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Effects of oxygen and strontium vacancies on the superconductivity of single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$

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Single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$ (2201 phase) were grown from CuO-rich melts. The Sr concentration in the crystals was varied from $x=0.1$ to 0.5 by adjusting the starting composition of the melt, and the oxygen content of the crystals was reversibly adjusted between $y=0$ and 0.5 by 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 9 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). A bond-valence sum analysis suggests that oxygen is removed from the Bi_2O_2 layers.

I. INTRODUCTION

The compound $Bi_2Sr_2CuO_6$ was the first phase discovered[1] in a large family of superconducting compounds $(BiO)_2Sr_2Ca_{n-1}Cu_nO_{2n+2}$ ($n=1,2,3$),[2-4] and $(TlO)_2Ba_2Ca_{n-1}Cu_nO_{2+2n}$ ($n=1,2,3$).[5-7] To understand the nature of superconductivity in these materials we have focused on the "simplest" member, $Bi_2Sr_2CuO_6$ also referred to as the 2201 phase or the 2201 structure. The ideal stoichiometry, $Bi_2Sr_2CuO_6$, is based on crystal-structure analysis.[3] Previous work on ceramics with the 2201 structure[8,9] demonstrated that the "ideal" 2201 phase is deficient in Sr with a range of Sr deficiency ($Bi_2Sr_{2-x}CuO_6$, $x=0.1-0.5$). For $x<0.1$ a collapsed 2:2:0:1 phase forms that appears to be a distinct layered ternary compound with a 1-Å smaller stacking repeat distance ($c=23.6$ Å). The collapsed phase is semiconducting.[8] 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.[8] We have recently discovered that the oxygen contents of these materials also can be reversibly altered, which results in changes in the physical properties of the 2201 crystals that are qualitatively similar to those observed in $YBa_2Cu_3O_{7-y}$ (Refs. 10 and 11) or $HoBa_2Cu_3O_{7-y}$ (Ref. 12) as the oxygen content is varied. To further complicate matters, the simple 2201 materials also exhibit a variable superstructure that depends on the Sr composition but is apparently unaffected by the O content of the crystals.[13]

The present work focuses on the growth of the 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.

II. CRYSTAL GROWTH

Single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$ were grown by slowly cooling melts (2–10 °C/h) of Bi_2O_3 (Johnson Matthey 99.998% purity), $SrCO_3$ (Johnson Matthey 99.999% purity), and CuO (Johnson Matthey 99.999% purity) from 950 °C in either air or pure flowing oxygen. The starting compounds were thoroughly ground together and prereacted in air at 800 °C before melting and were close to stochiometry with the exception of an excess of 0.2–0.5 CuO per formula unit that ensured that the resulting solid phases were only $Bi_2Sr_{2-x}CuO_{6-y}$ and CuO.[8] The prereacted material was melted at 950 °C for 1–2 h, then cooled to 400 °C at a rate of 5 °C/h, after which the furnace was turned off. The as-grown crystals were micaeous and typically $5\times5\times0.02$ mm^3 in size. Thermogravimetric measurements on as-grown crystals indicated a deficiency in oxygen that varied from about 0.1–0.5 oxygen per formula unit depending on the proximity of the crystal to the surface of the melt. Crystals were grown in yttria-stabilized-zirconia (YSZ), alumina, or gold crucibles. The superconducting properties of crystals grown in alumina crucibles were not reproducible. A few of the crystals showed a resistive transition, but none showed significant evidence of magnetic shielding in ac susceptibility measurements. In contrast, the superconducting properties of crystals grown in either YSZ crucibles or gold crucibles were reproducible and both resistivity and ac susceptibility measurements indicated bulk superconductivity at the same temperature. Energy dispersive x-ray analysis (EDX) and x-ray diffraction were used to determine the Bi, Sr, and Cu content of the crystals and to investigate possible contamination of the crystals by the crucible. No significant differences could be detected using these techniques between superconducting crystals grown in YSZ or gold crucibles and nonsuperconducting crystals grown in alumina crucibles. Since neither EDX or x-ray diffraction are sensitive to trace impurities, the crystals were analyzed further using spark-source mass spectrometry. As expected, Al was found in crystals grown in alumina crucibles, but at the relatively low levels of 10–50 ppm. Crystals grown in YSZ crucibles had larger concentrations of both Zr (20–70 ppm) and Y (50–120 ppm). Crystals grown in gold crucibles had no detectable concentrations of Au (<5 ppm). At present it is not understood why such small amounts of Al have such a deleterious effect on T_c. The cation compositions of the crystals studied are summarized in Table I.

