RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 13 1 MAY 1990

^{17}O NMR spectroscopy of $Bi_2Sr_2CaCu_2O_{8+x}$ high-T_c superconductor

A. Trokiner
Laboratoire de Physique Thermique, École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris 10, rue Vauquelin 75231 Paris CEDEX 05, France

R. Mellet, A-M. Pougnet, D. Morin, Y. M. Gao, J. Primot, and J. Schneck
Centre National d'Etudes des Télécommunications 196, rue Henri Ravera 92220 Bagneux, France

(Received 16 January 1990)

We have investigated at room temperature and at 7 K the ^{17}O NMR spectrum of a chemically and structurally characterized ^{17}O-enriched powder of $Bi_2Sr_2CaCu_2O_{8+x}$ superconductor. Using the frequency dependence of the spectrum and T_1 relaxation-time measurements, we were able to infer that the two lines constituting the spectra can be assigned to the oxygen nuclei in the SrO planes and to the oxygen nuclei in the CuO_2 planes. The absence of the expected BiO line is accounted for, on the basis of the incommensurate superstructure existing in these compounds.

The interest of ^{17}O nuclear magnetic resonance (NMR) measurements of high-T_c superconducting oxides has been often underlined. Indeed, band-structure calculations have shown that the 2p O orbitals in the CuO_2 planes contribute in a central manner to the formation of the charge-carrier bands.[1] Up to now, ^{17}O NMR results concerning $YBa_2Cu_3O_{7-x}$ powders[2,3] and oriented powders,[3-8] $LaSrCuO_4$-oriented powders[6] and some oxides, precursors to the high-T_c superconductors,[9] have been published. ^{17}O NMR studies of $YBa_2Cu_3O_{7-x}$, with $x=0$ and 0.35, have confirmed experimentally that the doped holes are predominantly (O 2p)-like rather than (Cu 3d)-like, and that the spin susceptibility originates from the CuO_2 plane.[6] Moreover, these measurements have allowed the specification that, at the O_2, O_3, and O_4 oxygen sites, the spin density involves the p_σ orbitals.[4] In the Bi-Sr-Ca-Cu-O system, NMR studies were essentially performed on the copper nuclei by nuclear quadrupole resonance (NQR) in the compounds $Bi_2Sr_2Ca_2Cu_3O_y$ (Ref. 10) and $Bi_2Sr_2CaCu_2O_{8+x}$.[11]

Very recently, Oldfield *et al.*[12] have published an extensive study of ^{17}O NMR in high-T_c superconductors which includes spectra concerning the so-called 2:2:1:2 phase of the Bi-Sr-Ca-Cu-O system whose building blocks contain two copper planes. The authors pointed out difficulties in interpreting the spectra; namely only two lines were observed where three are expected. Difficulties in the interpretation of the NMR spectra in superconductors are not specific to the bismuth compounds. Indeed, the assignment of ^{17}O NMR peaks is still controversial in $YBa_2Cu_3O_7$, though the studies were performed on oriented powders.[3,4]

In this Rapid Communication, we present new experimental results concerning the ^{17}O NMR of a chemically and structurally characterized enriched ^{17}O powder sample of the 2:2:1:2 phase of the Bi-Sr-Ca-Cu-O type of superconductors. Using the frequency dependence of the spectrum and an appropriate pulse sequence, as well as T_1 measurements, we were able to infer an assignment of the lines in the spectra, which is in agreement with the structural data available for this phase. In addition, we present the first preliminary results at temperatures located well below the critical temperature.

With the view of elaborating ^{17}O-enriched material, pellets of the 2:2:1:2 phase were prepared by standard solid-state reactions. The ^{17}O isotopic exchange was realized by two consecutive annealings of the pellets at 800 °C, in a static atmosphere of enriched ^{17}O oxygen gas (39.7%) and inside an air-tight silica tube; the duration of each annealing was 24 h. The resulting ^{17}O concentration inside the samples was analyzed by secondary-ion mass spectrometry (SIMS). The measurements were performed over the whole cross section of a cut pellet, showing that the isotopic exchange is homogeneous in the bulk of the samples. The data yield a proportion of oxygen substituted by ^{17}O, approximately equal to 28%. The persistence of the 2:2:1:2 phase during the exchange process has been established by checking that this treatment does not induce significant change in the x-ray powder spectra of the ceramics. It has been also verified that the superconducting properties of the ^{17}O enriched samples were preserved by investigating their resistivity: zero resistivity was observed near 65 K with an onset temperature of 80 K, which corresponds to a behavior similar to that of the nonenriched samples. As a final step, we have ground the ^{17}O enriched pellets and used a few grams of powder for each NMR experiment.

