Local probing of Hg neighborhood in HgBa$_2$CuO$_{4+δ}$

J. G. Correia$^{a,b}$, J. P. Araújo$^b$, S. M. Loureiro$^c$, P. Toulemonde$^d$, S. Le Floch$^d$, P. Bordet$^d$, J. J. Capponi$^d$, R. Gatt$^e$, W. Tröger$^f$, B. Ctortecka$^f$, T. Butz$^g$, H. Haas$^g$, J. G. Marques$^a$, J. C. Soares$^a$ and the ISOLDE collaboration$^h$.

$^a$Istituto Tecnológico e Nuclear, Estrada Nacional 10, P-2685 Sacavém, Portugal and CFNUL, Av. Prof. Gama Pinto 2, P-1699 Lisboa Codex, Portugal

$^b$IFIMUP, Phys. Dept., FCP, Rua do Campo Alegre 687, P-4150 Porto, Portugal

$^c$Princeton Univ., Chemistry Dept., Princeton NJ 08544, USA

$^d$Lab. de Cristallographie, CNRS, Av. des Martyrs 25, F-38042 Grenoble CEDEX 9, France

$^e$Phys. Dept. (M/C 273), 2168 SES, Univ. of Illinois, Chicago, IL, USA 60612

$^f$Fakultät für Physik und Geowissenschaften, Univ. Leipzig, Linnéstraße 5, D-04103 Leipzig, Germany

$^g$Bereich Festkörperphysik, Hahn-Meitner-Institut Berlin GmbH, D 14109 Berlin, Germany

$^h$CERN-EP/SC, CH-1211 Geneva 23, Switzerland

Electric field gradients (EFG) on mercury sites of the Hg1201 high-$T_C$ superconductors were measured with the perturbed angular correlation (PAC) technique. In Hg1201 samples where PAC detects higher oxygen content the EFGs have decreased to lower values indicating an elongation of the Hg-apical oxygen dumbbell. On the same samples the asymmetry parameter of the EFG becomes non-zero below 100 K, showing that the charge distribution near the Hg-apical oxygen chain becomes non-axially symmetric at low temperature.

1. INTRODUCTION

The family of Hg$_x$Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+δ}$ materials are among the most interesting high-$T_C$ superconductors due to their simple tetragonal lattice structure and high $T_C$ values [1]. However, the Hg planes are particularly disordered due to vacancies, impurities replacing Hg and the presence of the non-stoichiometric oxygen $O_x$ that is considered to be the dopant that regulates $T_C$. Neutron diffraction [2] as well as more local methods such as EXAFS [3] pointed to the existence of local distortions in these compounds. So far it is not clear if such effects are linked to the superconductivity mechanism or are simply due to crystal-impurity interaction effects.

Nuclear hyperfine techniques like nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are extremely useful in providing atomic scale information on the probe-element interactions with the lattice host [4]. Unfortunately, NQR on stable Hg isotopes is not efficient. Alternatively, we have recently shown [5] that using the time differential perturbed angular correlation of γ rays (PAC) technique [6] and the 42.6 minutes half-life 199mHg excited nuclei, the electric field gradients (EFG) at the Hg site in Hg1201 (n=1) can be measured. The interaction of the EFGs, which are generated by the charge distribution around the probe 199mHg nuclei, with the quadrupole moment (Q) of the 5/2→158 keV intermediate state of the nuclear cascade leads to this level energy splitting. That induces a time dependent modulation G(t) on the intensity of the angular correlation of the first γ-ray ($γ_1$), that populates the 158keV state, and the second γ-ray ($γ_2$) emitted when this state decays. Experimentally, G(t) is observed as a modulation of the half-life of the 158 keV state. In the present work, the PAC technique was applied to investigate the EFGs on Hg sites of the Hg1201 (n = 1)
compound. For comparison, first results performed on Hg1212 \((n=1)\) are included.

2. EXPERIMENTAL

Hg1201 (and Hg1212) powder samples were produced by solid state reaction under high pressure \[7\]. To reduce the \(O\) concentration two sets of Hg1201 samples were annealed at 523K under 1 bar Ar flow during 24h \((\text{set A}, a = 3.8785(4) \text{ Å}, c = 9.4998(13) \text{ Å}, T_c = 88K)\) and 86h, \((\text{set B}, a = 3.8780(4) \text{ Å}, c = 9.488(3) \text{ Å}, T_c = 85K)\). \(\delta\) was roughly estimated from the \(a\) parameter in the set A and set B to be ~ 0.1. Homogeneous samples were prepared and compacted in 5 mm diameter and 0.5 mm thick pellets which were manipulated in Ar atmosphere to avoid degradation. Small samples were cut off the disks to be used in the PAC experiments.

