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Defects that Control the Properties of Tl- and Hg-based Superconductors

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Defects that affect T_c in $Tl_2Ba_2CuO_{6+\delta}$ and $HgBa_2CuO_{4+\delta}$ have been characterized by neutron powder diffraction. In $Tl_2Ba_2CuO_{6+\delta}$, the dominant defect is interstitial oxygen between the two Tl-O planes, but Cu substitution on the Tl site also affects properties and there is evidence for a second oxygen defect for compositions in the vicinity of maximum T_c. In $HgBa_2CuO_{4+\delta}$, there are two competing oxygen defects in the Hg layer. The relative concentrations of these defects switches upon passing from the underdoped region, through the maximum T_c, to the overdoped region. This remarkable behavior could result from a change in the topology of the Fermi surface upon passing through the van Hove singularity.

1. INTRODUCTION

The $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) [1] and $HgBa_2CuO_{4+\delta}$ (Hg-1201) [2] superconducting compounds are of particular importance for the study of the physics of HTS because these materials exhibit the highest T_c's observed for any material with one CuO_2 layer, they have simple crystal structures, and the doping can be varied over a wide range. For Tl-2201, the maximum T_c is ~94K and the compound can be overdoped into the normal-metal regime. For Hg-1201, the maximum T_c is ~98K and the compound can be both underdoped and overdoped.

To enable the reproducible synthesis of these materials and to interpret the physical measurements, one must understand the defects that control the properties. Multiple defects form in both compounds. In this paper, we describe these defects and their effects on T_c. We also comment on what this complex defect chemistry may teach us about the underlying electronic structure — specifically, that the competition between slightly different oxygen defects can be strongly affected by crossing the van Hove singularity.

2. $Tl_2Ba_2CuO_{6+\delta}$

Two defects have previously been described in the literature for Tl-2201 [3]. T_c is affected most strongly by an interstitial oxygen defect O4 located between the two Tl-O layers. T_c is maximum (~94K) for the minimum amount of defect oxygen and decreases as more oxygen is added, eventually reaching the normal metallic state.

The second defect is Cu substitution at the Tl site. This defect was discussed in some of the earliest papers about Tl-2201, but the experimental evidence was not strong. More recently, Aranda et al. [4] used anomalous x-ray diffraction (at the Cu edge) to prove the existence of this defect. By comparing two samples, they showed that the unit cell tends to have a smaller orthorhombic strain (or appear tetragonal within experimental resolution) for higher concentrations of this defect. However, they did not correlate superconducting properties to the concentration of this defect.

To investigate the defect chemistry more fully, we prepared samples of Tl-2201 by a conventional solid-state-reaction technique for various Tl/Cu starting compositions from 2.3/1.0 to 2.0/1.1 [5]. Portions of each of these samples were then annealed in oxygen at 400° C and various oxygen partial pressures to vary the oxygen contents. This synthesis technique yielded samples with a wide range of structural and superconducting properties. For each sample, the amount of oxygen on the O4 interstitial site was determined by Rietveld refinement using neutron powder diffraction data.

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The T_c's of these samples vs. the oxygen content on the O4 site are shown in Fig. 1. From the wide scatter in the data, it is immediately obvious that O4 oxygen content is not the only factor controlling T_c. The T_c's and also the structural data show that these differences result from the different Tl/Cu starting compositions. We assume, but cannot prove directly from the neutron diffraction data, that these samples differ in the amount of Cu on the Tl site. The variation of orthorhombic strains vs. Tl/Cu ratio for our samples (see Fig. 2) agrees with the results of Aranda et al. [4], supporting our assumption. Samples with more Cu on the Tl site have smaller orthorhombic strains. For these samples, the maximum T_c that can be achieved by varying the oxygen content is also slightly (5-10° K) lower.

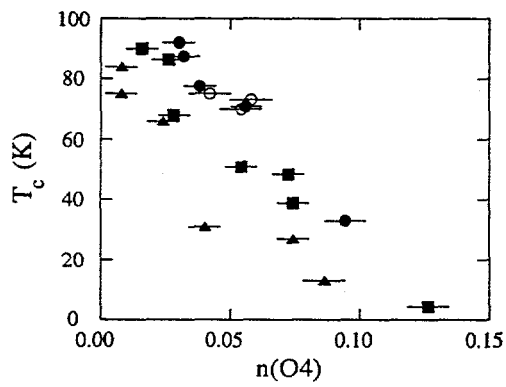

Fig. 1. T_c vs. oxygen content at the O4 site for Tl-2201. The different symbols are for samples with different Tl/Cu starting compositions.

