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^{63}Cu NMR in the normal state of $HgBa_2Ca_2Cu_3O_{8+\delta}$

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We present a ^{63}Cu NMR study of $HgBa_2Ca_2Cu_3O_{8+\delta}$ underdoped single crystals with $T_c \simeq 115$ K. While the uniform spin susceptibility decreases below $T_0 \simeq 370$ K, relaxation rate measurements demonstrate the opening of a spin-gap at $Q = (\pi, \pi)$ below $T^* \simeq 230$ K, the highest temperature reported so far. The characteristic energy of spin fluctuations is shown to be higher than in underdoped $YBa_2Cu_3O_{7-\delta}$, and the analysis of the quadrupole and hyperfine couplings suggests that the in-plane Cu-O hybridization is also stronger. The T-dependence of T_1 is the same in the three CuO_2 planes which seems hardly compatible with the pure interlayer spin-pairing picture.

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1. INTRODUCTION

In the past years, strong experimental evidence has been accumulated for a drastic change in the electronic properties of high-T_c superconductors, when one goes from the underdoped regime (where T_c increases with hole doping) to the overdoped one (where T_c decreases). This difference was first evidenced in the magnetic response at $q = 0$[1] and $Q = (\pi, \pi)$,[2,3] where a pseudogap (or "spin-gap") shows up *in underdoped compounds.* Latter, a variety of transport measurements have revealed related anomalies,[4–7] and recently a pseudogap around $q = (0, \pi)$ has been observed by angle-resolved photoemission.[8] However, many aspects of the pseudogap phase remain to be explored and/or clarified. Here, we present a ^{63}Cu NMR investigation of underdoped $HgBa_2Ca_2Cu_3O_{8+\delta}$ single crystals. It is shown that (i) the

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spin-gap at (π, π) opens at higher temperature than in underdoped YBCO, (ii) the characteristic energy of magnetic fluctuations and the in-plane Cu-O hybridization are also comparatively higher in this very high T_c compound.

2. SAMPLE

The sample is a mosaic of 23 single crystals[9] with common c-axis. Although AC susceptibility measurements have revealed a broad superconducting transition between 134 K and 110 K, subsequent specific heat measurements on selected crystals have shown that the bulk T_c was in the range 113-116 K. Therefore the broad transition observed in the susceptibility is ascribed to a surface inhomogeneity. This conclusion is also supported by the fact that no sign of oxygen distribution could be detected from the NMR measurements, namely we observed well defined lines and no distribution of the relaxation rates.

3. SPECTRA AND QUADRUPOLE COUPLINGS

For $H_0 \parallel ab$-plane, we identified two lines corresponding to the two copper sites : Cu(2) in the outer planes and Cu(1) in the inner plane. For $H_0 \parallel c$, the lines overlap completely. From the position of the NMR lines we have extracted the ^{63}Cu quadrupole coupling frequencies ν_Q which characterize the interaction between nuclear quadrupole moments and electric field gradients: $\nu_Q[^{63}Cu(1)] = 9.7$ MHz and $\nu_Q[^{63}Cu(2)] = 13.7$ MHz are the smallest values ever reported in the cuprates, for the square and pyramidal coordination of copper respectively. We have proposed[10] that the small values of ν_Q may be related to the absence of buckling in the CuO_2 planes of Hg-based materials, i.e., the Cu-O-Cu bond angles are very close to 180°. Although the origin of electric field gradients is still controversial, both current approaches, namely the point charge approximation[11] and the on-site electronic model,[12] appear to be compatible with this explanation.

4. MAGNETIC HYPERFINE SHIFT

Assuming that the quadrupole coupling is T-independent, we may extract the magnetic hyperfine shift of copper (^{63}K) from the positions of the NMR lines (Fig. 1). As usual, K is expressed as the sum of an orbital contribution, and a spin part K_s solely responsible for the T-dependence. As seen in Fig. 1, K_s shows a continuous decrease with T, typical of underdoped compounds.[1] This decrease starts well above T_c, at T_0 which we estimate $\simeq 370$ K, in close correlation with the anomalous curvature of the in-plane

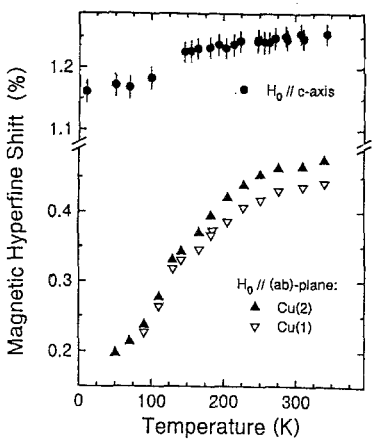

Fig. 1. Magnetic hyperfine shift of Cu.

