

^{17}O NMR Evidence for a Pseudogap in the Monolayer $\text{HgBa}_2\text{CuO}_{4+\delta}$

J. Bobroff,¹ H. Alloul,¹ P. Mendels,¹ V. Viallet,² J.-F. Marucco,² and D. Colson²

¹LPS, URA2 CNRS, 91405 Orsay Cedex, France

²CEA-Saclay, Service de Physique de l'Etat Condensé, DRECAM/SPEC, 91191 Gif sur Yvette Cedex, France

(Received 20 December 1996)

Measurements of the spin shift $^{17}\text{K}_s$ have been performed for the ^{17}O NMR line in the monolayer cuprate $\text{HgBa}_2\text{CuO}_{4+\delta}$, and yield the spin susceptibility $\chi_s(T)$ of the CuO_2 planes. In the underdoped regime, χ_s is found to extrapolate to zero at $T \geq 0$. This indicates that a pseudogap opens at $T^* > T_c$, as in $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$. Therefore, the pseudogap features cannot be explained in terms of a magnetic coupling between CuO_2 planes in bilayer systems. In the overdoped regime, $\chi_s(T)$ obeys a Pauli-like law, as found in the overdoped $\text{Ti}_2\text{Ba}_2\text{CuO}_6$. Comparing the different monolayer systems, we suggest some correlation between T_c and distortion effects in the planes, as monitored by the ^{17}O NMR linewidth. [S0031-9007(97)03066-4]

PACS numbers: 74.25.Nf, 74.72.Gr

The existence of a pseudogap in the spin excitations of the underdoped cuprates is a very surprising and central characteristic of the magnetic properties of high- T_c superconductors. A decrease of the static spin susceptibility $\chi_s(\mathbf{q} = \mathbf{0}, \omega = 0)$ is observed with decreasing T in NMR shift experiments on ^{89}Y [1], ^{17}O [2], or ^{63}Cu nuclei [3]. In the same temperature range, the opening of a spin pseudogap at $\mathbf{q}_{\text{AF}} = (\pi, \pi)$ is known to occur in the CuO_2 planes between room T and T_c in bilayer and trilayer compounds as probed by ^{63}Cu NMR T_1 [4] and/or neutron scattering experiments [5].

The $\mathbf{q} = 0$ pseudogap is characterized by the fact that $\chi_s(T)$ extrapolates to zero at $T \geq 0$. In other words, if the superconducting transition were not to occur, the magnetic uniform susceptibility would show up a gap at a positive temperature. The situation is quite different in the monolayer $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, where $\chi_s(T)$ extrapolates to positive values at $T = 0$ K, whereas $^{63}\text{T}_1$ does not show the opening of a spin pseudogap [6]. Recent theories [7] argue that these two features can be interpreted as a manifestation of a spin density wave instability in this monolayer compound. In opposition, the same authors claim that the spin pseudogap observed in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ may be interpreted as a spin singlet pairing in adjacent CuO_2 layers, due to a sufficient coupling within the bilayer. The spin pseudogap would appear in this scheme as a peculiarity of bilayer compounds in the underdoped regime. Various experiments which probe the existence and the magnitude of this coupling have been performed to test this idea [8].

$\text{HgBa}_2\text{CuO}_{4+\delta}$, which can be synthesized with an optimum $T_c^{\text{max}} = 95$ K, is an appropriate candidate to probe the existence of a pseudogap in monolayers, as it can be underdoped, in contrast to $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$. We present ^{17}O measurements of $\chi_s(T)$ on a full range of oxygen contents. In the underdoped regime, the observed extrapolation of $\chi_s(T)$ to zero at $T \geq 0$ and its quantitative similarity to the $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ susceptibility proves that a pseudogap occurs in this monolayer system, which contradicts Ref. [7].

