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High resolution STM/STS studies of the role of oxygen in superconductivity of Bi-2122 and optimization of T_c

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Abstract. The presence of excess oxygen intercalated in Bi–O redox layers has been found to be detrimental to the T_c of the Bi-2122 phase. High resolution STM has been effectively used to locate intercalated oxygen and STS studies have revealed Bi–O layers becoming more insulating with intercalation. By suitable nitrogenation when the excess oxygen is depleted, more conducting redox layers give rise to an improved coupling between Cu–O planes of the neighbouring demi-unit cells in the c -direction, and it is this improved coupling that is responsible for enhanced T_c . In this way it has been possible to optimize $T_c(R=0)$ for the single phase Bi-2122 cuprate at 96 K with a transition width of 3 K, which is the best value reported to date for the bulk ceramic sample of this material.

1. Introduction

The recent observation of Raveau *et al* [1, 2] that the oxidation state of Bi in Bi-based high T_c cuprates is lower than 3+ has emerged as a milestone in understanding the occurrence of superconductivity in these materials. Purely from the charge balance considerations, the classical trivalent Bi should make Cu in Bi-2122 divalent and the stoichiometric compound would become just an insulator. In the Aurivillius phase where the valency of Bi is 3+, the Bi atom is bonded strongly to eight oxygen atoms and weakly to another, giving a total coordination of nine. In contrast to this, in high T_c cuprates, Bi has only a sixfold coordination with respect to oxygen, which implies that the electron transfer from Bi to oxygen is incomplete to yield a 3+ oxidation state of Bi. Raveau and his collaborators [1, 2], from L_{111} edge spectra of XANES studies of Bi-2122, have provided convincing experimental evidence that Bi is indeed in a lower oxidation state than 3+ in this compound. They have attributed this to hybridization of the 6s, 6p orbitals of bismuth with 2p orbitals of oxygen, resulting in the formation of a narrow band and stabilization of some deep levels. The electrons are transferred from Cu to these deep levels, leading to the formation of holes on Cu and electrons on Bi, following the reaction



Thus, a decrease in the valency of Bi corresponds to an increase in the valency of Cu, which is responsible for the conducting and superconducting behaviour of the

compound. This apart, Bi-O layers in Bi-cuprate are all the more significant as they constitute the redox layers [1] possessing the remarkable ability to intercalate and deintercalate oxygen. As a result of oxygen intercalation in the Bi-O layers the oxidation state of Bi can become altered, with the effect that the carrier transport properties of the compound may dramatically change.

Interestingly, the aforesaid change in the valence state of Bi owing to excess oxygen is reflected in the electronic properties of the Bi-O redox layers. Our recent studies [3] relating to the partial substitution of Dy^{3+} at the Ca^{2+} -site in Bi-2122 have revealed, using STM (scanning tunnelling microscopy), the presence of excess oxygen in Bi-O layers, and subsequent STS (scanning tunnelling spectroscopy) studies have shown that these layers gradually turn from quasimetallic to insulating in the presence of increasing excess oxygen. It was further suggested that completely insulating redox layers would inhibit the maintenance of superconducting phase coherence between Cu-O planes across the neighbouring demi-unit cells along the *c*-direction, giving rise to a drastic decrease of T_c ($R = 0$).

In this paper we present the results pertaining to the optimization of the critical temperature of bulk single-phase Bi-2122 superconductor. Normally, this cuprate possesses the T_c -onset of about 100 K and $T_c(R = 0)$ of 82 to 85 K. By incorporating the quenching process [4] in its synthesis we had previously succeeded in raising the $T_c(R = 0)$ to 91 K with the T_c -onset, however, remaining nearly invariant at 99 K. Since T_c -onset was still significantly higher than $T_c(R = 0)$, it was felt that there was still room left for further optimization to achieve an even higher $T_c(R = 0)$ closer to 99 K. The quenching process, which had yielded the T_c enhancement from 82 K to 91 K, is primarily known to reduce the oxygen content of the sample. This motivated us to investigate the samples formed with varying oxygen intercalations in Bi-O layers. With the help of high resolution STM, it was possible to observe directly the excess oxygen atoms in the Bi-O monolayers at the sample surface. The resulting changes in the metallicity of the Bi-O layers are studied using an STS technique. By using a suitable nitrogenation treatment and by making the Bi-O layers more conducting, the coupling between superconducting Cu-O layers across the redox layers has been improved to realize an optimum T_c of 96 K for the bulk single phase Bi-2122 superconductor.

