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Stability and diffusion of Hg implanted $YBa_2Cu_3O_{6+x}$

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Abstract

The radioactive isotope ^{197m}Hg was implanted at 60 keV with low fluences (10^{13} ions/cm^2) into $YBa_2Cu_3O_{6+x}$ (YBCO) superconducting thin films at ISOLDE/CERN. We report on the Hg dynamics and stability inside the YBCO lattice as a function of annealing temperature up to 890 K in a vacuum or O_2 atmosphere. The perturbed angular correlation (PAC) technique was used for probing the Hg behavior at the atomic scale, while by monitoring the sample's activity in situ the Hg outdiffusion was studied. We found that Hg ions occupy unique lattice sites and that Hg should be bound to two apical oxygens. Hg diffusion occurs only for annealing temperatures above 653 K, in vacuum. The Hg migration energy was estimated to be $E_M = 1.58 \pm 0.15$ eV.

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1. Introduction

Since the discovery of $YBa_2Cu_3O_{6+x}$ (YBCO) [1] intensive work has been done, in order to produce high quality bulk and thin film materials free from parasitic phases. Doping studies have shown that the superconducting properties of YBCO are always degraded, except when doping with Au or Hg, which increases the critical temperature (T_c) by 2 K [2] and 10 K, respectively [3]. In these studies several atomic percent of Hg were introduced during sintering by changing the composition of the reactants. Therefore the Hg site was not experimentally determined, and the presence

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of different crystalline phases or different compounds cannot be excluded. Recently [4] we combined the emission channeling (EC) and perturbed angular correlation (PAC) techniques [5] to show that Hg occupies a unique highly symmetric site in the YBCO lattice, directly after implantation. In such studies a first annealing stage where point defects diffuse away from the Hg neighborhood was identified at 511 K, and it was further observed that the Hg is stable in the YBCO lattice up to 653 K.

In the present work radioactive ^{197m}Hg was introduced into YBCO thin films by ion implantation at very low fluences. The atomic environment of Hg was studied using the $e^- - \gamma$ PAC technique and the Hg out diffusion was studied by monitoring in-situ the sample's activity.

2. Experimental details

Poly-and [0 0 1] single-crystalline high quality YBCO thin films (100–3000 nm) were deposited by Pulsed Laser Ablation or Metal Organic Chemical Vapor Deposition on [1 0 0] $SrTiO_3$, and [1 0 0] MgO substrates. The crystalline quality was checked using the Rutherford Backscattering/Channeling (RBS/C) with a 1.6 MeV He^+ beam, and X-ray diffraction measurements. For control of the superconductivity, T_c was measured with the Alternate Susceptibility (χ_{ac}) technique [4]. The ^{197m}Hg radioactive isotope was implanted into the films at room temperature (RT) and an energy of 60 keV at the ISOLDE facility [6]. To avoid the production of unknown crystalline phases the beam was swept to get a homogeneous low fluence of 1.0×10^{13} Hg^+/cm^2 over the implanted area, covering ~95% of the 5×5 mm^2 film's surface. The Hg projected range is $R_P = 16$ nm, and the peak concentration is 7×10^{18} at/cm^3, i.e. about 0.01 at% [7].

The PAC measurements were performed using the well-known 165–134 keV cascade from the decay of the 24 h half-life ^{197m}Hg isomeric state [8]. Details of the experimental set-up and procedures can be found in Ref. [9]. The PAC technique is particularly suitable to probe the vicinity of the implanted Hg nuclei at an atomic level [10]. Its sensitivity is given by the electric field gradient (EFG) which is caused by the deviation from cubic symmetry of the charge distribution around the probes. This results in a modulation of the PAC spectrum, $R(t)$. For a cascade with an intermediate level with spin $I = 5/2$, three frequencies are observable per EFG. From these frequencies the coupling constant of the interaction, $\nu_Q = eQV_{zz}/h$, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ can be extracted. V_{zz} is the principal component of the EFG tensor, which is produced from the extra nuclear charge distribution. Q is the quadrupole moment of the 134 keV excited state. The interaction with randomly distributed defects leads to a distribution of frequencies instead of a sharp frequency. Here we assume such distributions to be Gaussian-like, with average value $\langle\nu_Q\rangle$ and standard deviation σ_Q, depending on the density and variety of the lattice defects.

