General trends in oxygen stoichiometry effects on T_c in Bi and Tl superconductors

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We have previously shown that T_c for Bi₂(Sr, Ca)_{n+1}Cu_nO_{2n+4+\delta} (n=1, 2 and 3) varies with oxygen stoichiometry δ determined by annealing in a variety of oxygen partial pressures and temperatures. Annealing results are now also presented for several Tl-superconductors in the series Tl_m(Ba, Sr)₂Ca_{n-1}Cu_nO_{2n+m+2+\delta}, for both m=1 and 2, revealing two general results for this class of Bi or Tl superconductors: (1) effects on T_c due to labile oxygen occur for all m=2 compounds but are absent in m=1 compounds with Sr. m=1 compounds with Ba do have variable oxygen but the effects on the *c*-axis are the opposite to m=2 compounds. This suggests for the latter that the labile oxygen resides in interstitial sites within the Bi₂O₂ or Tl₂O₂ bi layers; (2) the hole concentration per Cu decreases in progressing from n=1 to 2 to 3 in either class so that the parent n=3 and n=2 compounds lie respectively on the low- and high-hole concentration sides of the peak in T_c while the n=1 compounds extend out into the non-superconducting domain at very high hole concentration.

1. Introduction

Oxygen stoichiometry is known to play an important role in the behaviour of high- T_c superconducting cuprates. The effect is most noticeable for $YBa_2Cu_3O_{7-\delta}$ in which oxygen is readily inserted into or extracted from the Cu(1)-O(1) chains at temperature above 400°C with marked effects on the superconducting properties [1]. We have reported less dramatic, but proportionately much larger effects of oxygen loading on the physical properties of the $Bi_{2,1}(Ca_xSr_{1-x})_{n+1}Cu_nO_{2n+4+\delta}$ (n=1, 2, 3) series of superconducting oxides, in particular determining the conditions of annealing temperature and oxygen partial pressure for maximising $T_c[2,3]$. For the n=2material T_c is raised to 90 K by annealing at high temperature (700-800°C) in a low partial pressure of oxygen, while for n=3 material annealing at low temperature (~400°C) in 1 atm of oxygen raised $T_{\rm c}$ to 105 K. Though these effects were noted in an early investigation of the n=1, 2 and 3 compounds [4] they do not appear to have been widely recognised until much later. Subsequently, however, similar observations, including those on Tl analogues, have been made by others [5-10].

In the present work results are presented for several Tl superconductors in the series $Tl_m(Ba, Sr)_2Ca_{N-1}Cu_nO_{2n+m+2+\delta}$ for both m=1 and 2. We arrive at a general picture for the effect of oxygen stoichiometry on the physical properties of these Tl and Bi compounds. Changes in T_c due to labile oxygen occur for all m=2 compounds investigated, but are absent in the m=1 compounds with Sr, thus suggesting that the labile oxygen resides in interstitial sites in the Bi_2O_2 or Tl_2O_2 bilayers as proposed previously [11]. The systematic trends for n=1, 2 and 3 compounds can be understood in terms of the general phase behaviour of T_c as a function of hole doping.

2. Experimental

The compounds investigated here are those of nominal composition $Tl_2Ca_2Ba_2Cu_3O_{10}$, $Bi_{1.9}Pb_{0.2}Sr_2Ca_{0.9}Cu_2O_8$, $TlCaSr_2Cu_2O_7$, $Tl_{0.5}Pb_{0.5}Ca_{1-x}Y_xSr_2Cu_2O_7$,

 $\begin{array}{ll} Tl_{0.5}Pb_{0.5}CaSr_{2-x}La_{x}Cu_{2}O_{7} & \text{and} \\ Tl_{0.5+x}Pb_{0.5-x}CaSr_{2}Cu_{2}O_{7}. & \text{Our previous investiga$ tions include the \$n=1\$, 2 and 3 members of the Bihomologous series for various Pb-substitution levelsand Sr:Ca ratios [2,3], and $<math>Tl_{0.5}Pb_{0.5}Ca_{0.8}Y_{0.2}Sr_{2}Cu_{2}O_{7}$ [11]. Shimakawa et al. [8] have undertaken similar studies on $Tl_{2}Ba_{2}CuO_{6}$, Schilling et al. [9] on $Tl_{2}Ca_{2}Ba_{2}Cu_{3}O_{10}$ and Sales and Chakoumakos [10] on $Bi_{2}Sr_{2-x}La_{x}CuO_{6}$.

Single superconducting phase Tl₂Ca₂Ba₂Cu₃O₁₀ has been produced by reacting oxide mixtures of stoichiometry Tl₂Ca₆Ba₂Cu₆O₁₇ at 860°C in oxygen [12]. Using Tl₂O₃, Ca₂CuO₃, BaCuO₂ and CuO which was milled, pressed into 0.5 g, 10 mm diam. pellets and sealed, under an oxygen atmosphere, into gold bags, we reacted for 2 h and obtained n=3 material of composition $Tl_{1.9}Ca_{2.1}Ba_{2.0}Cu_{3}O_{10+\delta}$ as confirmed by electron microprobe analysis. This material had a single-step transition to the superconducting state determined by AC susceptibility measurements, but contained non-superconducting Ca- and Cu-rich impurity phases. The X-ray diffraction pattern from the surface of this pellet is shown in fig. 1(a) where reflections due to impurity phases are marked by dots. There is some evidence of preferential orientation of crystallites but crystal lattice parameters could be readily derived from the patterns, with an uncertainty of ± 0.001 Å in the aparameter and ± 0.005 Å in the *c*-parameter.

