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NUCLEAR HYPERFINE INTERACTIONS AND CHEMICAL BONDING  
IN HIGH  $T_C$  SUPERCONDUCTORS\*

by

J. Danon

Centro Brasileiro de Pesquisas Físicas - CNPq/CBPF  
Rua Dr. Xavier Sigaud, 150  
22290 - Rio de Janeiro, RJ - Brasil

Present address:  
Observatório Nacional  
Rua General Bruce, 586 - São Cristóvão  
20921 - Rio de Janeiro, RJ - Brasil

\*In homage to Ricardo Ferreira for its 60<sup>th</sup> birthday.

## ABSTRACT

Nuclear quadrupole resonances of  $\text{Cu}^{63}$  and  $\text{Fe}^{57}$  Mössbauer spectroscopy of the high temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\gamma}$  are described together with synchrotron radiation studies of the copper oxidation states in this material. The Mössbauer spectra of  $^{57}\text{Fe}$  in the two distinct crystallographic sites of the Cu atoms in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\gamma}$  are very similar from the quadrupole coupling point of view although exhibiting markedly different values for the isomer shift. The role of oxygen vacancies in the hyperfine interactions is discussed.

Key-words: High temperature superconductor; Nuclear hyperfine interaction; Nuclear quadrupole resonance; Mössbauer spectroscopy.

The discovery of superconductivity above 90 K in the oxides Y-Ba-Cu-O has generated experimental and theoretical excitement on an unprecedented scale. There is no doubt that this discovery has been quite unexpected and an explanation of these extraordinary high  $T_c$  has defied all theoretical efforts. There is a contrast between the highly sophisticated theories of superconductivity and the chemical complexity of such ternary oxides. These include dissimilar elements such as rare-earths, alkali-earths and a transition element, besides structural and solid state defects which probably are relevant for the presence of the superconductive state. In such situation the use of chemical concepts related to valence, ionic radii etc., such as electronegativity and others can be powerful for elucidating these kind of phenomena. Moreover, if one of the aims of a theoretical explanation is its predictive character, solid state chemistry has shown in the last years an impressive development and it become possible now in many instances to choose the materials which are most appropriate to provide the desired properties. As regards the high  $T_c$  superconductors the situation can be illustrated by the title of a recent paper<sup>1</sup>: "High  $T_c$  superconductivity - a chemical phenomena".

If we analyse the hundreds of papers<sup>2</sup>, most in the form of pre-prints, since the beginning of this year, we are also puzzled by the fact that practically any of them report work involving hyperfine interactions. Possibly this is due to the fact that several limitations exist for the use of these techniques, which can be summarized as follows:

1 - In nuclear hyperfine interactions the nucleus is a probe for electron-nuclear interactions. The phenomena of electrical conductivity involve electrons which participate in bands and are in a certain sense "distant" from the nucleus. In other words, the nuclear interactions are not very sensitive to conduction phenomena and in the past only very limited correlations have been found between the superconductivity transition and nuclear hyperfine parameters.

2 - In the new high  $T_c$  oxides only the rare-earths present a variety of nuclear transitions which are adequate for hyperfine interactions measurements. Among the alkali earths no practical isotope exists for hyperfine experiments and Cu has isotopes which are adequate for microwave measurements such as nuclear quadrupole resonance (NQR).

In spite of these limitations, we will describe recent Mössbauer and nuclear quadrupole resonance experiments which give relevant information on the electronic and structural properties of the Y, Ba, Cu, O superconductors.

The relevance of the Cu ions in these superconductor oxides is illustrated by the fact that one can prepare high  $T_c$  superconductors with a variety of rare-earths and by substitution of Ba for Sr, but none has been obtained by eliminating the Cu ions.

By detailed X-ray and neutron diffraction measurements the structure of the most popular of these high  $T_c$  superconductors,  $Y Ba_2 Cu_3 O_{7-\gamma}$  where  $\gamma$  represents the oxygen deficiency in this oxide, has been precisely determined.<sup>3,4,5</sup> In this perovskite structure the Cu atoms occupy two distinct crystallographic sites. One site Cu (1) is surrounded by a square planar oxygen configuration. The second site Cu (2) is fivefold coordinated by a square pyramidal arrangement of oxygens. This site has double occupancy in the unit cell structure. The Cu atoms in this structure can be visualised as forming planes and chains. One of the main question which arises is the following: what are the oxidation states and the bonding characteristics of these two type of Cu atoms?

