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Microscopic studies of radioactive Hg implanted in $YBa_2Cu_3O_{6+x}$ superconducting thin films

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Abstract

$YBa_2Cu_3O_{6+x}$ (YBCO) superconducting thin films implanted with low doses of radioactive ^{197m}Hg and ^{199m}Hg isotopes were studied with a combination of nuclear and non-nuclear characterization techniques. We show that after implantation Hg lies on a unique site in the YBCO lattice and the critical temperature increases slightly with the increase of the ^{197}Au concentration from the nuclear transmutation of ^{197}Hg. © 1998 Elsevier Science B.V. All rights reserved.

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The $YBa_2Cu_3O_{6+x}$ (YBCO) compound is one of the most studied and interesting high-T_C superconducting materials for applications. Doping studies have shown that the superconducting properties of YBCO are always degraded, except when doping with Au or Hg, which increase T_C by 2 K [1] and 10 K [2], respectively. In these studies the Hg site in the YBCO lattice was not known, and since it was earlier introduced during sintering by changing the composition of the reactants, the presence of different phases cannot be excluded.

Radioactive isotopes have received an increased application with non-nuclear techniques [3]. In particular, in the field of semiconductors, it was shown that the concentration of active carriers can be measured in a precise way even in complex situations, by performing measurements as a function of time and correlating these with the characteristic decay half-life of the radioactive isotope [4]. In the present work, radioactive Hg was introduced into YBCO thin films by ion implantation. The microscopical environment of Hg was studied with the e^-–γ perturbed angular correlations (PAC) [3] nuclear technique and determinations of the critical temperature, T_C, through electrical resistivity measurements were performed during the decay of ^{197}Hg to ^{197}Au.

The PAC technique is particularly suitable to probe the vicinity of the implanted Hg nuclei at an atomic level. The sensitivity of this technique comes from the electric field gradient (EFG), caused by the deviation from cubic symmetry of the charge distribution around the probes. This results in a modulation of the PAC spectrum, $R(t)$, which is described by the coupling constant, $\nu_Q = eQV_{zz}/h$, and the asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{zz} is the principal component of the EFG tensor. The interaction with randomly distributed defects does not lead to the measurement of a sharp frequency but rather to a distribution of frequencies, with an average value $\langle \nu_Q \rangle$ and a standard deviation σ_Q.

Poly- and single-crystalline-like high-quality YBCO thin films (1500 and 3500 Å) were deposited by pulsed laser ablation on $\langle 1\,0\,0 \rangle$ $SrTiO_3$ substrates. Their crystalline quality was checked by X-ray diffraction, scanning electron microscopy and α-particle Rutherford

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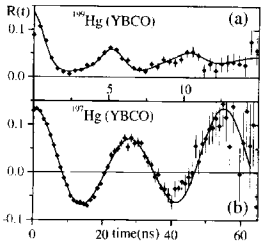

Fig. 1. e$^-$–γ PAC experimental, $R(t)$, functions measured after implantation of (a) ^{199m}Hg and (b) after annealing of the ^{197m}Hg implanted single-crystalline-like YBCO thin film. Different x-axis scales are due to the different quadrupole moments of the states where the PAC experiments are measured in each isotope.

backscattering. In order to avoid the production of unknown crystalline phases, the films were doped by ion implantation with low doses of 2×10^{12} at/cm^2 of the ^{199m}Hg ($T_{1/2} = 43$ min) and 1×10^{13} at/cm^2 of the ^{197m}Hg ($T_{1/2} = 24$ h) radioactive isotopes which are produced and accelerated to 60 keV energy at ISOLDE [3]. The samples implanted with ^{197m}Hg were annealed under flowing oxygen at 723 K for 6 h to recover the implantation damage, and then slowly cooled down (1 K/min) to room temperature.