III. EXPERIMENTAL METHODS

Resistivity was measured using the standard four-probe method between room temperature and 4.6 K using a dc current of 2 mA or less, the polarity of which was alternated approximately twice a second. Contacts to the crystals were made with silver paint or sputtered gold and spring clips. The temperature was measured with a Si diode which was accurate to ± 0.3 K.

The ac magnetic susceptibility of randomly packed single-crystal fragments was measured between room temperature and 4.2 K at a frequency of 200 Hz and with an excitation field of 1.5 mG using standard techniques. Temperature was measured with a Si diode.

Powder and single-crystal x-ray diffraction were performed with a SCINTAG automated diffractometer with a solid-state Ge detector using Cu $K\alpha$ radiation. Only the $(00l)$ reflections were recorded from the large single crystals. To obtain the lattice constants, the crystals were ground into a fine powder, packed into recessed plexiglass holders, and scanned at 1° in 2θ per min over the range from 2°–80°. Reported cell parameters are derived from peak positions corrected for instrumental errors with respect to the NBS standard Si 640*b*.

EDX analysis data were collected with a a SiLi detector on an International Scientific Instruments ISI-40 SEM operated at 15 keV and processed with a Princeton Gamma-Tech System IV analyzer. Thermogravimetric measurements over the temperature range from 25°–1000 °C were made with a Perkin-Elmer TGS-2 system interfaced to an automatic data analysis system.

IV. EFFECT OF VARIABLE OXYGEN CONTENT

As noted above, 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 usually 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 become metallic in character and the crystals exhibited superconductivity at ~9 K. This effect is illustrated in Fig. 1, where the resistance in the *a-b* plane of the same crystal ($Bi_2Sr_{1.85}CuO_{6-y}$) was measured before and after the oxygen heat treatment. The same sputtered Au contacts were used in both measurements to ensure that any change in the measured resistance was due to the oxygen treatment. The uptake of oxygen by this crystal reduced the room temperature resistance by about a factor of 3 and changed the overall shape of the resistance curves from semiconducting to metallic. The resistance curve for the fully oxygenated crystal is nearly linear over the entire temperature range of 30–300 K. For the fully oxygenated crystal the estimated magnitude of the resistivity (about 180 $\mu\Omega$ cm at 300 K) and the linear temperature dependence are consistent with data reported by others on 2201 crystals that presumably had similar oxygen and strontium contents.[14,15] It is assumed, based on the crystal structure work of Torardi *et al.*,[3] that the fully oxygenated crystals have six oxygens per formula unit ($y=0$).

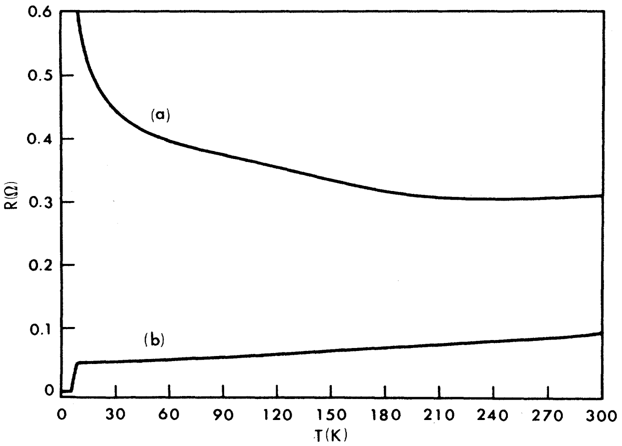

FIG. 1. Resistance vs temperature for (a) an as-grown crystal of $Bi_2Sr_{1.85}CuO_{6-y}$ and (b) the same crystal after a heat treatment in flowing oxygen at 800 °C for 15 h. For this sample a resistance of 0.1 Ω corresponds to a resistivity of about 180 $\mu\Omega$ cm.