2. Experimental aspects

Samples were prepared by solid-state reaction of appropriate mixtures of Bi_2O_3 , CaCO_3 , SrCO_3 and CuO , each of 4N purity. The powders were mixed, pulverized and calcined at 820 °C, 830 °C and 840 °C successively for 12 h each, followed by furnace cooling. In the final step, the samples were partially melted at 930 °C and then subjected to sustained heating at 860 °C for 12 h and finally quenched to room temperature [4]. The samples of this batch are denoted by (a). Some of the samples from (a) were oxygenated at 860 °C for 12 h and then furnace cooled to room temperature over a span of 6 h: this batch of samples are denoted by (b). Some samples from (b) were nitrogenated at 600 °C for 12 h and furnace cooled in the nitrogen environment over a span of 5 h; these samples are termed as (c). Finally, a few samples from (a) were separately nitrogenated for 12 h at 400 to 650 °C and subsequently furnace cooled in the nitrogen atmosphere over a span of about 5 h: these samples are denoted by (d).

Four-probe DC resistivity data of rectangular slab samples were obtained in the temperature range of 50 K to 300 K, in a liquid helium bath cryostat, using a carbon

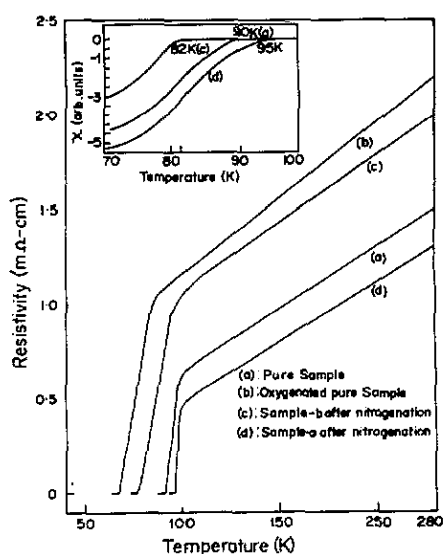


Figure 1. Resistivity-temperature curves for four different samples (a) to (d)—see text. The inset: AC susceptibility of samples (a), (c) and (d) in the temperature range of 100 to 70 K.

glass resistor temperature sensor. The entire measurement system, consisting of a nanovoltmeter (Keithley 181), a constant current source (Keithley 224), a temperature controller and an indicator (Lakeshore model 820), was hooked to an HP 216 system controller for automatic data acquisition and control. Magnetic susceptibility measurements were carried out with a fully computer controlled AC susceptometer (Lakeshore 7000). The samples were characterized for phase identification, homogeneity and the lattice parameters through x-ray diffraction using a Siemens D-500 diffractometer with Cu K_α radiation.

For STM studies, the Bi-based cuprates present the unique advantage that they always cleave across the twin Bi-O layers. Thus, one of the difficulties of ascertaining the orientation of the surface is circumvented as, at the sample surface, one is invariably looking at the monolayers of Bi-O. All the samples were freshly cleaved before mounting them on an STM (Nanoscope II, Digital Instruments), which was operated at the ambient temperature, using nanotips of Pt-Ir. Real-space grey-scale images were obtained in the constant current mode with the bias voltage (negative) in the range of a few mV to about 1500 mV, and with the tunnelling occurring from the filled state in the sample to the empty state in the tip. For STS observations, initially well-resolved images of Bi-O layers were obtained in the STM mode and subsequently, the instrument was switched into STS mode through the software program. This way, for any specific layer, a tunnelling spectra giving I - V , dI/dV (i.e. conductance), or $d \ln I / d \ln V$ (which is same as $(dI/dV)/(I/V)$ i.e. the normalized conductance) as a function of the bias voltage could be readily recorded.

