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^{17}O nuclear-magnetic-resonance evidence for distinct carrier densities in the two types of CuO_2 planes of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$

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A study of ^{17}O NMR spectra in the normal phase of ^{17}O-enriched powder samples of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (2:2:2:3 phase) has allowed us to distinguish the NMR lines of the CuO_2 planes having, respectively, pyramidal and square coordination for copper. The observed differences in the magnitude and temperature dependence of the ^{17}O Knight shift of the two types of planes are consistent with the occurrence of stronger electron correlations, or smaller carrier density, in the plane-square coordinated planes, in accordance with recent theoretical predictions.

In the search for a mechanism of high-T_c superconductivity in the bismuth and thallium cuprates, an important issue is the understanding of the dependence of the properties of these materials as functions of the number n of CuO_2 planes per elementary structural unit. There are some experimental indications[1-3] that there is a maximum value of T_c at $n=3$. With the view of explaining this situation it has been predicted very recently that for $n \gtrsim 3$, charge-carrier distribution differs strongly in the different CuO_2 planes, with a depletion in those planes most distant from the BiO or TlO planes.[4] However no experimental evidence of this inference has yet been disclosed.

Nuclear magnetic resonance (NMR) is adapted to produce such experimental evidence, through separation of the ^{17}O NMR shift contributions from the different CuO_2 planes, which are not all crystallographically equivalent for $n>2$.

We present in this paper a ^{17}O NMR investigation of the $n=3$ phase (with $T_c \approx 110$ K) of the bismuth cuprate superconductors, and compare the results to those recently reported for the $n=2$ phase.[5] The latter phase (with $T_c \approx 80$ K) contains two structurally equivalent CuO_2 planes (type I) per half unit cell, each CuO_2 plane being surrounded by a SrO and a Ca plane. The $n=3$ phase contains in addition to two planes of this type (type I), one additional CuO_2 plane (type II), surrounded by two Ca planes. The environment of a type-I CuO_2 plane determines a pyramidal oxygen coordination for copper, while the environment of a type-II CuO_2 layer determines a planar-square coordination for copper.[6]

We describe, hereafter, the identification of the ^{17}O NMR contribution of the two types of planes and discuss the magnitude of the observed Knight shifts and their temperature dependence on the basis of the mentioned theoretical predictions[4] as well as of similar available experimental data for other high-T_c superconductors.[7-9]

The ^{17}O-enriched material was prepared by a gas exchange procedure using as starting material, a nearly-single-phase ceramic of the $n=3$ phase. The ceramics used[10] had the nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{9.8}$. X-ray diffraction and resistivity measurements and chemical analysis showed that this ceramic had a proportion of 92% of the $n=3$ phase, an average composition $Bi_{1.7}Pb_{0.3}Sr_{2.15}Ca_{1.8}Cu_{3.15}O_y$, and zero resistivity at 105 K. The ^{17}O isotopic exchange was achieved by annealing the pellets (≈ 2.5 g) for 18 h in a static atmosphere of enriched ^{17}O (39.6%) in an air-tight silica tube connected to a storage vessel containing ^{17}O enriched gas. We have studied by NMR two samples of ^{17}O enriched material differing in the temperature and pressure conditions used during the gas exchange. The first sample (sample 1) was annealed at 800 °C under a gas pressure of 1 atm. The x-ray-powder spectrum of this sample reveals a partial transformation of the $n=3$ phase into the $n=2$ phase and also into nonsuperconducting phases Ca_2PbO_4 and $CaPbO_3$. However, the $n=3$ phase remains the dominant phase in the sample, occupying approximately twice the volume fraction of the $n=2$ phase.

The second sample (sample 2) was prepared using a partial pressure of the enriched gas equal to $\frac{1}{5}$ atm at room temperature, and an annealing temperature of 880 °C. Its x-ray-powder spectrum shows that the initial proportion of the $n=3$ phase is preserved ($>90\%$ of the ceramic volume). However, the resistivity measurements disclose a modification of the resistive transition: though zero resistivity is achieved at 100 K, this state is the result of two successive downward jumps onsetting at 113 and 103 K with a small plateau at about 105 K. It is not clear, at the present time, whether this behavior is related to a composition inhomogeneity within the $n=3$ phase, or to the appearance of another superconducting phase in the sample. It is worth noting that a similar behavior has been pointed out[3] in ceramics, having various nominal compositions within the system $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, and attributed to the presence of the $n=4$ superconducting phase, i.e., having four CuO_2 planes in each elementary unit,[3] two with pyramidal coordination and two with plane-square coordination. From the x-ray data we can infer that if this $n=4$ phase is possibly present in sample 2, it only occupies a small fraction of the volume.

