Perturbed Angular Correlations Studies in the HgBa$_2$CaCu$_2$O$_{6+\delta}$ 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$_2$CaCu$_2$O$_{6+\delta}$ (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 the La-Ba-Cu-O system [1] opened a new area of materials properties to be explored. 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$_\delta$, in these planes [11, 12]. Thus, the role of O$_\delta$ 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$_\delta$ 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 Kα 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 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 [15, 16], Hg-1212 samples were implanted with 199mHg (T1/2 = 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 BaF2 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 199mHg decay cascade. The experimental R(t) function is calculated from the time spectra following the equation:

\[
R(t) = 2 \sqrt{\prod_{j}^{6} N_j(180°, t) - \sqrt{\prod_{i}^{24} N_i(90°, t)}}
\]

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

\[
R_{\text{fit}}(t) = 2 \frac{W(180°, t) - W(90°, t)}{W(180°, t) + 2W(90°, t)}
\]

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 \((\nu_Q)\), 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 \(Pnma\) with cell parameters \(a = 3.8690(8)\ Å and \(c = 12.6746(6)\ Å\) in agreement with the values reported in literature [10, 20]. An extra oxygen content of 0.22(3) was inferred from the XRD data. The samples were found to be almost single phase though a small amount of CaHgO2 (<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 (Fig. 1(a)) shows a dominant EFG distribution, named EFG\(_a\), is given by 69(10)% of the 199Hg probe atoms, which are interacting with it. This EFG\(_a\) is described by \(ν_{Qa} = 1267(63)\ MHz\) and an asymmetry parameter, \(η_a = 0.25(4)\). 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 Fig. 1(b), shows the same EFG...