3. Results

3.1. Resistivity and susceptibility

Figure 1 depicts the resistivity versus temperature plots for the samples (a) to (d) in the temperature range of 40 K to 280 K. The inset shows AC susceptibility curves for samples

(a), (c) and (d) in the temperature range of 70 K to 100 K. All four samples show a wide but systematic change in both T_c -onset and $T_c(R = 0)$. It may be seen that sample (a) has a T_c -onset of 99 K and $T_c(R = 0)$ at 91 K with a transition width of 8 K, as also reported earlier by the present authors [4]. After oxygenation of (a), (i.e. sample (b)), a significant decrease in the T_c -values is shown, the former dropping to 82 K while the latter to 70 K, resulting in the transition width of 12 K. After nitrogenation of these samples (i.e. batch (c)) there is an increase in T_c -onset to 88 K, and in $T_c(R = 0)$ to 78 K, corresponding to a transition width of 10 K. In contrast to this, the samples of batch (d), which represent the nitrogenated samples (a) at varying temperatures from 400 °C to 600 °C, all showed $T_c(R = 0)$ above 91 K with T_c -onset remaining invariant at 99 K. The optimum results obtained at a temperature of 600 °C are presented by curve (d). It shows a T_c -onset of 99 K with $T_c(R = 0)$ at 96 K, giving a transition width of 3 K. For bulk single-phase ceramic samples of Bi-2122, these values are, to our knowledge, perhaps the best reported to date. However, for the samples that had been annealed above 600 °C, both the T_c -onset and $T_c(R = 0)$ were found to be lower (the curves are not shown).

It is interesting to note that although the four curves of figure 1 exhibit a metallic behaviour in the temperature range above T_c , their normal state resistivity values, near T_c -onset are significantly different. In particular, the oxygenated sample (b) possesses a maximum resistivity while the sample (d), which has the highest T_c , shows the smallest resistivity value.

The susceptibility measurements (inset in figure 1) corroborate the above T_c data measured resistively. As may be seen, the diamagnetic behaviour occurs at a temperature of 95 K for sample (d) while at 90 K for sample (a), indicating the bulk superconductivity at these temperatures. Sample (c) however, shows the diamagnetic behaviour 4 K above $T_c(R = 0)$. This indicates the presence of local regions of higher T_c which are not forming a continuous path for $R = 0$ at that temperature. Since $T_c(R = 0)$ for sample (b) was at 70 K, and the fact that the susceptibility measurements were made above this temperature, no diamagnetic behaviour was observed for this sample in the present study and its susceptibility curve does not, therefore, appear in the inset. It may be noted that although the susceptibility data shown is in arbitrary units, the relative superconducting volume fraction at 70 K is the largest for sample (d).

3.2. XRD data

The XRD (x-ray diffraction) data for the above four samples, with T_c values increasing from 70 K to 96 K, are shown one above the other in figure 2. Also their a and c parameters are given. All four diffractograms show the characteristic lines of Bi-2122 phase. No new phase or additional lines are detected. There is no systematic variation in the intensity of any particular line(s) which could be related to the observed change in the T_c values. There is only a marginal shift in the line positions which has resulted in a change in the c -parameter and which is less than 0.5% between the samples possessing extreme T_c values. Also, the spectra presented give no convincing indication of orthorhombic-tetragonal splitting of the lines. Consequently, T_c enhancement due to any structural aspects is ruled out.

