Possible Microscopic Doping Mechanism in Tl-2201

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Abstract

X-ray absorption spectroscopy on oxygen-annealed, self-flux-grown single crystals of Tl\textsubscript{2}Ba\textsubscript{2}CuO\textsubscript{6+\delta} suggests a microscopic doping mechanism whereby interstitial oxygens are attracted to copper substituted on the thallium site, contributing holes to both the planes and to these coppers, and typically promoting only one hole to the plane rather than two. These copper substituents would provide an intrinsic hole doping. The evidence for this is discussed, along with an alternative interpretation.

1. Introduction

Among correlated electron systems, high-temperature superconductivity (HTSC) in the cuprates remains the greatest unresolved problem. Their anisotropy and line nodes in the superconducting gap make them highly susceptible to impurities, thus accurate measurements of their electronic properties rely crucially on highly perfect, high-quality single crystals. To maximize homogeneity and fully understand experimental results, the carrier doping mechanism must be understood.

On the less-studied overdoped side of the cuprates’ phase diagram, Tl\textsubscript{2}Ba\textsubscript{2}CuO\textsubscript{6+\delta} (Tl-2201) stands out for its particularly flat CuO\textsubscript{2} plane, a relatively simple crystal structure without (CuO\textsubscript{2})\textsubscript{n} multilayers or CuO chain layers, and for reaching $T_c = 0$. Besides being suitable for bulk transport measurements\textsuperscript{2, 3}, Tl-2201 has a non-polar cleavage plane within its Tl\textsubscript{2}O\textsubscript{3} double layer that allows surface-sensitive single-particle spectroscopies to provide information characteristic of the bulk\textsuperscript{4, 5}. Many details of its chemical doping are understood\textsuperscript{6, 7}, but not how chemical doping effects carrier doping.

In this article, details of Tl-2201’s doping mechanism are inferred from X-ray absorption spectroscopy (XAS) measurements on the copper L edge. This technique measures the absorption of synchrotron X-rays as their energy is tuned through the Cu 2p – 3d atomic absorption edge. These spectra are sensitive to the electronic structure; because of electric dipole selection rules, the polarization-dependence provides information on which orbitals participate in each feature.

2. X-ray Absorption Spectroscopy

Copper L edge XAS data were collected at beamline 8.0.1 of the Advanced Light Source \textsuperscript{8}, with a 0.70 eV energy resolution, via total fluorescence yield, and normalized by incident intensity, then against each other using energy ranges far from the edge. Self-flux grown, oxygen-annealed Tl-2201 single crystals \textsuperscript{9} were studied, using etched square-millimetre-sized as-grown ab-plane faces. Spectra were collected at room temperature on overdoped crystals with $T_c$ of 9.5, 60 and 69 K for several angles between $E$ and $c$ from 0° to 70°, allowing a reliable point-by-point extraction of the $E \parallel c$ main peak weight.

![Figure 1: Doping evolution of Cu L\textsubscript{1} edge E \parallel c main peak weight.](image)

The spectra for $E \parallel c$ at the L\textsubscript{1} edge, associated with excitations into vacant states with Cu3d\textsubscript{3z2-r\textsuperscript{2}} character, are shown in Fig. 1. The left inset demonstrates that this feature’s energy differs from the in-plane peak, indicating a different band or chemical environment. The right inset shows the doping evolution of the peak’s integrated weight.
— hole dopings were extracted from $T_c$ via Presland’s phenomenological formula. This feature’s intensity changes far more rapidly than would be expected if it were proportional to CuO$_2$-plane hole doping, extrapolating to zero at $p \sim 0.18$, not $p \sim 0$.

It may be possible to attribute the anomalously steep increase in $c$-axis weight with doping to the copper substituents present at the 4-8% level in the Tl$_2$O$_2$ double layer. Cu$^{2+}$ in a Ti$^{3+}$ site would provide an intrinsic hole doping, potentially explaining the difficulty in underdoping Ti-2201. An interstitial oxygen atom in the Tl$_2$O$_2$ double layer could create one hole oxidizing a nearby copper substituent to Cu$^{3+}$ and contribute only one hole to the CuO$_2$ plane. Occupancy of this interstitial reaches zero near optimal doping, consistent with the trend observed. However, since only a few percent of thallium sites are occupied by copper and there are at most 0.1–0.15 excess oxygens per formula unit, the odds of an oxygen interstitial being adjacent a copper atom remain low at most dopings. The strength and doping dependence of the observed peak may imply that oxygen dopants preferentially fill sites adjacent copper substituents.

Traversing the overdoped regime (changing $p$ by 0.11 requires changing cation-substituted Ti-2201’s oxygen content by 0.08–0.12 per formula unit, leaving 0.05 to 0.13 holes unaccounted for, consistent with the concentration of copper substituents. Previous reports have linked elevated cation substitution with lower $T_c$, but this remained unexplained.

Such a doping mechanism would have several important implications. First, ensuring a homogeneous dopant distribution may require making the cation dopants homogeneous, significantly more difficult due to their very low mobility. Second, if the oxygen dopants are randomly distributed after a quench from high temperature, and if they are mobile at the storage temperature, the transition temperature should increase over time as oxygens become trapped near copper substituents and supply fewer holes to the CuO$_2$ plane. It may be possible to take advantage of such time-dependence to controllably change the doping with minimal changes to disorder, as has been done for underdoped YBa$_2$Cu$_{3-x}$O$_{6.6-x}$ particles. The addition of new states at the Fermi level may produce new Fermi surfaces (thus far, only CuO$_2$-plane bands have been observed). Such a doping mechanism could also be at work in other compounds, including potentially LSCO.

Alternatively, the extra 3$d_{3z^2-r^2}$ character could originate from the CuO$_2$ plane. Holes doped into the plane are shared amongst oxygen ligands at lower dopings, to avoid the strong copper on-site repulsion. If high ligand hole concentrations produce a high enough oxygen on-site repulsion, some holes may end up on copper atoms, with primarily 3$d_{3z^2-r^2}$ character. This would imply a fundamental breakdown in our current understanding of the doped CuO$_2$ plane, making it a very interesting possibility. More work will be required to determine which picture is correct; observation of dopant-clustering or aging, site-specific studies such as NMR, or the observation of an extra Fermi surface sheet could all help clarify this matter.

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