The Hole Concentration on Oxygen Sites in the High $T_c$ Superconductor $Y_1 - Ba_2 - Cu_3 - O_{7-x}$

P. Steiner$^1$, S. Hüfner$^1$, V. Kinsinger$^1$, I. Sander$^1$, B. Siegwart$^1$, H. Schmitt$^2$, R. Schulz$^2$, S. Junk$^3$, G. Schwitzgebel$^3$, A. Gold$^4$, C. Politis$^5$, H.P. Müller$^6$, R. Hoppe$^6$, S. Kemmler-Sack$^7$, and C. Kunz$^8$

$^1$ Fachrichtung Experimentalphysik, Universität des Saarlandes, Saarbrücken, Federal Republic of Germany
$^2$ Fachrichtung Technische Physik, Universität des Saarlandes, Saarbrücken, Federal Republic of Germany
$^3$ Fachrichtung Physikalische Chemie, Universität des Saarlandes, Saarbrücken, Federal Republic of Germany
$^4$ Fachbereich Physik, Technische Universität München, Federal Republic of Germany
$^5$ Institut für Nukleare Festkörperphysik, Kernforschungsanlage Karlsruhe, Federal Republic of Germany
$^6$ Institut für Anorganische Chemie, Universität Gießen, Federal Republic of Germany
$^7$ Institut für Anorganische Chemie, Universität Tübingen, Federal Republic of Germany
$^8$ Firma Villeroy und Boch, Mettlach, Federal Republic of Germany

Received October 14, 1987

From XPS core level spectroscopy the average copper charge on the Cu sites in the high temperature superconductor $Y_1 Ba_2 Cu_3 O_{7-x}$ is determined as function of the oxygen vacancy concentration $x$. Analysis of these data leads to the suggestion that there are holes on the oxygen sites in the basal plane of the crystal structure. The probability for holes on these oxygen ions is rather constant for $0 \leq x \leq 0.3$ with a value of 0.64 and decreases to zero for $x = 0.5$. The dependence of the superconducting transition temperature on the hole concentration is discussed. An energy level diagram for $Cu^{2+}$ and $Cu^{3+}$ in $YBa_2Cu_3O_{7-x}$ is constructed.

Introduction

The discovery of high temperature superconductivity in ceramic compounds with transition temperatures around 40 K by Bednorz and Müller [1] was soon followed by the discovery of ceramics based on the $Y-Ba-Cu-O$ system with transition temperatures around 90 K [2]. This stimulated large research activities both experimentally and theoretically [3]. Until now the physical origin for the extraordinary properties of these systems is unclear. In this communication we present results, based mainly on XPS core level spectroscopy, which show that in well prepared samples of $Y_1 Ba_2 Cu_3 O_{7-x}$ ($0 \leq x \leq 0.8$) both $Cu^{3+}$ and $Cu^{1+}$ can be detected, together with the dominant $Cu^{2+}$ species. Their concentration depends on the annealing conditions of the samples, which is now known to tune reversibly the oxygen defect concentration $x$.

Many investigations have shown [4] that oxygen annealing at low temperatures between 300°C–500°C is essential for a good quality of the superconducting ceramic samples. The crystal structure of the $Y_1 Ba_2 Cu_3 O_{7-x}$-compound has been established by x-ray diffraction [5], neutron diffraction [6] and high resolution transmission electron microscopy [7]. This
structure is sketched in Fig. 1 for clarity. It consists of a cubic triple perovskite with an ordered Y-Ba-Y stacking along the c-axis. The Cu ions are
located at two inequivalent lattice sites. One is Cu(1) – which is located between two BaO layers has a planar corner shared coordination with 4 oxygen ions – O(1) and O(4) – within the c-a plane. The oxygen sites on the a-axis between the two Cu(1) atoms are completely empty in the orthorombic superconducting phase with b > a. The second Cu site is Cu(2) at z = 0.35 – is again nearly planar coordinated to four oxygen ions parallel to the a-b plane – O(2) and O(3) – with a slight buckling of the oxygens towards the Y-ion. The Cu(2) – O(1) distance with ~2.3 Å is much larger than the Cu(2) – O(2, 3) distance of ~1.94 Å. This latter coordination of the Cu(2) site is very similar to the one in CuO and therefore the Cu(2) is believed to be in a Cu$^{2+}$ valence state. While the Cu(1) – O(4) distance is also around 1.94 Å, the Cu(1) – O(1) distance is only 1.86 Å. This bonding is typical for Cu$^{3+}$ as in NaCuO$_2$. Using formal oxidation states Y$^{3+}$, Ba$^{2+}$, O$^{2-}$ – which are the only stable oxidation states of these ions – one arrives at the conclusion that 30% of the Cu ions should be in a formal Cu$^{3+}$ charge state in the fully oxygenated compound (with x = 0).