3.3. STM/STS studies

The STM images of all the above four samples were consistent with the (001) plane, with the interatomic distances agreeing with the reported distances of the Bi-O layer. As

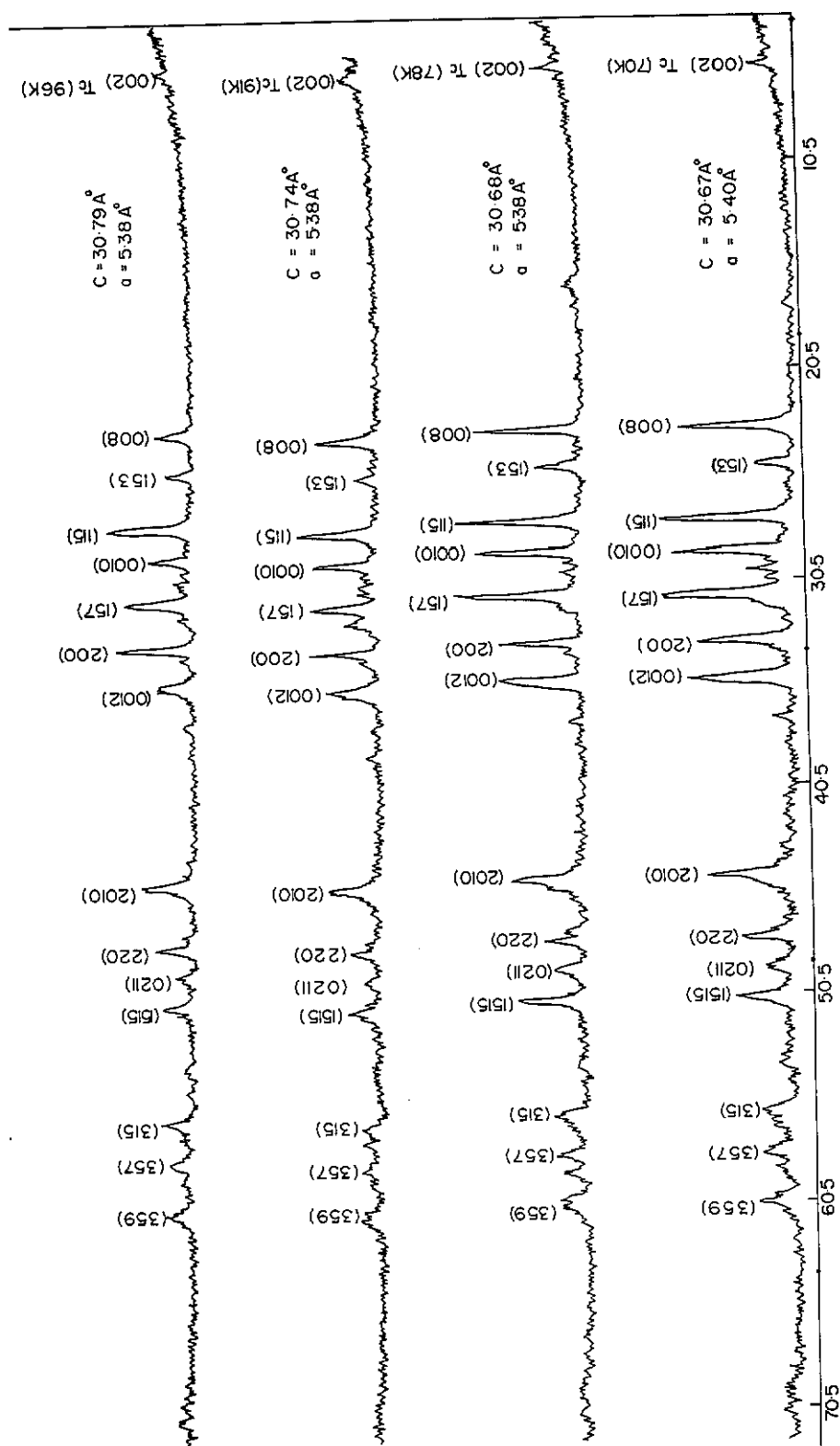


Figure 2. xrd patterns from top to bottom in the sequence of decreasing T_c . Sample (d) ($T_c = 96$ K); sample (c) ($T_c = 78$ K); and sample (b) ($T_c = 70$ K). The abscissa shows 2θ and the ordinate shows intensity in arbitrary units.