Secondary-ion-mass-spectroscopy (SIMS) analysis of the two samples yielded a proportion of substituted ^{17}O approximately equal to 21%, and showed that this proportion is uniform in the bulk of the samples.

The NMR measurements were carried out on a Bruker spectrometer CXP 300 at a Larmor frequency $\nu_L=40.7$ MHz. Signals were obtained with a $90°$-τ-$90°$ spin-echo sequence, with $\tau=30$ μs and $90°=1.3$ μs, and Fourier transformed starting at a time $\tau+2$ μs after the second pulse. Data at temperatures between 95 and 360 K were obtained with a nitrogen Bruker cryostat.

The room temperature ^{17}O NMR spectra of the two $n=3$ samples are represented in Figs. 1(a) and 1(b) while the spectrum of the $n=2$ phase, previously reported by us,[5] is represented in Fig. 1(c). The three spectra have some common characteristic features: (i) a broad line (BL1) with a high-frequency shift $K=0.19\pm0.01\%$ ($K=\Delta\nu/\nu$, where ν is the frequency line shift of the line, relative to the position of the ^{17}O line in tap water) and (ii) a narrow line (NL) only weakly shifted towards high frequencies ($K=0.02\%$). The spectra relative to the $n=3$ samples present a main difference with respect to the spectrum corresponding to the $n=2$ phase. An additional broad line (BL2) is found at an intermediate position between BL1 and NL, corresponding to a shift $K=0.12$ $\pm0.01\%$.

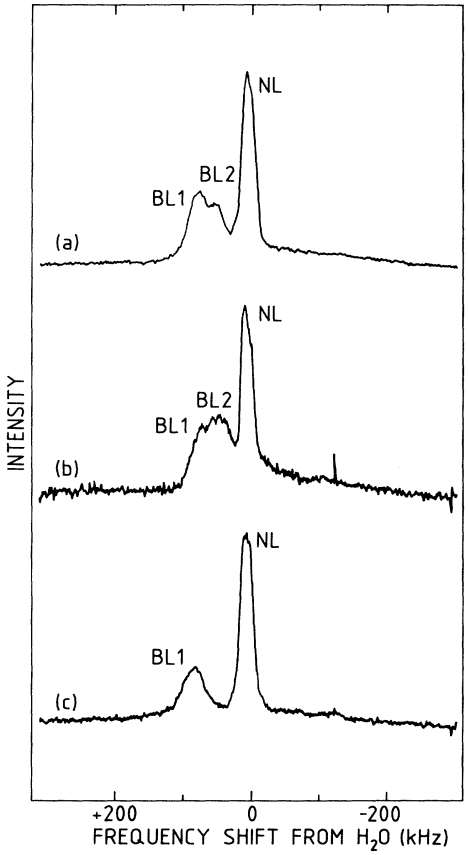

FIG. 1. Room temperature ^{17}O spectra ($\nu_L=40.7$ MHz) of enriched powdered samples of bismuth superconductor cuprates. (a) Sample 1 (see the text) of the $n=3$ phase. (b) Sample 2 of the $n=3$ phase. (c) The $n=2$ phase (see Ref. 5). The BL1 and BL2 lines have been, respectively, assigned to the oxygen of the type-I CuO_2 planes, with pyramidal coordination for copper, and to the oxygen of the type-II CuO_2 planes with plane-square coordination for copper. Line NL is associated to the SrO planes.

The spin-lattice relaxation time T_1 is nonexponential for the three lines of the spectra corresponding to the $n=3$ compounds. We have fitted the largest exponential component of T_1. It appears that BL1 and BL2 have short spin-lattice relaxation times, respectively, 5 and 70 ms, while NL has a much larger spin-lattice relaxation time of about 2 s.

The temperature dependence of the three characteristic lines of the spectra of the $n=3$ compounds has been investigated between 360 and 95 K. The shift of line NL is temperature independent in the whole temperature range. The shift of line BL1 (Fig. 2) is nearly temperature independent down to (T_c+20 K) before displaying a steep decrease. These two results are very similar to those previously reported for the $n=2$ phase for which only line BL1 was found to be sensitive to the onset of superconductivity.[5,11] The new remarkable result is that the shift of the BL2 line (Fig. 2) exhibits a continuous decrease on cooling which starts at room temperature.