Results presented here were obtained at three different Larmor frequencies 40.69, 54.3, and 67.8 MHz with Bruker spectrometers CXP 300, MSL 400, and MSL 500, respectively. Most experiments were performed at $\nu_L=40.69$ MHz. In all cases, signals were obtained with a 90°-τ-90° spin-echo sequence. The signal was then Fourier transformed at a time $\tau+2$ μsec after the second pulse. We have also evaluated the spin-lattice relaxation time T_1, with a classical inversion-recovery method, at 40.69 MHz. Data at temperatures below T_c were obtained with a helium Bruker cryostat.

The spectrum presented in Fig. 1(a) has been obtained at room temperature and at 40.69 MHz with $\tau=40$ μsec. One can distinguish the following features: (i) an intense narrow line (labeled NL), with a full width at half height

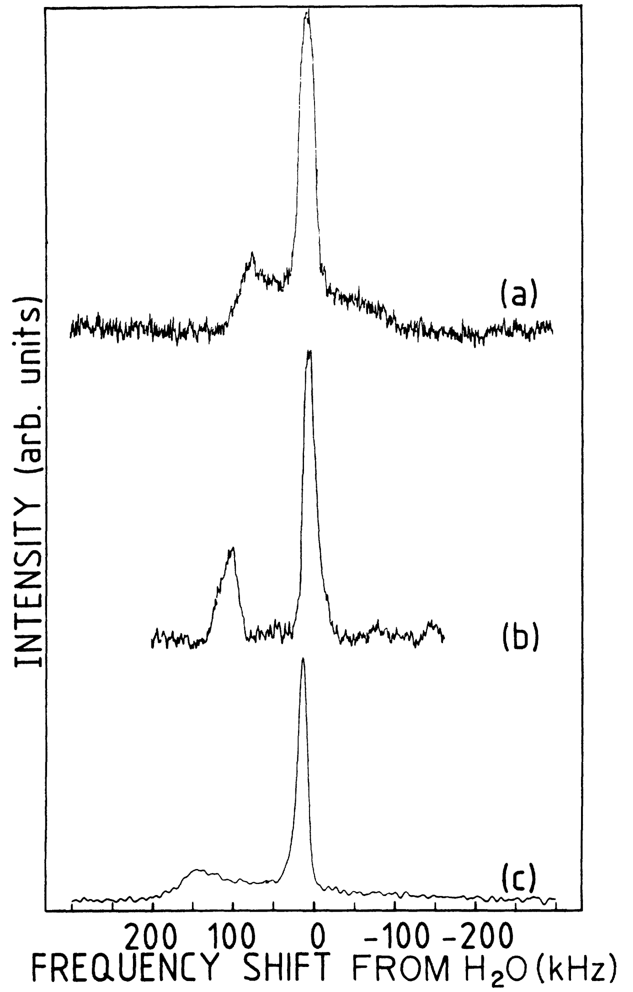

FIG. 1. Room-temperature ^{17}O NMR spectra of an enriched powdered sample of $Bi_2Sr_2CaCu_2O_{8+x}$. (a) The Larmor frequency ν_L is 40.69 MHz (7 T), the pulse length is 2.5 μsec, $\tau = 40$ μsec, where τ is the delay between the two pulses, the repetition rate is 12 sec; (b) $\nu_L = 54.3$ MHz (9.4 T), the pulse length is 3.5 μsec and $\tau = 50$ μsec; and (c) $\nu_L = 67.8$ MHz (11.7 T), the pulse length is 0.7 μsec and $\tau = 30$ μsec.

(FWHH) of 22 kHz, weakly shifted towards high frequency, and (ii) a broad line (BL) with a high-frequency shift $K = 0.19 \pm 0.01\%$ ($K = \Delta\nu/\nu_L$, where $\Delta\nu$ is the frequency shift of the line, relative to the position of the ^{17}O line in tap water). For each line, we find a maximum in signal intensity for a 2.5-μsec pulse length, while for water we find a 7.5-μsec pulse length. This implies that for both lines the quadrupolar interaction is intense compared to the radio frequency (rf) field strength and thus, that the rf field irradiates only the so-called central line ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$). As a result, in order to have a maximum signal in our sample, one has to use a pulse length equal to the 90° pulse length in water divided by $(I + \frac{1}{2})$, where $I = \frac{5}{2}$ is the ^{17}O spin.[13]

Figures 1(b) and 1(c) show the room-temperature spectra obtained at 54.3 MHz with $\tau = 50$ μsec and at 67.8 MHz with $\tau = 30$ μsec. The FWHH of line NL are 18 and 14 kHz, respectively. For both frequencies the shift K of line BL is the same as the one measured at 40.69 MHz.