The compounds TlCaSr₂Cu₂O₇ and Tl_{0.5}Pb_{0.5}CaSr₂Cu₂O₇ were prepared in a similar fashion but using stoichiometric mixtures and reacting at 920°C for 2 h. X-ray diffraction patterns for the latter, nearly single-phase, material is shown in fig. 1(b). Samples traversing the compositional $Tl_{0.5}Pb_{0.5}Ca_{1-x}Y_xSr_2Cu_2O_y$, ranges $Tl_{0.5}Pb_{0.5}CaSr_{2-x}La_{x}Cu_{2}O_{7}$ and $Tl_{0.5+v}Pb_{0.5-v}CaSr_2Cu_2O_7$ for $0 \le x \le 1$ and $0 \le y \le 0.3$ were prepared by first milling CaCO₃, SrCO₃, CuO and Y₂O₃ or La₂O₃ in stoichiometric proportions, then calcining in air for 12 h at 920°C. These were ground, mixed and milled with stoichiometric proportions of Tl₂O₃ and PbO, die-pressed into pellets, wrapped in gold foil and reacted in flowing oxygen for several hours at 950°C. The result was singlephase material, as confirmed by XRD and illustrated in fig. 1(c) for x=0.2, except near the end points x=0 and x=1 where small quantities of im-



Fig. 1. X-ray diffraction patterns obtained using $CoD\alpha$ radiation. Lines from impurity phases are marked with dots. (a) $Tl_2Ca_2Ba_2Cu_3O_{10}$; (b) $Tl_{0.5}Pb_{0.5}Ca_5r_2Cu_2O_7$, the major impurity being n = 1 compound; (c) $Tl_{0.5}Pb_{0.5}Ca_{0.8}Y_{0.2}Sr_2Cu_2O_7$.

purity phases appeared. The oxygen content across the compositional range was estimated by standard iodometric titration [13].

Singlc-phase $Bi_{1.9}Pb_{0.2}Sr_2Ca_{0.9}Cu_2O_8$ was prepared by reacting a stoichiometric mixture of Bi_2O_3 , PbO, $Sr(NO_3)_2$, $Ca(NO_3)_2$, and CuO at 830°C for 6 h, after decomposing the nitrates at 700°C. The material was ground, repressed and reacted at 830°C several times before a final reaction at 865°C for 6 h was carried out. The reaction at 830°C is an essential step to ensure homogenisation and prevent phase-separation in the final reaction at 865°C.

Pellets of each compound were annealed at different temperatures in open gold boats in flowing oxygen or air at 1 atm pressure, quenched into liquid nitrogen to fix the stoichiometry, then weighed. Because of the sensitivity of the Tl/Ba compounds to moisture, the pellets were sealed in plastic film and T_c measured from the temperature dependence of ac susceptibility. Taken at the onset of flux exclusion from the pellet, T_c was determined reproducibly to within 0.5 K. Annealing in any set of conditions was repeated until a stable value of T_c was obtained. At 700°C the equilibration time was less than 1 h, while at 400°C annealing was continued for 16 h. The repeatability of shifts in T_c was checked by returning the conditions of annealing to 600°C in 1 atm oxygen for 4 h at intervals through the series of measurements.

Electron diffraction patterns on the [001] zone axis were obtained (as described previously [14]) from Bi n=2 material annealed such that the resistivelydetermined T_c (R=O) ranged from 89 K down to 63 K.

3. Results

3.1. m = 1 compounds

Of the two m=1 compounds TlCaSr₂Cu₂O₇ and Tl_{0.5}Pb_{0.5}CaSr₂Cu₂O₇, neither showed any change in $T_{\rm c}$ with annealing conditions i.e., with changing temperature and oxygen partial pressure. This is consistent with the absence of annealing effects previously reported [11] for $Tl_{0.5}Pb_{0.5}Ca_{0.8}Y_{0.2}Sr_2Cu_2O_{7+\delta}$. For this compound the oxygen partial pressure was varied between 10^{-4} atm to 1 atm and the temperature from 400°C to 700°C, conditions under which T_{c} for $Bi_2CaSr_2Cu_2O_{8+\delta}$ rose by 30 K, maximised at 95 K, then fell by 20 K due to changes in oxygen stoichiometry [11]. Indeed, all Bi and Tl m=2 compounds which we have investigated, exhibit a systematic and reproducible dependence of T_c , lattice parameters and resistivity on the temperature and oxygen partial pressure of annealing. We tentatively deduce the absence of oxygen loading and insensitivity of T_c to annealing conditions to be a general feature for the m=1 compounds with Sr on the perovskite A-site.