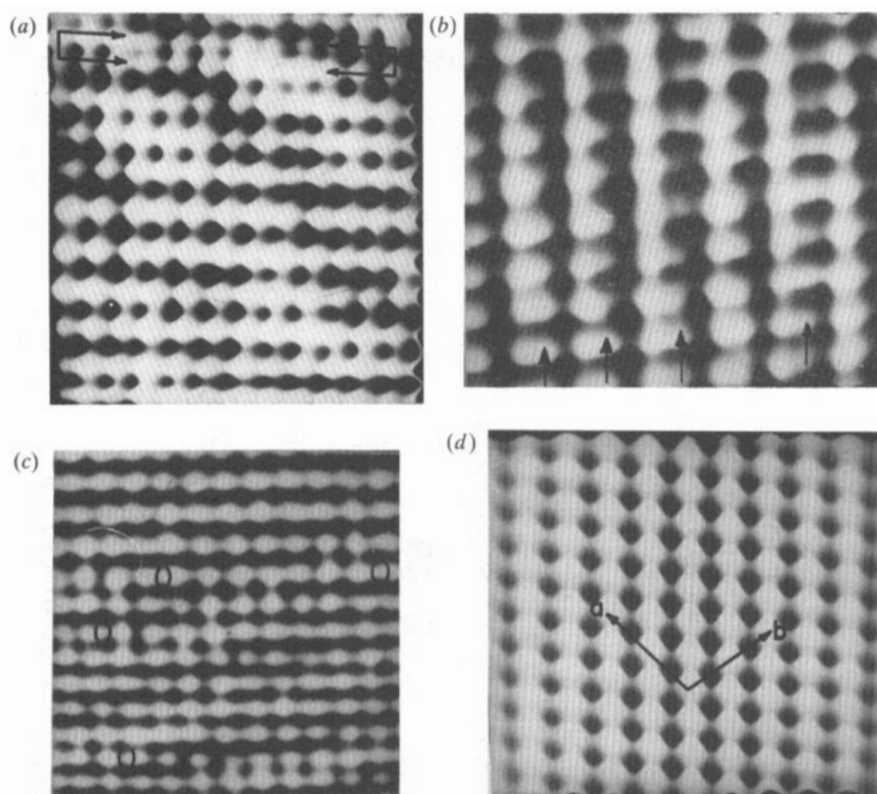


Figure 3. (a) STM image of pure sample (a) showing Bi–O layer; scan size $3\text{ nm} \times 3\text{ nm}$ and image in 3D perspective at 60° pitch. In the region (vertical row) enclosed by the arrows the interatomic distances are compressed. (b) Image of oxygenated sample (b) showing Bi–O layer with intercalated rows of excess oxygen indicated by arrows. Scan size $1.2\text{ nm} \times 1.2\text{ nm}$ and in 3D perspective at 60° pitch. (c) Image of Bi–O layer of sample (b) after nitrogenation (i.e. sample (c)). Top view image, scan size $4\text{ nm} \times 4\text{ nm}$. Circles drawn indicate the locations of excess oxygen. (d) Image of sample (a) after nitrogenation (i.e. sample (d)). Scan size: $3.2\text{ nm} \times 3.2\text{ nm}$ and image in 3D perspective at 60° pitch; note the regularity of the Bi–O layer, free from intercalation effects.

pointed out earlier [3], since the electronic states at E_f are mainly 0–2p states, primarily oxygen atoms are imaged at low bias scans of about -3 mV . At higher negative voltages of a few hundred mV, both species of atoms could be imaged. Figure 3(a) depicts a typical image of a Bi–O layer for pure sample (a) having the $T_c(R=0)$ of 91 K. The effect of oxygenation (i.e. sample (b) with a low T_c of 70 K), as revealed through the STM images, was the presence of extra rows or string of atoms intercalated in the successive Bi–O subunit cells, as marked by arrows in figure 3(b). This leads to a change in the local composition from BiO to BiO_2 . The excess atoms are intercalated along one of the basal plane axes, giving rise to a local increase in the bond length along that direction while there is no change in the periodicity in the other direction. Neutron diffraction studies of Sequeira *et al* [5] agree with this observation. The effect of nitrogenation of this sample, as revealed from the STM images, was to reduce considerably the excess intercalated oxygen from the Bi–O layer (figure 3(c)) although the presence