The relevance of this question for a theoretical explanation of superconductivity has been analysed by L. Pauling in a recent paper.<sup>6</sup>

In its oxides and other compounds, Cu copper has three oxidation states,  $Cu^I$ ,  $Cu^{II}$ , and only rarely  $Cu^{III}$ . Let us fix on the trivalent state of Cu. Two important papers on this rather rare oxidation state of Cu have been published about 15 years ago.<sup>7,8</sup> Under oxygen pressure a new  $Cu(III)$  compound  $Sr La Cu O_4$  has been prepared and from X-ray structure and magnetic measurements the low-spin state of  $Cu^{III}$  has been characterized.

The situation of the valence state of copper in the superconducting oxides is still controversial.

From structural analysis of the neutron diffraction data it has been concluded that  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  ions preferentially occupy the square pyramidal Cu(2) and square planar sites. An explanation for the occurrence of Cooper pairs is the disproportionation of  $(d^9)\text{Cu}^{2+}$  into  $(d^{10})\text{Cu}^+$  and  $(d^8)\text{Cu}^{3+}$ . This leads to an electron configuration of  $(d_{x^2-y^2})^0$  and  $(d_{x^2-y^2})^2$  on alternate copper sites, which is equivalent to a dynamic localization of electron pairs. The dynamic emptying and filling of the  $d_{x^2-y^2}$  orbitals is then involved in the superconduction mechanism.

The presence of  $\text{Cu}^{3+}$  has been identified using the NSLS synchrotron radiation source by Cu K-edge X-ray absorption near-edge structure, comparing oxides of monovalent, divalent and trivalent copper with  $\text{L}_{a2-x}(\text{Sr},\text{Ba})_x\text{CuO}_y$  superconductor<sup>9</sup>.

However, recent XPS and UPS photoemission experiments with  $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$  have revealed only a  $\text{Cu}^{2+}$  contribution and the presence of mixed  $\text{Cu}^{2+}/\text{Cu}^{3+}$  valence state in these superconductors is denied<sup>10</sup>.

$\text{L}_{2,3}$  XANES by using synchrotron radiation of LURE of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  with variable oxygen content denies also the presence of  $\text{Cu}^{3+}$  ions with a  $3d^8$  configuration<sup>11</sup>. Evidence for  $\text{Cu}^{2+}\text{O}^-$  pairs and  $\text{Cu}^+\text{O}^-$  pairs is provided. No energy gap is observed between the  $\text{Cu}^{+1}(3d^9\text{L})$  and  $\text{Cu} 3d^{10}\text{L}$  configuration like in  $\text{Cu}^+\text{O}^-$  pairs where L indicates a hole in the oxygen derived valence band. This is a direct consequence of a very large metal oxygen covalency, which is in fact confirmed by several theoretical calculations of the copper-oxygen bands  $3d - 2p$  in these oxides<sup>12</sup>.

These results are in agreement with photoelectron core level spectra (XPS) of the single phase superconductor  $YBa_2Cu_3O_{7-\gamma}$ . Although the presence of non-equivalent Cu sites, fivefold coordinated Cu(2) and fourfold coordinate Cu(1) sites in the  $YBa_2Cu_3O_{7-\gamma}$  crystal structure the Cu ions are presumed to exhibit an homogeneous valence state<sup>13</sup>. The formation of  $Cu^{2+}O^-$  pairs is preferred to the formation of  $Cu^{3+}$  ions with  $3d^8$  configuration. As mentioned above, oxygen should form holes in the oxygen band with increasing concentration of  $3d^9L$  configuration. The mechanism of conductivity in the high  $T_c$  superconductor could then be associated with the holes in the oxygen valence band which form both  $3d^{10}L$  and  $3d^9L$  configurations i.e.,  $Cu^+O^-$  and  $Cu^{++}O^-$  pairs.

The role of microstructure vacancies and oxygen ordering in these high  $T_c$  superconductors has been emphasized after results from high-temperature X-ray diffraction studies showed a transition from orthorhombic to tetragonal structure at about  $750 K$ <sup>14</sup>. The tetragonal phase is stabilized by a rapid quenching of the material. This quenched sample has a much higher resistivity and  $T_c$  is considerably depressed.

These results indicate that most of the vacancies are formed in the sublattice containing Cu-O chains, which play a relevant role in the high temperature superconductivity.

