A new monoclinic phase of superconducting $Tl_2Ba_2CuO_{6+\delta}$

D. R. Pederzolli, G. M. Wltschek and J. P. Attfield

[a] *Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, UK CB3 0HE*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*

High-resolution time-of-flight neutron and synchrotron X-ray powder diffraction studies of the 'orthorhombic' form of the high-T_c superconductor $Tl_2Ba_2CuO_{6+\delta}$ evidence both the orthorhombic (*Fmmm*) phase and a new monoclinic (*F*112/*m*) form at high excess oxygen contents δ.

$Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) is the first member of the $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ series of high critical temperature (T_c) copper oxide superconductors. Unlike the other homologues, which are all tetragonal, Tl-2201 exhibits both tetragonal and orthorhombic symmetries and the physical properties of both forms vary from non-superconducting to superconducting with T_c values up to 90 K.[1] Physical measurements[2] and a resonant synchrotron X-ray diffraction study[3,4] have shown that the two forms have slightly different compositions $(Tl_{2-x}Cu_x)Ba_2CuO_{6+\delta}$. The orthorhombic form obtained at 800–850 °C is cation stoichiometric ($x = 0$) whereas tetragonal Tl-2201 formed above 850 °C has a significant degree of Cu substitution at the Tl site with $x = 0.1$. The synchrotron diffraction study also detected a possible phase separation in orthorhombic Tl-2201, evidenced by small splittings of certain diffraction peaks *e.g.* 040. Here we report further high-resolution synchrotron X-ray and time-of-flight (TOF) neutron powder diffraction studies of 'orthorhombic' Tl-2201. These have led to the discovery of a new monoclinic form of this important superconductor.

A 20 g batch of orthorhombic $Tl_2Ba_2CuO_{6+\delta}$ was synthesised at 820 °C under flowing O_2 and quenched to room temperature. Portions of this 'as-prepared' sample were annealed for 5 h under flowing Ar at temperatures between 200 and 700 °C to systematically decrease the excess oxygen content δ, and a further portion was treated under 600 atm O_2 pressure at 600 °C to increase δ. Synchrotron X-ray powder diffraction patterns were recorded on diffractometer 9.1 at the Synchrotron Radiation Source, Daresbury, UK and TOF neutron diffraction data were collected from instrument HRPD at the Rutherford Appleton Laboratory, UK. Rietveld refinements[5] were performed using the GSAS package.[6] Diffraction peaks from traces of $BaCO_3$ and Tl_4O_3[7] were also observed in some of the profiles and were fitted in the refinements. Magnetisations were measured on a Quantum Design SQUID magnetometer in a field of 500 G.

The neutron diffraction pattern of the as-prepared $Tl_2Ba_2CuO_{6+\delta}$ sample contained small splittings of many *hk*0 and *hkl* diffraction peaks *e.g.* 220 (Fig. 1) although the *h*00 and 0*k*0 diffraction peaks were unsplit. These splittings are inconsistent with orthorhombic symmetry and with the previously reported phase separation model,[4,5] and show that the crystal symmetry is monoclinic. Lowering the symmetry of the structural model from orthorhombic *Fmmm* to monoclinic *F*112/*m* (a non-standard setting of space group *C*2/*m* with the *c*-axis unique) gave a good fit to the profile (R_{wp} = 8.8%). Monoclinic splittings were not observed for the 700 °C Ar-annealed sample (Fig. 1) and the data were fitted by the orthorhombic *Fmmm* model (R_{wp} = 9.7%). Results are summarised in Tables 1 and 2.

The synchrotron X-ray diffraction profiles showed monoclinic splittings for the high pressure O_2-annealed, as-prepared, and 200 and 400 °C Ar-annealed Tl-2201 samples, but the 600 and 700 °C Ar-annealed samples were orthorhombic. Good fits to the data with R_{wp} ranging from 5.4 to 9.7% were obtained using the monoclinic *F*112/*m* or orthorhombic *Fmmm* models as appropriate (Table 1).