Moreover, an analysis based on the measured width of the NMR line is proposed in order to explain the difference between mercury and lanthanum compounds. We shall show that mercury is a prototype system for superconducting monolayer compounds, for which the oxygen content range can be probed.

The powder samples were prepared by a single step gold amalgamation technique, described in [9]. As ^{16}O has no nuclear spin, we have performed $^{17}\text{O}(I = \frac{5}{2})$ exchange. This has been done by annealing the sample at 300 °C, during one or two days in about 0.3 bar oxygen atmosphere, with an $^{17}\text{O}_2$ content of 40%. Further heat treatment allowed us to control the oxygen content in the mercury plane, and therefore the hole doping of the CuO_2 plane. The transition temperature T_c has been determined from zero-field cooling ac-susceptibility or SQUID measurements. For an as-quenched sample, we obtained $T_c = 89$ K, while slow cooling yields overdoped samples with T_c as low as 16 K. Heating the samples up to 450 °C in N_2 atmosphere allowed the synthesis of underdoped samples with T_c down to 75 K.

NMR experiments were performed in a 7.5 T field, using a standard $\frac{\pi}{2} - \tau - \pi$ pulse sequence. The ^{17}O NMR spectrum was obtained by Fourier transform of the spin echo. The spectra in Fig. 1 show the central transition $-\frac{1}{2} \longleftrightarrow \frac{1}{2}$ of the quadrupole splitted NMR spectrum, for a given sample, before and after the N_2 deoxidation step. Two well separated groups of lines are observed. The low frequency set of lines around 43.25 MHz is nearly unchanged, as seen in the inset. In contrast, the high frequency line shifts with oxidation state. By analogy with ^{17}O NMR in all other cuprates [2,10–12], the high frequency line is identified as being the plane oxygen O(2,3) line. The apical oxygen line is part of the low frequency group of lines, which has a long T_1 of the order of 1 sec. No simple assignment of the mercury plane additional oxygen line could be done, as we did not detect any marked change in this group of lines while reducing the concentration δ by about a factor 6.

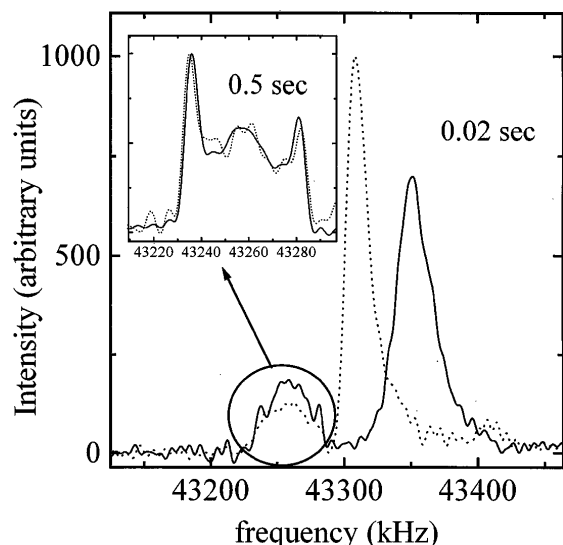


FIG. 1. Spectrum at $T = 300$ K before deoxidation (full line, $T_c = 61$ K) and after deoxidation (dashed line, $T_c = 75$ K) corresponding to a loss in oxygen content of $\Delta\delta \approx 0.15$. The repetition time of the NMR pulse sequence is 20 msec, which reduces artificially the low frequency group of lines (T_1 of the order of 1 sec). In the inset, this group of lines is shown for a repetition time of 0.5 sec.

