^{43}Ca NMR Study of Bismuth-Based High-T_c Superconductors *

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As a first step of a study of the electronic properties of CuO_2 planes by probing calcium nuclei in the bismuth-based high-T_c materials we report here the structural assignment of Ca NMR lines measured in ^{43}Ca-enriched samples of $n=2$ ((Bi,Pb)$_2$Sr$_2$CaCu$_2$O$_{8+x}$) and $n=3$ ((Bi,Pb)$_2$Sr$_2$-Ca$_2$Cu$_3$O$_{10+x}$) bismuth compounds. Powdered samples were investigated as well as oriented powders, achieved by uniaxial alignment of the grains in a 7 T magnetic field. For the main calcium site (Ca between two CuO_2 planes), we could determine the quadrupolar as well as the shift tensors. The results indicate that, in the same way as yttrium nuclei in YBaCuO, calcium nuclei are sensitive to the magnetic susceptibility of the metallic CuO_2 planes.

Key words: ^{43}Ca NMR, High-T_c superconductors, Quadrupolar parameters, Shift parameters, Metallic state.

1. Introduction

High T_c superconducting cuprates have a layered structure and among the various layers of the unit cell, the CuO_2 planes are greatly responsible for the electronic properties. In the (Bi,Pb)$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4+x}$ family, the various compounds differ from one another mainly by the number of metallic CuO_2 planes, n, present in the unit cell. For instance, in the $n=2$ compound ((Bi, Pb)$_2$Sr$_2$CaCu$_2$O$_{8+x}$, transition temperature $T_c = 85$ K) there are two CuO_2 planes in the unit cell whereas in the $n=3$ compound ((Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$, $T_c = 110$ K), there are three planes. Thus, in order to understand the variation of the electronic properties from one compound to the other it is of great interest to study the local properties of the metallic CuO_2 planes.

Calcium atoms have the great advantage to be located between two CuO_2 metallic planes. Thus it should be possible to get information on the electronic properties of these planes by probing calcium nuclei. Furthermore, calcium sites in bismuth compounds are very similar to yttrium sites in YBa$_2$Cu$_3$O$_{6+x}$ system, and ^{89}Y NMR studies [1] have shown that ^{89}Y nuclei probe the spin susceptibility of the metallic copper planes.

Up to now, very few ^{43}Ca NMR studies have been performed in the solid state [2–4] because of the low natural abundance of this isotope, so that not much information concerning NMR properties of this nucleus is available in the literature.

As a first step of a study of the electronic properties of CuO_2 planes by probing calcium nuclei in Bi-based high-T_c materials we report here the structural assignment of ^{43}Ca NMR lines measured in ^{43}Ca-enriched powdered samples and oriented powders of $n=2$ and $n=3$ bismuth compounds as well as the quadrupolar and shift tensors of the main Ca line.

2. Experimental

a) Sample Preparation

Three samples were studied, two $n=2$ samples (with and without lead) and one $n=3$ sample (with lead).

The $n=2$ compounds, both with and without lead-substitution, can be prepared as a pure phase whereas it is quite difficult to synthetise $n=3$ compounds as a pure phase without including lead atoms, which are believed to substitute mainly bismuth atoms in the BiO plane [5].

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The samples have been prepared by usual powder ceramic technique from Bi_2O_3, $SrCO_3$, CuO, $CaCO_3$ and PbO, $CaCO_3$ being enriched with ^{43}Ca (57.9% enrichment, compared with 0.13% natural abundance). PbO was only used for samples with lead. The powders mixed in the proportions corresponding to $Bi_2Sr_2CaCu_2O_x$, $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_y$ and $(Bi_{1.6}Pb_{0.4})Sr_{1.7}Ca_{2.3}Cu_3O_z$ were first homogeneized for 12 hours at 800 °C, and after grinding (in liquid ether) were calcinated at 820 °C for 16 hours in air. The products were then pressed and the pellets sintered at 860 °C for 18 hours in an oxygen flow followed by slow cooling. For the $n=3$ compound an additional step is needed which consists in a new grinding and a final heat treatment at 845 °C for 120 hours in oxygen flow. The values of T_c according to ac-susceptibility measurements were 84 K, 85 K and 106 K for $n=2$ without Pb, $n=2$ with Pb and $n=3$ samples, respectively.