3. Results

Fig. 1 shows the RBS/C spectra measured in the thick (>2 μm) YBCO film. The ratio between the random and [0 0 1] aligned spectrum gives a

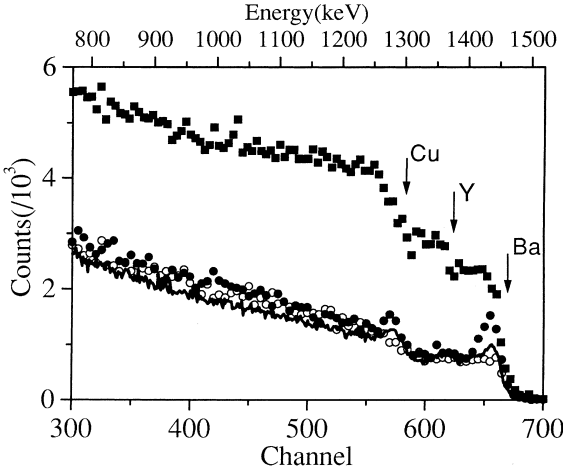

Fig. 1. Random *as-grown* (■) and [0 0 1] aligned RBS spectra taken before (○) and after(●) implantation of 1×10^{13} Hg^+/cm^2, and after subsequent 6 hours annealing at 723 K under O_2 flow (–). Notice the recovery of the implantation defects after the annealing.

minimum yield of 30% which indicates an epitaxial film with a fairly good crystalline quality. The Hg signal, which should appear in front of the Ba signal, is below the detection limit due to the low Hg concentration and detector pileup background. On the other hand, the implantation disorder and annealing recovery of the YBCO lattice can be seen in the corresponding Y, Cu and Ba [0 0 1] aligned signals. Still, due to the Y and Cu signal overlapping and smaller RBS crossections, only the Ba aligned spectra could be quantitatively checked. After implantation the surface peak in the [0 0 1] spectrum increases, revealing the production of near surface defects. From the area of the Ba peak we calculate the number of Ba displaced atoms to be 2.6×10^{15} at/cm^2. The thickness of the damaged region is 26 nm. After 6 h annealing at 723 K under O_2 flow the lattice significantly recovers in the implanted region as the [0 0 1] aligned spectrum shows. This agrees with previous PAC experiments which showed that annealing above 511 K in a vacuum or oxygen atmosphere removed the point defects from the Hg neighborhood [4,11]. With these low implantation doses and annealing conditions, T_c can return to the as-grown values [4].

Fig. 2 (a) shows the PAC spectrum measured at RT, after implantation and annealing at 723 K in flowing O_2, of a single-crystalline-like film placed with its normal ($\vec{n}$) in the detector's plane, making an angle of 45° with each electron detector directions. X-ray diffraction showed that the film was epitaxially grown, with the c-axis pointing towards $\vec{n}$. The $R(t)$ spectrum was fitted assuming that all Hg probe nuclei interact with the same EFG_1 characterized by a sharp ($\sigma_{Q1}=0$) frequency centered at $\langle\nu_{Q1}\rangle = 121.5\pm0.4$ MHz, where V_{zz}^1 is aligned along c, and a small $\eta = 0.19\pm0.02$. $\sigma_{Q1}=0$ reflects the fact that no point defects remain in the Hg atomic vicinity [4,11]. Fig. 2 (b) and (c) show refined measurements of the EFG orientation where $R(t)$ spectra have been measured with $\vec{n}$ placed in the detector plane but now making 18° and 72° with each electron detector directions, respectively. In these pictures the continuous lines are just simulations of the $R(t)$ spectra, assuming that V_{zz}^1 is fully aligned with $\vec{n}\|c$, but making now an angle of 18° or 72° with the electron detector.

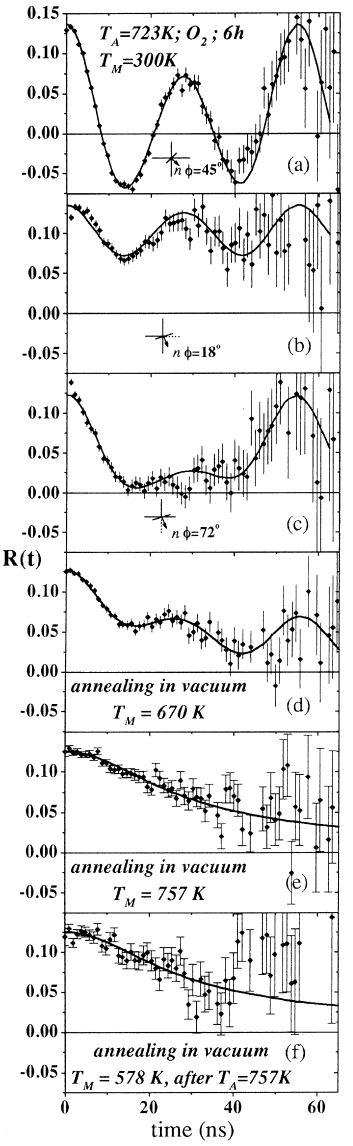

Fig. 2. PAC spectra measured on a single-crystalline-like film at RT after implantation and annealing under flowing O_2 at 723 K with $\vec{n}$ making 45° with both electron detectors (a), and making angles of 18° (b) and 72° (c). PAC spectra taken on a slightly textured film during annealing in vacuum at 670 K (d) and 757 K (e). The spectrum measured at 578 K (f) was obtained after annealing at 757 K.

