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Perturbed Angular Correlations Studies in the $HgBa_2CaCu_2O_{6+\delta}$ high-T_C superconductor

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Abstract The electric field gradients at ^{199m}Hg nuclei have been measured via the perturbed angular correlation (PAC) technique, allowing a full characterization of the Hg neighborhood charge distribution at high oxygen doping on the Hg planes. The PAC technique has been applied to investigate the effect of high oxygen pressure during the measurement. Polycrystalline $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) samples have been annealed at 152 bar pressurized oxygen. The influence of oxygen pressure during the experiment was then investigated by measuring the samples at atmospheric pressure and under 152 bar oxygen pressure.

The present set of PAC experiments shows that at high oxygen concentrations there is a non-uniform oxygen distribution. Moreover, the Hg environment is not free from oxygen and the results hint to a new type of ordering.

Keywords Hg-based superconductors · oxygen ordering · Local probe techniques

1 Introduction

The discovery of superconductivity in La-Ba-Cu-O system [1] opened a new area of materials properties to be explored.

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More than 20 years after this remarkable discovery, the relationship between doping and charge ordering is still under review [2,3]. Although some aspects related to the properties of these compounds are generally accepted, the topic of inhomogeneous distribution of charge carriers is still in debate [4]. Moreover, evidence of organized patterns were reported and terms like phase separation, stripes and checkerboard patterns are concepts still heavily discussed [5–7].
From all high-T_C superconductors, the Hg-based family [8–10] is one of the most promising systems due to their simple tetragonal crystalline structure and the highest superconducting transition temperatures (T_C). Although these compounds present simple structures, disorder at the Hg planes is believed to be related to the location of excess oxygen, O_δ, in these planes [11,12]. Thus, the role of O_δ in the formation of charge inhomogeneities and its influence on the local electronic and structural properties is not yet clear and of great importance.
In the present work, the perturbed angular correlation (PAC) technique was applied to investigate the electric field gradients (EFG) at the Hg sites of the 2nd member of this family of compounds (Hg-1212), under high oxygen doping concentrations. The measurement of the EFGs allows the full characterization of the Hg neighborhood contributing as local information for O_δ rearrangements in the Hg planes.

2 Experimental

Hg-1212 polycrystalline samples were synthesized using the high pressure - high temperature technique (HP-HT) [13] at 1.6 GPa, 1073 K for one hour. The quality of the samples was controlled via X-ray diffraction (XRD) measurements, which were performed using a Siemens D5000 diffractometer, with Cu K_α radiation (λ=1.541 Å), in a 2θ range between 10° and 90°. The lattice parameters were refined using the LeBail method with the program Full Prof Suite [14]. Magnetic characterization was performed using a Quantum Design SQUID magnetometer under an applied field of 0.005 T in the range 4-150 K in zero field cool (ZFC) and field cool procedure (FC).

The study of oxygen ordering, at high concentrations, in the mercury planes was performed using the Perturbed Angular Correlation (PAC) technique. Similarly to refs. [15, 16], Hg-1212 samples were implanted with ^{199m}Hg ($T_{1/2}$= 42 min) at the ISOLDE/CERN facility [17]. After implantation, the effect of high oxygen pressure during the measurement was investigated. The samples were annealed at 463(10)K under 152 bar pressurized oxygen for 25 minutes. After annealing, two different procedures were followed: for measurements at atmospheric pressure, the pressure was released and the samples were then sealed inside copper containers; for the measurements under 152 bar oxygen pressure, the temperature was lowered and the samples were kept under pressure. Both measurements were performed using a highly efficient PAC γ-ray BaF_2 detector setup [18], at room temperature.