The \(^{199}\text{Hg}\) isotope was produced at the ISOLDE/CERN \[8\] on-line mass separator and implanted with 60 keV energy, in swiping mode, to achieve a homogenous low dose of \(5 \times 10^{11}\) at/cm\(^2\), under vacuum at room temperature (RT). The \(^{199}\text{Hg}\) implanted range is \(R_p = 170 \text{ Å}\) with straggling \(\sigma = 70 \text{ Å}\). Implantation tests were made for different beam energies and implantation doses up to \(4 \times 10^{13}\) at/cm\(^2\). After 15 minutes annealing at 473K all spectra are as clear and equivalent, which let us to believe that the implantation damage has been eliminated from the \(^{199}\text{Hg}\) neighbourhood.

The PAC setup records 30 \(\gamma_1\) coincidence time spectra, \(N_0(\theta, t)\), from detector pairs at \(\theta = 180^\circ\) \((k=1...6)\) and \(0 = 90^\circ\) \((k=1...24)\). By constructing the experimental ratio \(R(t)\) (eq.1) the half-life component is eliminated to reveal the perturbation function that contains all the relevant information.

\[
R(t) = 2 \left( \sqrt[3]{\prod_{i=1}^{6} N_i(180^\circ, t)} - \sqrt[3]{\prod_{i=1}^{24} N_i(90^\circ, t)} \right) + \sqrt[3]{\prod_{i=1}^{24} N_i(180^\circ, t)} \]

For each angle \(\theta\), the angular correlation functions \(W(\theta, t)\) are calculated numerically by taking into account the full Hamiltonian for the nuclear quadrupole hyperfine interaction \[9\]. Eq. 2 defines the theoretical function, \(R_{th}(t)\), whose parameters are fitted to the \(R(t)\) function.

\[
R_{th}(t) = \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + 2W(90^\circ, t)}
\]

For spin \(5/2\), three frequencies are observable per EFG from which the coupling constant of the interaction \(v_Q = eQV_{zz}/\hbar\) and the asymmetry parameter \(\eta = (V_{xx} - V_{yy})/V_{zz}\) are extracted. \(V_{zz}\) is the principal component of the EFG tensor that is produced by the charge distribution outside the probe nucleus. \(V_{xy}\) and \(V_{xz}\) are the components of the tensor along the y and x-axes, which are chosen according \(|V_{zz}| > |V_{xy}| > |V_{xx}|\). In the case of an interaction with randomly distributed defects a distribution of frequencies is observed, which broadens the frequency spectrum and attenuates the \(R(t)\) function. In this work only weak distributions are found, which were assumed to be Lorentzian-like. These are characterised by the average value \(v_Q\) and standard deviation \(\Delta v_Q\).

3. RESULTS AND DISCUSSION

Figure 1 shows (left) the experimental \(R(t)\) functions and (right) the corresponding Fourier transforms (FT) obtained during Ar annealing on: (i) Hg1201-set A, \(T_m=490K\); (ii) Hg1201-set B, \(T_m=520K\); (iii) Hg1212, \(T_m=520K\). The theoretical fit functions and the corresponding FT of the fit functions are included as continuous thick lines on the \(R(t)\) and FT plots, respectively. The spectrum obtained on Hg1201-set A shows a frequency triplet that reveals only one axially symmetric EFG 1 , characterised by \(v_{Q1} = 1448(5)\) MHz and \(\eta_1 = 0\). That corresponds to 100% of the \(^{199}\text{Hg}\) nuclei placed on regular sites of the Hg1201 lattice with local tetragonal symmetry \[5\]. A small attenuation of the \(R(t)\) spectra is observable that is characterised by \(\Delta v_{Q1} = 35(3)\) MHz, most likely due to long-range disorder of the Hg planes. Differently, the spectra obtained on Hg1201-set B exhibit a fraction \(f_1 = 43(5)%\) of Hg nuclei interacting with an axially symmetric but slightly weaker EFG 1 , characterised by \(v_{Q1} = 1362(7)\) MHz. A fraction \(f_2 = 57(5)%\) of \(^{199}\text{Hg}\) nuclei interact with a non-axially symmetric EFG 2 , characterised by \(v_{Q2} = 1199(9)\) MHz and \(\eta_2 = 0.20(2)\). Thus a large fraction of Hg atoms are on lattice sites with lower than tetragonal symmetry.
Figure 1. (left) $R(t)$ functions and (right) their FT measured under Ar annealing (i) Hg1201 set A, (ii) Hg1201 set B and (iii) Hg1212 samples.

