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Short communication

 ^{17}O NMR in planes and chains of $\text{YBa}_2\text{Cu}_3\text{O}_7$

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Résumé.— Nous présentons les premiers résultats de spectres RMN de l'isotope ^{17}O de l'oxygène obtenus après échange gazeux à 300 et 850°C. Nous sommes en mesure d'attribuer le signal étroit (et faiblement déplacé) à la transition $1/2, -1/2$ des atomes des chaînes Cu O et le signal large (fortement déplacé) aux sites d'oxygène appartenant aux plans.

Abstract.— We report the first observation of ^{17}O NMR spectra in $\text{YBa}_2\text{Cu}_3\text{O}_7$ obtained after selective gas exchanges performed at 300 and 850°C. We are able to assign the narrow (weakly shifted) signal to the $(1/2, -1/2)$ transition of oxygen atoms in CuO chains and the broad (strongly shifted) signal to the O-sites in CuO_2 planes.

Up to now high temperature superconductivity has only been observed in oxygen containing materials (ternary or quaternary copper oxides). The structure of these materials reveals the existence of either CuO_2 planes or a combination of CuO_2 planes and CuO chains as in the orthorhombic phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Oxygen atoms play a crucial role in these materials.

- i) The concentration of oxygen atoms determines the actual valence state of Cu.
- ii) It has been argued that charge carriers in $\text{YBa}_2\text{Cu}_3\text{O}_7$ are holes in the predominantly oxygen 2p band of the CuO_2 planes.

Furthermore, oxygen is known to be fairly mobile in the structure even temperatures as low as 300°C. Neutron diffraction studies [1] of the orthorhombic structure $6.5 < 7 - \delta < 7$ have shown

that oxygen atoms can occupy five different crystallographic sites. Sites O(1) and O(5) are lying within the ab-plane but only O(1) sites are filled as long as δ is small forming Cu-O chains along the b-direction. O(2) and O(3) sites lie in CuO_2 layers adjacent to Y atoms whereas O(4) sites are located in planes parallel to the c-direction.

We report an NMR study of ^{17}O nuclei allowing a clear-cut assignment of NMR signals to planes and chains sites. The starting material was prepared by a chemical route [2] using liquid nitrate precursors in order to achieve an excellent chemical homogeneity checked by electron microprobe. After a post-treatment (2 hours at 850°C in O_2) this process leads to powders exhibiting a monomodal distribution of particles

centered at $\approx 0.7 \mu\text{m}$ which give rise to superconductivity with a T_c of 92 K as measured by dc-Meissner effect [3]. Several heat treatments were carried out in order to modify the ^{17}O distribution among the four occupied O-sites of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure. In a first treatment (leading to sample 1) the isotopic exchange was carried out on the powder with a treatment of five days at 300°C in a confined gaseous mixture enriched up to 51% in ^{17}O . The $^{17}\text{O}/^{16}\text{O}$ ratio in the gas was monitored with a quadrupole mass spectrometer during the exchange process. Due to some unknown exchange with various parts of the equipment we could not ascertain the exact amount of exchanged ^{17}O in the sample. However, after annealing for 120 hours no further variation of the $^{17}\text{O}/^{16}\text{O}$ ratio could be detected. Thus, assuming a total exchange reaction in the solid we estimate that no more than 25% of the ^{16}O has been exchanged by ^{17}O . According to the X-ray analysis performed on the exchanged sample there was no evidence of any significant change in lattice parameters ($a = 3.83 \text{ \AA}$, $b = 3.88 \text{ \AA}$, $c = 11.68 \text{ \AA}$).

The ac-susceptibility displays a superconducting transition for exchanged samples at about 90 K in zero applied field [4].

In a second treatment (leading to sample 2) the exchange was conducted in the same confined environment for three days at 850°C . The $^{17}\text{O}/^{16}\text{O}$ ratio was similarly monitored during exchange and after reaching equilibrium. The sample was cooled slowly down to room temperature in the surrounding gas at a rate of $100^\circ\text{C}/\text{h}$ in order to keep the high oxygen content of the oxide. In a third step (leading to sample 3) a part of batch 2 was back-exchanged in a pure ^{16}O atmosphere at a temperature of 300°C for three days.

The X-ray analysis of sample 3 gives $a = 3.827 \text{ \AA}$, $b = 3.881 \text{ \AA}$, $c = 11.679 \text{ \AA}$. In addition there is little doubt that samples 2 and 3 have the same structure since the procedure allowing to pass from # 2 to # 3 is rather harmless chemically speaking.

It is known that oxygen is fairly mobile in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure and can be easily exchanged with a gas phase in a reversible way. Oxygen insertion reaches a maximum at about 450°C and a quasi-reversible loss arises above this temperature. Upon cooling, oxygen insertion is observed in the temperature domain ($300\text{--}360^\circ\text{C}$) depending on time, tempera-

ture and surface reactivity of the powder. *In situ* neutron powder diffraction experiments carried out in vacuum [5] have shown that $\text{YBa}_2\text{Cu}_3\text{O}_7$ looses its oxygen on the O(1) sites (pertaining to Cu-O chains) while the other sites remain unaffected. Similar experiments, under oxygen atmosphere [1] show that the O(1) occupancy drops smoothly with no significant occupancy of the normally empty O(5) sites.