This contrasts with the behaviour of m=1 compounds with Ba on the perovskite A-site. Nakajima

et al. [15] demonstrated clear shifts in T_c from 80 K to 109 K due to changes in oxygen content in TlCaBa₂Cu₂O_y. Evidently the larger Ba ion expands the lattice in the *a-b* plane (*a*=3.855 Å) sufficiently compared to the Sr-containing lattice (*a*=3.798 Å) that additional oxygen can be incorporated. This idea is supported by the observation of Shimakawa et al. [16] that replacing 50% of Ba by the smaller La ion in TlBa₂CuO₅ (*a*=3.840 Å) nearly eliminated variability in oxygen stoichiometry. Similarly there is a reduced range of variation in T_c upon oxygen loading in TlCaBaSrCu₂O₇ (*a*=3.827 Å) in which 50% of Ba²⁺ is replaced by the smaller Sr²⁺ [17].

The nature of oxygen loading in the m=1 compound TlCaBa₂Cu₂O_y must be different from all m=2 compounds. In the latter, oxygen is loaded interstitially between the Bi-or Tl-double layers [11,18–20] and all show the *c*-axis contracting as oxygen is added. This is as expected for intercalation of oxygen between positively charged layers. For TlCa-Ba₂Cu₂O_y the *c*-axis expands with oxygen content [15] indicating that the excess oxygen is incorporated either in, or above and below the TlO layer or in the Ca layer. Moreover the Ca layer may be excluded as TlBa₂CuO₅ also has variable oxygen is associated with the TlO layer only.

The compounds $Tl_{0.5}Pb_{0.5}Ca_{1-y}Y_ySr_2Cu_2O_7$ and $Tl_{0.5+x}Pb_{0.5-x}CaSr_2Cu_2O_7$ present a series which spans the entire superconducting domain [22]. $T_{\rm c}$ values are plotted in fig. 2 as a function of x and yand these range from zero to a maximum of 107 K and back to zero. Rietveld refinement of atomic coordinates using neutron diffraction data [23] reveals that the oxygen molar content is 7 when x=0and y=0. If we assume that Pb is tetravalent [24] and the oxygen content remains fixed at 7 mol across the substitution range the doped hole concentration p may be calculated. The hole concentration calculated in this manner is shown on the top scale of fig. 2 and the inverted parabolic behaviour of $T_{\rm c}$ agrees closely with that observed for $La_{2-r}Sr_{r}CuO_{4}$ [25]. The agreement is nearly exact for p > 0.1 but for $p < 0.1 T_c$ does not fall as rapidly as expected (see the dashed curve in fig. 2) we suspect because of additional oxygen being incorporated at high levels of Y substitution. This is probably a simple charge compensation process but at low Y substitution it does



Fig. 2. Zero-resistance T_c for $Tl_{0.5+y}Pb_{0.5-y}Ca_{1-x}Y_xSr_2Cu_2O_7$ plotted as a function of y (with x=0) and of x (with y=0). The upper scale shows the hole concentration assuming that the oxygen content remains fixed at 7. The dashed curve shows the expected curve based on $La_{2-x}Sr_xCuO_4$ suggesting that additional oxygen is incorporated for large values of x.

not occur because the lattice is too dense to allow intercalation of additional oxygen. However, the lattice expands with increased Y substitution due to adding electrons to the antibonding hybridised σ orbitals and ultimately it becomes sufficiently large to allow the intercalation of interstitial oxygen.

Titration measurements yielded mean effective copper valencies, and thus oxygen contents, which were too high by about 0.2 across the composition range. This arises from systematic partial reduction of TI^{3+} and Pb^{4+} and renders the technique unusable for these compounds. The phase curve shown in fig. 2 is probably a reliable diagram of T_c versus hole concentration at least for p>0.1, and we shall interpret the effect of oxygen stoichiometry on T_c for all of the m=2 compounds discussed below in terms of this general phase curve.

3.2. m=2, n=3: $Tl_2Ca_2Ba_2Cu_3O_{10}$

Figure 3 shows a series of AC susceptibility curves as a function of temperature for the m=2 compound



Fig. 3. AC inductance versus temperature for quenched $Tl_2Ca_2Ba_2Cu_3O_{10}$ (a) Annealed in oxygen at the various temperatures shown in °C. (b) Annealed at 600°C in oxygen (solid line) and in air (dashed line).

Tl₂Ca₂Ba₂Cu₃O_{10+ δ} annealed at temperatures between 400°C and 700°C in oxygen and in air. The values of T_c (diamagnetic onset) over the whole range of annealing conditions examined are displayed in fig. 4 together with a summary of some of the previously reported data for a variety of n=2 and 3 Bi superconductors annealed in air. The behaviour for the n=3 Tl superconductor is markedly similar to that for its Bi analogue $-T_c$ is maximised by low temperature annealing, implying that oxygen loading is required to maximise T_c for both Tl and Bi n=3compounds. This means that this compound lies on the low hole concentration side of T_c (max).