resistivity.[13,14] Since K_s is proportional to the uniform spin susceptibility χ_s, this behaviour is rather anomalous in a Fermi-liquid picture. In the framework of the ionic model proposed by Mila and Rice,[15] one has:

$$^{63}K_s = (A + 4B)\chi_s/g\mu_B, \tag{1}$$

with A and B being the on-site and transferred hyperfine coupling constants respectively. Assuming the same values of A as in YBCO:[16] A_{ab} = 70 kOe and A_c = -332 kOe, we derive that $B^{Cu(2)}$ =136 kOe and $B^{Cu(1)}$ = 146 kOe (absolute values ±15%).[17] These values are much higher than for YBCO (B = 83 kOe), revealing a stronger hybridization between Cu and O orbitals. This, again, is compatible with the absence of buckling. According to Zheng *et al.*,[12] the relatively low value of K^c_{orb} ($\sim$ 1.19 %) has also the same origin. On the other hand, the values of the spin susceptibility ($\sim 5 \times 10^{-5}$ emu/mole) are comparable to those of typically underdoped YBCO.[18] It is conceivable that a higher Cu-O hybridization for the same doping level should lead to a higher value of the in-plane antiferromagnetic superexchange J.

5. SPIN-LATTICE AND SPIN-SPIN RELAXATION RATES

In Fig. 2 we show the T-dependence of $(^{63}T_1T)^{-1}$ for both sites and $H_0 \parallel ab$, along with preliminary data for the nuclear spin-spin relaxation rate $(^{63}T_{2G})^{-1}$. For the latter measurements H_0 was $\parallel c$, and so each $(^{63}T_{2G})^{-1}$ value is an average of the Cu(1) and Cu(2) sites. However, in light of the $^{63}K_s$ and $(^{63}T_1)^{-1}$ data, we do not expect a large difference in the magnitude and

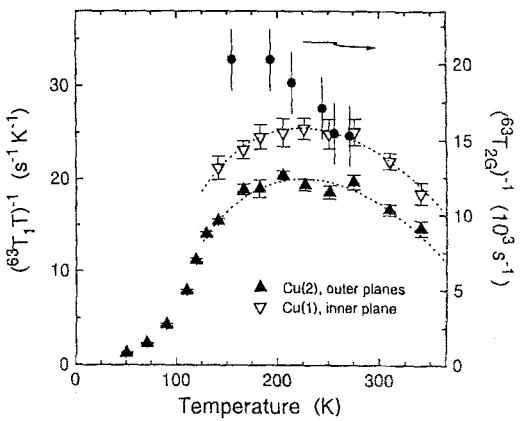

Fig. 2. Cu Spin-lattice relaxation rates ($H_0 \parallel ab$), and gaussian spin-spin relaxation rate ($H_0 \parallel c$).

the T-dependence of $(^{63}T_{2G})^{-1}$ for the two Cu sites. The results of Magishi *et al.* in optimally doped Hg-1223 have fully justified this assumption.[19] Note also that the sizeable error bars reflect more uncertainties in the absolute values of $(T_{2G})^{-1}$, than in the T-dependence.

While $(^{63}T_1T)^{-1}$ increases with decreasing T and starts to drop at $T^* \simeq 230$ K, $(^{63}T_{2G})^{-1}$ continues increasing and eventually saturates below ~ 200 K. The combination of these two behaviors demonstrates unambiguously the opening of a spin-gap at (π, π) with redistribution of spectral weight from low to high energies as is observed in underdoped YBCO.[20]

It is remarkable that the characteristic temperature for this spin-gap $T^* \simeq 230$ K is higher than in all other systems studied so far (typically 120 K $\leq T^* \leq$ 165 K), suggesting that T^* may be the characteristic energy scale for the pairing. Indeed, Hg-1223 has the highest T_c among the cuprates ($T_c^{max} \sim 135$ K at ambient pressure, and ~ 160 K at 30 GPa[21]).

A quantitative analysis of the relaxation data has been presented elsewhere;[14] we refer the reader to this reference and to Ref.[22] for more details. The spirit is that of the RPA calculation of Millis, Monien and Pines,[23] modified in order to fit with neutrons data in YBCO. We show that one can define a magnetic pairing energy as $\Omega_{sf} = \omega_{sf}\xi$, regardless of the absolute value of the AF correlation length ξ, as soon as $\xi \geq 2$ (ω_{sf} is the characteristic frequency of spin fluctuations at (π, π)). In other words, no T-dependence has to be assumed. Then, we calculate that for Hg-1223 $\Omega_{SF} =$ 95 meV and for $YBa_2Cu_3O_{6.63}$[24] $\Omega_{SF} = 75$ meV. The magnetic energy scale Ω_{SF} is clearly higher for the Hg-compound, a fact which appears compatible

with the proposal that J is higher in Hg-1223. This result supports quite naturally a pairing which is mediated by spin-fluctuations, as in the model proposed by Monthoux and Pines in the so-called "nearly antiferromagnetic Fermi-liquid" scenario.[25] Recently, the same conclusion has been reached from a similar analysis of the nuclear relaxation of Cu in underdoped Tl-2223[26] and optimally doped Hg-1223.[19] Of course, a proper description of spin dynamics in the cuprates is far from being settled down, and our conclusion may be model-dependent. In any case, the pairing is very likely to be associated to an electronic energy scale.