For a spin $\frac{5}{2}$ and an applied field along the crystalline \mathbf{c} axis, the shift of the central transition, with respect to a liquid reference sample, is given by

$$(\nu - \nu_0)/\nu_0 = K_{\text{orb}} + K_s^c + \frac{2}{9}(\nu_a - \nu_b)^2/\nu_0^2, \quad (1)$$

where K_{orb} is the orbital shift, K_s^c the spin shift along \mathbf{c} , ν is the frequency, ν_0 is the reference frequency, and the last term is due to quadrupole effects. As usual in these systems, the temperature dependence of the shift is associated with K_s^c . The diamagnetic shift is supposed to be negligible. For the O(2,3) site, the quadrupole second order frequency shift $\delta\nu_q = \frac{2}{9}(\nu_a - \nu_b)^2/\nu_0$ has been obtained by comparing the measured shifts for two different fields $H_0 = 11.75$ T and $H_0 = 7.5$ T applied along \mathbf{c} in an aligned sample. Taking ν_0 as the position of ^{17}O in water, we find $\delta\nu_q = 17.7 \pm 3$ kHz in the 7.5 T field. This is near the value $\delta\nu_q = 19.4$ kHz found in $\text{Tl}_2\text{Ba}_2\text{CuO}_y$ [11], as could be expected from the similar geometries of the CuO_2 planes in the two compounds. The data for K_s of the CuO_2 planes are plotted versus T in Fig. 2, for various doping levels. Here, the orbital part of the shift has been taken to be $^{17}K_{\text{orb},c} = ^{17}K_{\text{orb},a} = 0.01\%$, as found in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [2]. From the uncertainty on both K_{orb} and $\delta\nu_q$, we expect the $K_s = 0$ position to be defined with an error bar of $\pm 0.01\%$.

Two distinct behaviors are observed. The spin shift of the underdoped compounds decreases with decreasing T , similarly to the underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, the $x = 0.6$ case being reported on the same figure. In contrast, as found for the slightly overdoped $\text{YBa}_2\text{Cu}_3\text{O}_7$ case (see

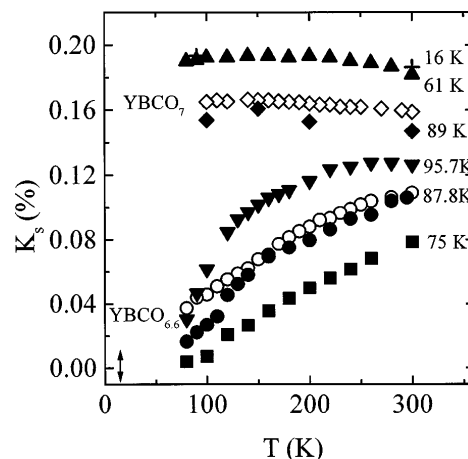


FIG. 2. K_s as a function of T for different doping levels for Hg compounds with the indicated T_c (solid symbols) and for YBaCu_{6+x} with $x = 0.6$ and 1 (empty symbols). The zero value for K_s is determined within an error bar of $\pm 0.01\%$ represented by the arrow.

Fig. 2), the overdoped regime is characterized by a nearly T -independent K_s [13]. For the highest doping levels, the variation of the shift is flat and increases with hole doping as found from ^{63}Cu NMR data in the overdoped monolayer $\text{Tl}_2\text{Ba}_2\text{CuO}_y$ [14].

Contrary to the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [12], the data shown in Fig. 2 for the underdoped regime allow us to stress here that $\chi_s(T)$ unambiguously extrapolates to zero at $T \geq 0$. $\text{HgBa}_2\text{CuO}_{4+\delta}$ being a monolayer system, this experimental fact proves that *pseudogap manifestation in underdoped cuprates is not characteristic of just the bilayer systems*. In such monolayer cuprates, the coupling between adjacent layers is known to be so weak from neutron scattering data in the AF state [15] that it cannot be invoked to produce a pseudogap. Itoh *et al.* [16] have performed a simultaneous work on the ^{63}Cu T_1 of the same underdoped materials where they find a pseudogap at $\mathbf{q} = (\pi, \pi)$. The link between these $\mathbf{q} = \mathbf{0}$ and $\mathbf{q} = (\pi, \pi)$ pseudogaps has been questioned in monolayer systems in view of the data found in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Thus, one important point disclosed by Ref. [16] and our work is the occurrence of both gaps in the present Hg monolayer compound, just as in bilayers.