For Tl₂Ca₂Ba₂Cu₃O_{10+ δ} the *a*-lattice parameter is found to remain constant for all conditions of annealing (*a*=3.851±0.001 Å) while the *c*-axis parameter increased as the temperature of annealing



Fig. 4. The effect of annealing temperature, T_a , on transition temperature (T_c) for a variety of Bi and Tl superconductors. Open symbols are for annealing in air, solid symbols for annealing in oxygen. Compounds include: n=2 Bi₂Ca_{1.5}Sr_{1.5}Cu₂O₈ (Δ), Bi₂CaSr₂Cu₂O₈ (∇); and n=3: Bi₂Ca₂Sr₂Cu₃O₈ (+), Bi_{1.8}Pb_{0.35}Ca₂Sr₂Cu₃O₁₀ (\times) (all data from ref. 2); Tl₂Ca₂Ba₂Cu₃O₁₀ (\bigcirc).

was raised, and T_c decreased as shown in fig. 5(a). It is evident that the results for annealing in oxygen at 1 atm and at 0.21 atm are scattered about the same curve, implying an equilibrium between oxygen content of the lattice and the ambient atmosphere. In fig. 5(b), T_c for Bi₂CaSr₂Cu₂O_{8+ δ} is plotted against the *c*-axis parameter and the reverse dependence is found – T_c increases with the increase in the *c*-axis. A similar result was reported [8] for $Tl_2Ba_2CuO_{6+\delta}$ and for $Bi_2Sr_{2-x}La_xCuO_6$ [10] with varying oxygen content. This is clear evidence that these n=1 and n=2 compounds lie on the high hole concentration side of $T_{\rm c}({\rm max})$ because expansion of the lattice along the *c*-axis is caused by the unloading of oxygen as the annealing temperature is raised and/or the oxygen partial pressure is lowered. The contrasting dependence of $T_{\rm c}$ on lattice parameter between $\Gamma l_2 Ca_2 Ba_2 Cu_3 O_{10+\delta}$ and $Bi_2 Ca Sr_2 Cu_2 O_{8+\delta}$ is thus entirely consistent with the data in fig. 4 which shows



Fig. 5. T_c plotted as a function of *c*-axis parameter for a single pellet annealed at different temperatures in oxygen (full symbols) and in air (open symbols). (a) Tl₂Ca₂Ba₂Cu₃O₁₀ (Δ); (b) Bi₂CaSr₂Cu₂O₈ (\Box). One data point for annealing in 2% oxygen is also shown (\diamondsuit).

 $T_{\rm c}$ increasing with oxygen loading in the former case and decreasing in the latter case, i.e. the n=3 and n=2 compounds lie on opposite sides of the peak in $T_{\rm c}$ versus carrier concentration.

3.3. m=2, n=2: $Bi_{1.9}Pb_{0.2}Sr_2Ca_{0.9}Cu_2O_{8+\delta}$

Previous data on T_c and lattice parameters as functions of anneal temperature and oxygen partial pressure have been reported elsewhere [3] for this compound. The same trend occurs as shown by the inverted triangles (∇) in fig. 4 for the unsubstituted compound Bi₂Sr₂CaCu₂O₈ with T_c maximising by unloading oxygen in high temperature anneals at an oxygen partial pressure less than that of air. The *c*axis lattice parameter shows systematic variation with annealing conditions and the relationship between T_c and *c* is plotted in fig. 5(b). The square data points are for annealing and quenching in air at 500, 600, 700 and 800°C respectively, while the diamond is for annealing at 600°C in 2% oxygen in nitrogen. The effect of changing the oxygen partial pressure at 600°C from 0.21 atm to 0.02 atm is to raise T_c by nearly 10 K but the *c*-axis elongates due to oxygen desorption with the result that the data point still lies on the curve of T_c versus *c*. This is clear evidence that the transition temperature and lattice constant are functions of equilibrium oxygen stoichiometry.

In fig. 6 T_c is plotted as a function of resistivity and changes in oxygen content for Bi_{1.9}Pb_{0.2}Sr₂Ca_{0.9}Cu₂O_{8+ δ}. The resistance was determined using four permanent electrodes deposited using silver paint, then bakcd for 1 h at 750°C in flowing oxygen. After annealing at a given temperature and oxygen partial pressure the sample was quenched into liquid nitrogen, then resistance mea-



Fig. 6. Transition temperature T_c for the n=2 compound Bi_{1.9}Pb_{0.2}Ca_{0.9}Sr₂Cu₂O_{8+ δ} subjected to various annealing treatments. (a) Plotted as a function of the resistance ratio $R_0/R(\Delta\delta)$. R_0 is the room temperature resistance obtained after the sample is slow by cooled in oxygen ($\Delta\delta$ =0). Circles and squares are for two different samples. (b) Plotted as a function of the change in oxygen stoichiometry $\Delta\delta$ determined from changes in the mass of a 3 g sample.

