

ANTIFERROMAGNETISM IN HYDRATED 123 COMPOUNDS

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Copper nuclear quadrupole resonance and zero field nuclear magnetic resonance studies of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ show that a magnetic phase appears in underdoped 123 superconductors treated in ambient wet air. The studies give convincing evidence that the "empty" CuO chains play the role of easy water insertion channels. The reaction occurs first in ordered regions of the crystallites. The final product of the reaction is a non-superconducting antiferromagnetic compound characterized by at least two types of magnetically ordered copper ions with ZFNMR spectra respectively in the frequency ranges of 46-96 and 96-135 MHz respectively. Even for powder samples fixed in an epoxy resin, the reaction is found to occur partly after a few years.

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The idea of co-existence of superconductivity and local antiferromagnetism in high-temperature superconductors (HTSC) is appearing more and more frequently in theoretical and experimental papers. Recently we found [1] that in aged samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x < 0.8$ packed in paraffin and kept at room temperature for about 6 years the superconducting volume fraction had essentially decreased. In the same samples, we also found, along with the typical copper nuclear quadrupole resonance (NQR) spectrum of the superconducting 1-2-3 system, copper zero field nuclear magnetic resonance (ZFNMR) spectra in the frequency range 46-135 MHz, indicating the presence of a magnetically ordered phase which remains observable up to 200 K.

The initial goal of this study was to find a way of artificially aging the compound to produce the magnetic phase. At the time of our previous report [1], we considered the presence of the magnetic phase as a result of stripe pinning due to the Ortho-III phase, which was well-ordered during the very long-term room temperature annealing, so we began the artificial aging experiments with attempts to accelerate the oxygen ordering process. It is known [2] that the temperature boundary of the Ortho-III phase is about 75 °C, so the first experiments were devoted to annealing at 55-60 °C for a few weeks, but this failed to produce the magnetic phase. Thus, further attempts were undertaken at somewhat higher temperatures. Finally we managed to get a small amount of magnetic phase exhibiting the characteristic ZFNMR spectra [1]. However, the mass of the samples during the ambient air annealing had increased, and controlled annealing of dry powder sealed in an ampoule showed neither the mass changes nor the appearance of the magnetic phase.

The most natural explanation of the mass increase is the occurrence of a chemical reaction of YBCO with components of the air, in particular, with water vapour, since the significant reactivity of 123 with water is well established. Most of the early papers on the reaction of 123 with water reported reaction products such as Y_2BaCuO_5 ("green phase"), CuO , BaCO_3 and some others. Some of these compounds are antiferromagnets having either low Néel temperature (15-30 K) or ZFNMR spectra very different from the one we observed in Ref.[1]. More recent studies (see Ref.[3] and references therein) using high-resolution electron microscopy and X-Rays have shown that the 123 superconductors react with water vapour via a topotactic mechanism. The final product of this reaction, occurring in a bulk material at 75–250 °C, is a so-called pseudo-248 phase $\text{H}_{2z}\text{YBa}_2\text{Cu}_3\text{O}_{6+z+z}$ (isostructural with the familiar 248 structure but with 50% of the Cu(1) sites vacant and referred to as phase *B* in Ref.[3]).

To study the changes occurring in 123 HTSC under reaction with water vapour by NQR and NMR a number of samples with different water content were prepared. As starting material, we used samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ ($T_c=56$ K) in the form of free powder with a particle size of about 30 μm , freshly synthesized using conventional solid state reaction of powdered Y_2O_3 , BaO and CuO at about 940 °C interrupted periodically for grinding. The free powder annealing was done in air at 150 °C. A vapour pressure (about 35 mbar at 150 °C) was established in a closed furnace by evaporation. The samples were weighed periodically to measure the water uptake. After annealing all samples were packed in Stycast 1266A epoxy. With this procedure, we obtained a number of samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}(\text{H}_2\text{O})_z$ with water concentrations $z = 0; 0.14; 0.24; 0.55$ and 1.2, the last value being the maximum water uptake, beyond which further annealing did not yield a mass increase.