One may wonder why $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compounds do differ in this respect, and whether this difference has any relationship with its low optimal T_c value $T_c^{\text{max}} = 38$ K. We attempt here to assign these differences to structural disorder effects. Those can be directly probed by measuring the NMR linewidth $\Delta\nu$ of the plane oxygen line. This width at room T measures distributions of K_s as we found it to scale with the applied magnetic field from 7.5 to 11 T, in the mercury compounds. This should be generally true, since second order quadrupole effects varying as the inverse of the applied magnetic field are much smaller than the width for ^{17}O in cuprates. For

our samples, the distribution of K_s might be ascribed to an inhomogeneity of the oxygen content. The full widths presented in Fig. 3 were found to be of about 50% of K_s , and were as low as 30% for the underdoped samples at 300 K, which are compatible with a distribution of K_s . This hypothesis of a macroscopic distribution of the oxygen content is confirmed by the existence of some correlation between $\Delta\nu$ and the superconducting transition width. The inhomogeneity and the linewidth could therefore certainly be reduced with better heat treatments.

In comparison, the linewidth of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.24$) is about 120% of K_s [12], while T_c is still defined. Such a large linewidth cannot be explained by a macroscopic distribution of Sr content. This disorder might as well induce the extrapolated positive χ_s at low T .

In this regard, Table I shows that the ^{17}O linewidth is somewhat correlated with T_c^{max} in the different monolayer compounds. The monolayer cuprates may be grouped into two families: Tl and Hg monolayers with large T_c and small $\Delta\nu$, and La and Bi monolayers with lower T_c and larger $\Delta\nu$. One might associate the low values of T_c in Bi and La compounds with an intrinsic disorder in the CuO_2 plane probed by $\Delta\nu$. As a matter of fact, both $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ are known to exhibit structural distortions which could be linked to this disorder. For La compounds, the tilt of the oxygen octahedra leads to the well-known magnetic nonsuperconducting phase at $x = \frac{1}{8}$. For Bi compounds, the crystal structure is found to display incommensurate distortion effects, in which the atomic positions are modulated in the \mathbf{c} direction. In this latter case, it has indeed been shown by x-ray analysis that substitution of La and Pb induce altogether an increase of T_c^{max} and a decrease of the structural distortions along the \mathbf{c} axis [17]. In bilayer systems, disorder within the CuO_2 planes also induces a strong reduction of T_c [18].

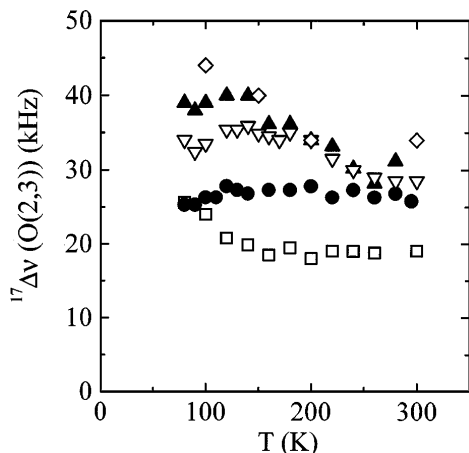


FIG. 3. Full width, taken at half maximum of the plane ^{17}O line, is plotted versus T with the same symbols as in Fig. 2 for the mercury compounds (some have been emptied for clarity).

In contrast to the Bi and La systems, the CuO_2 planes of $\text{HgBa}_2\text{CuO}_{4+\delta}$ are known to be rather flat, which explains the low values of $\Delta\nu$. Moreover, this linewidth is found almost T independent. One would expect a $1/T$ behavior for $\Delta\nu$ if a significant amount of magnetic defects were to occur within the planes. In $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, it has even been shown that “nonmagnetic” defects as Zn substituted on Cu site in CuO_2 planes also induce magnetic perturbations and the corresponding $1/T$ broadening [19,20].