surements were made at room temperature. Changes in oxygen content $\Delta \delta$ were determined from mass changes in a 3 g pellet. Taking as a reference point, $\Delta \delta = 0$, the oxygen stoichiometry corresponding to slow cooling and annealing at 400°C in flowing oxygen, we plot in fig. 6(a) T_c as a function of the resistance ratio $R(\Delta \delta = 0)/R(\Delta \delta)$ and in fig. 6(b) T_c as a function of $\Delta \delta$. This resistance ratio is proportional to the normal-state carrier concentration induced by changing oxygen stoichiometry. There is seen to be a clear dependence of T_c on δ and carrier concentration which exhibits a peak such as that shown in fig. 2. Though the changes in oxygen content are a factor of 10 smaller compared to those occuring in YBa₂Cu₃O_{7- δ} (123) and Y₂Ba₄Cu₇O_{15- δ} (247), the proportionate changes in T_c are much larger. The maximum slope $\partial T_c/\partial \delta$ in fig. 6(b) is 2400 K/vacancy, while that for 123 and 247 is only 250 K/vacancy [26,27]. This is because the major changes in carrier concentration per vacancy for 123 and 247 occur in the chains with only a small charge transfer to the planes.

The incommensurate superlattice modulation in the n=1, n=2 and n=3 Bi-homologous superconductors observed by electron diffraction has been known from the earliest investigations [28,4] but only recently has the origin of the modulation been solved. Le Page et al. [29] showed that the modulation probably arises from the incorporation of an additional 0.2 oxygen per unit cell in the Bi_2O_2 bilayer in the form of perovskite-like bridging oxygens. One might expect, therefore, to see changes in the incommensurate superlattice length which accompany changes in the oxygen stoichiometry. Thus, upon increasing T_c from 64 K to 92 K, by removing 0.05 oxygen per unit cell (refer to fig. 6(b)) one might expect to see the superlattice length increase from 4.75 to 6.25. Our early investigations [4] failed to find any dependence of the superlattice length on annealing conditions and Chakoumakos et al. [30] found no change in superlattice length for single crystals of $Bi_2Sr_2CuO_{6+\delta}$ when the oxygen content was varied by as much as 0.5. However, in the Pbsubstituted compound $Bi_{1,9}Pb_{0,2}Ca_{0,9}Sr_2Cu_2O_{8+\delta}$, we have observed a discontinuous change in the superlattice length as oxygen is loaded and T_c falls. Preliminary results are given in table 1. We have previously described two b-axis superstructures in Pb-

Table 1 *b*-Axis superstructure ratios for $Bi_{1.9}Pb_{0.2}Sr_2Ca_{0.9}Cu_2O_{8+\delta}$ annealed to attain the T_c listed

Τ _c (K)	Superstructure ratios	
	S1	S2
89	6.65±0.10	4.5 ± 0.2
83	6.65	4.5
70	6.65	4.5
67	$4.82 \pm .08$	Not observed
65	4.82	Not observed
63	4.82	Not observed

substituted m=2 Bi compounds [3,14]. In the latter paper we noted that the first superstructure possesses a characteristic length which expands as Pb is substituted into the Bi₂O₂ bilayer and that the second superstructure, apparent only at Pb additions ≥ 0.2 mol, had a constant characteristic length of \sim 4.5 times the *b*-axis lattice constant. We note in table 1 that both superstructures are present in the oxygen-deficient material annealed and quenched at high temperature. As oxygen is loaded into the lattice the first superstructure abruptly shortens and the second superstructure disappears. On either side of the discontinuity the superstructure lengths show no sign of variation with annealing temperature, oxygen content and transition temperature, $T_{\rm c}$. However, the location of the discontinuity shifts to higher oxygen partial pressure in such a way as to suggest that the controlling factor is oxygen content rather than Pb content. We have found that substitution of Pb²⁺ for Bi^{3+} , which reduces the oxygen content of the lattice for a given oxygen partial pressure, displaces the discontinuity to a higher oxygen partial pressure or, equivalently, a lower temperature of annealing.

4. Discussion

The above results show that, for the m=2 Tl- or Bi-bilayer compounds, there occurs a systematic and reversible variation of T_c with annealing temperature and oxygen partial pressure with accompanying changes in mass, *c*-axis parameter, superstructure and carrier concentration which provide a clear picture of changing oxygen stoichiometry with accompanying doping of holes onto the superconducting CuO₂ planes. Though the changes in oxygen stoichiometry are much smaller than that exhibited by YBa₂Cu₃O_{7- δ} the changes in T_c per oxygen vacancy are an order of magnitude higher than for that compound. In contrast, the m=1 single-layer Tl compounds display mixed behaviour with the small aparameter compounds, which incorporate Sr^{2+} in the perovskite A-site, showing no changes in oxygen stoichiometry and in $T_{\rm c}$ arising from varying annealing conditions. On the other hand, the larger aparameter compounds, which incorporate Ba²⁺, exhibit varying oxygen content with consequent changes in $T_{\rm c}$ and lattice parameters. The nature of the oxygen loading in these m=1 compounds is clearly different from the m=2 compounds because the *c*-axis parameters increase with oxygen loading.