The PAC technique is based on the hyperfine interaction of nuclear moments with extra EFGs, which are generated by the charge distribution in the Hg surroundings. The information taken from the PAC experiments is obtained from the time perturbation function, R(t), modulated by the interaction of the quadrupole moment of the 158 keV intermediate state in the ^{199m}Hg decay cascade. The experimental R(t) function is calculated from the time spectra following the equation:

$$R(t) = 2\frac{\sqrt[6]{\prod_{j}^{6} N_j(180^\circ,t)} - \sqrt[24]{\prod_{i}^{24} N_i(90^\circ,t)}}{\sqrt[6]{\prod_{j}^{6} N_j(180^\circ,t)} + 2\sqrt[24]{\prod_{i}^{24} N_i(90^\circ,t)}} \qquad (1)$$

where N_j/N_i are γ-γ coincidences spectra measured at 180° and 90°, after subtraction of the chance coincidences background. This ratio eliminates the half-life exponential component revealing the perturbation function, which contains the relevant information. For each angle θ, the angular correlation functions, W(θ,t), are calculated numerically by taking into account the full Hamiltonian for the nuclear quadrupole hyperfine interaction [19]. The theoretical function, whose parameters are fitted to the experimental R(t) function, is given by:

$$R_{fit}(t) = 2\frac{W(180^\circ,t) - W(90^\circ,t)}{W(180^\circ,t) + 2W(90^\circ,t)} \qquad (2)$$

For a γ-γ cascade with the intermediate level of spin I=5/2, three frequencies are observable per EFG. From these frequencies the coupling constant of the interaction (ν_Q), given by $\nu_Q = eQV_{zz}/\hbar$, and the asymmetry parameter, η, are calculated. V_{zz} is the principal component of the EFG tensor that is produced by the charge distribution surrounding the probe nucleus. V_{xx} and V_{yy} are the components of the EFG tensor along *x* and *y* axes, which are chosen according to $|V_{zz}| > |V_{yy}| > |V_{xx}|$. In the case of an interaction with randomly distributed defects a distribution of frequencies is observed, which broadens the frequency spectrum and thus attenuates the R(t) function.

3 Results and Discussion

To control the sample quality, XRD and magnetization measurements have been performed. The raw Hg-1212 samples crystallize in the tetragonal structure, space group P_4mmm with cell parameters a=3.8690(8)Å and c=12.6746(6)Å in agreement with the values reported in literature [10,20]. Extra oxygen content of 0.22(3) was inferred from XRD data. The samples were found to be almost single phase though a small amount of $CaHgO_2$ (<8% Vol.) was observed. Magnetic measurements show an onset T_C of 128 K, in excellent agreement with the values reported for the same doping [10, 20].

Figure 1 displays the experimental perturbation function R(t) (left) and corresponding Fourier transforms (right), for measurements at atmospheric pressure and under 152 bar pressurized oxygen. The fits are shown by continuous lines in the R(t) spectra. The resulting fit parameters are summarized in Table 1. The analysis of the data showed two representative EFG distributions present in these samples. However, a third EFG distribution had to be included to account for the attenuation observed in the spectra and improve the quality of the fit. This EFG is believed to be related to a random distribution of defects and/or to probes out of regular sites in the Hg-1212 lattice. Thus this EFG is considered of not being representative of regular Hg sites in the Hg-1212 lattice. Further analysis will not take into account the presence of this EFG distribution.

The experiment performed at atmospheric pressure (Figure 1(a)) shows a dominant EFG distribution, named EFG_a, is given by 69(10)% of the ^{199m}Hg probe atoms, which are interacting with it. This EFG_a is described by ν_{Qa}=1267(63) MHz and an asymmetry parameter, η_2=0.25(4). The second EFG distribution found, EFG_b, is described by ν_{Qb}=800(40) MHz and η_b=0.76(2). This highly asymmetric EFG distribution accounts for 31(8)% of the probes interacting with it. The measurement performed under 152 bar pressurized oxygen, displayed in Figure 1(b), shows the same EFG distributions. However, the fractions of probes interacting with EFG_a and EFG_b were found to be slightly different. A dominant fraction of 83(5)% was again found to be interacting with EFG_a, which is characterized by ν_{Qa}=1175(70) MHz and η_a=0.24(6). Similarly to the atmospheric pressure measurement, the highly asymmetric EFG_b was also found, and is characterized by ν_{Qb}=904(70) MHz and η_b=0.69(5). EFG_b

Table 1 EFG fitting parameters of the experimental R(t) functions.