The oxygen content of the crystals could be reversibly varied between $y=0$ and $y=0.5$. This is illustrated in Fig. 2, which shows thermogravimetric data from a stack of single crystals of the approximate composition $Bi_2Sr_{1.85}CuO_{6-y}$. Oxygen-deficient crystals were heated in flowing oxygen at 734 °C for ~20 h. The crystals gained 0.9% in weight due to the uptake of oxygen which corresponds to a change in y of about 0.5. The same crystals were then heated in flowing He gas at 741 °C for

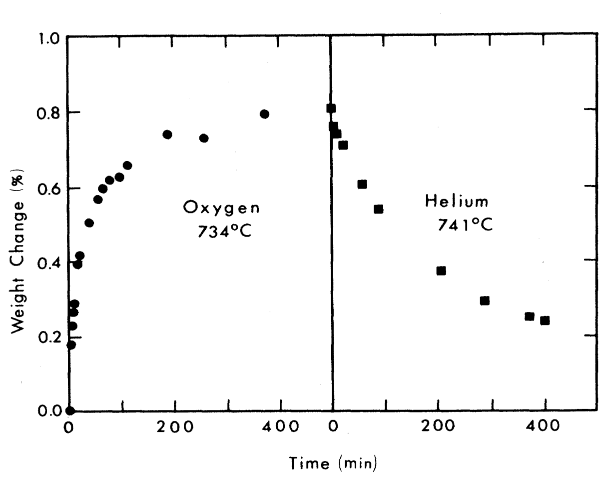

FIG. 2. Weight change vs time for a group of single crystals of the approximate composition $Bi_2Sr_{1.85}CuO_{6-y}$ heated in (●) oxygen and (■) helium (see text for details).

20 h, and during this time the crystals lost about 0.9% (only part of the weight gain and loss data are shown in Fig. 2). Attempts to remove more than 0.5 oxygens per formula unit from the crystals by heat treatments above 800 °C resulted in the decomposition of the 2201 structure and the formation of orthorhombic $Bi_2Sr_2O_5$.[16] A detailed investigation of the kinetics of oxidation and reduction of 2201 crystals will be reported elsewhere.[17] The removal of small amounts of oxygen ($y=0.1$) from these crystals resulted in the depression of T_c below 4.2 K (our lowest measuring temperature). Superconductivity could be restored, however, by simply heating the crystals in oxygen at 700–800 °C for several hours. The reversible change in T_c with oxygen content is illustrated in Fig. 3, which shows ac magnetic susceptibility data for the same crystals that were made sequentially superconducting-normal-superconducting by varying the oxygen content. The width of the superconducting transition, as measured magnetically, is unusually broad as is evident by the lack of complete magnetic shielding at 4.2 K. The reason for this large transition width is not known but could be related to either penetration depth effects for some crystals or could simply reflect some chemical inhomogeneity of the crystals.

Changing the oxygen content from $y=0.5$ to $y=0$ caused the lattice to expand by 0.02 Å in the **c** direction while **a** and **b** remained essentially the same. An expanded cell volume would be expected if extra oxygen is somehow added to the Bi_2O_2 layer through a structural reorganization.