All the three compounds were studied as powdered samples and as oriented powders. Oriented samples were obtained as follows: the powders were carefully ground and then mixed with epoxy in a magnetic field of 7 T at room temperature [6, 7]. With this procedure, the crystallographic *c*-axes of the grains are aligned along the magnetic field direction, *a*- and *b*-axes being random in the plane perpendicular to the field. X-ray patterns showed that a small fraction of the powders is not well oriented. Compared to YBaCuO compounds, powders of bismuth compounds are far more difficult to orient, and only one NMR work concerning ^{63}Cu in an $n=3$ bismuth powder oriented in a 12 T magnetic field, has been published [8].

b) NMR Experiments

The ^{43}Ca NMR spectra were measured at 20.198 MHz on a BRUKER CXP 300 spectrometer in a field of 7 T. The ^{43}Ca NMR line of a solution of $^{43}CaCl_2$ in D_2O was used as a reference for the frequency shifts. Signals were obtained with a $90°-\tau-90°$ spin echo sequence with $\tau=40$ µs and a pulse length of 3 µs. Signals were then Fourier transformed at a time $\tau+2$ µs after the second pulse. It is worth noting that the 90° pulse length for which we obtain the maximum signal is about one quarter of the 90° pulse length for the solution; this indicates the existence of quadrupolar interaction.

Static as well as MAS experiments, with a rotation speed of 5 kHz, were performed on the powdered samples.

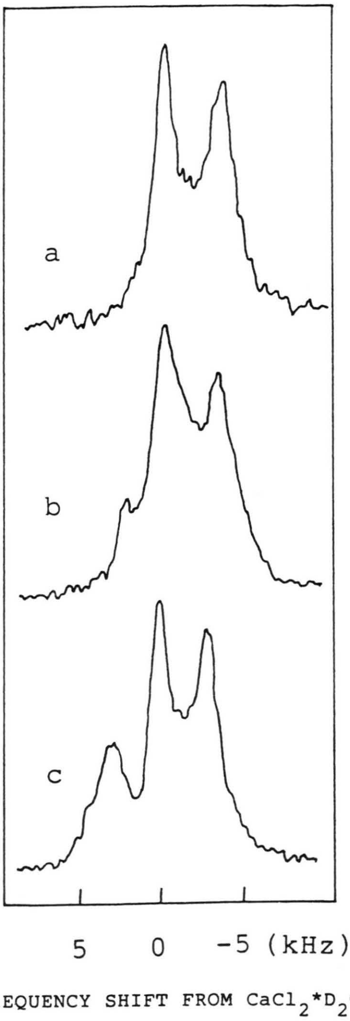

Fig. 1. Room temperature ^{43}Ca NMR spectra ($\nu_L=20.19$ MHz) of powdered samples. a) $n=2$ sample with Pb, b) $n=2$ sample without Pb, c) $n=3$ sample.

Temperature measurements were performed between 105 and 300 K with a nitrogen Bruker cryostat.

3. Results

The room temperature ^{43}Ca NMR spectra of the two $n=2$ powder samples are represented on Figs. 1 a and 1 b while the spectrum of the $n=3$ powder sample is shown in Figure 1 c. The three spectra have a common characteristic feature: a double peak situated at $+100$ Hz and -3100 Hz for the $n=2$ samples, and at $+250$ Hz and -2400 Hz for the $n=3$ one.