Lastly, within a simple RPA calculation of the dynamic susceptibility χ'' of three CuO_2 planes coupled by a weak $J_\perp$,[27] one finds that χ'' is more strongly enhanced by $J_\perp$ in the inner layer than in outer ones. As within experimental accuracy, no difference can be detected in the T-dependence of $1/T_1T \propto \chi''(Q)$ for both Cu sites, we conclude that $J_\perp$ has no significant impact on the T-dependence of the planar spin dynamics. Consequently, this first clear observation of a spin-gap at (π,π) in a three-layered compound does not seem to be in favor of a *pure* interlayer spin-pairing.[28] Recently, the interplane singlet order has also been questionned from theoretical works on the $t-J$ model.[29,30]

6. CONCLUSION

Summarizing our results, we have performed a Cu NMR investigation of Hg-1223 single crystals. The sample has a doping level comparable to that of underdoped YBCO with $T_c \sim$ 60-70 K. However, the in-plane Cu-O hybridization, the temperature $T^* \simeq 230$ K at which a spin-gap opens at $q = (\pi,\pi)$, and the characteristic magnetic energy $\omega_{sf}\xi$ are found to be comparatively higher. The interlayer spin-singlet pairing seems unlikely to be the origin of the spin-gap.

REFERENCES

1. H. Alloul, T. Ohno and P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989).
2. H. Yasuoka, T. Imai and T. Shimizu, in *Strong Correlations and Superconductivity*, Ed. by H. Fukuyama, S. Maekawa, and A.P. Malozemoff (Springer Verlag, Berlin, 1989) p. 254.
3. M. Horvatić *et al.*, Phys. Rev. B **47**, 3461 (1993).
4. B. Battlogg *et al.*, Physica C **235-240**, 130 (1994).
5. K. Mizuhashi, K. Takenada, Y. Fukuzumi, and S. Uchida, Phys. Rev. B **52**, R3884 (1995) and references therein.
6. J.W. Loram *et al.*, Phys. Rev. Lett. **71**, 1740 (1993).
7. C.C. Homes *et al.*, Physica C **254**, 265 (1995) and references therein.
8. A.G. Loesser *et al.*, preprint; D.S. Marshall *et al.*, preprint.

9. D. Colson *et al.*, Physica C **233**, 231 (1994).
10. M.-H. Julien *et al.*, to be published.
11. T. Shimizu *et al.*, Bull. Magn. Res. **12**, 39 (1990).
12. G.-q. Zheng, Y. Kitaoka, K. Ishida, and K. Asayama, J. Phys. Soc. Jpn. **64**, 2524 (1995).
13. A. Carrington *et al.*, Physica C **234**, 1 (1994).
14. M.-H. Julien *et al.*, Phys. Rev. Lett. **76**, 4238 (1996).
15. F. Mila and T.M. Rice, Physica C **157**, 151 (1989).
16. M. Takigawa *et al.*, Phys. Rev. B **43**, 247 (1991).
17. Note that these values of B precisely account for the anisotropy of T_1.
18. On the basis of our results, it is difficult to make an accurate comparison with the doping level of typically underdoped YBCO samples. Carrington *et al.*[13] have suggested from a scaling analysis of resistivity data that the doping level of Hg-1223 crystals having the same bulk T_c as those presented here was presumably intermediate between that in $YBa_2Cu_3O_{6.72}$ and $YBa_2Cu_3O_{6.77}$, for which T_c= 67 K and 81 K, and T_0 = 233 K and 210 K, respectively. This could possibly imply that T_0 is higher in the compound having a higher T_c, at equal doping levels.
19. K.-i. Magishi *et al.*, J. Phys. Soc. Jpn. **64**, 4561 (1995).
20. C. Berthier *et al.*, Physica C **235-240**, 67 (1994) and references therein.
21. M. Nũnez-Regueiro *et al.*, Science **262**, 97 (1993); C.W. Chu et al., Nature (London) **365**, 323 (1993).
22. T. Auler *et al.*, Physica C **235-240**, 1677 (1994).
23. A.J. Millis, H. Monien and D. Pines, Phys. Rev. B **42**, 167 (1990).
24. M. Takigawa, Phys. Rev. B **49**, 4158 (1994).
25. P. Monthoux and D. Pines, Phys. Rev. B **49**, 4261 (1994).
26. G.-q. Zheng *et al.*, J. Phys. Soc. Jpn. **64**, 3184 (1995); Physica C **260**, 197 (1996).
27. A.J. Millis and H. Monien, preprint cond-mat/9506088.
28. B.L. Altshuler, L.B. Ioffe, and A.J. Millis, Phys. Rev. B **53**, 415 (1996) and references therein.
29. R. Eder, Y. Ohta, and S. Maekawa, Phys.Rev. B **52**, 7708 (1995).
30. B. Normand, H. Kohno, and H. Fukuyama, J. Phys. Soc. Jpn. 64, 3903 (1995).