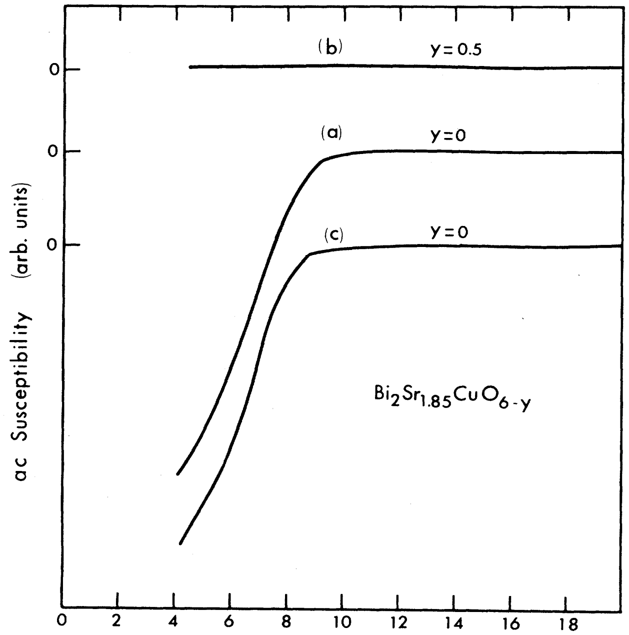

FIG. 3. ac magnetic susceptibility data for a group of single crystals of the approximate composition $Bi_2Sr_{1.85}CuO_{6-y}$ after (a) heating in oxygen at 800 °C for 15 h, (b) helium at 740 °C for 15 h, and (c) oxygen at 800 °C for 15 h. The susceptibility curves have been shifted vertically for clarity.

V. EFFECTS OF VARIBALE STRONTIUM CONTENT

The maximum Sr concentration that was incorporated into any of the 2201 crystals was 1.9 Sr per formula unit. Attempts to grow crystals with higher Sr contents resulted in the formation of the collapsed phase, another related layered structure with a somewhat smaller **c** lattice constant. This phase is semiconducting and has been investigated previously.[8,9,18] The actual amount of Sr incorporated into the crystals depended on the amount of Sr in the starting melt composition and the degree of reaction between the melt and the crucible walls. For crystals grown in alumina or YSZ crucibles the removal of Sr was a more serious problem than for crystals grown in gold boats. The starting melt compositions and the resulting compositions of the crystals as determined by EDX analysis are given in Table I.

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. 4. For these data a resistance of 0.02 Ω corresponds to a resistivity of about 45 $\mu\Omega$ cm. Before measuring, 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. 4

TABLE I. Cation compositions of $Bi_2Sr_{2-x}CuO_6$ crystals as determined by EDX and spark-source mass spectrometry analysis. The estimated errors in the major cation concentrations of the crystals are Bi, ±0.05; Sr, ±0.05; Cu, ±0.1. * indicates "not determined."

Starting powder	Crystals	Crucible	Crucible contamination (ppm)
$Bi_2Sr_2Cu_{1.5}O_{6.5}$	$Bi_2Sr_{1.9}Cu_1O_6$	Au	Au, <5
$Bi_2Sr_2Cu_{1.5}O_{6.5}$	$Bi_2Sr_{1.85}Cu_1O_6$	YSZ	Y, 100; Zr, 60
$Bi_2Sr_2Cu_{1.5}O_{6.5}$	$Bi_2Sr_{1.85}Cu_1O_6$	Al_2O_3	Al, 40
$Bi_2Sr_{1.8}Cu_{1.5}O_{6.3}$	$Bi_2Sr_{1.80}Cu_1O_6$	YSZ	*
$Bi_2Sr_{1.75}Cu_{1.5}O_{6.25}$	$Bi_2Sr_{1.75}Cu_1O_6$	YSZ	*
$Bi_2Sr_{1.5}Cu_{1.5}O_6$	$Bi_2Sr_{1.7}Cu_1O_6$	Al_2O_3	*
$Bi_2Sr_{1.25}Cu_{1.5}O_{5.75}$	$Bi_2Sr_{1.5}Cu_1O_6$	Al_2O_3	*