We had previously analyzed the spectrum of the $n=2$ phase[5] and shown that, in accordance with other existing NMR data,[12] the line NL results from a quadrupolar interaction and has to be associated to the oxygen in the SrO planes, while line BL1 results from a hyperfine interaction between the spins of the ^{17}O nuclei and the charge carriers in the CuO_2 planes having pyramidal coordination for copper. The absence of the expected BiO line had been explained by the existence of an incommensurate superstructure in this compounds, which introduces a large dispersion of the oxygen environment in these planes.[13]

Note that, similarly to the situation in the $n=2$ phase,

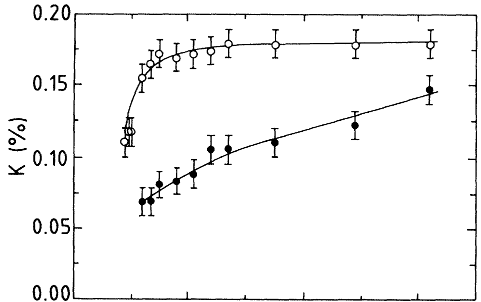

FIG. 2. Temperature dependences of the shift of line BL1 (open circles) and of line BL2 (solid circles) of the spectra corresponding to the $n=3$ phase.

the contribution of the Bi-O planes to the NMR spectra of the $n=3$ phase is unlikely to be detected since these planes are known to be affected by incommensurate modulations with close characteristics in the two phases.[13]

Hence, the BL2 line, specific of the $n=3$ phase, can reasonably be assigned to the oxygens of the additional CuO_2 planes (type II). Furthermore, the relatively short T_1 (70 ms) as well as the pronounced temperature dependence of this line suggests that the corresponding shift results from a Knight-shift interaction with the carriers expected to exist in this metallic plane.[14] In the framework of the above assignments the paramagnetic shifts corresponding to BL1 and BL2 correspond to Knight shifts, respectively, associated to the CuO_2 planes of type I and type II.

Note that, consistently with the possible presence of some $n=4$ phase a slight broadening and an enhanced intensity of line BL2 in sample 2 [Fig. 1(b)] can be attributed to the fact that CuO_2 planes of type II are also present in the $n=4$ phase.

In the view of interpreting the striking differences pointed out between the ^{17}O Knight shifts of the oxygen nuclei in the square coordinated (type I) and in the pyramidal coordinated (type II) CuO_2 planes, it is worth noting first that the Knight shift is the sum of two contributions:[9] a spin contribution K_{spin} and an orbital one K_{orb}. The latter contribution is expected to be temperature independent. In general, its magnitude can be deduced from the residual value of the total Knight shift at $T=0$ (in practice at temperatures well below T_c) since K_{spin} is expected to cancel out due to the pairing of the spins which occurs in the superconducting state. Existing data for the ^{17}O Knight shift relative to the CuO_2 planes in high-T_c superconductors,[9] and in particular for the case of the $n=2$ phase in the bismuth cuprates,[5] show that K_{orb} is weak, and that, above T_c, the total Knight shift is almost equal to its spin contribution. We can reasonably assume that this situation remains valid for the type I and II shifts in the $n=3$ phase and consider that the observed differences in the Knight-shift behavior essentially reflect differences in K_{spin}. The latter quantity is the product of the paramagnetic spin susceptibility of the carriers and of a hyperfine factor which reflects the electron probability density at the site of the nuclei. For the two types of CuO_2 planes, the orbital hybridization corresponding to the charge carriers is expected to be the same, essentially determined by the structure of the CuO_2 planes.[15]

Hence, the observed differences in the type-I and type-II Knight shifts can be assigned to differences between the paramagnetic spin susceptibility of the charge carriers in the two types of planes.

In this respect, the standard situation expected in a normal metallic phase is the observation of the temperature-independent Pauli-type susceptibility of a free-carriers gas. This type of behavior matches well the observations of the Knight shift in the type-I planes, where a temperature dependence is only found nearby T_c, when the free-carrier gas picture is expected to breakdown. In the type-II planes there is clearly a departure from the free-carrier gas situation already at room temperature.

We assign this departure to the occurrence in these planes of significant correlations between the carriers. This assumption allows us to interpret satisfactorily the two differences pointed out above in the behavior of the type-I and type-II Knight shifts. Indeed, the occurrence of electron correlations is expected to decrease the value of the spin susceptibility χ_s via a lowering of the effective one-electron density of states at the Fermi level with respect to the ideal free-electron gas: some amount of spin-spin correlations takes place which decreases the paramagnetic spin response. Moreover, a temperature dependence of χ_s, namely a decrease on cooling, will be determined by the extension, on cooling, of the antiferromagnetic type of ordering which is normally expected to result from the antiparallel spin correlations.

