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MEASUREMENTS OF THE ELECTRIC FIELD GRADIENT AT CADMIUM IN

$\text{YBa}_2\text{Cu}_3\text{O}_x$ ,  $\text{Y}_2\text{BaCuO}_5$  AND  $\text{Y}_2\text{Cu}_2\text{O}_5$

by

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**ABSTRACT**

The Electric Field Gradient (EFG) at diluted  $\text{Cd}^{111}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  was measured by Angular Correlation (AC). In order to determine the atom-probe localization, AC measurements were also performed on  $\text{Y}_2\text{BaCuO}_5$  and  $\text{Y}_2\text{Cu}_2\text{O}_5$ . A nuclear electric quadrupole interaction frequency (NQIF) was associated with  $\text{Cd}^{111}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  Cu(1) site.

Key-words: Angular Correlation; Electric Field Gradient; High Tc Superconductor.

## INTRODUCTION

Since the discovery of high  $T_c$  superconductor  $YBa_2Cu_3O_x$ ,  $x > 6.5$ , a great deal of effort has been done, using a variety of bulk and microscopic techniques, to understand its structure, composition<sup>[1,2]</sup>, as well as its lattice particle-hole dynamics<sup>[3]</sup>. Within this context, some studies had already been done on  $YBa_2Cu_3O_x$  and on the related materials, such as  $Y_2BaCuO_5$  and  $Y_2Cu_2O_5$ <sup>[4-11]</sup>, among them the perturbed angular correlation (PAC) measurements. These are most frequently performed via the  $Cd^{111}$  atom-probe. In the case of  $YBa_2Cu_3O_x$  and the related compounds, the use of  $Cd^{111}$  as an atom-probe may give rise to some uncertainties concerning its position(s) in the lattices, for the following reasons: a)  $Cd^{111}$  is not among its constituents, b) the existence of several different substitutional and/or interstitial sites in a single phase material. Furthermore  $Cd^{111}$ , as a substitute element, could give rise to structural inhomogeneities, precipitations and unidentified complex clusters. All these uncertainties make the safe identification of the atom-probe site an essential point.

In this paper we report PAC measurements on  $YBa_2Cu_3O_x$ ,  $Y_2BaCuO_5$  and  $Y_2Cu_2O_5$ , and identify the possible  $Cd^{111}$  atom-probe site in  $YBa_2Cu_3O_x$  and the related NQIF. We also show that other PAC parameters which have already been suggested in the early studies<sup>[9,11]</sup>, in the case of  $YBa_2Cu_3O_x$ , may be highly questionable.

## EXPERIMENTAL DETAILS

Polycrystalline samples of  $YBa_2Cu_3O_x$ ,  $Y_2BaCuO_5$  and  $Y_2Cu_2O_5$

were prepared from stoichiometric mixtures of  $Y_2O_3$ ,  $BaCO_3$  and  $CuO$ , under oxygen flow, at 970C, for 15hs, and then cooled slowly with a decay rate of 50C/h. The X-ray diffraction pattern of  $YBa_2Cu_3O_x$  and  $Y_2BaCuO_5$  showed the orthorombic structures. In the case of  $Y_2Cu_2O_5$ , X-ray pattern did not show the reagents lines, suggesting a full reaction. The characterization of superconductivity was done by the magnet test (Meissner effect) after cooling the  $YBa_2Cu_3O_x$  samples to 77K; some of them were also checked by magnetic susceptibility measurements: all of them showed a transition near 90K; they also kept the superconductivity property for several months after preparation.