We also conclude that, for the m=2 compounds investigated, the n=3 compounds require additional hole doping by oxygen loading in order to maximise T_c while the n=2 compounds require a reduction in hole doping by oxygen unloading in order to maximise T_c . To these results we may add the following results from other studies:

(1) n=2 TlCaBa₂Cu₂O_y lies on the high hole-concentration side of $T_c(max)$ with T_c variable from 80 K to 109 K with decreasing oxygen content [15] and similarly for n=2 Tl₂CaBa₂Cu₂O₈ with T_c varying from 87 K to 112 K [16].

(2) n=1 Tl₂Ba₂CuO₆ lies well on the high holeconcentration side of $T_c(\max)$ with T_c variable from 0 to 90 K [31].

(3) n=1 Bi₂Sr₂CuO₆ has such a high hole concentration that it is unstable. La-substitution in the composition range Bi₂Sr_{2-x}La_xCuO₆ reduces the hole concentration and ensures stability of the superconducting phase for $x \ge 0.2$. $T_c(\max) = 23$ K for x = 0.4 [10].

(4) n=3 Tl₂Ba₂Ca₂Cu₃O₁₀ lies on the low hole concentration side close to $T_c(max)$ with T_c varying from 110 to 116 K [16] similar to the result we report above.

The general picture which emerges from all of these results is that the bismuth or thallium oxide layers transfer a given total charge to the CuO_2 planes and the greater the number of planes the more diluted is the charge on each. Thus the CuO_2 planes in n=1compound are doped to high hole concentration, and may lie in the non-superconducting metallic domain, while the CuO₂ planes in the n=2 and n=3 compounds are superconducting but lie respectively on the high- and low-concentration sides of $T_c(max)$. The variable oxygen stoichiometry in the m=2 compounds, which arises by loading an interstitial site in the (Bi, Tl)₂O₂ bilayer, allows a variable range of hole concentration which narrows on progressing from n=1 to 2 to 3 because of this dilution. These ideas may be quantified as follows.

4.1. Superconducting phase diagram

The shape of the curve of $T_{\rm c}$ versus hole concentration shown in fig. 2 was first demonstrated for $La_{2-x}Sr_{x}CuO_{4}$ and appears to be a general feature in the phase diagram of the cuprate superconductors. It has been confirmed using a variety of atomic substitutions in Bi₂CaSr₂Cu₂O₈ [32] and also for 123 using bond valence sums to determine charge distribution between CuO chains and CuO₂ planes [33]. Indeed the dependence of T_c on hole concentration may have wider generality, as pointed out by Hirsch and Marsiglio [34] who draw attention to the striksimilarity between the behaviour for ing $La_{2-r}Sr_{x}CuO_{4}$ and transition metal alloys. In fig. 7 we present a universal phase diagram based on the



Fig. 7. Schematic phase diagram for cuprate superconductors showing the parabolic superconducting domain for $La_{2-x}Sr_xCuO_4$. The data points are those from fig. 6(b) for $Bi_{1,9}Pb_{0,2}Ca_{0,9}Sr_2Cu_2O_8$. The upper brackets show the range of hole concentrations and T_c values of the bismuth n=3, n=2 and ideal n=1 compounds annealed in air over a range of temperatures. The lower brackets show the range of hole concentrations and T_c values for the thallium n=3, n=2 and n=1 compounds.

data for $La_{2-x}Sr_{x}CuO_{4}$ found by Takagi et al. [35] and Torrance et al. [25] which summarises some of the above results. The curve is, in fact, the parabola $T_{\rm c}/T_{\rm c}({\rm max}) = 1-82.6 \ (p-0.16)^2$, where p is the number of holes per Cu. The upper bracketed regions show the domains spanned by n=2 and n=3bismuth superconductors annealed in air at temperatures between 300 and 800°C. For the n=2 compound T_c ranges from 64 K to $T_c(max) = 92$ K. If the phase curve for these materials is identical to that shown in fig. 7 then the hole concentration ranges from p=0.22 to 0.16. For the n=3 compound T_c ranges from $T_{c}(max) = 107$ K to 90 K and consequently the average value of p ranges from 0.16 to 0.116. These values are close to 2/3 of the limits for n=2 suggesting that the holes transferred from the Bi₂O₂ bilayer are distributed uniformly onto the three superconducting CuO₂ layers. On this basis one expects the hole density in the ideal n=1 compound to range from p=0.44 to 0.32, as indicated by the n=1bracket, and would not be expected to be superconducting. As prepared in air this compound is evidently unstable and Bi³⁺ tends to substitute on the Sr^{2+} site, giving compositions such as $Bi_{2,2}Sr_{1,8}CuO_{\nu}$. This altervalent substitution would displace the domain of hole concentration to lower values and superconductivity is observed in these compounds. Alternatively the structure may be stabilised by La substitution in the compounds $Bi_2Sr_{2-x}La_xCuO_y$ which again displaces the n=1 domain to overlap the superconducting domain.