Fig. 1a shows the $R(t)$ spectrum obtained after implantation of ^{199m}Hg in a polycrystalline film. From the analysis of this spectrum, it is seen that after implantation 70(7)% of the ^{199}Hg nuclei interact with a well-defined EFG, characterized by $\nu_Q = 1240(12)$ MHz and $\eta = 0.25(2)$. This shows that there is a unique site occupation for the Hg atoms in the YBCO structure. The presence of defects around the Hg probes is shown by the small damping, $\sigma_Q = 115(11)$ MHz, observed. Fig. 1b shows the spectrum obtained after implantation and annealing of ^{197m}Hg in a single-crystalline-like film. During the annealing, about 20% of the implanted Hg atoms diffused out of the film, from the comparison of the sample's activity before and after the annealing. The analysis of this spectrum shows that the ^{197m}Hg nuclei are all interacting with the same EFG as in the as-implanted state, now characterized by a non-damped frequency $\nu_Q = 121.5(5)$ MHz, and $\eta = 0.19(2)$. The quadrupole coupling frequencies scale with the known ratio of the quadrupole moments of the $\frac{5}{2}$ levels of ^{199}Hg and ^{197}Hg [5]. Orientation measurements performed in this sample (not shown here) confirm that V_{zz} is aligned with the crystalline c-axis. Furthermore, the fact that the ν_Q and η values are very close to those measured in HgO doped with ^{199m}Hg ($\nu_{Q\text{-HgO}} = 1162(10)$ MHz, $\eta_{HgO} = 0.185(13)$) [5] suggests that Hg has a close-to-linear coordination with neighboring oxygen atoms, along the c-axis, which is compatible with the position found for Au, i.e., the Cu(1) site [1].

The critical temperature was determined before and after implantation and annealing, through electrical

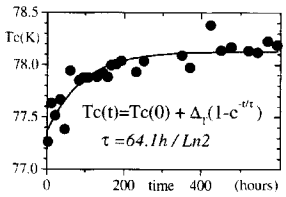

Fig. 2. Plot of T_c measured as a function of time, after implantation and annealing of ^{197}Hg. The continuous line is proportional to the increase of the ^{197}Au concentration due to the transmutation of ^{197}Hg into ^{197}Au.

resistivity measurements, $\rho(T)$, as a function of temperature, using the four-contacts geometry technique and a closed-cycle He refrigerator. T_C was estimated by the maximum of the curve the derivative, $d\rho/dT$, with a fitting error of 0.01 K. After annealing, T_C always decreased 5–10 K relative to the value measured in the as-grown samples, indicating that the oxygen content of the thin films changed during the annealing. In order to distinguish between the T_c variations which are due to the implanted Hg atoms and the variations due to the remaining implantation damage or induced by the annealing, T_C was determined during a succession of cooling–heating cycles (10–300 K) for several days, during the decay of ^{197}Hg to stable ^{197}Au ($T_{1/2} = 64$ h). Fig. 2 shows a plot of T_C as a function of time where it is observed that T_C increases by about 1 K, following the characteristic increase in the ^{197}Au concentration due to nuclear transmutation.

In conclusion, these experiments have shown that already after implantation, the Hg nuclei lie on a unique site in the YBCO lattice, behaving rather differently from other impurities, including isovalent Cd, implanted into YBCO compounds [6]. It has also been observed that the critical temperature is sensitive to the Hg atoms, even when these are present at a low-concentration dose of about 10^{13}Hg/cm^2. The measurement of the superconducting properties during the elemental transmutation from Hg to Au allows us to separate the effects initiated by the impurity doping from those due to the remaining implantation damage or annealing.

References

[1] G. Ganakas, M.J. Morgan, G. Jakovidis, J. Mater. Sci.: Mater. Electron 6 (1995) 244.
[2] A.K. Chakraborty, K. Bose, G. Som, B.K. Chaudhuri, J. Mater. Sci.: Mater. Electron 5 (1994) 22.
[3] J.G. Correia, Nucl. Instr. Meth. B 113 (1996) 501.
[4] G. Rohrlack, K. Freitag, R. Vianden, R. Gwilliam, B.J. Sealy, J.G. Correia, D. Forkel-Wirth, Nucl. Instr. Meth. B 106 (1995) 267.
[5] T. Butz, Th. Völkel, O. Nuyken, Chem. Phys. 149 (1991) 437.
[6] A. Bartos et al., J. Less-Comm. Metals 164–165 (1990) 1121.