Exp.	Preliminary Annealing Conditions	Measurement Conditions	f_a %	ν_{Qa} MHz	EFG_a $\lvert V_{zz}\rvert_a$ V/ Å^2	η_a	δ_a	f_b %	ν_{Qb} MHz	EFG_b $\lvert V_{zz}\rvert_b$ V/ Å^2	η_b	δ_b
(a)	Pressurized O_2 (152 bar)	Atmospheric Pressure	69 ±16	1213 ±60	744 ±86	0.26 ±0.01	0.07 ±0.01	31 ±8	854 ±43	524 ±60	0.76 ±0.02	0.07 ±0.03
(b)	Pressurized O_2 (152 bar)	152 bar	83 ±5	1175 ±60	721 ±60	0.24 ±0.06	0.06 ±0.01	17 ±4	904 ±70	555 ±50	0.69 ±0.05	0.06 ±0.03

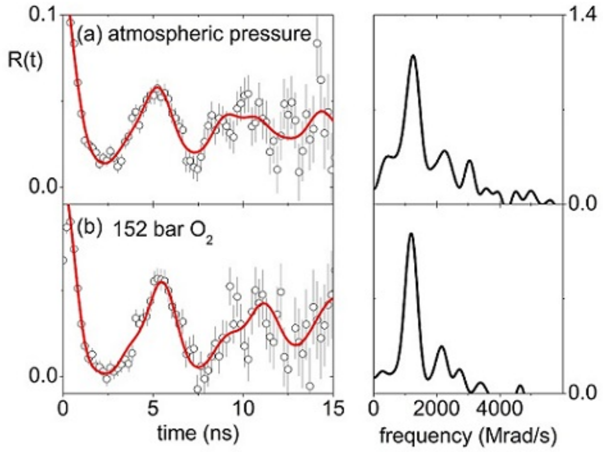

Fig. 1 (left) Experimental perturbation functions, R(t), and (right) corresponding Fourier transforms, for measurements performed at (a) atmospheric pressure and (b) under 152 bar pressurized oxygen. The thicker lines over the spectra are the fitting functions.

affects 17(4)% of the ^{199m}Hg probe atoms.
At a first glance, the non-axially symmetric EFG_a could be assigned to ^{199m}Hg nuclei placed in lattice sites with symmetry lower than tetragonal due to the location of oxygen in the Hg mesh, as obtained in Hg-1201 [15,16]. However, one would expect that the measurement under 152 bar oxygen would lead to strong changes in the fractions of probes interacting with the different EFGs, due to the continuous doping. The slight increase of the fraction of probes interacting with EFG_a for the measurement under 152 bar pressurized oxygen together with the fact that Hg-1212 as opposed to Hg-1201 can trap more oxygen, suggests a different ordering than the one reported [15,16].

The observation of a highly asymmetric EFG distribution, EFG_b, hints to a new oxygen ordering scenario. EFG_b cannot be assigned to any of the configurations reported in refs. [15,16], since those EFG parameters have not been experimentally observed. Furthermore, such high local oxygen concentrations have not been calculated and thus the present experimental results require new simulations.

Moreover, this set of results show that there is a non-uniform oxygen distribution given by the presence of two EFG distributions, which are observed for both measurements. This result is in agreement with a recent study in La_2CuO_{4+y} superconductor where it was observed that the oxygen interstitials order is highly inhomogeneous, being this ordering characterized by a fractal distribution of dopants [21]. Also, the present data show that the Hg environment was found to be not free from oxygen as obtained from the EFG parameters where both η_a and η_b are different from zero. The correct assignment of each experimental EFG shall be done with the help of the new simulations, which shall account for high oxygen concentrations.

4 Conclusions

The EFGs at the Hg site in Hg-1212 have been measured via the PAC technique. For high oxygen concentrations, there is non uniform local oxygen distribution and the Hg local environment is not free from oxygen. The results suggest the existence of a new oxygen ordering.

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