The  $YBa_2Cu_3O_x$  off stoichiometric sample,  $x < 6.5$ , was prepared by heating it at 500C for 2hs, under argon flow, and its X-ray diffraction data showed the well known tetragonal structure; the same procedure was also applied to  $Y_2BaCuO_5$ . The  $In^{111}$  activity, obtained via the nuclear reaction  $Ag^{109} (\alpha, 2n) In^{111} \rightarrow Cd^{111}$ , was carrier free extracted and the carrier free solution was dropped directly onto the reagents mixtures, and so  $In^{111}$  was introduced in the samples lattices during sinterization, with an indium concentration below an upper limit of  $10^{-4}$  at %. Using the  $Cd^{111}$  (172-247)KeV nuclear cascade, the PAC measurements, were carried out with a fast-slow coincidence timing electronics four detector setup - NaI(Tl) scintillation crystals mounted on photomultipliers in a plane  $90^\circ$  intervals. The resolving time was about 3.5 Nsec, and an electronic router allowed to store four simultaneous coincidence spectra, which were then combined to eliminate the exponential decay of  $W(\theta, t)$  and to obtain the intensity ratios  $R(t)$  (Fig. 1), which were fitted in a manner described elsewhere [12]

$$R(t) = \frac{2}{3} \left\{ \frac{N_{13}(180^\circ, t) N_{24}(180^\circ, t)}{N_{14}(180^\circ, t) N_{23}(180^\circ, t)} \right\}^{1/2} - 1 \quad (1)$$

where  $N_{ij}(\theta, t)$  represent the coincidence rate at a certain angle and detector configuration.

## RESULTS AND DISCUSSIONS

PAC measurements parameters on  $YBa_2Cu_3O_x$ ,  $Y_2BaCuO_5$  and  $Y_2Cu_2O_5$  are displayed in Table I; except in the  $Y_2Cu_2O_5$  sample, the other two exhibited a common quadrupole interaction ( $\sim 5\%$  relative fraction) indicating the presence of  $In_2O_3$ ; this interaction will not be discussed here.

As far as the  $YBa_2Cu_3O_x$  is concerned, measurements were performed in several samples and the results could be divided in two groups, Sample I and Sample II, with the main difference between them being the presence of an extra interaction in Sample I; this interaction is the dominant one in  $Y_2BaCuO_5$  sample. This suggests that Sample II was better sintered than Sample I, since Sample I showed an  $Y_2BaCuO_5$  extra phase. In the following  $YBa_2Cu_3O_x$  will always refer to Sample II. Measurements on  $Y_2Cu_2O_5$ , another phase which may occur as a result of sample preparation, displayed PAC parameters quite different from  $YBa_2Cu_3O_x$  ones.

The two NQIF we measured in  $YBa_2Cu_3O_x$  are quite close, with one of them highly predominant - in the light of this result, we could perhaps advance that we are dealing with

only one NQIF, the predominant one, with the second less significant; this is probably due to slight site distortions and/or different oxygen coordination. In order to check this possible  $\text{Cd}^{111}$  site,  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and  $\text{Y}_2\text{BaCuO}_5$  were reduced for their oxygen content: X-ray measurements on these oxygen reduced samples displayed the tetragonal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_x$ ,  $x < 6.5$ , whereas no change was observed in  $\text{Y}_2\text{BaCuO}_5$ ; furthermore, PAC measurements on the oxygen reduced samples showed noticeable change in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  parameters and no change in  $\text{Y}_2\text{BaCuO}_5$ . These features seem to reveal, as far as  $\text{YBa}_2\text{Cu}_3\text{O}_x$  is concerned, that the position(s) of the  $\text{Cd}^{111}$  is (are) quite sensitive upon environmental oxygen content; and it is well known that these are the Cu(1) sites. So, we are tempted to assume  $\omega_Q = 6.0(0)\text{Mrad/sec}$  of Table I (or a value very near to it) is related to NQIF undergone by  $\text{Cd}^{111}$  in Cu(1) site.

Recently<sup>[11]</sup> two NQIF were observed in  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , which were attributed to Cu(1) site with different second nearest neighbours,  $\omega_{Q1} = 21.92\text{ Mrad/sec}$  and  $\omega_{Q2} = 24.47\text{ Mrad/sec}$ , at room temperature. A slightly different NQIF  $\omega_Q = 24.18\text{ Mrad/sec}$ , attributed to the Cu(1) site was observed in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  by a second group<sup>[9]</sup>; PAC measurements performed by the same group in  $\text{Y}_2\text{Cu}_2\text{O}_5$  displayed parameters remarkably close to the

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The NQIF from other references are normalized to the units we are using:

$$\omega_Q [\text{rad/sec}] = \frac{\pi}{2Q} \gamma_Q [\text{Hz}]$$

$\text{YBa}_2\text{Cu}_3\text{O}_x$  ones values. The oxygen reduction they performed on  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , heated during one hour at 710C in high vacuum lead it to  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , which displayed a NQIF  $\omega_0 = 21.04$  Mrad/sec, also took as undergone by  $\text{Cd}^{111}$  in the Cu(1) site of the oxygen reduced phase.