Note that a similar situation exists in the case of oxygen-deficient $YBa_2Cu_3O_{6+x}$.[7-9] A temperature-independent spin susceptibility has been found for the CuO_2 planes in oxygen saturated $YBa_2Cu_3O_7$,[9] while for the oxygen-deficient compounds two results have been pointed out: (i) a decrease of χ_s with decreasing values of the oxygen content x;[7,9] (ii) for $x<1$, a temperature dependence[8,9] similar to that reported here for the type-II planes in the bismuth cuprates. In $YBa_2Cu_3O_{6+x}$, these results have been assigned, similarly, to the occurrence of electron correlations.[7,16] The likelihood of this interpretation is strongly supported by the observations that electron correlations of antiferromagnetic nature exist in these substances, and that they are enhanced by a lower oxygen content and by a decreasing temperature.[7,8,9,16]

Let us now discuss, for the bismuth cuprates, the physical basis supporting the assumption of a different degree of electron correlations in the two types of planes.

In the high-T_c cuprates the occurrence of electron correlations in the CuO_2 planes is known to depend closely on the degree of filling of an antibonding hybridized one-electron conduction band Cu(3*d*)-O(2*p*).[14,17] If the CuO_2 planes are isolated, this band is half filled. Such a circumstance is known[14,17] to favor the occurrence of electron correlations, and can determine the CuO_2 planes to be antiferromagnetic Mott insulator at zero temperature. This type of situation is believed to be realized in stoichiometric La_2CuO_4 (Ref. 18) and in $YBa_2Cu_3O_{6+x}$ for $x<0.4$.[19]

In the case of the $n=2$ phase of the bismuth based family of compounds, electronic band calculations have shown that there are transfers of electrons from the type-I CuO_2 planes to the Bi-O planes of the structure via the bridging oxygens situated at the top of the pyramidal environment of the coppers atoms.[20] The Bi-O planes thus act as reservoirs for the creation of holes in the type-I CuO_2 planes and deplete the antibonding electron band associated with these planes, which accordingly is less than half filled. As a consequence the correlation effects are attenuated and a metallic normal state is possible.

In the $n=3$ compound, one expects that transfer of electrons from the type-II CuO_2 planes to the Bi-O planes will be less important from the type-I layers to the Bi-O ones. This has been shown theoretically for the similar thallium layered structure on the basis of a simplified electrostatic model,[4] which considers the distribution of the density of holes among the different CuO_2 planes of an elementary structural unit. In the framework of this model, there is an accumulation of 90% of the holes in the type-I planes that are closest to the reservoir planes Bi-O or Tl-O. The type-II planes, more distant from the reservoir planes, only contain 10% of the holes. This predicted difference between the two types of planes is qualitatively consistent with preliminary results of electronic band calculations, carried out for the $n=3$ phase.[21] These calculations show that the number of holes in the type-II planes is 90% of that in the type-I planes. Hence there are converging theoretical arguments, somewhat differing quantitatively, asserting that the density of holes in the type-II CuO_2 planes is smaller than in the type-I planes, in agreement with our assignment of stronger correlations in the former planes.

An attempt to estimate qualitatively the holes distribution among the type-I and type-II planes in the $n=3$ phase can be based on a comparison of our NMR data with those previously reported in the case of $YBa_2Cu_3O_{6+x}$ (see Refs. 8 and 9). Thus, the relative magnitude of the ^{17}O Knight shifts, as well as the temperature dependences of χ_s in the type-I and type-II planes, can be put in correspondence with the behavior of χ_s in $YBa_2Cu_3O_{6+x}$ for the two values $x=1$ and 0.85. Consistently with our preceding discussion we can assume that the ratio of the density of holes in the type-I and type-II planes is the same as the corresponding ratio for $x=1$ and 0.85 in $YBa_2Cu_3O_{6+x}$. Depending on the description adopted for the latter material, the density of holes, i.e., the excess in oxygen content with respect to the half-filled band situation, can be assumed proportional either[7,22] to $(x-0.4)$ or to x. On this basis, we obtain for the $n=3$ bismuth cuprates phase, a density of holes 15%–25% smaller in the type-II planes than in the type-I planes. This result appears closer to the predictions of the band-structure calculations[21] than to those of the electrostatic model.[4]

In conclusion, we have shown that our NMR measurements for the $n=3$ phase are consistent with the heterogeneous distribution of carriers recently conjectured.[4] We find the coexistence, in the same compound, on the one hand, of CuO_2 planes (type I) having a high density of holes, and no pronounced manifestations of antiferromagnetic correlations and of CuO_2 planes (type II) which present a hole deficiency, and where antiferromagnetic correlations exist and are apparently enhanced in the normal phase when the temperature is decreased.

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