The frequency shift of line BL is observed to depend linearly on ν_L. Despite the fact that the pulse-length measurements evidence quadrupolar interaction, there is no detectable quadrupolar-shift effect. This implies that only a Knight-shift interaction with conduction electrons and/or a chemical shift due to an orbital contribution provoke the observed shift. There is a wide weak line looking like a "tail" of line BL, and extending to the right-hand side of line NL. Owing probably to instrumental limitations, this signal is not apparent on the spectra performed at 54.3 MHz [Fig. 1(b)]. Considering the very large width of this tail, we believe that the FWHH measurements for line BL cannot be safely determined when the spectra are obtained through an echo Fourier transform.

From the frequency dependence of the weak shift of line NL, we could not infer any definite interaction. However, the FWHH of this line is proportional to $1/\nu_L$, showing thus a quadrupolar interaction (see Fig. 1).

Our T_1 data show that for both lines, the recovery of the magnetization as a function of the delay t between rf pulses is nonexponential. The longest component of T_1 for line NL is about 1 sec while for line BL, it is a few milliseconds.

Clearly, the frequency dependence of the spectra and the T_1 data show that the oxygen nuclei contributing to line NL and line BL have a very different behavior, the former mostly experiencing a quadrupolar interaction and the latter a hyperfine interaction.

Analyzing the above data requires consideration of the structural characteristics of $Bi_2Sr_2CaCu_2O_{8+x}$. This compound has a complex structure involving a twofold superstructure along the a crystallographic axis, as well as an incommensurate superstructure with wave vector parallel to the b crystallographic axis.[14] The approximate structure is tetragonal with one chemical formula per elementary unit cell. For this approximate structure, one can distinguish three different oxygen sites belonging to the CuO_2, SrO, and BiO planes, respectively. From a NMR point of view, the two oxygen atoms in the CuO_2 plane are inequivalent and are thus expected to give rise to two lines. However in our experiment, where only the central transition is detected, we expected, as in $YBa_2Cu_3O_7$,[4] that the lines of the two oxygen atoms in the copper plane overlap. Hence, only three lines are expected in the NMR spectra.

Based on the analogy of line positions and on the value of T_1 in other high-T_c oxides, Oldfield *et al.*[12] have assigned line BL to the copper plane and line NL to the remaining SrO and BiO planes. The existence of a single peak while two are expected, corresponding to one oxygen in the SrO plane and one in the BiO plane, was not clearly accounted for.

The assignment of line BL to the oxygen in copper planes is reasonable, beyond the mere analogy with the NMR spectra of high-T_c superconducting oxides.[6] Actually, theoretical calculations[15] of the band structure as well as experimental results[16] have shown that the SrO and BiO planes are insulating and that the carriers are localized in the copper planes. Thus, the large paramagnetic shift with very short T_1 of line BL can be attributed to a hyperfine interaction between the spins of the nuclei and these carriers.

As said before, we find in addition to lines BL and NL, a wide weak signal looking like a tail of line BL and overlapping with line NL. This signal has not been reported by Oldfield *et al.*[12] In the aim of assigning this signal, we have represented in Fig. 2(a) the spectrum performed at 40.69 MHz by the inversion-recovery method with a pulse delay $t = 38$ msec, chosen in order to cancel line NL. In Fig. 2(b), the spectrum of line NL is represented, obtained by difference of spectra. The very broad line described above, shows a T_1 in the same range as line BL and thus is likely to involve an interaction with charge carriers. Hence, it cannot be attributed to the SrO or BiO missing line and, is rather to be due to the oxygen in the copper planes. It is not yet clear whether this line is a part of a satellite transition or a part of the central transition. In the latter case, the asymmetry of the BL line shape could be related to the shift anisotropy.

In view of accounting for the absence of a ^{17}O line corresponding to either the BiO or the SrO plane, it is worth recalling that the incommensurate modulation of these compounds essentially affects the BiO planes.[17] The amplitude of the modulated displacements are at least twice as large in these planes as any other displacements in the structure. Besides, structural models of the modulation[18] have shown that the modulation will lead to a large variety of environments for the oxygen in the BiO planes. Hence the NMR line corresponding to this oxygen is expected to be very wide. Actually, NMR powder spectra on quadrupolar nuclei have never been detected in incommensurate materials,[19] probably due to this characteristic. For this reason there is a great probability that the oxygen in the BiO planes is not detected. Let us emphasize that the ^{17}O spectra available for $Tl_2Sr_2CaCu_2O_{8+x}$,[12] in which no modulation or a weak one at most exists, the line of the corresponding TlO plane is clearly observed.