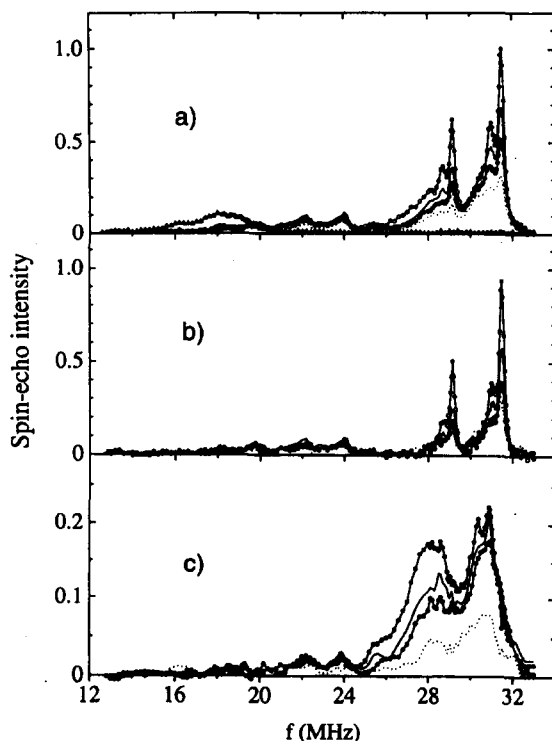


Fig.1. Copper NQR spectra for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ with different water uptake z (open circles, solid line, solid circles, dotted line and open triangles correspond to $z = 0; 0.14; 0.24; 0.55$ and 1.2, respectively): a) as-taken spectra; b) slow-relaxing part of the spectra (Cu(1) spectra); c) fast-relaxing part. For details see text

Home-built pulsed NMR spectrometers were used to measure NQR and ZFNMR spectra at 4.2 K. The copper NQR spectra of the free-powder annealed samples are shown in Fig.1. Since the nuclear spin-lattice relaxation rate of the "chain" copper is significantly slower than that of the "plane" copper [1], it is possible to separate their spectra (Fig.1b,c). The large difference in their transverse relaxation rates can also be used for separation. The assignment of different NQR lines to the nuclei of Cu(1) residing in different oxygen coordinations is done in Ref. [4]. The fast relaxing part of the copper NQR spectrum (Fig.1c) is usually assigned to the plane copper nuclei. It consists of two groups of lines at frequencies 30.8 and 28 MHz for the isotope $^{63}\text{Cu}(2)$. To simplify the discussion, hereafter we will discuss only the frequencies and intensities of the NQR lines for this isotope; naturally, the corresponding ^{65}Cu lines are also observed.

One can see in Fig.1 that the intensity of the copper NQR spectrum decreases with increasing water uptake. It is remarkable that at the initial stage of the reaction (at a small water uptake) the narrow ^{63}Cu NQR lines at 31.5 and 31 MHz, i.e. the lines of $^{63}\text{Cu}^+$ nuclei belonging to the "empty" ... - Cu - Cu - ... chains located between two "full" ... - Cu - O - Cu - ... chains (31.5 MHz, Ortho-II phase) and between "full" and "empty" chains [4], begin to disappear first. At the same time the broad fast-relaxing line at 28 MHz (the plane $^{63}\text{Cu}^{2+}(2)$) also decreases. At water uptake of approximately 0.5 molecules of H_2O per $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, the narrow lines of Cu(1) and the Cu(2) line at 28 MHz are practically absent in the NQR spectrum, and the intensity of the NQR line of Cu(2) at 30.8 MHz has decreased by a factor of 2 compared to the unreacted compound. The intensity of the NQR line belonging to the triply-coordinated copper nuclei (located at the ends of the chains, 24 MHz) doesn't change significantly, though a small increase of its intensity at the first stages of water uptake was noted. At maximum water uptake (1.2 molecules) the copper NQR spectrum typical for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ has disappeared, giving way to a broad copper NQR line at 18.4 MHz.

The copper ZFNMR spectra of free-powder annealed samples are shown in Fig.2. At small water uptake ($z < 0.5$) the spectrum, as in Ref.[1], consists of two groups of well-resolved lines. The low-frequency group (46-96 MHz) resembles the Cu(2) ZFNMR spectrum of antiferromagnetic $\text{PrBa}_2\text{Cu}_3\text{O}_7$ [5] and corresponds to a hyperfine magnetic field of ~ 64 kOe at the copper nucleus and quadrupolar frequency of $\nu_Q \approx 30$ MHz. A field of about 103 kOe and $\nu_Q \approx 16$ MHz produces a high-frequency group (96-135 MHz), this part of the spectrum is practically identical to that of the Nd_2CuO_4 antiferromagnet [6]. The relative intensity of the two groups corrected for the difference in transverse relaxation rate and the (square) frequency dependence is estimated to be $I_{LFG}/I_{HFG} = 1 \pm 0.5$.