At oxygen contents near those that give the maximum T_c, we see evidence for a second oxygen defect. In the vicinity of maximum T_c, with continuously decreasing oxygen content, the c-axis lattice parameter increases, passes through a maximum, and then decreases again (see Fig. 3). Such behavior is not consistent with a monotonically changing concentration of a single defect. By comparing the oxygen content on the O4 site (determined by neutron diffraction) with the total oxygen uptake determined by TGA, we conclude that, for these low oxygen concentrations, there is apparently an oxygen defect that is not at the O4 site. We have been unable to locate this second oxygen defect by neutron diffraction (which is not surprising, due to its small concentration). However, the observation of a similar phenomenon in Hg-1201 at compositions in the vicinity of maximum T_c (to be discussed in the next section) suggests that our conclusions are correct and may provide some clues about what different kind of oxygen defect is being formed.

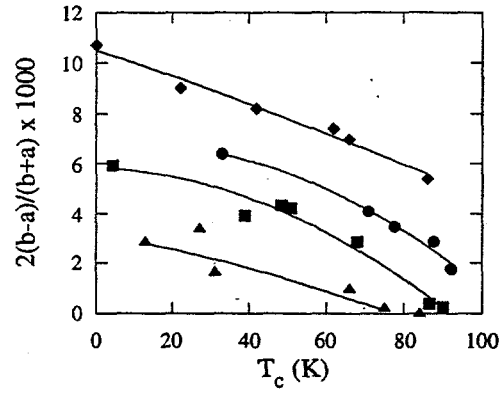

Fig. 2. Orthorhombic strain vs. T_c for Tl-2201 samples with different Tl/Cu starting compositions and oxygen contents: closed circles and closed squares, Tl/Cu=2.0/1.0, closed triangles 2.0/1.1; diamonds are the data of Ref. 3.

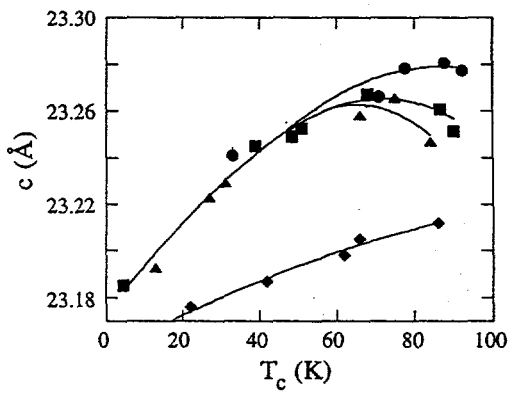

Fig. 3. c-axis length vs. T_c for Tl-2201 samples (same format as Fig. 2).

3. $HgBa_2CuO_{4+\delta}$

Less is known about the defect chemistry of Hg-1201 than for Tl-2201. There is general agreement that the defect that most influences T_c is an interstitial oxygen defect in the center of the Hg plane. There are conflicting reports that Cu may substitute at the Hg site with additional oxygen bonded to this Cu [6-8]. In this work, we do not investigate this Hg-site substitutional defect. We focus on the oxy-

gen defect chemistry as the oxygen content is varied over a wide range extending from the underdoped to the overdoped region. We see a remarkable change in the oxygen defect chemistry upon passing through the maximum T_c.

To avoid confusion from possible differences in metal-site defect chemistry, the measurements reported here were performed by oxygen annealing small samples from a single larger sample. Repeated annealings of the same small samples confirmed that the results are reproducible and do not depend significantly on sample history. The oxygen anneals were performed at 300-400° C in oxygen pressures from 10^{-7} to 150 atm. Structural parameters were obtained by Rietveld refinement using neutron powder diffraction data obtained on the SEPD at IPNS [9].

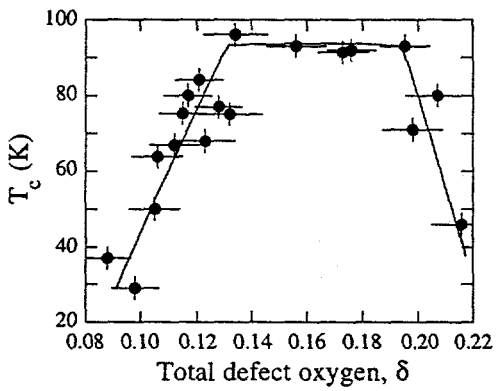

Fig. 4. T_c vs. total defect oxygen content, δ, for Hg-1201 samples annealed in various oxygen environments.

Two slightly different oxygen defects were identified in the Rietveld refinements. One of these is the previously reported interstitial oxygen site in the Hg plane (site O3) [2,6-8]. The second site (O4) is also in the Hg plane, but is at an (x,x,0) site that is displaced towards one of the Hg atoms, and the Hg atom is displaced slightly in the same direction, to form a Hg-O4 bond 2 Å in length.

The T_c vs. total defect oxygen content, δ (combined occupancies of the O3 and O4 sites determined from neutron powder diffraction), is shown in Fig. 4. Data from the present samples are in good agreement with those from the literature, when total defect oxygen contents are used. A surprising feature of the data is the plateau at maximum T_c, where T_c is nominally constant (>90K) for total oxygen contents from 0.13 to 0.19.