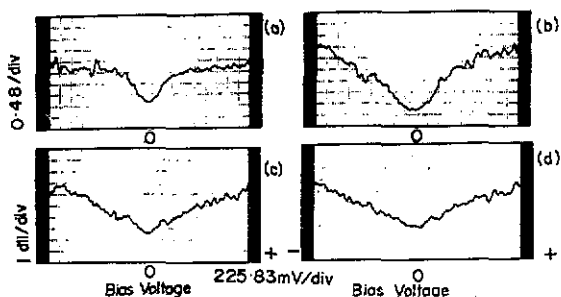


Figure 4. Normalized conductance spectra over a bias scan voltage of ± 2.25 V under similar conditions for samples (a) to (d).

of excess atoms can be seen in the figure—indicated by circles. It is worth mentioning that as the excess oxygen atoms influence the Bi–O bond lengths, the resulting lattice pattern may get locally disturbed. This can be seen even in the image of pure sample (a) of figure 3(a) where the interatomic distances on the extreme right of the photograph, in the region shown, are significantly compressed. However, for this sample when nitrogenated to yield the optimum T_c of 96 K, its STM image (figure 3(d)) was found to be remarkably symmetric and devoid of any noticeable intercalation effect.

The influence of oxygen intercalation on the electronic structure of the Bi–O layers was studied by the STS technique. Figures 4 (a–d) are typical STS spectra showing the normalized conductance versus bias scan voltage obtained for all four samples, (a), (b), (c) and (d), at room temperature under identical conditions. The conductance is proportional to the local density of states (LDOS), but as it is influenced by the tip–sample transmission factor it is usual to plot the normalized conductance instead, which is less sensitive to the experimental parameters.

The observed behaviour of the normalized conductance is indicative of a localized gap in the energy spectrum of the Bi–O monolayer at the sample surface whose value close to E_f for pure sample (a) is around (0.4 ± 0.08) eV (figure 4(a)). This value seems consistent and lies in the range 0.3 to 1 eV reported by other workers [6, 7]. The effect of oxygenation is to enhance the gap and to decrease the LDOS closer to zero (figure 4(b)). Figure 4(c) shows the effect of further nitrogenation of the oxygenated sample which is found to lower the gap and to increase the LDOS, closer to its parent value (sample (a) in figure 4(a)). When pure sample (a) was nitrogenated the conductance spectra (figure 4(d)) revealed no noticeable gap and the LDOS was enhanced, exhibiting a metallic type of behaviour. The above observations confirm that oxygenation tends to make the Bi–O redox layers more insulating while nitrogenation restores and improves the conductivity of these layers.

The described behaviour of the Bi–O layers may be understood in terms of (1). To begin with, the lower oxidation state of Bi in the pure, stoichiometric Bi-2122 allows the Bi–O redox layers to contain some free electrons available for *n*-type conduction. Consequently, the parent sample (sample (a)), prepared by quenching, having Bi–O layers with relatively low concentration of intercalated oxygen is expected to exhibit metallic or quasimetallic conduction. However, as the redox layers are progressively loaded with excess oxygen (sample (b)), the valence state of Bi is expected to rise towards 3+. As a consequence, the Bi–O layers would become more insulating. Disintercalation from the layers by nitrogenation has the obvious reverse effect on the Bi valency and as a result the *n*-type conductivity of the Bi–O layers is either partly restored (sample (c)) or even improved (sample (d)).