The agreement between the experimental data and the simulations is remarkable thus confirming that Hg is located at unique sites of the YBCO lattice and surrounded by a charge distribution with the

lattice symmetry. These measurements confirm our previous work where preliminary EC experiments shown that Hg lies along the Cu or Y/Ba c-axis rows. The fact that the magnitude of $|V_{zz}^1|$ is very close to $|V_{zz}|$ measured in ^{199m}Hg doped HgO enhances the supposition that Hg in YBCO has two linear coordinated (apical) oxygen atoms as first neighbors, as is the case for the Cu(1) lattice site [4].

Fig. 2 (d) shows a PAC spectrum measured at $T_M = 670$ K in vacuum (2.10^{-6} mbar), slightly above the temperature at which diffusion starts (~653 K). The $R(t)$ spectrum has clearly changed and was fitted by considering that the Hg ions are now interacting with two different EFGs. A fraction $f_1 = 35 \pm 2\%$ of the Hg nuclei was still interacting with the same EFG_1, while $f_2 = 65 \pm 2\%$ was interacting with a distribution, EFG_2, characterized by $\langle \nu_{Q2} \rangle = 18 \pm 3$ MHz and $\sigma_{Q2} = 19 \pm 5$ MHz. After further increasing T_M to 757 K the $R(t)$ spectrum shows no more evidence of EFG_1 (Fig. 2 (e)). Only EFG_2 is present with parameters $\langle \nu_{Q2} \rangle = 23 \pm 3$ MHz and $\sigma_{Q2} = 25 \pm 9$ MHz. Moreover this effect is irreversible when returning to low annealing temperatures. This can be seen by annealing in vacuum at $T_M = 578$ K (a temperature where diffusion should be hindered) after annealing at 757 K (see Fig. 2 (f)). EFG_2 is now characterized by $\langle \nu_{Q2} \rangle = 23 \pm 3$ MHz and $\sigma_{Q2} = 24 \pm 13$ MHz. The fact that $\nu_{Q2} \ll \nu_{Q1}$ hints that diffusion of the Hg ions must take place by lattice sites with a higher symmetry, most likely not bound to oxygen anymore.

The Hg out diffusion was studied by measuring the γ count rate CR_γ of the 134 keV transition and the PAC coincidence rate CR_{PAC} at constant temperature, as a function of annealing time. At temperatures higher than 653 K both CR_γ and CR_{PAC} decreased faster than it would be expected if it were only due to the natural ^{197m}Hg decay. The relative decrease of CR_γ and CR_{PAC} was the same, thus indicating that Hg was diffusing out. If Hg would only diffuse within the film, then CR_{PAC} would decrease faster than CR_γ, due to higher absorption and scattering of the conversion electrons through the film. Four measurements were done at $T_{M=}$ 684, 757, 800 and 888 K. When analyzing the data, the count rates were corrected for the natural decrease due to the radioactive decay, and normalized to unity at the beginning of each measurement. In Fig. 3 (a) we show the average (I_N) of the CR_γ and CR_{PAC} corrected normalized intensities, for the three highest temperatures. It is clearly seen that the rate of Hg losses increases with T_M. For the clearness of the picture we did not include the measurements at 684 K, for which I_N changed only slightly. I_N is proportional to the remaining ^{197m}Hg nuclei into the film, thus I_N is proportional to the integral of the Hg depth profile. The solid lines in Fig. 3 (a) are fits assuming a simple one-dimensional Gaussian-like diffusion model on a semi-infinite film without surface traps.