For the bismuth n=2 compound the data in fig. 6(b) showing T_c as a function of the change in oxygen content, is replotted in fig. 7. Noting that $\Delta p = \Delta \delta$ we assume that $T_c = 64$ K, for the maximum oxygen content lies precisely on the universal phase curve. The remaining points are plotted using this point as a reference and can be seen to match the curve extremely well. It can be seen in fig. 4 that by increasing the Ca:Sr ratio from 1:2 to 1:1 in this compound (i.e. to $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_8$), the peak in the superconducting phase curve is displaced to a lower annealing temperature. This means that the hole concentration is reduced in this compound so that the accessible domain spans either side of $T_{\rm c}(\max)$. This almost certainly arises from increased Bi3+ substitution on the Sr²⁺ site due to the reduced Sr content, which will lower the hole concentration on the CuO_2 planes.

Data for the thallium compounds also are entirely consistent with the universal phase curve. Martin et al. [36] find for $Tl_{1.96}CaBa_2Cu_2O_8$ that $T_c = 96$ K may be raised to $T_c(max) = 118$ K by reducing the hole concentration by 0.04 holes per copper. By reading off $T_{\rm c}$ values from the universal curve one expects a reduction of 0.044 holes per copper in good agreement with the measured value. Shimakawa et al. [16], by annealing $Tl_2Ba_2CuO_6$, $Tl_2CaBa_2Cu_2O_8$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$ in atmospheres ranging from oxygen to argon, found T_c to rise from 0 K to $T_c(max) = 90$ K for n=1, from $T_c = 87$ K to $T_{\rm c}({\rm max}) = 112$ K for n=2 and $T_{\rm c}$ to fall from $T_{\rm c}(\max) = 116$ K to 110 K for n = 3. Again reading off fig. 7 these correspond to changes in hole density of $\Delta p \sim 0.9$, 0.5 and 0.26, close to the ratios of 1: 1/ 2:1/3 and indicating that holes transferred from the Tl_2O_2 bi-layer are uniformly distributed on the CuO₂ planes. Presumably the n = 1 compound overlaps the superconducting domain because of Tl³⁺ substitution on the Ba^{2+} or Cu^{2+} site. The hole density ranges for these thallium compounds are shown by the lower brackets. Though more rigorous data would be preferred these few results help confirm the universality of the superconducting phase curve which can be partially spanned in many of these compounds by varying the oxygen stoichiometry. It appears that $T_{\rm c}({\rm max})$ is the only quantity which varies from one compound to another.

4.2. Oxygen sites for variable stoichiometry

The contrasting behaviour of the m=1 and m=2compounds implies that the latter possess a site for labile oxygen which is absent in the structure of the m=1 compounds and the obvious assignment is an interstitial site in the Tl or Bi bilayer. Evidence for an interstitial oxygen site has been found in Tl₂Ba₂CuO_{6+ δ} [19] and confirmed by Shimakawa et al. [20]. This compound is variously reported to be a non-superconductor or superconducting with T_c ranging between 0 and 90 K, depending upon preparation conditions. In agreement with our results, the determining factor appears to be the oxygen stoichiometry as controlled by oxygen partial pressure and Parise et al [19] found, in their neutron scat-

tering studies of high- $T_c Tl_2Ba_2CuO_{6+\delta}$, evidence for 0.1 oxygens located in the interstitial site, tetrahedrally coordinated to Tl, in the Tl₂O₂ block. The $Tl_2Ba_2CuO_{6+\delta}$ materials reported by Shimakawa et al. [8] displayed a range of oxygen contents with $T_{\rm c}$ ranging from 0 to 90 K and for these $T_{\rm c}$ was a linear increasing function of the *c*-axis lattice parameter. We deduce from this that as oxygen is progressively unloaded from the interstitial site the *c*-axis lattice parameter increases, due to reduction in cohesive energy of the double layer, and the hole concentration decreases, driving T_c to higher values. The decrease in c-axis parameter with oxygen unloading during annealing at progressively higher temperatures is consistently observed for the compounds $Bi_2CaSr_2Cu_2O_{8+\delta}$ and $Tl_2Ca_2Ba_2Cu_3O_{10+\delta}$ discussed here.

It would be considerably more difficult to similarly deduce the equivalent site of labile oxygen in the Bi m=2 materials because of their incommensurate superstructure. However, Le Page et al. [29] have solved the isostructural compound $Bi_{10}Sr_{15}Fe_{10}O_{46}$, which has a 5× commensurate superstructure in the *a*-*b* plane. They show that the superstructure modulation arises from the insertion of extra oxygen atoms every 10 Bi rows, giving a short region of perovskite-like Bi-O-Bi bonding between the Bi-layer planes regularly interspersed between the regular rocksalt arrangement of parallel BiO planes. This insertion corrugates the bilayer. They suggest the incommensurate superstructure in that $Bi_2Sr_2CaCu_2O_{8,2}$ is generated by a random sequence of single and double insertions of oxygen atoms near the tops of the corrugations. These extra oxygens could be the labile oxygen which is loaded or unloaded according to annealing conditions, except for the fact that we do not see a continuous lengthening of the modulation as oxygen is removed from the compound. Our observation that the modulation remains unchanged with progressive unloading, then discontinuously splits into two distinct modulations with no further change, would suggest that the bridging oxygens are not labile. In addition, most investigations have failed to observed incommensurate superstructures in the m=2 Tl compounds [37] which still exhibit variable oxygen stoichiometry. The incommensurate superstructure appears to be a stable consequence of the 6s² lone pair of electrons in

Bi³⁺ [37]. Tl³⁺ does not possess a lone pair of electrons and, for those few cases where a superstructure is evident in non-stoichiometric Tl compounds, it is attributable to the presence of Tl¹⁺ which does. Moreover, the close similarity between the annealing behaviour for the n=3 Bi and Tl superconductors would imply that the nature of the oxygen loading is very similar in both cases in spite of the fact that the superstructure is present only in the former compound. We believe that the labile oxygen site in both sets of Bi and Tl homologues is the interstitial site identified by Parise et al. [19].