It is interesting to observe that the question remains if it is oxygen ordering or the presence of  $Cu^{3+}$ , copper in a trivalent oxidation state which is responsible

for the high temperature superconductivity. The nuclear hyperfine investigations can give some informations about this questions.

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) can be performed directly in the  $YBa_2Cu_3O_{7-\gamma}$  superconductor. Mössbauer spectroscopy in this superconductor doped with Fe-57 can give structural and chemical informations on this oxide, particularly by comparing with the hyperfine interactions measured at the Cu nuclei.

NQR of a superconductive sample ( $T_c = 89.5$  K) with an oxygen deficiency of  $\gamma = 0.02$  has been obtained<sup>15</sup> at 170K and two pairs of lines were found at 20.5, 22 MHz and 28.7, 31.2 MHz respectively. Each pair corresponds to the  $^{65}\text{Cu}$  and  $^{63}\text{Cu}$  resonances of a particular site as evidenced by the frequency and intensity ratios of magnetic moments and abundances of the isotopes. The site giving  $^{63}\text{Cu}$  resonance at 22.0 MHz is referred as site A and that at 31.2 MHz as site B. The intensity of site B is three to four times less than that of site A.

A second sample of  $YBa_2Y_3O_{2-\gamma}$  has been prepared by further annealing of the previous sample in oxygen atmosphere. NQR of this sample showed a resonance at the same 22.0 MHz position, but with much narrow linewidth. This sample is still under investigation.

A tentative assignement of sites A and B to crystallographic sites can be made by taking into account that in the unit cell of  $YBa_2Cu_3O_7$  structure there are two inequivalent Cu sites. Site A with 22.0 MHz most probably



corresponds to the more abundant Cu site situated in the Cu-O planes, with five-fold oxygen coordination and a nearly tetragonal symmetry, which is agreement with the asymmetry parameter  $\eta = 0$  in the NQR spectrum.

Site B with 31.2 MHz and  $\eta \neq 0$  corresponds to the square planar oxygen configuration which forms the Cu-O chains. The larger quadrupole resonance in this site can be attributed to the presence of the oxygen vacancies. Neutron diffraction studies indicate that these vacancies concentrate at site B, which will clearly induce a larger efg at the Cu nucleus<sup>16</sup>.

These results are to be compared with the Mössbauer spectra of <sup>57</sup>Fe doped  $YBa_2Cu_3O_{7-\gamma}$ , prepared by the solid state reaction with respective oxides. With diluted Fe proportions ( $\leq 1\%$ ) obtained with highly enriched <sup>57</sup>Fe, the resulting material remains superconductor with practically no decrease in  $T_c$ . Several groups have investigated the Mössbauer spectra of such samples, treated in a variety of oxygen conditions.<sup>17,18,19,20</sup> A detailed Mossbauer investigation of the role of oxygen vacancies has been recently performed<sup>21</sup>.

The Mössbauer spectrum results mainly from several quadrupole splitted ( $\Delta E$ ) lines, with relative intensity which is markedly dependent on the oxygen treatment of the sample. The isomer shifts (IS) relative to Fe metal for both spectra are either close to zero or assume negative shift values. We shall discuss the meaning of these IS values in a next paper. The spectra exhibit the usual variation of  $\Delta E$  and IS with temperature and no particular changes are confirmed on going through the superconductive state.

The Mössbauer spectrum can be more clearly assigned in two distinct situations.

- a - with samples quenched from high temperature in which the tetragonal phase is stabilized and with large concentration of oxygen vacancies. In this situation the spectrum is dominated by the presence of a quadrupole interaction  $\Delta E \sim 2 \text{ mm.s}^{-1}$  and IS  $\sim 0.0 \text{ mm.s}^{-1}$ .
- b - with well oxygenated samples, exhibiting high  $T_c$  superconductive behaviour, with orthorhombic phase stabilized. In this situation the Mössbauer spectrum is dominated by two pair of doublets, with large overlap, giving the values  $\Delta E_1 = 1.54 \text{ mm.s}^{-1}$  and IS =  $-0.15 \text{ mm.s}^{-1}$  and  $\Delta E_2 = 1.60 \text{ mm.s}^{-1}$ , IS =  $+0.20 \text{ mm.s}^{-1}$ . Spectrum 1 present about the double intensity of that of spectrum 2.

On the basis of the intensity ratio has been attributed to spectrum 1 to site A (Cu-O planes) and spectrum 2 to site B (Cu-O chains).

