Phase Separation and Cation Distributions in Tl-2201 from Resonant Synchrotron X-ray Diffraction

J.P. Attfielda, M.A.G. Arandab, and D.C. Sinclaira,c

aInterdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, and Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

bDepartamento de Química Inorgánica, Universidad de Malaga, Aptd. 59, 29071 Malaga, Spain

cSchool of Materials, University of Leeds, Leeds LS2 9JT, UK

Orthorhombic and tetragonal Tl-2201 (Tl2Ba2CuO6+5) samples have been studied using resonant synchrotron X-ray powder diffraction data at energies just below the Cu K and Tl LIII absorption edges. The resonant contributions enable us to demonstrate that Cu substitutes at the Tl site; the tetragonal structure is stabilised by a higher (5.5%) degree of substitution than the orthorhombic material where it is <1%. A slight splitting of some diffraction peaks of orthorhombic Tl-2201 is consistent with separation into two phases due to the segregation of interstitial oxygens, giving one phase with \( \delta = 0 \) and another with \( \delta = 0.3 \) that displays an incommensurate superstructure. These two phases are respectively too under- and over-doped to superconduct.

1. INTRODUCTION

Tl-2201 (Tl2Ba2CuO6+5) is of interest as the first member of the double TI series of copper oxide superconductors. Unlike the other higher homologues, this phase is found in both tetragonal and orthorhombic forms, and varies from non-superconducting to having \( T_c \)s up to 110 K [1]. Shimakawa [2] has recently suggested that the variation in crystallographic symmetry is due to the degree of substitution of Cu for Tl, high levels of substitution being necessary to stabilise the tetragonal form. We have used resonant powder X-ray diffraction to investigate this proposed substitution, as well as the effects of oxygen interstitials upon the structures of orthorhombic and tetragonal Tl-2201.

2. EXPERIMENTAL

Tl-2201 samples were prepared from high-purity powders of Tl2O3, BaO2 and CuO. The pellets were wrapped in gold foil envelopes during sintering and were reground and reheated several times. Orthorhombic Tl-2201 (starting composition Tl: Ba: Cu = 2.10: 2.00: 1.06) was sintered at 820 °C and the tetragonal sample (initial Tl: Ba: Cu = 2.10: 2.00: 1.15) was heated at 865 °C. Both samples were cooled to room temperature at 10 °C/min under flowing oxygen, and were found to be non-superconducting.

Synchrotron X-ray powder diffraction was carried out on diffractometer 2.3 at the EPSRC Synchrotron Radiation Source, Daresbury, UK. For each sample, resonant diffraction patterns were recorded at \( \lambda = 0.97966(3) \) Å, 12 eV below the Tl LIII edge, and \( \lambda = 1.38181(3) \) Å, 10 eV below the Cu K edge. These resonant wavelengths give rise to large anomalous dispersion effects, calculated \( f'(\text{Tl}) = -17.0 \) electrons/atom at the former wavelength and \( f'(\text{Cu}) = -6.6 \) electrons/atom at the latter. The crystal structure of each phase was fitted to the two patterns simultaneously, using the GSAS program [3], to make use of the contrast between Tl and Cu.

3. RESULTS

3.1. Tetragonal Tl-2201

All the sharp Bragg peaks of this single phase sample were indexed on a tetragonal P4/nmm unit cell (Table 1). The occupation factors of Tl and the proposed substituent Cu were refined independently during the simultaneous refinement, giving values of 0.936(8) and 0.052(16), respectively. The total Tl+Cu occupancy of the Tl site, 0.988(18), clearly indicates that no significant Tl vacancy formation occurs. Hence, in the subsequent refinements the Tl and Cu occupancies were constrained to sum to 1.0. Refinement of the occupancy of the interstitial O site between the TlO layers gave a value of 0.001(1). Final overall R factors for the joint refinement were \( R_{wp} = 6.9\% \), \( R_p = 4.9\% \) and \( R_F = 7.7\% \).
Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>(x)</th>
<th>(\delta)</th>
<th>(a (\text{Å}))</th>
<th>(b (\text{Å}))</th>
<th>(c (\text{Å}))</th>
<th>(V (\text{Å}^3))</th>
</tr>
</thead>
</table>
| Tetragonal | 0.11(1) | 0.18(3) | 3.86409(2) &nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&n

3.2 Orthorhombic Tt-2201

The pattern was indexed on an orthorhombic unit cell with Fmmm symmetry. Several very weak peaks due to an incommensurate structural modulation [4] were also observed. The variable components of the propagation vector were refined from the positions of five well-resolved satellite peaks, giving the vector \(<0.046(1), 0.217(1), 1>\).

Anisotropic strain broadening of the diffraction peaks was evident in the orthorhombic Tt-2201 pattern and was fitted in the refinement. The strain in the ab plane is approximately twice that in the c-direction. A further slight splitting of some peaks was also observed. This could not be fitted as a lattice distortion, but was found to be consistent with separation of the sample into two phases (Orthol and Ortho2) with slightly different a and b cell parameter values (Table 1). The Orthol: Ortho2 ratio was 0.444(7): 0.556. Refinement of the interstitial oxygen sites occupancies for the two phases showed that this site is vacant in Orthol, but has a 0.15(3) occupancy in Ortho2. No significant substitution (i.e. \(<1%) of Tt by Cu was found. Final overall R-factors for the joint refinement were Rwp = 8.2%, Rp = 5.6% and Rf = 9.4%.

4. DISCUSSION

Our results confirm that the main difference between orthorhombic and tetragonal Tt-2201 is the degree of Cu substitution at the Tt site [2]. Our orthorhombic sample is essentially stoichiometric in Tt, but in the tetragonal sample 5.5% of the Tt cations are substituted by Cu. The disorder caused by the substitution of Cu for Tt gives a macroscopic tetragonal symmetry, although orthorhombic microdomains may be present. The Cu substitution also suppresses the oxygen segregation and superstructure observed in the orthorhombic sample.

The tetragonal Tt-2201 sample is overdoped and hence non-superconducting due to the presence of interstitial oxygen. This was confirmed by post-annealing a small bar of the tetragonal sample in Ar at 480 °C for 5 hrs and quenching into liquid N2, after which d.c. resistivity measurements demonstrated a sharp resistive superconducting transition at Tc(0) = 49 K.

The previously unknown oxygen phase separation in orthorhombic Tt-2201 is consistent with the formation of an unmodulated, underdoped Orthol phase with \(\delta = 0\) and a structurally modulated, overdoped Ortho2 phase with \(\delta = 0.3\). A similar phase separation is seen in La2CuO4+\(\delta\) [5] although in this case less oxygen is incorporated between the two LaO layers, as they are less flexible than TtO layers, and the oxygen rich phase with \(\delta = 0.08\) is superconducting with Tc = 40 K.

REFERENCES