The intensities of both groups of the spectrum scale with water uptake for $z < 0.5$ (Fig.2b), while for $z > 0.5$ a new component appears and grows to maximal intensity in the sample with maximum water uptake. Although the separate lines of this component are not well-resolved, it can be assigned to copper nuclei located in a hyperfine field of approximately 80 kOe, just like in $\text{YBa}_2\text{Cu}_3\text{O}_6$ compound.

Changes in the superconducting volume fraction were determined by measuring ac diamagnetic susceptibility ($H_1 \approx 1$ Oe, $f = 1$ kHz). The superconducting volume fraction decreases with water uptake (Fig.3) while T_c remains practically unchanged. The sample with maximum water uptake is completely non-superconducting.

So, in accordance with [3], we conclude that insertion of water into a 123 compound proceeds in two stages. The first stage ($z < 0.5$) is characterized by the presence of

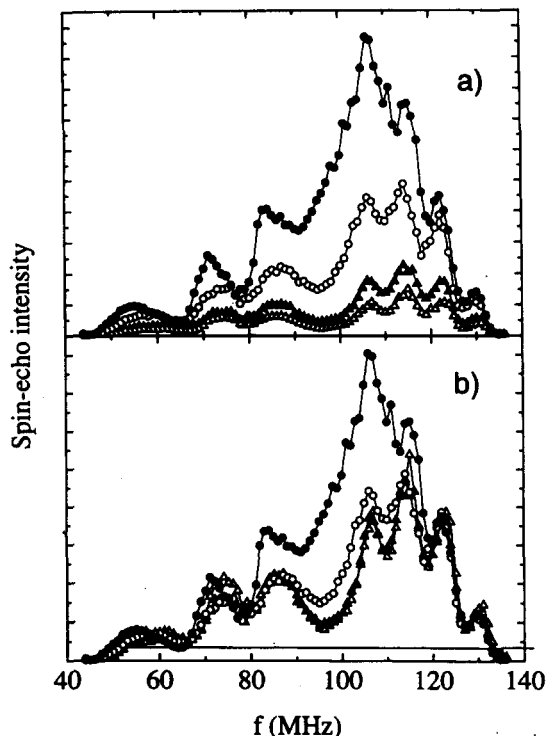


Fig.2. Copper ZFNMR spectra for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ with different water uptake z (open and solid triangles and open and solid circles correspond to $z = 0.14; 0.24; 0.55$ and 1.2 , respectively): a) as-taken spectra; b) spectra normalized by water uptake; the spectrum for $z = 1.2$ is normalized by 0.6

two types of magnetically ordered copper ions whose nuclei experience internal magnetic fields of 64 and 100 kOe. The changes of the copper NQR spectra described above provide straightforward evidence that Cu(1) chains that contain no oxygen and belong to the well-developed Ortho-II phase present an easy diffusion path for the insertion of water or other related species (e.g. hydroxide ions). The superconducting volume fraction decreases at this stage approximately at the same rate as the sharp Cu(1) NQR lines do, but twice as fast as the total NQR intensity in the 21-33 MHz range (Fig.3). The superconducting volume fraction for the sample with $z = 0.55$ is only 14% of that for $z = 0$. The simultaneous disappearance of the broad fast-relaxing NQR line at 28 MHz allows us to assign it to Cu(2) nuclei belonging to the well-developed Ortho-II phase. It is quite reasonable to suppose [3] that water diffusion is hampered in areas of oxygen-disorder within the crystallites, i.e. in areas where the empty-chain diffusion channels are blocked by oxygen in O5 positions, twin boundaries, etc. From this, we assign the "residual" NQR spectrum of the $z = 0.55$ sample primarily to such areas. A small increase of the intensity of the terminating Cu(1) NQR line (at 24 MHz) at the initial stage of the reaction is thus most likely due to the destruction of long Cu(1) chains.