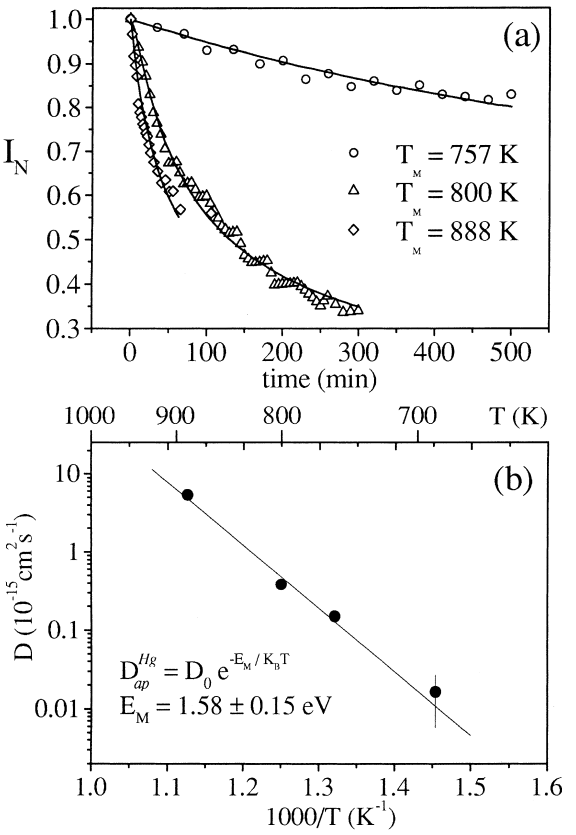

Fig. 3. (a) I_N plotted as a function of annealing time (I_N = average of $CR\gamma$ and CR_{PAC} count rates after half-life correction and normalization, see text); (b) Arrhenius plot of the apparent Hg diffusion coefficient. Solid lines are fits explained into the text.

Under these assumptions, the solution of the diffusion equation is given by

$$\frac{1}{\sqrt{\pi(4Dt+2\sigma_0^2)}}\left(\exp\left(-\frac{(x-x_0)^2}{4Dt+2\sigma_0^2}\right)-\exp\left(-\frac{(x+x_0)^2}{4Dt+2\sigma_0^2}\right)\right),$$

where x_0 is the initial range corresponding to the maximum of the gaussian profile, σ_0 is the standard deviation, D is the diffusion coefficient, and t is the time. For each temperature the fit function to I_N is the integral of the depth profile. This is an error function with $x_0/\sqrt{4Dt+2\sigma_0^2}$ as argument and only D and σ_0 as free parameters. The time is the independent variable. TRIM [7] was used to estimate $x_0 = R_P$ (that was kept constant during the fit), as well the initial as-implanted straggle $\sigma_0 = 5.6$ nm. Within this model an apparent diffusion coefficient D_{ap}^{Hg} (T_M) is found, that is plotted in Fig. 3 (b) as a function of reciprocal temperature. In this plot the error bars for the three highest temperature values are smaller than the point size. The solid line is a linear fit to an Arrhenius plot assuming that $D_{ap}^{Hg}(T) = D_0 \exp(E_M/kT)$. The migration energy for Hg in YBCO was found to be $E_M = 1.58 \pm 0.15$ eV. On the other hand the prefactor $D_0 = \exp(-12.4 \pm 2.3)$, with most probable value $\bar{D} = 4 \times 10^{-6}$ cm^2 s^{-1}, could not be accurately determined.

4. Discussion and conclusions

In this work we have combined PAC, RBS/Channeling and X-ray diffraction measurements to study the stability and diffusion of implanted Hg into thin YBCO films. The results are shown to be fully reproducible in all films that we studied, independently of their production method. The RBS/C analysis shows that after annealing the lattice damage has partially recovered, significantly reducing the defect concentration in the implanted region. Combining X-ray diffraction with PAC refinement orientation measurements we determined that the principal axis of the EFG was aligned with the major symmetry (c) axis of the YBCO lattice.

By measuring the γ and the PAC coincidence rates during annealing in vacuum, we observed that Hg starts to out-diffuse above 653 K. With a simple model that neglects surface trapping and surface reflection, we were able to estimate the Hg diffusion coefficients at different temperatures, and the migration energy for Hg in an oxygen deficient (due to vacuum annealing) YBCO lattice [4]. We stress that both the γ and PAC coincidence rates are proportional to the integral of the Hg ions that still remain in the film, and thus cannot hint about the real Hg profile or microscopic diffusion mechanisms. On the other hand, the low frequencies that characterize the $R(t)$ PAC functions, which were taken during diffusion, suggest that Hg is diffusing via highly symmetric lattice sites, not bounded to oxygen, probably the Y or Ba sites [4]. Also, a big σ_{Q2} was found for all measuring temperatures. When measuring at $T_M = 578$ K (Fig. 2 (f), a temperature where diffusion should be hindered, but after annealing at 757 K, σ_{Q2} remained unchanged. This excludes a correlation with a dynamical diffusion process. σ_{Q2} is probably due to Hg that occupies lattice sites with oxygen vacancies in its surroundings, due to vacuum annealing. Furthermore, we should also consider that Hg could now be interacting with remaining implantation and surface defects. Finally, the abundance of oxygen in the YBCO lattice seems to hinder the Hg diffusion because the Hg losses are much smaller when annealing at 723 K under O_2 flow, and only EFG_1 was observed (Figs. 2 (a)–(c)).

These results are motivating new experiments, in which the transport properties of YBCO doped by diffusion with higher concentrations of Hg will be studied.

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