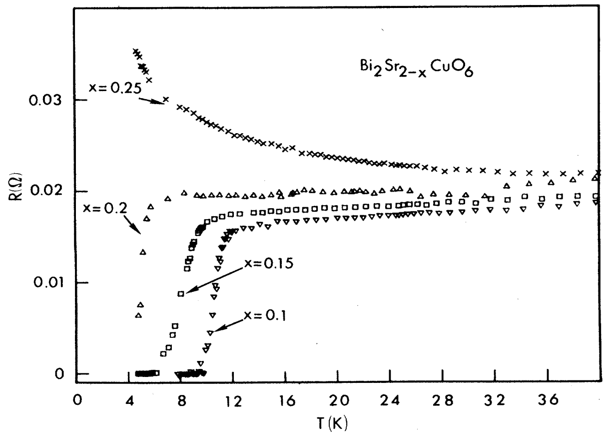

FIG. 4. Resistance vs temperature for single crystals of the approximate composition $Bi_2Sr_{2-x}CuO_6$ for values of x of 0.1, 0.15, 0.2, and 0.25. For these samples a resistance of 0.01 Ω corresponds to a resistivity of about 45 μΩ cm.

($x = 0.25$), no evidence of superconductivity is observed and the resistance of the crystal increases with decreasing temperature. This semiconducting behavior becomes more pronounced in crystals where the Sr deficiency is increased beyond $x = 0.25$ (these data are not shown in Fig. 4). The transition from a metal to a semiconductor with decreasing Sr content was also previously observed by us in ceramic samples (Ref. 8, Fig. 7) and the data reported in that work are qualitatively similar to the single-crystal data shown in Fig. 4.

VI. DISCUSSION

Although the maximum superconducting transition temperature measured for the $Bi_2Sr_{2-x}CuO_{6-y}$ crystals investigated was only 10 K, these materials display a rich variety of physical properties that are similar to those exhibited by other cuprate superconductors. The ability to change the 2201 crystals from a metal to a semiconductor with the removal of oxygen from the structure is similar to the behavior of the 123-phase cuprate superconductors such as $HoBa_2Cu_3O_{7-y}$.[12] To destroy superconductivity in 123 materials, however, it was necessary to remove a much larger amount of oxygen from the structure ($y = 0.5$) than for the 2201 phase materials ($y = 0.1$). The oxygen content in the $n = 2$ member $Bi_2Sr_2CaCu_2O_8$ of the series can also be varied somewhat, but the net effect is to change T_c over the range 65–85 K with the maximum T_c for samples with the smallest oxygen content.[19] For example, the T_c of the same $n = 2$ sample can be reversibly adjusted between 84 and 67 K by varying the quench rate of the samples in oxygen from 10^4 K/min to 0.1 K/min, respectively. As far as we are aware no metal-to-semiconducting transition as a function of oxygen content has been reported for the $n = 2$ member $Bi_2Sr_2CaCu_2O_8$.

The oxygen that is reversibly removed from the ideal 2201 structure most likely comes from the O(3) site. This oxygen is positioned within the Bi_2O_2 layer in the crystal structure and is probably off center in its distorted octahedral shell of 5 Bi and 1 Sr, shifted parallel to and closer to one Bi.[3] This creates a distorted octahedral coordination geometry for Bi, with two short (2.09 and 1.98 Å), two medium length (2.69 and 2.69 Å), and two long (3.27 and 3.21 Å) bonds to oxygen. The lone $6s^2$ electron pair of Bi^{+3} is probably directed between the two long bonds, which is a direction towards the adjacent BiO layer. This would explain the large (3.21 Å) separation of the adjacent BiO layers and the perfect (00*l*) cleavage exhibited by these crystals. Given this positional model, a bond-valence sum analysis (Table II) assigns reasonable values to all atomic sites except O(3). The bond valence sum to Sr is significantly less than two valence units, which is consistent with the observed Sr deficiency in both crystals and ceramics.[8] The sum to Cu being significantly greater than 2.0 is consistent with a formal valence of Cu between 2+ and 3+. The grossly underbonded sum to O(3) suggests that its position may not be exactly correct. However, if the O(3) position is correct then bond-valence analysis suggests that of the three oxygens, O(3)

TABLE II. Empirical bond-valence analysis[a] for $Bi_2Sr_2CuO_6$.