The important point here is that the Mössbauer spectra of  $^{57}\text{Fe}$  in the two distinct crystallographic sites of the Cu atoms in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are very similar, from the quadrupole splitting point of view (although they are markedly distinct from the IS point of view).

The large  $\Delta E$  observed in the tetragonal phase possibly arises from the additional contribution to the efg originating from oxygen vacancies, which, as has been mentioned before, concentrates at site B (Cu-chains).

Further confirmation of this interpretation arises from the observation that the ratio of the two NQR frequencies of  $^{63}\text{Cu}$  for sites A and B (in tetragonal symmetry)  $\frac{\nu_A}{\nu_B} = \frac{22}{31.2} = 0.7$  is about the same as the ratio of quadrupole splittings  $\Delta E_A / \Delta E_B = 1.6 / 2.0 = 0.8$ .

These ratios represent the ratio of values of the electric field gradient in both sites. The fact that the values are about the same for  $^{63}\text{Cu}$  and  $^{57}\text{Fe}$  means that these nuclei are interacting with about the same efg in each site.

The efg arises from contributions of the electronic configuration of the atom and from external charge distribution at the site. It is thus possible that the main contribution to the efg arises from the structure of the copper sites, the role of oxygen vacancies being dominant in this respect.

## FIGURE CAPTIONS

- FIGURE 1 - Orthorhombic and tetragonal phases of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .  
Note the disordering of the chains and that the oxygen are drawn with dotted lines indicating partial (<5%) occupancy in the tetragonal phase.
- FIGURE 2 - Nuclear quadrupole resonance spectra at 170 K, (ref.15)  
Sample I - oxygen deficient.  
Sample II- after further oxygenation of sample I.

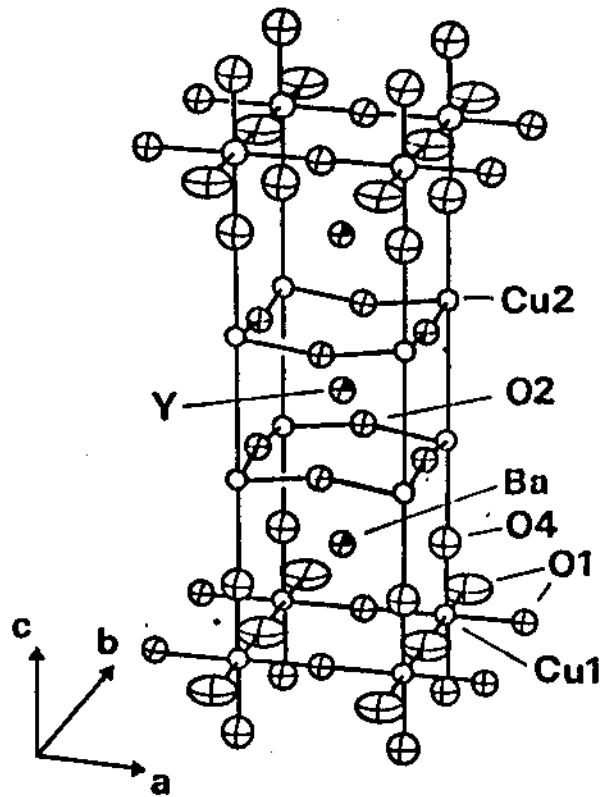
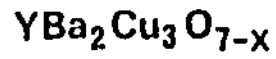
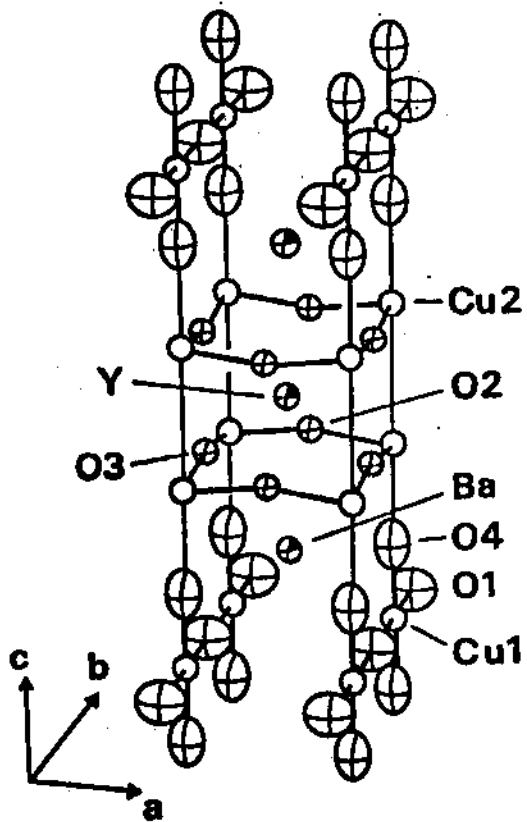