The Tl-2201 superconductor is notable for having three different macroscopic symmetries due to small variations in chemical composition. The extent of the monoclinic distortion (Table 1) is dependent upon the oxygen content, as the largest

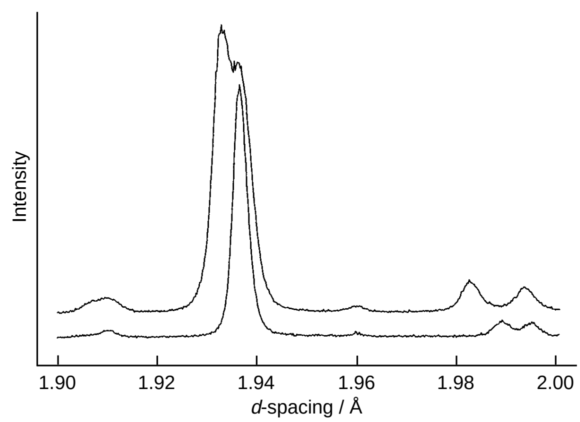

Fig. 1 Part of the TOF neutron powder patterns of as-prepared (upper curve) and 700 °C Ar-annealed (lower curve) Tl-2201 samples. A monoclinic splitting of the 220 peak (d = 1.935 Å) is seen for the as-prepared sample and the relative magnitudes of the orthorhombic distortions are apparent from the separation of the 208 and 028 reflections at 1.98–2.00 Å.

Table 1 Cell data for monoclinic ($\gamma > 90°$) and orthorhombic ($\gamma = 90°$) $Tl_2Ba_2CuO_{6+\delta}$ samples from high-resolution synchrotron X-ray (X) (λ = 0.871 94 Å) and TOF neutron (N) refinements, with e.s.d.s in parentheses. Samples are listed in order of decreasing excess oxygen content δ

Sample treatment	a/Å	b/Å	c/Å	γ/°	$10^3\ 2(b-a)/(b+a)$
600 atm O_2 X	5.43846(7)	5.50419(8)	23.1563(3)	90.189(1)	12.01(2)
As-prepared X	5.44667(8)	5.50601(9)	23.1556(3)	90.120(1)	10.84(2)
As-prepared N	5.44760(6)	5.50496(7)	23.1560(3)	90.114(1)	10.47(2)
200 °C, Ar X	5.44527(11)	5.50388(12)	23.1494(4)	90.119(2)	10.71(2)
400 °C, Ar X	5.44989(10)	5.50152(11)	23.1638(4)	90.124(2)	9.43(2)
600 °C, Ar X	5.46383(8)	5.49577(9)	23.2168(4)	90	5.83(2)
700 °C, Ar X	5.46622(7)	5.49173(8)	23.2223(3)	90	4.66(2)
700 °C, Ar N	5.46576(7)	5.49766(7)	23.2265(3)	90	5.82(2)

Table 2 Atomic parameters from neutron refinements of the as-prepared *F*112/*m* (normal type) and 700 °C Ar-annealed *Fmmm* (in italics where different) Tl-2201 samples, with e.s.d.s in parentheses

Atom	Multiplicity	x	y	z	U_{iso}/Å^2	Occupancy
Tl	16	−0.0049(6) *0*	0.0260(3) *0.0175(8)*	0.20253(3) *0.20271(5)*	0.0226(3) *0.0210(4)*	0.5
Ba	8	0.5	0	0.08388(4) *0.08271(7)*	0.0196(3) *0.0159(4)*	1
Cu	4	0	0	0	0.0184(2) *0.0132(4)*	1
O(1a)[a]	4	0.25	0.75	0	0.0207(2) *0.0152(3)*	1
O(1b)[a]	4	0.25	0.25	0	0.0207 *0.0152*	1
O(2)	8	0	0	0.11573(4) *0.11651(7)*	0.0207 *0.0152*	1
O(3)	16	−0.0203(6) *0*	0.0740(3) *0.0587(5)*	0.28895(8) *0.28838(11)*	0.0514(6) *0.0471(8)*	0.5
O(4)	8	0.25	0.25	0.25	0.0207 *0.0152(3)*	0.096(2) *0.075(3)*

[a] These sites are equivalent in orthorhombic *Fmmm* symmetry.