Samples used in the NMR experiments were kept in quartz ampoules filled with 1 atm of either $^{17}\text{O}_2$ (# 1 and 2) or $^{16}\text{O}_2$ (# 3). NMR spectra of $^{17}\text{O}(I = 5/2)$ nuclei have been obtained with a pulsed spectrometer tuned at a frequency $\nu_o = 27.112\text{MHz}$. H_2^{17}O was taken as the reference signal for shifts. We have worked with the usual spin echo sequence selecting a pulse length of $\pi/6$ in order to preferentially excite the $(1/2, -1/2)$ transition of the quadrupolar spectrum. Delays between pulses in the echo sequence were in the range of 130 to 250 μs . After a 4 to 5 hours accumulation (repetition time = 0.5 s) the Fourier-transform was performed on half of the spin echo signal. The Fourier-transform of the spin echo in sample 2 (Fig. 1) shows clearly two distinct signals which

Fig. 1.— Fourier transform NMR spectrum of plane and chain ^{17}O (sample 2, gas-exchanged at 850°C).

can be attributed to the $(1/2, -1/2)$ transitions of ^{17}O ($I = 5/2$) nuclei. The field-swept spectrum of ^{17}O in Cu-O chains has been reported in another publication [4]. The narrow signal is centered at 240 ppm (as referred to ^{17}O enriched H_2O) with a linewidth of about 200-400 ppm. The other signal (much broader) is shifted to higher values of the frequency (≈ 1400 ppm) with a linewidth of about 1000-1400 ppm.

The assignment of the two signals in figure 1 is provided by the data obtained with sample 1, where only a narrow and weakly shifted signal is obtained (Fig. 2). As ^{17}O is likely to populate only the O(1) sites in sample 1 which was treated at 300°C the comparison between spectra in (Figs. 1 and 2) allows an unambiguous assignment of the 240 and 1400 ppm signals to chain and plane sites respectively. We believe that the large linewidth of the 1400 ppm signal can be attributed to unresolved shifts of the two O-sites in the CuO_2 planes and to the O(4) sites.

Fig. 2.— Fourier transform NMR spectrum of chain ^{17}O (sample 1, gas-exchanged at 300°C).

As far as sample 3 is concerned, both signals are observed, (Fig. 3). The signal at 1400 ppm

has about the same amplitude as in sample 2. However, the ^{17}O signal at 240 ppm is slightly smaller than in sample 2. apparently the back-exchange is not complete. This feature can be understood since, i) as for the first treatment only a small fraction of oxygen sites are exchanged during the heat treatment and, ii) the treatment performed on sample 2 has progressively increased the size of the crystallites with a concomitant slowing down of the oxygen diffusion [6]. A back-exchange performed at a higher temperature and for a longer period of time should result in a more complete destruction of the 240 ppm signal. This argument is only valid provided that statistical plane-chain interdiffusion may be neglected when the temperature is not too high.

Fig. 3.— NMR spectrum of sample 3.

The spectrum in figure 4 has been obtained after subtracting the signal of # 1 out of # 2. Figure 4 is therefore likely to display the NMR signal of ^{17}O in the planes.

Several mechanisms could contribute to the positive shifts of the NMR lines. First, the chemical shift (possibly anisotropic) coming from

the filled oxygen levels and, secondly, shifts related to the existence of partially filled bands. Chemical shifts are still unknown. However, plane and chain oxygens are both squeezed between two Cu atoms. It sounds plausible they experience similar chemical shifts, less than 200 ppm or so, as suggested by the empirical relation between the atomic radius and the chemical shift which has been proposed for some transition metal oxides [7]. We feel confident that the weakly shifted signal can be attributed to the easily exchanged site i.e. O(1) in the Cu-O chains, whereas the more shifted line is related to O(2,3) plane sites in agreement with the dominant contribution to the susceptibility coming from the planes [8]. Some orbital contribution to the positive Knight shift [9] cannot be ruled out *a priori*, but a crude estimate based on the derivation of reference (9) leads to about 10 ppm, using a bandwidth of 1 eV and $\langle 1/r^3 \rangle_p = 3 \times 10^{25} \text{ cm}^{-3}$ [10]. Thus the large and positive Knight shift of plane oxygens can be attributed to the d-character of the hybridized 2p-5d wave functions giving a non-zero electron density on oxygen sites.

In conclusion, an appropriate gas-exchange treatment of $\text{YBa}_2\text{Cu}_3\text{O}_7$ has made possible the unambiguous assignment of ^{17}O NMR signals to plane and chain O-sites. It has been shown that internal magnetic fields (Knight shifts) are much stronger in planes than on chains in agreement with the dominant role of the density of states

Fig. 4.— Plane ^{17}O NMR spectrum after subtraction of (Fig. 2 out of Fig. 1).

at the Fermi level in the planes [8].

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