From the above arguments it is believed that it is the Cu on the Cu(1) site which is Cu$^{3+}$. When equilibrated in temperatures above 600 °C and quenched to room temperature [4, 9] oxygen can reversibly be removed from the structure up to x ≈ 1 (or even more), depending on the equilibration temperature and oxygen partial pressure. Neutron spectroscopy has shown [6] that mainly the O(4) oxygen sites are emptied in this procedure, with the conclusion that the Cu(1) ions are successively reduced from Cu$^{3+}$ to Cu$^{2+}$, being purely Cu$^{2+}$ at x = 0.5, where the crystal transforms from the orthorombic to a tetragonal structure with a = b, and even to Cu$^{1+}$ for x > 0.5 with purely Cu$^{1+}$ at x = 1. In this situation Cu(1) is twofold coordinated to O(4), a situation which is similar to Cu$^{1+}$ in Cu$_2$O. The good superconducting properties decrease or even vanish when x ≥ 0.5 It has therefore been speculated, that the presence of Cu$^{3+}$ is essential for the good superconducting properties of the samples.

Numerous attempts to detect the Cu$^{3+}$ directly by XPS spectroscopy [10], X-ray absorption spectroscopy [11] or electron spin resonance spectroscopy [12] gave controversial results. In most cases only little Cu$^{3+}$ could be detected even for samples, which were good superconductors with a $T_c$ ≈ 90 K, for which the oxygen content should be close to x = 0.

Conversely in samples with small oxygen content 0.5 ≤ x ≤ 1, where by simple ionic arguments Cu$^{1+}$ should be present, this species could not be detected. We have performed XPS core level measurements together with $T_c$ measurements (DC-resistivity and AC-susceptibility) on samples annealed under 1 bar flowing oxygen at temperatures between 350 °C and 1000 °C for about 15 h, and subsequently quenched to room temperature. The main results will be presented here. A full documentation of these experiments will be given in a forthcoming longer paper [13].

At this point it is seems useful to discuss in more detail the question of the valency of the Cu ions because it has become quite a controversial point and in addition the nonobservation of Cu$^{3+}$ has been puzzling to some researchers.

The electronic structure of a system like YBa$_2$Cu$_3$O$_{7-x}$ can, with respect to the Cu ion, be described to a first rough approximation by a molecular orbital approach involving the Cu 3d electrons and the oxygen ligands (L). Thus for YBa$_2$Cu$_3$O$_{6.5}$, assuming that all the Cu ions are divalent, the groundstate would be $3d^9 + 3d^{10}$. Here $L^{-1}$ is a hole in the oxygen ligand band. Conversely for x < 0.5, the Cu$^{3+}$ ions would have a groundstate $3d^8 + 3d^9 L^{-1}$. It is, however, known from photo-emission data that in CuO, which is electronically probably not too different from the situation found in YBa$_2$Cu$_3$O$_{6.5}$, the $3d^8$ configuration is ~10 eV above the $3d^9 + 3d^{10} L^{-1}$ groundstate. If therefore in the range 0 ≤ x ≤ 0.5 formally Cu$^{3+}$ ions are produced their wavefunctions will be dominated by the $3d^9 L^{-1}$ component because of the high excitation energy of the $3d^8$ configuration. For the conductivity in YBa$_2$Cu$_3$O$_{7-x}$ with x < 0.5 this means that it is pro-