FIGURE 1

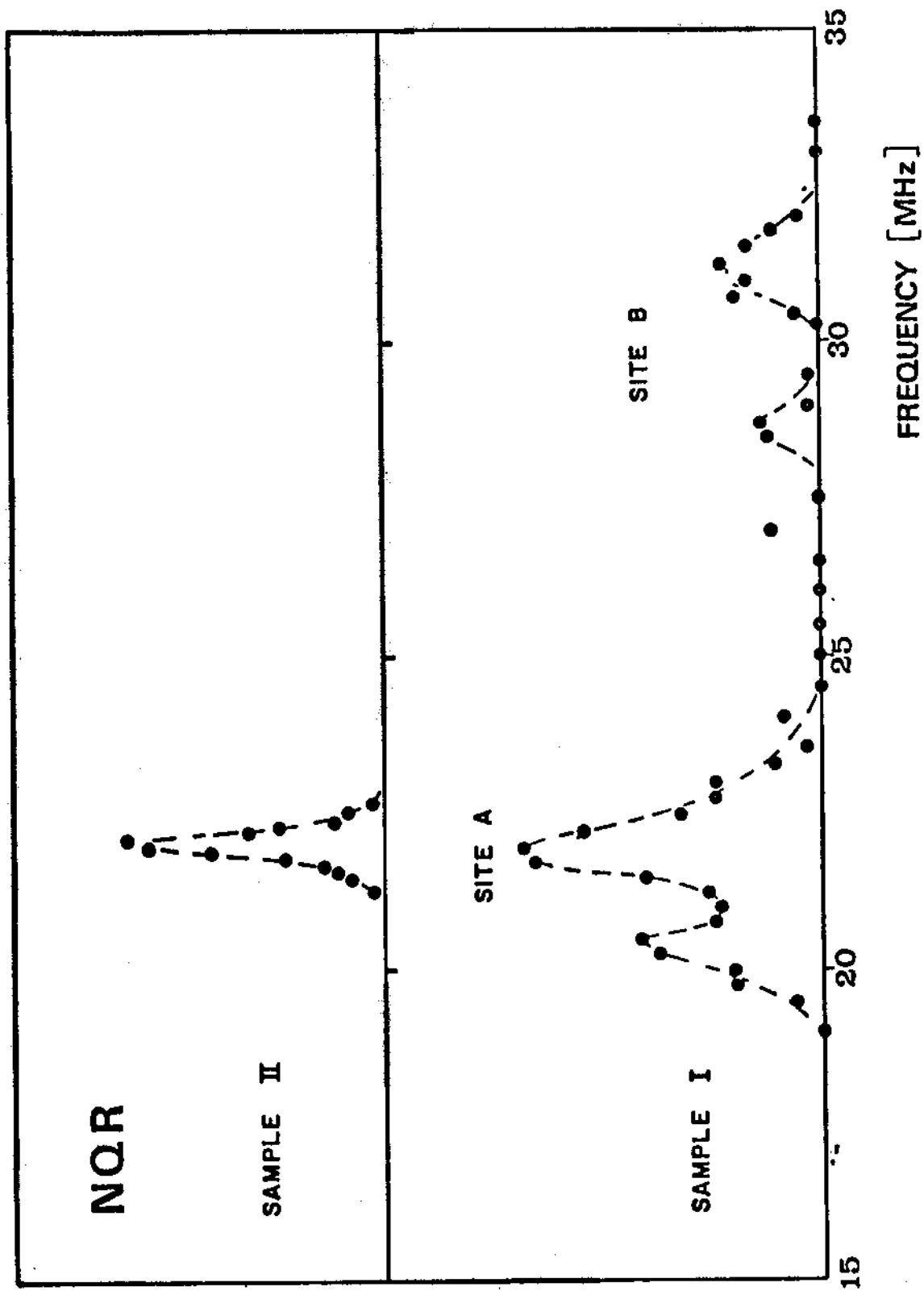


FIGURE 2

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