So both the magnitude and the temperature independence of $\Delta\nu$ show that mercury monolayers are clean compounds.

Let us finally comment on the variation of $K_s(300\text{ K})$ with hole content. At high temperature, K_s is found to increase regularly with δ (Fig. 2). Unfortunately, because of our ^{17}O exchange procedure, we could not perform thermogravimetric measurements of δ on the NMR samples. But we could scale in Fig. 4 the T_c variations versus K_s with the T_c variations versus δ , obtained from measurements on nonenriched samples [21]. This scaling corresponds to a linear fit $K_s = 0.063 + 0.64\delta$. In this analysis, the zero reference for δ and K_s is not certain but from the slope 0.64 ± 0.05 , $K_s(300\text{ K})$ appears to give an independent determination of the relative doping levels of different samples. This holds at least for samples for which the pseudogap effects have disappeared at room T , namely for $\delta > 0.05$. We therefore confirm a similar analysis made in $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [22] and extend its validity to a very large range of doping content.

In conclusion, $\text{HgBa}_2\text{CuO}_{4+\delta}$ is the best experimental monolayer compound, as a large range of hole contents can be investigated, with minimal magnetic disorder effects. Its static spin susceptibility is found to display exactly the same T dependence as in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds, which establishes that the pseudogap at $\mathbf{q} = 0$ is not restricted to multilayer underdoped cuprates. A pseudogap temperature T^* may be defined as a crossover temperature between the low part of $\chi_s(T)$, which decreases with decreasing T , and the flat high temperature part. High temperature measurements are missing to evaluate T^* . Still, from Fig. 2, T^* decreases from above 300 K for the underdoped compound to around 200 K for the optimally doped one and encounters T_c for slightly overdoped ones. This decrease of T^* with increasing doping is similar to that found in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, in which the pseudogap disappears only for $x = 1$, the optimal doping

TABLE I. The different monolayer compounds with the associated T_c and NMR oxygen width.

	T_c^{max} (K)	^{17}O full width kHz/% of K_s
$\text{HgBa}_2\text{CuO}_{4+\delta}$	95	30 kHz/50%
$\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$	85	15 kHz/20% [11]
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$	38	90 kHz/120% [12]
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	10	70 kHz/110% [10]

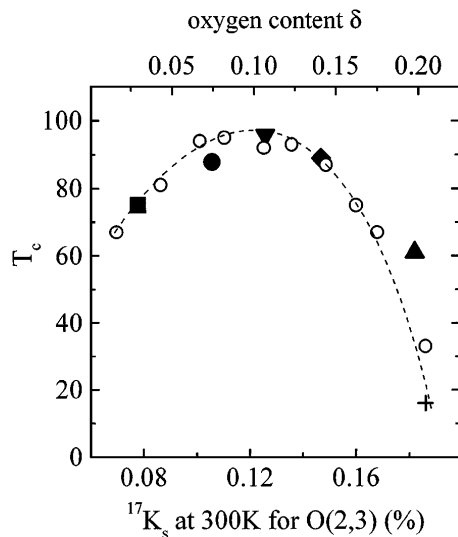


FIG. 4. T_c is plotted versus K_s (bottom axis) for the samples of Fig. 2 (same symbols). T_c versus thermogravimetric measurements of δ are reported (open circles) with the upper scale adjusted to bring the two T_c curves into coincidence [21]. The dashed line is a guide to the eye.

occurring for about $x = 0.95$. This proves once again the generality of the pseudogap behavior among the cuprates.