The similarity between our  $\text{Y}_2\text{Cu}_2\text{O}_5$  PAC parameters and that of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  [9,11] lead us to perform the same oxygen reducing procedure with our  $\text{Y}_2\text{Cu}_2\text{O}_5$ : the PAC parameters obtained in our case,  $\omega_0 = 21.70$  Mrad/sec and  $\eta = 0$ , including the R(t) pattern, are quite coincident with those measured on  $\text{YBa}_2\text{Cu}_3\text{O}_6$  [9]. The absence of  $\text{BaCO}_3$  in the  $\text{Y}_2\text{Cu}_2\text{O}_5$  we have prepared reveals the fact that it was not a sinterization of a  $\text{YBa}_2\text{Cu}_3\text{O}_x$  phase.

In the light of our results, the NQIF which have already been associated with the  $\text{Cd}^{111}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  Cu(1) site [9,11] are questionable. We believe that they are due to a  $\text{Y}_2\text{Cu}_2\text{O}_5$  phase segregation.

## CONCLUSIONS

- a) Different PAC parameters measured on  $\text{YBa}_2\text{Cu}_3\text{O}_x$ ,  $\text{Y}_2\text{BaCuO}_5$  and  $\text{Y}_2\text{Cu}_2\text{O}_5$  lead to the assumption that immersed  $\text{Cd}^{111}$  on those compounds don't form isolated clusters, independent of the host lattice, even if the compounds are prepared from the same reagents following the same heat treatment on their sinterization;
- b)  $\omega_{Q1} = 21.92$  Mrad/sec and  $\omega_{Q2} = 24.47$  Mrad/sec should not be associated to Cu(1) site in  $\text{YBa}_2\text{Cu}_3\text{O}_x$ ;

c)  $\omega_Q = 6.0$  Mrad/sec is a reasonable value to relate NQI undergone by  $Cd^{111}$  in Cu(1) site in  $YBa_2Cu_3O_x$ .

Further work is in progress on the subject.