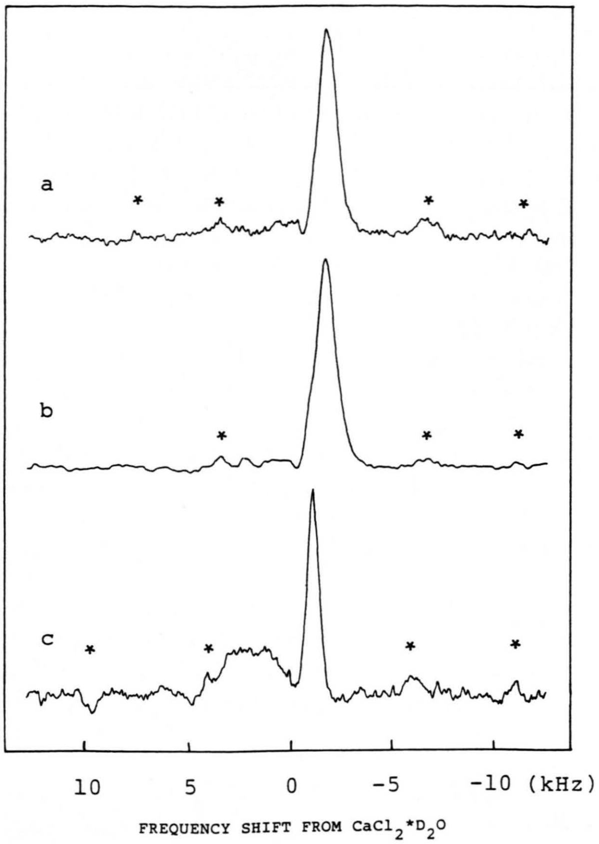

Fig. 2. Room temperature ^{43}Ca MAS NMR spectra ($\nu_L = 20.19$ MHz) of a) $n=2$ sample with Pb, b) $n=2$ sample without Pb, c) $n=3$ sample. The spinning sidebands are indicated by stars.

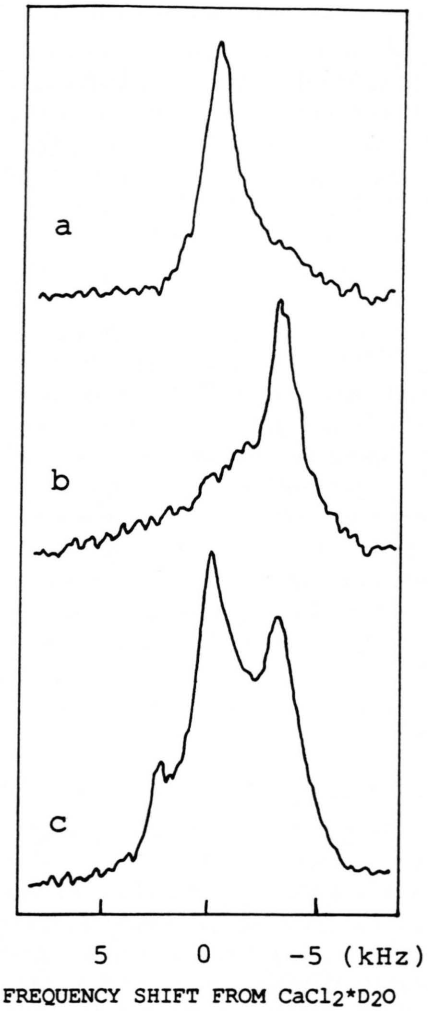

Fig. 3. ^{43}Ca NMR spectra ($\nu_L = 20.19$ MHz) of an oriented $Bi_2Sr_2CaCu_2O_{8+x}$ powder. a) c-axis perpendicular to the magnetic field B_0. b) c-axis parallel to B_0. c) non oriented powder of the same sample.

Compared to the $n=2$ sample synthetised with lead, there is an additional line in the spectra of the $n=2$ sample without lead and of the $n=3$ sample. This additional line is found at high frequency around 2200 Hz for the $n=2$ (without lead) sample and $+2800$ Hz for the $n=3$ sample.

Line separation could not be performed by varying the repetition time or the echo time τ since the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2 have the same order of magnitude for all lines, i.e. about 1 s and 5 ms, respectively.

For all three samples, MAS spectra (Fig. 2) show that the double peak merges to one narrowed line situated at -1600 Hz for both $n=2$ samples and at -1200 Hz for the $n=3$ sample. Compared to the lead-substituted $n=2$ sample, this line is narrower in the $n=3$ sample. On the other hand, as is seen on Fig. 2c, there is no MAS narrowing of the high-frequency line for the $n=3$ sample, whereas for the $n=2$ sample (without lead) the high-frequency line is narrowed, giving rise to a weak shoulder on the high-frequency side of the central line.

NMR spectra obtained in the oriented powder of the $n=2$ (without lead) compound with the c-axis perpendicular and parallel to the magnetic field B_0, are represented in Figs. 3a and b, respectively. The spectrum of the non-oriented powder is shown for comparison on Figure 3c. As it can be seen, for the c-axis perpendicular to B_0 only the high frequency component of the double peak is left, whereas for the c-axis parallel to B_0 only the low frequency component remains. Their non-symmetric shapes are mainly due to the fraction of non-oriented powder mentioned above, giving rise to a weak signal on the low frequency (high frequency) side of the line when the c-axis is perpendicular (parallel) to B_0.