For the m=1 compounds no such interstitial site exists but variable oxygen stoichiometry has been observed in those compounds, containing some Ba²⁺ on the perovskite lattice-A site, with an *a-b* plane lattice constant ≥ 3.82 Å. As argued in section 3.1, there appears to be a critically restricted volume available for interstitial oxygen above and below the Tl-O layer.

4.3. Implications of variable oxygen stoichiometry

The fact that variable oxygen stoichiometry has been overlooked in many previous studies on these compounds has considerable bearing on conclusions made in those studies. Thus, for example, investigations [38] of rare-earth (RE) substitution for Ca in the solid solution range $Bi_2Ca_{1-x}RE_xSr_2Cu_2O_8$ with undefined annealing treatment, showed $T_{\rm c}$ remaining constant at 73 K for values of x up to 0.35, then falling for values beyond. This rather low value of T_c even for x=0 suggests, with reference to fig. 4, that the samples were cooled slowly. Thus T_c was not optimised with respect to oxygen content in the lattice. Of course this would be necessary for each value of x. In the absence of such optimisation, no conclusions should have been drawn about the the behaviour of T_c as a function of x. In contrast, we found the optimised T_c rose to a maximum of 100 K for x=0.1 in the Y-doped system [39].

Similar comments also apply to the claim that T_c for the compounds $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$ and $Bi_2Ca_{n-1}Sr_2Cu_nO_{2n+4}$ maximises as a function of *n* at n=3, at the values 122 K for the former and 110 K for the latter. Until T_c is optimised as a function of oxygen stoichiometry for $n \ge 4$ no conclusion can be drawn about the *n* dependence of $T_c(max)$. In the case of the m=1 compounds, in which oxygen stoichiometry is not variable, this criticism does not apply. Ihara et al. [40] have prepared mixed phase m=1 Tl superconductors with n up to 6 by progressively evaporating Tl during high-temperature anneals. They find T_c does indeed maximise at 122 K for n=3 and n=4. Uniform dilution over the CuO₂ planes, of the fixed hole charge transferred from the TlO plane, a process circumstantially but strongly supported in this investigation, would produce a hole density less than the optimum for maximising T_c in materials with n>4.

A variety of transition temperatures has been recorded in studies of members of the $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4+\delta}$ series. Our observations show that this can, at least in part, be explained by failure to optimise the oxygen stoichiometry during processing. Of course, it is also evident that the maximum T_c for n=3 material which we achieved is 118 K, whereas Parkin et al. [12] report 125 K while others, using the same processing recipe, have reported 122 K [41] and 118 K [36]. Some of the discrepancies amongst reported values of T_c may be generated by intergrowths of fewer or additional Ca-CuO₂ layers which depress T_c in Tl₂Ca₂Ba₂Cu₃O_{10+ δ}. However, we and others have established the significance of oxygen stoichiometry in determining T_c in this structure. It is also notable in fig. 6 that $T_{\rm c}$ continues to increase with decreasing *c*-axis parameter. It likely, then, that more oxygen can be loaded in this system before T_c is maximised. The process of sealing the sample under oxygen in a gold tube [12] is probably instrumental in achieving this in that the reaction at 900°C would occur at 4 atm while slow cooling to load oxygen would produce an oxygen partial pressure of about 2 atm at 400°C.

In summary, we have investigated the effects on T_c of annealing in oxygen a variety of compounds within the homologous series $M_mCa_{n-1}A_2Cu_nO_{2n+m+2+\delta}$ where M is Bi (or partly Pb) or Tl, A is Sr or Ba, m=1 or 2 and n=1, 2 or 3. We find no oxygen-loading effects for m=1 compounds when A is Sr but, when A is Ba and for all m=2 compounds, the effects of ambient oxygen partial pressure and annealing temperature on T_c , sample mass, resistivity and lattice parameters present a clear picture of oxygen loading into the lattice and consequent hole doping in these compounds.

m=2 compounds we deduce that the oxygen is loaded in interstitial sites between the double Bi or Tl layer while in the m=1 compounds additional oxygen probably loads within, or above and below, the TlO single layer. All of these compounds exhibit a phase diagram similar to that for $La_{2-x}Sr_xCuO_4$ which shows a maximum in T_c versus hole concentration at p=0.17 holes/Cu atom. In general n=1and 2 compounds appear to lie on the hole-excess side of the maximum while n=3 compounds lie on the hole-deficient side of the maximum.

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