4. Discussion

A prominent way in which the Bi-2122 differs from Y-123 and La-214 systems is that whereas in the latter two, incorporation of oxygen generally promotes T_c , in the former it degrades T_c . It is worth noting that in both Y- and La-systems, Cu is the only cation showing a valence modification but in the Bi-based cuprates besides that of Cu, the valence state of Bi also changes. Consequently, although superconductivity resides in Cu-O layers, the superconducting behaviour of the Bi-system is influenced by both Cu-O and Bi-O layers, the former showing the p-type conduction while the latter, the n-type. Normally, the addition of oxygen is expected to enhance the valency of Cu, generating more holes in Cu-O layers, which promote the normal state conductivity (just above T_c), enhance the T_c -onset as well as the $T_c(R = 0)$ and, simultaneously, reduce the transition width. The resistivity-temperature curves of figure 1, on the other hand, show that oxygenation has lowered the normal state conductivity, reduced both T_c -onset and $T_c(R = 0)$ and has increased the transition width. Thus, it looks unlikely that Cu valence would increase with oxygenation; instead, the evidence suggests that it has decreased or at best it may have remained invariant. Our STS observations, discussed above, have revealed that in the presence of excess oxygen $\text{Bi}^{3-\delta}$ moves towards Bi^{3+} , making the Bi-O layers more insulating. Some of the band structure calculations [8, 9] performed on pure Bi-2122 show that the Bi-O bands above the Fermi level intercept E_F at several pockets suggesting the Bi-O layers take part in the electrical conduction. The increase in the resistivity of the intercalated Bi-O layer is perhaps responsible for the decreased normal state conductivity, just above T_c , of the oxygenated sample.

If we look at the crystal structure of Bi-2122 we find that the distance between the neighbouring Cu-O layers, across the Ca-layer is 0.32 nm, while their separation across the twin Bi-O redox layers is 1.26 nm. Since the superconducting coherence length of the compound in the *c*-direction is particularly small, around 0.2 to 0.3 nm, the above separation of 1.26 nm is too large to have their superconducting wave functions directly overlap each other, unless the intervening 0.32 nm thick twin redox layer is conducting. This would seriously impair the 3D superconductivity and degrade $T_c(R = 0)$, as observed for sample (b). On the other hand, sample (d), nitrogenated at 600 °C and having more conducting Bi-O redox layers, is expected to have a better coupling between the Cu-O layers in the *c*-direction, which is presumably responsible for the enhanced T_c . Since $T_c(R = 0)$ for this sample is just 3 K lower than the onset T_c of 99 K, we believe this to be the optimum value for the single phase Bi-2122. Apparently, nitrogenation at 600 °C almost completely disintercalates the excess oxygen of the Bi-O layers. The value of δ in (1) for the optimized sample is presumably the largest, i.e. the Cu-O superconducting layers carry the maximum number of holes for the optimum p-type conductivity and, simultaneously, Bi-O redox layers carry the maximum number of electrons for the optimum n-type conductivity. Nitrogenating the sample at higher temperature would deplete oxygen from other layers which is expected to bring down the hole density of Cu-O layers although the electron density in the Bi-O layers may remain unaffected. This explains our observations that nitrogenation beyond 600 °C led to T_c depression, enhancement of normal state resistivity and a reduced metallic conduction in the temperature range above T_c . Clearly, both types of conduction, i.e. p-type Cu-O layers and n-type Bi-O layers seem essential for T_c optimization.

To sum up, the present work has shown that the excess oxygen intercalated in the Bi-O redox layers, and revealed in the high-resolution STM images, is detrimental to the T_c of the Bi-2122 cuprate superconductor. The STS studies confirm that intercalation

makes the Bi-O layers more insulating with the result that the coupling between the Cu-O layers across the neighbouring unit cells is hindered and the T_c is lowered. By suitable nitrogenation heat treatment the optimum T_c attained is found to be 96 K. Finally, our results indicate that for the optimum T_c , along with the optimum p-type conduction in Cu-O planes, a simultaneous n-type conduction in the Bi-O redox layers seems necessary. We are tempted to suggest that the electrons in the redox layers perhaps play the role analogous to those of phonons in conventional superconductors and accordingly mediate hole pairing in Cu-O planes, giving rise to T_c in the 100 K range. However, this calls for theoretical attention.

Acknowledgments

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