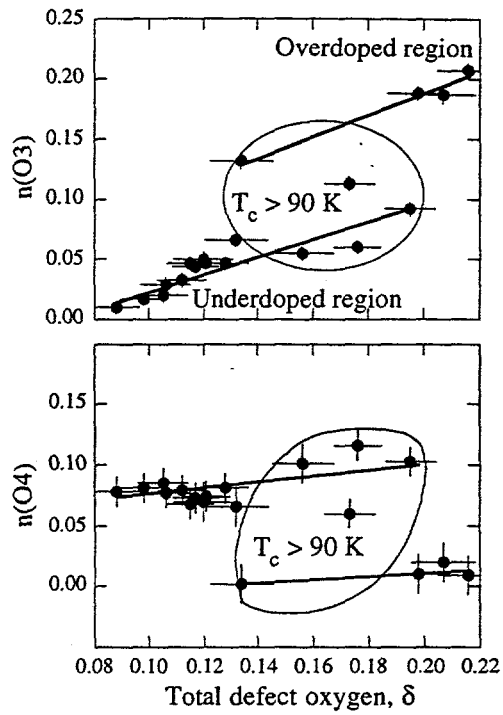

Fig. 5. O3 and O4 oxygen defect concentrations vs. total oxygen defect concentration [δ=n(O3)+n(O4)] for Hg-1201.

This plateau results from an unusual competition between the two oxygen defects, illustrated in Fig. 5. For underdoped samples (δ<0.13), the dominant defect is O4; for overdoped samples (δ>0.19), the dominant defect is O3. This unusual behavior in the defect chemistry also manifests itself in other structural parameters such as cell parameters and positions of the apical oxygen (O2) and Ba atoms. For example, the unit cell volume vs. δ is shown in Fig. 6. The monotonic behavior in the underdoped and overdoped regions is separated by a region (corresponding to T_c>90K) where the cell volume is nominally constant while the total oxygen content is changing.

From the bond lengths, the charge on Cu can be estimated by the bond valence sum method. The result of such a calculation is shown in Fig. 7. The charge on Cu increases with increasing oxygen content in both the underdoped and overdoped regions, but remains nominally constant for the plateau region (0.13≤δ≤0.19) where T_c is constant. Thus, the

T_c is controlled by the number of carriers and the number of carriers remains constant upon passing through the range of oxygen contents where the dominant defect switches from O4 to O3.

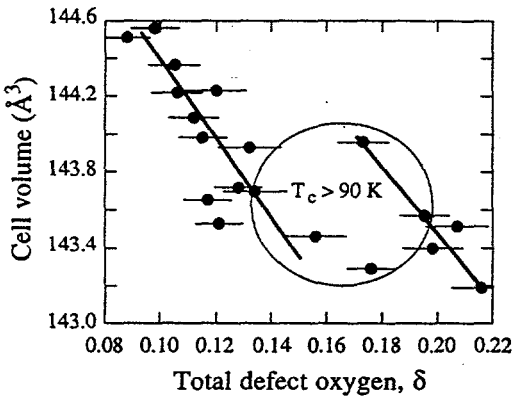

Fig. 6. Unit cell volume vs. total oxygen defect content, δ, for Hg-1201.

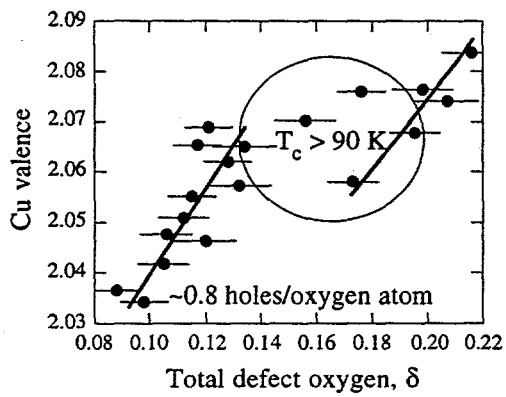

Fig. 7. Bond valence sum for Cu in Hg-1201 vs. total oxygen defect content, δ.

4. CONCLUSIONS

These data suggest that the formation energies for O3 and O4 oxygen defects in Hg-1201 differ by only a small amount and that this delicate energy balance is modified upon passing through the region of maximum T_c. A similar behavior (the appearance of a second oxygen defect in the region of maximum T_c) is suggested by our data for the Tl-2201 system, but the data are much less clear in that case because the underdoped region cannot be accessed. Such behavior could result from crossing the van Hove singularity at maximum T_c. The resulting topological transition in the Fermi surface could affect the defect chemistry by altering bands involving Hg (or Tl). This conjecture remains to be validated; but, if it is correct, the present data may be the first evidence for crossing the van Hove singularity at maximum T_c by varying the chemical composition. Such transitions have not been predicted to result in first-order changes in structural parameters [10]. But, the remarkable behavior observed here could result from the first-order response of the delicately balanced defect chemistry to the changes in electronic structure.

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