The best fit obtained on Hg1212 exhibit a fraction $f_1 = 41(3)\%$ of $^{199m}$Hg nuclei interacting with an axially symmetric EFG $1$, characterised by $\nu_{Q1} = 1431(8)$ MHz. A fraction $f_2 = 51(4)\%$ of $^{199m}$Hg nuclei interact with a non-axially symmetric EFG $2$, characterised by $\nu_{Q2} = 1314(8)$ MHz and $\eta_2 = 0.15(2)$. A third fraction $f_3 = 8(5)\%$ of Hg nuclei interact with a weaker but highly asymmetric EFG.

On the Hg1201-set A of samples a fraction of Hg nuclei that interact with EFG $2$, characterised by $\nu_{Q2} = 1229(14)$ MHz and $\eta_2 = 0.21(4)$, could easily be tuned on or off under oxygen or argon annealing, respectively [5]. First principle calculations of the EFGs [10] at the Hg site let us to assign EFG $1$ and EFG $2$ as due to Hg atoms without and with one single O in their neighbourhood, respectively [5]. The fact that under Ar annealing there are no evidence for O should be due to the near-surface implantation depth of the $^{199m}$Hg probe nuclei.

The values now found for $\nu_{Q1}$ and $\nu_{Q2}$ in the Hg1201-set B of samples are lower than the corresponding numbers obtained on Hg1201-set A. We further stress that on Hg1201-set B, during the annealing time (~3 hours) that PAC is measuring, the fraction $f_2$ of Hg nuclei could hardly be changed under Ar or O$_2$ annealing. On the other hand, the fact that the $c/a$ ratio on Hg1201-set B is smaller than the $c/a$ ratio on Hg1201-set A suggest that carbonate ions can be present. In order to learn what would be the observable EFGs at the Hg site under such contamination defects, theoretical calculations are being performed. Assuming that EFG $2$ corresponds to single oxygen atoms which are located nearby the centre of the Hg planes, the corresponding $\delta$ from the PAC data is $\delta_{PAC} = f_2/4 = 0.14(1)$ [5] on the $^{199m}$Hg probing region.

So far, in the absence of EFG calculations for the Hg1212 compound and by comparison with what has been measured in Hg1201 [5], we tentatively assign EFG $2$ to the presence of single O$_2$ atoms in the Hg neigboorhood and EFG $3$ to a still unknown defect.

It should be stressed that the ab-initio calculations have shown that the main contribution for the EFG at the Hg site comes from the tightly bound apical oxygen O(2). To a small increase of +0.01 Å on the O(2)-Hg distance we expect a decrease of $\Delta \nu \sim 2.1\%$ on the PAC observable frequencies. This explains why $\nu_{Q1}$ measured in the Hg1201-set A and Hg1212 samples are very similar, since the reported O(2)-Hg distances are quite close [7]. On the other hand, the O(2)-Hg distance in the Hg1201-set B should be bigger, by about +0.028(2) Å, than the equivalent distance in the Hg1201-set A of samples, within the $^{199m}$Hg probing region.

The high sensitivity of the PAC technique to local charge variations can be further seen in Figure 2 that shows the FT plot of the $R(t)$ data and of the fit functions obtained in the Hg1201-set B at low temperatures. There are put in evidence the position of the first two harmonics $\omega_1$, $\omega_2$ for EFG $1$ and EFG $2$, as obtained from the fits. Below $T_M=100$K, $\omega_1$ and $\omega_2$ for EFG $1$ get closer ($\omega_2<\omega_1$) indicating that even those Hg nuclei, which were in positions with tetragonal-like symmetry at RT, e.g., free of O$_2$ or other point defects, are now interacting with by slightly non-symmetric ($\eta \neq 0$) charge distributions. The origin of such effect is still unknown, since this could be just due to small lattice distortions induced at low temperature by the presence of impurities on
these samples.

In conclusion, the EFGs at the Hg site in Hg1201 and Hg1212 have been measured with the PAC technique. We have stressed on the high sensitivity of the technique for specific variations on the Hg-O(2) distance. This is a consequence from the fact that the apical oxygen is tightly bound to Hg and thus dominates the EFG at the Hg site. Future experiments should provide details on the O/G47 diffusion mechanisms as well as on the Hg electronic environment as a function of the O/G47 concentration and temperature. For the best success of such experiments, high quality samples should be used and the PAC results should be compared and complemented with crystallographic and transport properties characterisation techniques.

ACKNOWLEDGEMENTS

This work was partially funded by FCT, Portugal, through projects CERN/S/FIS/1048/98, PBICT/C/CTM/1891/95 and grants under the PRAXIS XXI Program (J.P.A.), and ITN (J.G.C.).

REFERENCES