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-7-

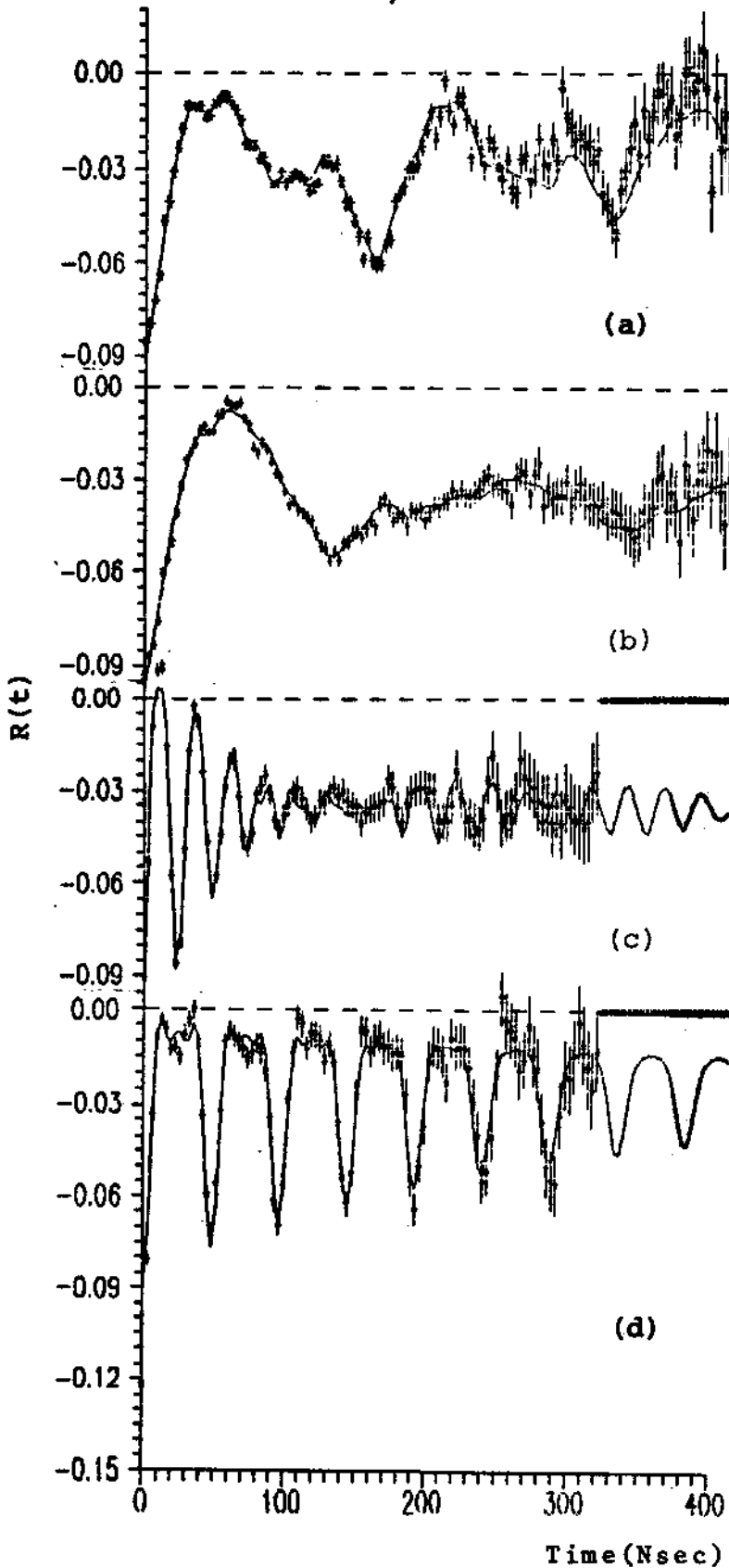


Fig. 1 - PAC  $R(t)$  fitted spectra of  $Cd^{111}$  in  $YBa_2Cu_3O_2$  and  $Y_2Cu_2O_5$

a)  $YBa_2Cu_3O_x$  - 296K

b)  $YBa_2Cu_3O_x$  reduced in argon flux - 296K

c)  $Y_2Cu_2O_5$  - 296K

d)  $Y_2Cu_2O_5$  heated at 710C, high vacuum - 296K

TABLE I: PAC measurements for  $\text{YBa}_2\text{Cu}_3\text{O}_x$ ,  $\text{Y}_2\text{BaCuO}_5$  and  $\text{Y}_2\text{Cu}_2\text{O}_5$  doped with  $\text{Cd}^{111}$ 

T	$f^I$	$\omega_Q^I$	$\eta^I$	$\delta^I$	$V_{zz}^I$	$f^{II}$	$\omega_Q^{II}$	$\eta^{II}$	$\delta^{II}$	$V_{zz}^{II}$	$f^{III}$	$\omega_Q^{III}$	$\eta^{III}$	$\delta^{III}$	$V_{zz}^{III}$
$\text{YBa}_2\text{Cu}_3\text{O}_x$															
296a	37(7)	6.2(1)	.31(4)	1(1)	1.96(3)	23(14)	7.0(2)	.49(4)	5(5)	2.22(6)	40	9.1(3)	.36(3)	11(3)	2.88(6)
200a	28(6)	6.3(0)	.23(5)	0(1)	1.99(0)	27(13)	6.8(1)	.49(3)	4(4)	2.15(3)	45	8.7(1)	.39(2)	8(2)	2.75(4)
296a1	33(6)	5.7(1)	.36(3)	2(2)	1.80(3)	19(8)	7.8(1)	.39(4)	0(2)	2.47(3)	48	9.3(1)	.0	11(3)	2.95(3)
296b	84(5)	6.0(0)	.34(1)	4(1)	1.90(0)	16(4)	6.7(1)	.58(4)	1(2)	2.12(3)					
77b	37(7)	6.5(1)	.0	4(2)	2.06(3)	63(7)	6.5(1)	.47(3)	7(1)	2.06(3)					
296b1	100	4.6(0)	.61(1)	13(1)	1.46(0)										
296c	30	24.4(1)	1.0		7.74(2)	45.0	21.9(1)	1.0		6.95(2)					
296d2	100	21.0(5)	0.	2	6.66(6)										
$\text{Y}_2\text{BaCuO}_5$															
296	46.	12.2(7)	.0	20(7)	3.87(2)	54(10)	8.9(1)	.27(2)	4(1)	2.82(3)					
2961	52.	19.8(1.7)	.0	21(9)	6.28(5)	48(7)	9.2(1)	.25(4)	3(2)	2.91(3)					
$\text{Y}_2\text{Cu}_2\text{O}_5$															
296	70(2)	24.8(1)	.90	.02	7.86(3)	30	21.0(1)	1.0	.02	6.66(3)					
2962	100	21.9(0)	.0	.01	6.94(0)										