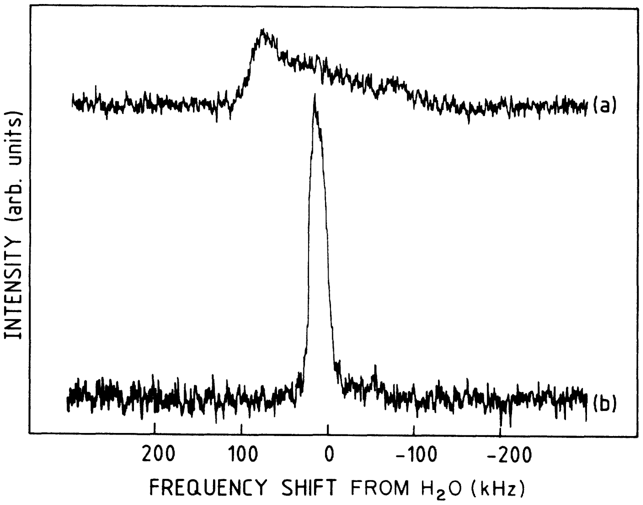

FIG. 2. (a) Room-temperature spectrum of line BL (see text). The spectrum was performed at 40.69 MHz by applying an inversion recovery sequence prior to the spin-echo sequence. The delay t between the inversion recovery pulses sequence has been chosen in order to cancel line NL, $t = 38$ msec. (b) Line NL is obtained by subtracting the spectrum in Fig. 2(a) to a spectrum obtained with $t = 12$ sec.

As a consequence, line NL is very likely to be associated with the oxygen nuclei in the SrO planes.

Low-temperature measurements give additional evidence of the assignment of line BL. We present the first results at temperatures in the superconducting phase, well below T_c. Figure 3 shows the spectrum obtained at 7 K. When cooling down, from T_c to 7 K, there is no variation of the shift of the SrO line. By contrast, line BL, due to the CuO_2 plane, exhibits a large diamagnetic (low-frequency) shift, showing the sensitivity of the corresponding oxygens to the onset of the superconductivity. The resulting line at 7 K is asymmetric and broad. The position of its maximum is $K = 0.05\%$.

For a classical superconductor below T_c, because of the pairing of the spins, the spin contribution to the Knight shift K_{spin} is expected to disappear on cooling. On the other hand, the orbital contribution K_{orb}, which is not affected by this spin pairing, is expected to remain down to $T = 0$ K. Hence, from the line position at $T = 0$ K one should get K_{orb}. Assuming that this is valid for the high-T_c superconductors, we can deduce both contributions to the Knight shift from the spectra displayed in Figs. 1 and 3. We find that for the oxygen in the copper planes, K_{orb} is $\simeq 0.05\%$, while at 300 K, K_{spin} is $\simeq 0.14\%$. The orbital contribution when compared to the spin contribution appears larger in $Bi_2Sr_2CaCu_2O_{8+x}$ than in $LaSrCuO_4$ (Ref. 6) and in $YBaCuO_7$.[4]

In conclusion, performing NMR experiments at three different Larmor frequencies has enabled us to deduce that the two lines, NL and BL, of the spectra are mostly concerned with a quadrupolar and Knight shift interaction, respectively. Line BL is attributed to the oxygen in the copper planes. On the basis of the structural information available, we have attributed line NL to the oxygen in the SrO planes, while we have argued that the signal of the oxygen in the BiO planes is likely to be smeared out by the modulation and thus difficult to be detected.

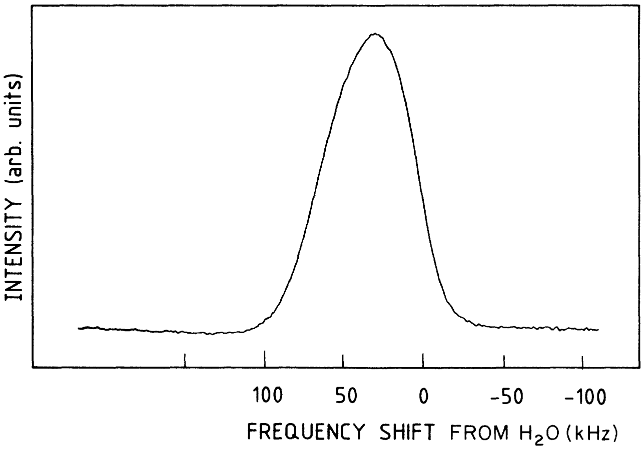

FIG. 3. ^{17}O NMR spectrum performed at $T = 7$ K and $\nu_L = 54.3$ MHz.

