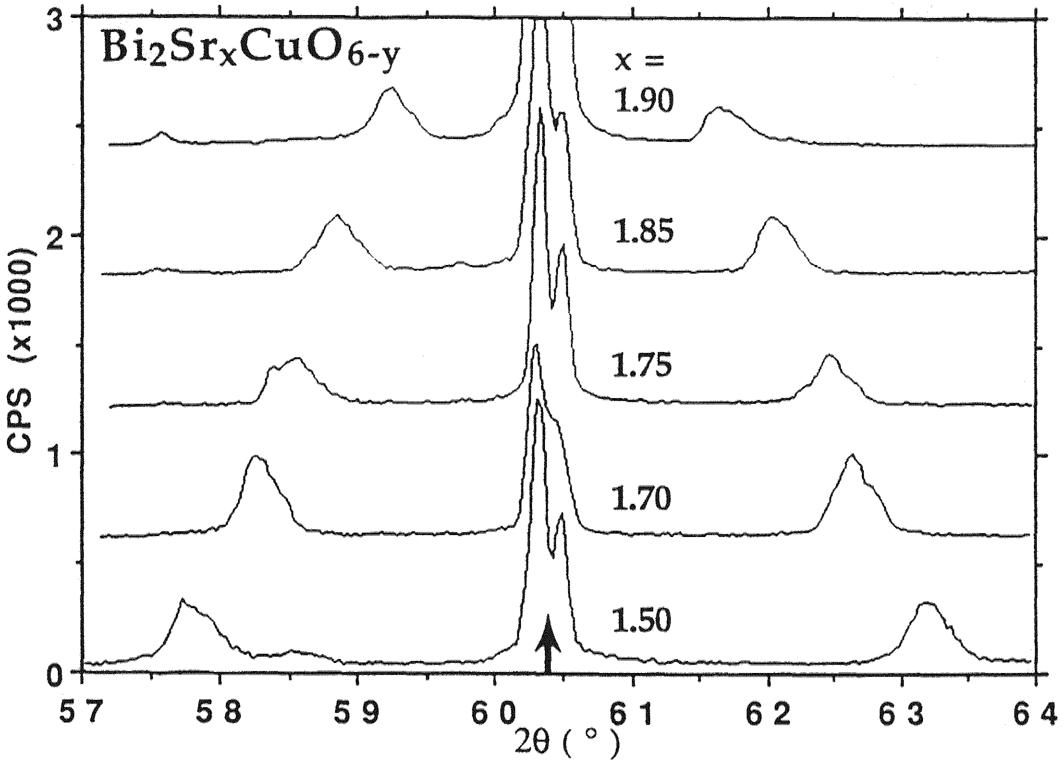

Fig. 1 For $Bi_2Sr_xCuO_6$ single crystals, (00l) x-ray diffraction patterns display satellite peaks around the main reflections, shown here for (0016) , which shift away from the main peak with decreasing Sr content. The Sr contents (± 0.05) labelled on each curve were determined for each crystal using EDAX and a set of ceramic standards.

The resistance curves in the **a-b** plane for $Bi_2Sr_{2-x}CuO_6$ crystals with $0.25 < x < 0.1$, are shown in fig 2. Prior to the resistivity measurements, these crystals were heated in oxygen at 830 °C for 15 h and are assumed to have the full complement of oxygen (y=0). As the Sr content is lowered the superconducting transition temperature of the crystals (defined as the temperature at which the resistance is 0) decreases from 10 K for x=0.1, to 6 K for x=0.15 to below 4.6 K for x=0.2. For the lowest Sr content shown in Fig. 2 (x=0.25), no evidence of superconductivity is observed and the resistance of the crystal increases with decreasing temperature.

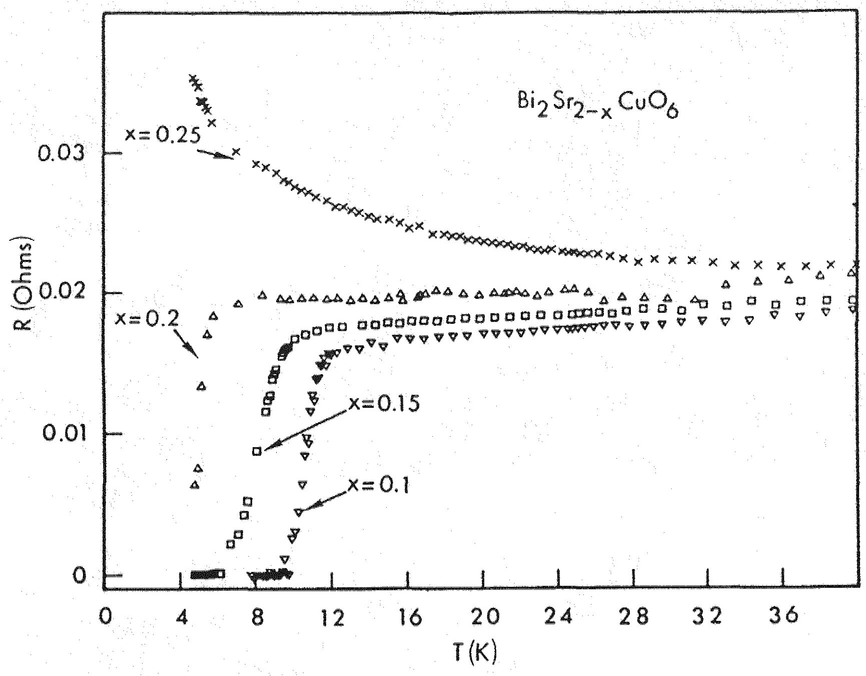

Fig. 2 Resistance versus temperature for single crystals of $Bi_2Sr_{2-x}CuO_6$ for values of x of 0.1, 0.15, 0.2 and 0.25. For these samples a resistance of 0.02 Ω corresponds to a resistivity of about 45 μΩ-cm.