T = temperature in K;  $f^i$  = relative fractions in %;  $\omega_Q^i$  = quadrupole frequency in Mrad/sec.

$\eta^i$  = asymmetry parameters;  $\delta^i$  = quadrupole frequencies relative widths in %.

$V_{zz}^i$  = electric field gradients in  $10^{17}$  Volt/cm<sup>2</sup>.

a this work Sample I

b this work Sample II

c refs. 9, 11

d ref. 9

1 reduced in argon flux at 500C

2 reduced in high vacuum at 700C.

## REFERENCES

- [1] F. Iseimi, H. Asano, T. Ishigaki, E. Takaiowa, Y. Uski, N. Watanabe, T. Nishicawa; J.J. Appl. Physics 26 n<sup>o</sup> 5 (1987) L649.
- [2] M.A. Beno, L. Sonderholm, D.W. Capone II, D.G. Hinks, J.D. Jorgensen, I.K. Schuller, C.V. Segre, K. Zheng, J.D. Grese; Appl. Phys. Lett. 59 (1987) 57.
- [3] E. Baggio Saitovitch, R.B. Scorzelli; I. Souza Azevedo, H. Micklitz; Physical Review B 41 n<sup>o</sup> 4 (1990).
- [4] E. Baggio Saitovitch, I.S. Azevedo, R.B. Scorzelli, H. Saitovitch, S.F. Cunha, A.P. Guimarães, P.R.J. Silva, A.Y. Takeuchi; Physical Review B 37 n<sup>o</sup> 13 (1988) 7967.
- [5] H. Saitovitch, P.R.J. Silva, E. Baggio Saitovitch, I.S. Azevedo, R.B. Scorzelli, S.F. Cunha, A.P. Guimarães, L.C. Sampaio, J.A. Martinez; Progress in High Temperature Superconductivity 9 (1988) 377.
- [6] H. Saitovitch, P.R.J. Silva, E.B. Saitovitch, I.S. Azevedo, R.B. Scorzelli, S.F. Cunha, A.P. Guimarães, L.C. Sampaio; Latin American Conf. on High Temp. Sup. (Proceedings), May/1988 Rio de Janeiro, Brazil; pages 377-380.
- [7] P. Singh, M.N. Nyayate, S.H. Devare, H.G. Devore; Physical Review B39 n<sup>o</sup> 4 (1984) 2308.
- [8] M. Uhrmacher, A. Bartos, K. Winzer; Journal of Less Common Metals 150 (1989) 185.
- [9] M. Uhrmacher, A. Bartos; HFI'89: B3-7, B3-32.
- [10] H. Plank, M.F. Mayer, W. Witthuhn; Physics Letters A 133 (1988) 451.

- [11] H. Plank, O. Baner, D. Forkel, F. Mayer, B. Roas, G. Saemann  
Ischenko, J. Ströbel, H. Wolf, W. Witthuhn; HFI'89; B3-23.
- [12] M. Forker, H. Saitovitch, P.R.J. Silva; J. Phys. C. Solid  
State Physics 17 (1984) 1055.