4. Discussion

The analysis of the above data requires consideration of the structural characteristics of the $n=2$ and $n=3$ compounds. These compounds have a complex structure involving an incommensurate superstructure with wave vector parallel to the crystallographic b-axis. The approximate structure is tetragonal with one chemical formula per elementary unit cell. For this approximate structure there is only one calcium site belonging to the calcium plane located between two CuO_2 metallic planes. In the $n=2$ compound this site is in a mirror plane, whereas in the $n=3$ compound this site is less symmetric, but nevertheless its local environment is roughly the same for both structures.

On the other hand, it has been reported in the literature that there could be cation disorder in bismuth compounds. It was assumed that some amount of calcium atoms could substitute bismuth or strontium sites [9, 10], and inversely strontium, bismuth and lead atoms could substitute calcium sites [9–12]. These studies, which concerned mainly the $n=2$ compounds, show that besides the NMR line of calcium in their main site, one could expect a signal from calcium atoms in this site but surrounded by other cations, or from calcium atoms in other planes.

The comparison of our static and MAS NMR spectra (Figs. 1 and 2) for all three samples, taking into account that for the $n=2$ sample (with lead) only the double peak is present, has led us to assign this double peak to the main calcium site, i.e. calcium nuclei in the calcium plane. This interpretation is consistent with the fact that this signal has the same shape for both structures in static as well as MAS experiments, as it is expected since the local environment is roughly the same in $n=2$ and $n=3$ compounds.

This assignment is in disagreement with the result of the only other ^{43}Ca NMR study which concerns an isomorphous $n=2$ thallium-based compound ($Tl_2Ba_2CaCu_2O_{8+x}$) [13]. The difference with our ^{43}Ca NMR spectra is that for the $n=2$ thallium sample the most intense line is a single line arising on the high frequency side of the double peak line. This high frequency line was thus attributed to the main calcium site. The origin of this discrepancy, as is clear now, is the presence of a certain amount of the spurious dielectric phase Ca_2CuO_3 originated from an excess of $CaCO_3$ and CuO in the starting nominal composition. The presence of this spurious phase led the authors of [13] to an incorrect assignment of this intense ^{43}Ca NMR line.

Before considering the high frequency line which is present in the $n=2$ compound (without lead) and in the $n=3$ compound, we would like to emphasize that for the lead-substituted $n=2$ sample our calcium NMR spectra show the absence of either an additional calcium site or a spurious phase containing calcium.

For the $n=2$ sample (without lead), MAS results (Fig. 2b) show a narrowing of the high frequency line, giving rise to a weak shoulder on the left side of the main line. By contrast, in the $n=3$ compound the high frequency line is not narrowed (Fig. 2c), showing thus an inhomogeneous broadening. This different behaviour led us to conclude that the high frequency line has not the same origin in the two samples. Furthermore, for the $n=2$ compound, static experiments showed no thermal variation of the high-frequency line, whereas in the $n=3$ sample the width of the line increases strongly with decreasing temperature.

Concerning the $n=2$ compound, it has been reported in [14] that for sample preparation conditions similar to ours one can get small amounts of spurious phases. Comparison of X-ray patterns of our two $n=2$ samples (with and without lead) demonstrates additional reflections for the sample without Pb. These additional X-ray reflections are consistent with the existence of a small amount of a copper free spurious phase [14]$Bi_2(SrCa)_4O_7$ or $Bi_2(SrCa)_3O_6$.

The situation is less clear concerning the origin of the additional line in the $n=3$ sample. Let us consider cation disorder as a possible origin. If calcium sites are substituted by another cation (Sr, Pb or Bi), we do not expect an additional ^{43}Ca NMR line since with ^{207}Pb NMR measurements in the lead-substituted $n=2$ sample we have confirmed the presence of lead atoms in the calcium plane [15], whereas no additional line is detected in the ^{43}Ca NMR spectrum (Fig. 1a). This is not surprising since oxygen and copper atoms are the two nearest calcium neighbours, lead atoms (or any other cation in the calcium plane) being at most the third nearest neighbour. On the other hand, as said above, calcium atoms may substitute bismuth or strontium atoms in BiO and SrO planes. If calcium atoms are in bismuth sites, the corresponding NMR line should be hardly detectable since ^{17}O NMR lines corresponding to BiO layers have never been seen [16, 17] due to the strong incommensurate modulation existing in this plane.