In contrast to these two systems, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ show large NMR linewidths, which is a signature of intraplane static distortion effects. We propose that their low value of T_c^{max} as compared to Tl and Hg compounds could be linked to these singular structural properties. Therefore, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with its specific phase-separation properties would not appear to be a generic compound for the monolayer cuprates. Finally, the overdoped regime has been studied and χ_s is found nearly constant with T , increasing with doping. Thus, the overdoped regime roughly belongs to the expected Fermi-Liquid behavior, in contrast with the strongly correlated underdoped regime.

We thank Arlette Trokner and P. V. Bellot for the use of the 11.5 T spectrometer at E.S.P.C.I., and Amit Keren for his constant interest and for stimulating discussions.

[1] H. Alloul, T. Ohno, and P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989).

- [2] M. Takigawa *et al.*, Phys. Rev. Lett. **63**, 1865 (1989); Y. Yoshinari *et al.*, J. Phys. Soc. Jpn. **59**, 3698 (1990).
- [3] R. E. Walstedt *et al.*, Phys. Rev. B **41**, 9574 (1990).
- [4] For a review, see C. Berthier, M. H. Julien, M. Horvatic, and Y. Berthier, J. Phys. I (France) **6**, 2205 (1996); M. H. Julien *et al.*, Phys. Rev. Lett. **76**, 4238 (1996).
- [5] J. Rossat Mignot *et al.*, Physica (Amsterdam) **169B**, 58 (1991).
- [6] S. Ohsugi, Y. Kitaoka, K. Ishida, and K. Asayama, J. Phys. Soc. Jpn. **60**, 2351 (1991).
- [7] B. L. Altshuler and L. B. Ioffe, Solid State Commun. **82**, 253 (1992); A. J. Millis and H. Monien, Phys. Rev. Lett. **70**, 2810 (1993); B. L. Altshuler, L. B. Ioffe, and A. J. Millis, Phys. Rev. B **53**, 415 (1996).
- [8] R. Stern, M. Mali, J. Roos, and D. Brinkmann, Phys. Rev. B **52**, 15734 (1995).
- [9] A. Bertinotti *et al.*, Physica (Amsterdam) **268C**, 257 (1996).
- [10] R. Dupree *et al.*, Physica (Amsterdam) **175C**, 269 (1991).
- [11] S. Kambe, H. Yasuoka, A. Hayashi, and Y. Ueda, Phys. Rev. B **47**, 2825 (1993).
- [12] G.-q. Zheng *et al.*, Physica (Amsterdam) **208C**, 339 (1993).
- [13] A nearly T -independent variation was also found in $\text{HgBa}_2\text{CuO}_{4+\delta}$ for the slightly overdoped composition by ^{63}Cu and ^{199}Hg NMR by B. J. Suh *et al.*, Phys. Rev. B **54**, 545 (1996).
- [14] Y. Kitaoka *et al.*, Physica (Amsterdam) **179C**, 107 (1991).
- [15] B. Keimer, N. Belk, and R. J. Birgeneau, Phys. Rev. B **46**, 14034 (1992), and references therein.
- [16] I. Itoh *et al.*, J. Phys. Soc. Jpn. **65**, 12 (1996).
- [17] Y. Dumont, Ph.D. thesis, University Paris XI, Orsay, 1996; (to be published).
- [18] A. Legris, F. Rullier-Albenque, and E. Radeva, J. Phys. I (France) **3**, 1605 (1993).
- [19] H. Alloul, P. Mendels, and H. Casalta, Phys. Rev. Lett. **67**, 3140 (1991); R. E. Walstedt and L. R. Walker, Phys. Rev. B **9**, 4857 (1974).
- [20] P. V. Bellot and A. Trokner (private communication): Recent results on Tl1212 show a $1/T$ broadening of $^{17}\Delta\nu[O(2,3)]$ of about 15 kHz between 100 and 300 K, in the scale of Fig. 3.
- [21] J.-F. Marucco *et al.*, Physica (Amsterdam) **275C**, 12 (1997).
- [22] J. L. Tallon *et al.*, Phys. Rev. B **53**, 11972 (1996).