We thank J-C. Toledano for helpful discussions and careful reading of the manuscript. We have appreciated stimulating discussions with H. Zanni. We are grateful to H. Foester and M. Smith, from the NMR Application Laboratory (Bruker, Karlsruhe), for giving us access to the 9.4 and 11.7 T spectrometers. A grant by Centre National d'Etudes des Télécommunications for partial support of this work is gratefully acknowledged by one of us (A.T.). Laboratoire de Physique Thermique is "Unité Associée au Centre National de la Recherche Scientifique No. 857."

---

[1] L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987); Jaejun Yu, A. J. Freemann, and J. H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).

[2] H. Bleier, P. Bernier, J. Jerome, J. M. Bassat, J. P. Coutures, B. Dubois, and P. Odier, J. Phys. (Paris) **49**, 1825 (1988); K. Ishida, Y. Kitaoka, K. Asayama-Yoshida, Y. Okabe, and T. Takahashi, J. Phys. Soc. Jpn. **57**, 2897 (1988).

[3] C. Coretsopoulos, H. C. Lee, E. Ramli, L. Reven, T. B. Rauchfuss, and E. Oldfield, Phys. Rev. B **39**, 781 (1989).

[4] M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, K. C. Ott, and J. D. Thompson, Phys. Rev. Lett. **63**, 1865 (1989).

[5] P. C. Hammel, M. Takigawa, R. H. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. Lett. **63**, 1992 (1989).

[6] Y. Kitaoka, K. Ishida, F. Fujiwara, T. Kondo, K. Asayama, H. Horvatic, Y. Berthier, P. Butaud, P. Segransan, C. Berthier, H. Katayama-Yoshida, Y. Okabe, and T. Takahashi (unpublished).

[7] M. Horvatic, Y. Berthier, P. Butaud, Y. Kitaoka, P. Segransan, C. Berthier, H. Katayama-Yoshida, Y. Okabe, and T. Takahashi, Physica C **159**, 689 (1989).

[8] P. Butaud, M. Horvatic, Y. Bethier, P. Segransan, Y. Kitaoka, C. Berthier, and H. Katayama-Yoshida, Physica C **166**, 301 (1990).

[9] S. Yang, K. D. Park, and E. Oldfield, J. Am. Chem. Soc. **111**, 7278 (1989).

[10] K. Fujiwara, Y. Kitaoka, K. Asayama, H. Sasakura, S. Minamigawa, K. Nakahi Gashi, S. Nakanishi, M. Kogachi, N. Fukuoka, and A. Yanase, J. Phys. Soc. Jpn. **58**, 380 (1989).

[11] A. K. Rajarajan, V. R. Palkar, N. C. Mishra, M. S. Multani, R. Vijayaraghavan, and L. C. Gupta, Solid State Commun. **71**, 835 (1989).

[12] E. Oldfield, C. Coretsopoulos, S. Yang, L. Reven, H. C. Lee, J. Shore, O. H. Han, and E. Ramli, Phys. Rev. B **40**, 6832 (1989).

[13] P. P. Man, J. Klinowski, A. Trokiner, H. Zanni, and P. Papon, Chem. Phys. Lett. **151**, 143 (1988).

[14] J. Schneck, L. Pierre, J. C. Toledano, and C. Daguet, Phys. Rev. B **39**, 9624 (1989).

[15] J. Ren, D. Jung, M. H. Whangbo, J.-M. Tarascon, Y. Le Page, W. R. McKinnon, and C. C. Torardi, Physica C **159**, 151 (1989).

[16] K. C. Shih, R. M. Feenstra, J. R. Kirtley, and G. V. Chandrashekhar, Phys. Rev. B **40**, 2682 (1989).

[17] Y. Gao, P. Lee, P. Coppens, M. A. Subramanian, and A. W. Sleight, Science **24**, 954 (1989).

[18] Y. Le Page, W. H. McKinnon, J. M. Tarascon, and P. Barboux, Phys. Rev. B **40**, 6810 (1989).

[19] R. Blinc, P. Prelovsek, V. Rutar, J. Seliger, and S. Zumer, *Incommensurate Phases in Dielectrics,* edited by R. Blinc and P. Levanyuk (North-Holland, Amsterdam, 1986), p. 143.