	Bi	Sr	Cu	O(1)	O(2)	O(3)	Σ	Σ_{expected}	CN
Bi				1.42		0.19×2 0.04×2 0.99	2.87	3	6
Sr				0.15×2 0.21 0.10	0.33×2 0.24×2	0.13	1.88	2	9
Cu				0.08×2	0.55×4		2.36	2	6
O(1)	1.42	0.15×2 0.21 0.10	0.08				2.11	2	6
O(2)		0.33×2	0.55×2				2.24	2	6
O(3)	0.19×2 0.04×2 0.99	0.13					1.58	2	6

[a] Bond valences in valence units calculated from curves of Altermatt and Brown (Ref. 20) using the structure data of Torardi *et al.* (Ref. 3).

is likely to be the most mobile. We propose that the observed oxygen gain of up to 0.5 oxygens per formula unit occurs at the O(3) site. Further crystal structure refinements of $Bi_2Sr_{2-x}CuO_{6-y}$ crystals with variable values of y are clearly needed in order to test this hypothesis.

The Sr deficiency and variable oxygen content appear to be crucial for superconductivity in $Bi_2Sr_{2-x}CuO_{6-y}$. Both the Sr deficiency and additional oxygen provide mechanisms for producing mobile holes in the CuO_2 layers. The presence of mobile holes in these planes is believed to be a necessary condition for all of the high-T_c cuprate superconductors. A deficiency of Sr in these materials is also suggested by the bond-valence analysis discussed above, the variation of the **c** dimension of the unit cell with Sr content,[8] EDX analysis, and the systematic variation of the superstructure modulation with Sr content.[13] The importance of Sr and Ca vacancies in the superconductivity of the $n=2$ phase has also been proposed.[21]

If small quantities of either oxygen ($y=0.1$) or Sr ($x=0.25$) are removed from the $Bi_2Sr_{2-x}CuO_{6-y}$ crystals, the low-temperature resistance of the crystals in the **a**-**b** plane increases with decreasing temperature. It is also known that the normal-state resistivity of these crystals is extremely anisotropic with the resistivity for conduction along the **c** axis about 10^5 times larger than the resistivity in the **a**-**b** planes.[14] Because of the highly two-dimensional nature of the electrical conductivity in these materials, the upturn in the resistance curve at low temperatures for oxygen or strontium-deficient crystals may be partially due to the phenomenon of weak localization. Weak localization is a quantum-mechanical effect that occurs in metallic thin films when the distance over which the phase coherence of a normal electron in a solid (mean-free path) becomes comparable to the thickness of the film. At low temperatures where inelastic scattering from phonons can be neglected the increase of the resistance with decreasing temperature is predicted to be linear when plotted versus $\log(T)$ for a two-dimensional system.[22,23] The present data are not sufficient, however, to prove or disprove the hypothesis of "weak localization." Further experiments are in progress to measure the resistance of these crystals at lower temperatures and as a function of applied magnetic field.

VII. CONCLUSIONS

(1) Single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$ with ($0.1<x<0.5$ and $0<y<0.5$) can be grown from CuO-rich melts in either YSZ, alumina, or gold crucibles.

(2) The superconductivity of crystals grown in alumina crucibles appears to be destroyed by small amounts of Al contamination (50 ppm).

(3) A substantial amount of oxygen (0.5 oxygen per formula unit) can be reversibly added or removed from the crystals by an appropriate heat treatment.

(4) A metal-semiconductor transition in single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$ was observed to occur if either small amounts of oxygen or strontium are removed from the structure.

(5) A bond-valence sum analysis suggests that oxygen is reversibly removed from the Bi_2O_2 layers.

(6) The increase in the resistance at low temperature for crystals near the metal-semiconductor transition may be due to weak localization.

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