THE SYSTEM La$_{2-x}$Sr$_x$CuO$_4$

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ABSTRACT. A complex phase diagram for the strontium-doped 214 lanthanum-copper-oxide superconductive system is systematically developed and interpreted. It is argued that below 300 K the superconductive phase is thermodynamically distinguishable from both the antiferromagnetic parent compound and the overdoped metallic phase. The mobile holes introduced by oxidation of the copper-oxide sheets form unconventional polarons characterized by covalent bonding within a polaron and ionic bonding without; molecular-orbital (MO) states inside a polaron are coupled vibronically to localized copper states without. Below 300 K, the polaron gas is unstable relative to the formation of a distinguishable normal state consisting of coupled polarons having extended vibronic states with a Fermi surface near the locus predicted by band theory, but with a band splitting at the half-band position.

1. INTRODUCTION

The superconductive system La$_{2-x}$Sr$_x$CuO$_4$, $0 \leq x \leq 0.34$, has been extensively studied both because of the relative simplicity of its crystal structure and because it can be prepared over the entire compositional range in which superconductivity is found. The parent compound La$_2$CuO$_4$ is an antiferromagnetic insulator, the overdoped samples with $x > 0.28$ are metallic with no apparent transition to superconductivity at lowest temperatures. The superconductive compositional range with maximum critical temperature $T_C$ is confined to the narrow compositional range $0.10 < x < 0.22$; I shall argue that this compositional range represents, in the temperature interval $T < 300$ K, a unique phase that is thermodynamically distinguishable from the antiferromagnetic phase of the parent compound on the underdoped side and from the metallic phase on the overdoped side. Moreover, in this system $x = p$ gives unambiguously the number $p$ of holes per Cu atom in the CuO$_2$ sheets; it appears that the maximum values of $T_C$ for all the $p$-type superconductors are found in the range $0.10 < p < 0.22$ holes per Cu atom in the superconductive CuO$_2$ sheets. I shall also argue that what makes the superconductive phase distinguishable is a condensation of an intermediate-size-polaron gas below 300 K to a polaron liquid in which extended vibronic states are formed that have a momentum vector $k$, an energy dispersion, and a Fermi surface locus in momentum space near that predicted by Fermi-liquid theory (FLT). However, molecular-orbital coupling within a polaron introduces an energy gap at the half-band position separating bonding from antibonding states within a polaron. This unusual electron-phonon coupling allows the system to accommodate to a coexistence of ionic and covalent Cu-O bonding.
FIG. 1. The structure of La$_2$CuO$_4$: (a) tetragonal T > T$_t$ phase and (b) cooperative CuO$_6$ rotation (arrows) in orthorhombic T < T$_t$ phase. In (a), x marks position of interstitial oxygen in La$_2$CuO$_4$+$\delta$.

2. THE La$_{2-x}$Sr$_x$CuO$_4$ PHASE DIAGRAM

At high temperatures, stoichiometric La$_2$CuO$_4$ has the tetragonal structure of Fig. 1; it consists of an intergrowth of CuO$_2$ planes containing 180° Cu-O-Cu bonds alternating with (001) rock-salt bilayers of LaO. We represent the structure as

\[
\text{LaO} \text{LaO} \text{LaO} \text{LaO} \text{CuO}_2 \text{LaO} \text{LaO} \text{LaO} \text{CuO}_2
\]

where the vertical lines represent the interfaces between intergrowth layers on traversing the c-axis. In this structure, the bond-length mismatch across an interface is expressed by a tolerance factor

\[
t = (\text{La-O}) / \sqrt{2} (\text{Cu-O})
\]

where La-O and Cu-O are the equilibrium bond lengths. Because the La-O bond has the larger thermal expansion, t decreases with decreasing temperature; at room temperature, a t < 1 can be calculated from the sums of the ionic radii. A t < 1 places the CuO$_2$ sheets under compression and the LaO-LaO layers under tension; below a transition temperature T$_t$ = 540 K, a cooperative rotation of the CuO$_6$ octahedra about [110] axes (arrows in Fig. 1) distorts the crystal from tetragonal to orthorhombic symmetry so as to relieve the internal stresses. The rotation bends the Cu-O-Cu bonds from 180° and creates some shorter La-O bonds.

The internal stresses are also relieved by an ordering of the 3d hole on the Cu$^{2+}$ : 3d$^9$ configuration into an $x^2$ - $y^2$ orbital (x and y axes directed towards nearest-neighbor Cu atoms of