EFFECTS OF VARIABLE OXYGEN CONTENT

As-grown crystals were deficient in oxygen by an amount between 0.1 and 0.5 oxygens per formula unit depending on the proximity of the crystals to the melt surface during growth. The resistance curves of the as-grown crystals were ususally semiconducting and showed no evidence of superconductivity above 4.2 K. After heating the crystals in flowing oxygen for several hours at temperatures of 650-830°C, however, the resistance curves became metallic in character and the crystals exhibited superconductivity at 9-10 K. The resistance curves for the fully oxygenated crystals are nearly linear over the temperature range from 30-300 K. The estimated magnitude of the resistivity (about 180 μΩ-cm at room temperature) and the linear temperature dependence are consistent with data reported by others on "2201" crystals that presumably have similar oxygen and strontium contents [8].

The oxygen content of the crystals could be reversibly altered by either heating the oxygen deficient crystals in oxygen at 650-800 °C for several hours or by heating the fully oxygenated crystals in flowing He gas ($PO_2 \approx 10^{-4}$ torr) at 750 °C. During a complete oxidation or reduction cycle the crystals typically exhibited a weight gain (or loss) of about 0.8%. If the crystals were completely stable this would correspond to 0.4 oxygens per forumla unit being added to or removed from the "2201" structure. Although most of this weight change appears to be associated with changes in the oxygen content of the "2201" phase, part of the weight change is due to the oxidation and reduction of CuO which forms as the crystals gradually decompose with repeated oxidation-reduction treatments. With prolonged heat treatments at elevated temperatures the crystals at least partially decompose into the true 2:2:1 semiconducting phase and CuO [3,7]. In spite of the formation of small amounts of additional phases, the superconducting properties of the crystals can be reversibly changed by the addition or removal of oxygen [5,9]. This is illustrated in Fig. 3 which shows ac susceptibility data for the same crystals that were made sequentially superconducting-normal-superconducting by varying the oxygen content.

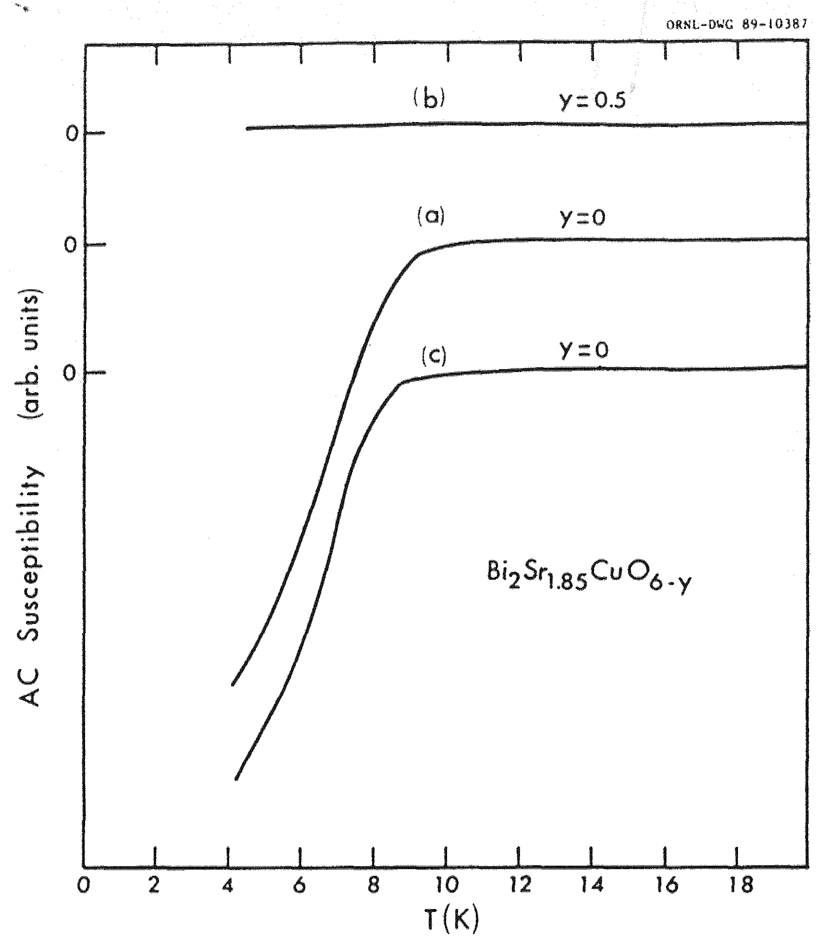

Fig. 3 ac magnetic susceptibility curves for a group of single crystals of the approximate composition $Bi_2Sr_{1.85}CuO_{6-y}$ after (a) heating in oxygen at 800 °C for 15 h (b) helium at 740°C for 15 h and,(c) oxygen at 800°C for 15 h. The susceptibility curves have been shifted vertically for clarity.

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