It is tempting to assign this additional line in the $n=3$ sample to Ca atoms in the SrO plane, but such an assignment cannot explain the very strong broadening of the line with decreasing temperature, which could be interpreted as due to the presence of localised magnetic moments. This strong broadening is consistent neither with the behaviour of the ^{17}O NMR line corresponding to the SrO plane, which showed no temperature variation [16, 17], nor with the ^{43}Ca NMR main line, whose linewidth did not show any thermal variation. Although no spurious phase was detected in the $n=3$ sample by X-ray measurements, an alternate more reasonable interpretation of the origin of this additional line is the presence of a small amount of a calcium rich spurious phase which does not contribute to X-ray patterns, being poor in heavy atoms. Taking into account the strong thermal dependence of the corresponding linewidth, which is consistent with the presence of localised magnetic moments, we think that this magnetic spurious phase could contain copper atoms.

Focussing now on the main calcium site, we have analyzed the experimental spectra (of powdered samples and oriented powders) with computer simulation taking into account both quadrupolar and shift interactions. Data obtained with oriented powders have enabled us to determine the shift tensor component along the *c*-axis and in the ab-plane. The quadrupolar frequency is defined as

$$\nu_q = \frac{3e^2qQ}{2I(2I-1)h},$$

where $I=7/2$, Q is the nuclear quadrupolar moment, and $eq=V_{zz}$ is the largest component of the electric field gradient tensor (efg). ν_q and the asymmetry parameter, $\eta=(V_{xx}-V_{yy})/V_{zz}$, of the efg are roughly the same for all the compounds, $\nu_q=110\pm10$ KHz and $\eta=0.05\pm0.05$. These results are consistent with the position of satellite lines corresponding to the $\pm1/2 \leftrightarrow \pm3/2$ transition obtained for the $n=3$ sample. The shift tensor, σ, is the sum of two contributions, an orbital or chemical shift part and a spin contribution due to the spin susceptibility of the CuO$_2$ planes. We have deduced the isotropic component $\sigma_{\text{iso}}=(\sigma_{zz}+\sigma_{yy}+\sigma_{xx})/3$ as well as the axial one $\sigma_{\text{ax}}=(2\sigma_{zz}-\sigma_{yy}-\sigma_{xx})/6$. For both $n=2$ samples we find $\sigma_{\text{iso}}=-60\pm8$ ppm and $\sigma_{\text{ax}}=-46\pm8$ ppm, whereas for the $n=3$ compound, $\sigma_{\text{iso}}=-43\pm8$ ppm and $\sigma_{\text{ax}}=-37\pm8$ ppm.

The negative isotropic shift of ^{43}Ca agrees quite well with that of ^{89}Y although we don't know yet the orbital contribution with accuracy. Therefore, and owing to the great analogy of the local environment of ^{43}Ca and ^{89}Y sites in bismuth and YBaCuO compounds, respectively, we believe that ^{43}Ca nuclear spins couple with the O(2p) orbitals of the eight near neighbour oxygens in the CuO$_2$ planes, in the same way as the ^{89}Y coupling in YBaCuO [1].

Furthermore, $|\sigma|$ is larger for the $n=2$ compounds than for the $n=3$ compound. This can be related to a ^{17}O NMR shift of oxygen nuclei in the CuO$_2$ planes, for which the spin contribution is larger for $n=2$ than for $n=3$ compounds [6, 16, 17].

These facts indicate that in the same way as yttrium nuclei in YBaCuO, calcium nuclei are sensitive to the electronic susceptibility of the copper planes.

4. Conclusion

The analysis of ^{43}Ca NMR spectra of powdered samples and oriented powders of various Bi-based high-T_c cuprates has enabled us to identify the main calcium site (Ca between CuO$_2$ planes) and to characterize the other calcium line as due to spurious phases. No calcium disorder was detected in the structure.

For the main site, we have separated the room temperature quadrupolar tensor from the shift tensor. This ^{43}Ca NMR investigation is the first step to the study of the thermal behaviour of the spin susceptibility of the conducting CuO$_2$ planes.

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