Our studies of water insertion allow us to tentatively clarify the often debated question: Do all the nuclei from the superconducting regions of 123 contribute to the NQR/NMR signal, i.e. does the RF fully penetrate superconducting 123? The observed correlation of the copper NQR intensity, superconducting volume fraction and water uptake allows us to conclude that *all* superconducting regions contribute to the NQR signal in the case of underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ of 30 μm -sized powder packed in Stycast. For comparison, our attempt to insert water (two hours 200 °C-annealing) into $\text{YBa}_2\text{Cu}_3\text{O}_7$ lead to a 30%

decrease of the superconducting volume fraction, but due to better RF field penetration into a "spoiled" superconductor we observed a 20% increase of the observed Cu(2) NQR intensity.

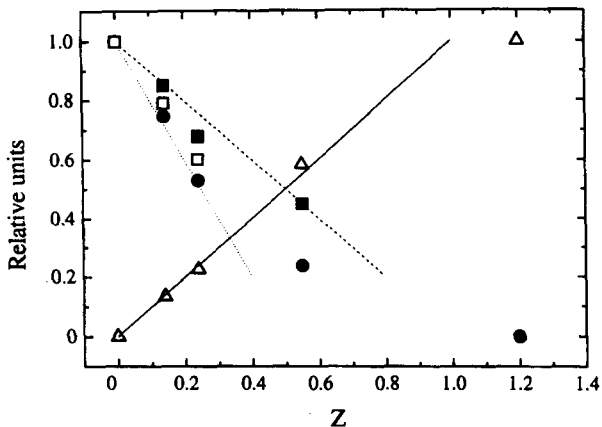


Fig.3. The dependence of the superconducting volume fraction (solid circles), copper NQR spectra intensity (solid squares), NQR intensity of slow-relaxing Cu(1) nuclei (open squares) and ZFNMR intensity (triangles) on water uptake z . Straight lines represent the functions $y = z$ (solid line), $y = 1 - z$ (dashed line) and $y = 1 - 2 \cdot z$ (dotted line).

The second stage of the reaction ($z > 0.5$) leads to total disappearance of superconductivity and to dramatic changes in the NQR spectrum (Fig.1). At maximum water uptake $z_{max} = 1.2$ (different from $z_{max} = 1$ in Ref.[3]) two new copper centers arise: one characterized by a hyperfine field ~ 80 kOe at the Cu nuclei, and another with a nuclear quadrupole frequency of 18.4 MHz and a lack of magnetic ordering. It should be mentioned that magnetically ordered areas which have appeared at $z < 0.5$, are still present and become even larger at $z = 1.2$. As estimated by relative intensities of ZFNMR spectra, they represent about 70-80% of the total number of Cu ions participating in well-ordered magnetic phase(s), which corresponds to about one water molecule ($z \approx 1$) involved in producing this phase.

X-Ray diffraction spectra taken for the sample with a maximum water uptake show that the final product of the reaction in our case is identical to the one considered in Ref.[3] as the tetragonal pseudo-248 structure with 50% defects at chain copper positions (phase B in Ref.[3]). In this structure there are 3 inequivalent Cu sites. We could identify at least 3 in the magnetically ordered phase, and we find an additional relatively weak copper NQR line at 18.4 MHz (not far from the 19.8 MHz Cu(1) NQR line in $YBa_2Cu_4O_8$). Further studies are necessary to relate the NMR spectra in detail to the structure.

Our copper NQR/ZFNMR studies of the reaction of $YBa_2Cu_3O_{6.5}$ compound with water vapour give straightforward evidence that "empty" CuO chains play the role of easy water insertion channels. The most ordered regions of the crystallites react most easily. The water insertion reaction proceeds very slowly at room temperature, but in 6 years in air, water reaches even samples packed in paraffin [1]. At 100-200 °C the reaction proceeds quickly (in few days). The final product of the reaction is a non-superconducting antiferromagnet characterized by at least two types of magnetically ordered copper ions with ZFNMR spectra at the frequency ranges of 46-96 and 96-135 MHz. This antiferromagnetic signal, indicating decomposition of the superconductor, was even detected in samples packed in Stycast and left at room temperature (normally deemed a safe storage procedure) for few years.

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