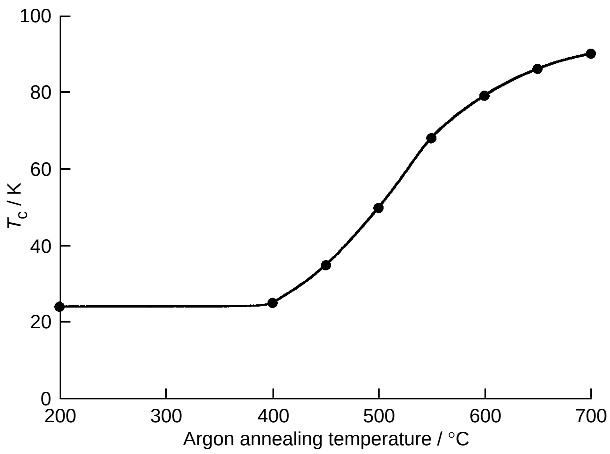

Fig. 2 Variation of T_c with Ar-annealing temperature in 'orthorhombic' Tl-2201

value of $\gamma = 90.2°$ is found in the sample treated under a high oxygen pressure, whereas the as-prepared material and samples annealed ⩽400 °C under Ar all have $\gamma \approx 90.1°$ and those annealed above 600 °C are orthorhombic. A similar reduction in the orthorhombic distortion, quantified by the orthorhombicity $2(b - a)/(b + a)$, is also observed with decreasing δ. The monoclinic to orthorhombic transition occurs between Ar-annealing temperatures of 400 and 600 °C and is accompanied by a sharp decrease in the orthorhombicity and an abrupt increase in c from 23.15–23.16 Å in monoclinic samples to 23.22–23.23 Å in the orthorhombic ones. The maximum slope in the variation of T_c with Ar-annealing temperature (Fig. 2) also occurs within this region, showing that the structural or chemical changes at the monoclinic to orthorhombic transition enhance T_c.

Comparing the neutron-refined atomic parameters of the monoclinic as-prepared and orthorhombic 700 °C Ar-annealed $Tl_2Ba_2CuO_{6+\delta}$ samples (Table 2) enables small structural changes to be discerned. The reduction in excess oxygen content from $\delta = 0.192(4)$ to 0.150(6) is consistent with the change from overdoped non-superconducting behaviour to superconductivity with $T_c = 90$ K. This is accompanied by a significant increase in the distance from Cu to the apical oxygen atom O(2) from 2.676(1) Å in the non-superconducting monoclinic structure to 2.702(1) Å in the $T_c = 90$ K orthorhombic sample, whereas the Tl–O(2) distance decreases slightly from 2.012(1) to 2.001(2) Å. Hence, the observed expansion of 0.07 Å in c is due to the overall increase of 0.10 Å in the four Cu–O(2) contacts which is partly offset by a total decrease of 0.04 Å of the four Tl–O(2) bonds. This adds to the large amount of evidence for the crucial role of the apical Cu–O bond distance in determining the value of T_c in these notable superconductors.[8,9]

In conclusion, small changes in the amount of excess oxygen in 'orthorhombic' $Tl_2Ba_2CuO_{6+\delta}$ play a critical role in determining the crystal symmetry and electronic properties. Oxygen-rich compositions with T_c values up to *ca*. 50 K are monoclinic whereas less oxidised samples with T_c values of 50–90 K are orthorhombic. The monoclinic to orthorhombic phase change occurs due to loss of interstitial oxygen, whereas the orthorhombic to tetragonal change at higher temperatures involves the loss of Tl_2O_3 from the structure accompanied by the substitution of 5% Cu at the Tl site.

References

1 Y. Kubo, Y. Shimakawa, T. Manaho and H. Igarashi, *Phys. Rev. B*, 1991, **43**, 7875.
2 Y. Shimakawa, *Physica C*, 1993, **204**, 247.
3 M. A. G. Aranda, D. C. Sinclair, J. P. Attfield and A. P. Mackenzie, *Phys. Rev. B*, 1995, **51**, 12 747.
4 M. A. G. Aranda, D. C. Sinclair and J. P. Attfield, *Physica C*, 1994, **235–240**, 965.
5 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
6 A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LA-UR-86-748, 1987.
7 R. Marchand and M. Tournoux, *C. R. Hebd. Seances Acad. Sci., Ser. C, Sci. Chim.*, 1973, **277**, 863.
8 Y. Ohta, T. Tohyama and S. Maekawa, *Phys. Rev. B*, 1991, **43**, 2968.
9 K. Eid, M. Matlak and J. Zielinski, *Physica C*, 1994, **220**, 61.

Received, 27th November 1996; Com. 6/08024C