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1990 J. Phys.: Condens. Matter 2 4153

(http://iopscience.iop.org/0953-8984/2/18/012)

J. Phys.: Condens. Matter 2 (1990) 4153–4159. Printed in the UK

The study of high-temperature superconducting $YBa_2Cu_3O_{7-x}$ ceramics using the positron annihilation method

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Received 3 March 1989, in final form 8 August 1989

Abstract. This paper presents the measurements of angular correlation spectra of annihilation γ-quanta in high-temperature superconducting $YBa_2Cu_3O_{7-x}$ ceramics annealed in vacuum (10^{-3} mm Hg) and in air in the temperature range between 80 and 1150 K. It is shown that the temperature dependence of positron annihilation parameters for Y–Ba–Cu–O is different when the samples are annealed in vacuum from that when the annealing was carried out in air. In the case of vacuum annealing, at temperatures between 700 and 800 K, one observes the lowering of the critical transition temperature to $T = 52$ K and an increase in the S-parameter from 0.371 ± 0.001 to 0.390 ± 0.001. With a further rise in the temperature the value of the S-parameter increased to 0.437 ± 0.001. In the case of air annealing there were no changes in the parameters of the angular correlation spectra of annihilation γ-quanta.

1. Introduction

The synthesis of superconducting ceramics with a high critical temperature of the superconducting transition has sharply activated the experimental and theoretical studies in the area of superconductivity aimed at obtaining information about the properties of these materials and at a better understanding of the physical nature of high-temperature superconductivity.

As is known, such physical properties of a material as its electrical resistance and magnetic permittivity are due to periodic spatial oscillations of the free-electron charge density, while the phase transitions are associated with changes in the electronic wavefunctions.

The positron annihilation method gives a unique possibility for obtaining information about the local electron density and its variation (lifetime method) and about the momentum distribution of electron–positron pairs (the Doppler and angular methods) without destroying the studied sample [1]. So, from observation of the presence or absence of a change in the annihilation parameters one can find whether a change occurs in the structure of high-T_c materials.

Physically, the positron annihilation method consists of the following. The positrons emitted by a radioactive source slow down to thermal energies and annihilate with electrons in the material, producing annihilation γ-quanta which are recorded with a detector. The angles between the annihilation photons and the changes in their energy

0953-8984/90/184153 + 07 $03.50

Table 1. Parameters for various Y–Ba–Cu–O ceramics.

Sample No.	T_c (K)	ΔT_c (K)	FWHM (mrad)
1	92	2.3	11.77 ± 0.06
2	92	1.6	11.40 ± 0.04

are determined by the kinetic energy of the annihilating electron–positron pair, while the lifetime of a positron in the studied material depends on the electron density at the vicinity of the annihilation point. It should be noted that the measurements of angular-correlation annihilation-photon (ACAP) spectra and of the Doppler broadening of the annihilation line (DBAL) give similar information, but the accuracy of the angular correlation method is about 10 times that of the Doppler method although the time of statistics accumulation in the former case is much longer.

In order to find the angular distribution function of annihilation photons, one measures the dependence of the coincidence counting rate on the turning angle of one of the detectors that detect the annihilation photons from a two-quantum decay.

The observed angular distribution $C(\theta)$ of annihilation photons is directly related to the momentum distribution density $\rho(\boldsymbol{p})$ of annihilating e^+–e^- pairs. In our experiments we used a set-up that had the so-called 'long-slit' geometry, i.e. the length of the slit in the collimator placed in front of the detector was much greater its width (in our case the size of the slit was 400 mm × 2 mm). In this case,

$$C(\theta) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p\rho(\boldsymbol{p})\, \mathrm{d}p_x\, \mathrm{d}p_y$$

and we see only the component p_z of the total momentum perpendicular to the sample plane.

In our present study we measured the ACAP spectra for Y–Ba–Cu–O ceramics annealed in a wide range of temperatures, from 77 to 1150 K, both in vacuum and in air.

2. Experiment

The samples of the high-T_c superconducting ceramics $YBa_2Cu_3O_{7-x}$ were manufactured according to standard technology from a mixture of $BaCO_3$, Y_2O_3 and CuO powders. The final caking of samples was done in air at about 1200 K for 12 h with subsequent slow cooling. The samples were tablet shaped, 2.5 mm thick and 12 mm in diameter. The samples had a perovskite structure, an orthorhombic elementary cell and a density of about 60–70%. The oxygen deficit x was about 0.25 ± 0.05.

In table 1 we present the superconductivity transition temperature T_c (at the 0.1R level), the transition width ΔT_c (0.1R–0.9R) and the FWHM of the ACAP spectra for various Y–Ba–Cu–O ceramics.

We have carried out two series of experiments. In the first series, sample 1 was annealed in vacuum and sample 2 was annealed in air within the temperature range between 77 and 840 K. In the second series of experiments, sample 1 was annealed in vacuum at temperatures from 77 to 1150 K and subsequently cooled to room temperature.

The ACAP spectra were measured with a spectrometer that has a long-slit geometry and an angular resolution of 1 mrad [2]. The positron source—copper 64 with activity 100 mCi—together with the studied sample were placed into a thermochamber located at the centre of the annihilation set-up. The vacuum in the working volume of the thermochamber that could be attained was about 10^{-3} mm Hg. The heating rate of the samples was about 10 K min^{-1}. The temperature was stabilised at a selected level and was kept constant during the whole of the ACAP spectra measurements, which typically took around 12 h.

The ACAP spectra were processed according to the LSM-SPLINE program [3], which approximates the experimental spectra with piecewise smooth cubic splines.

Then we determined the FWHM of the measured spectra and the lineshape parameters S and W. The S-parameter was found as the ratio of the area under the central section of the ACAP spectrum, within the range of angles between -4 and 4 mrad, to the total area under the ACAP curve. The W-parameter was taken to be the ratio of the sum of areas under the 'wings' of the distribution curve calculated, within the symmetric intervals from -10 to -4 mrad and from 4 to 10 mrad, to the total area under the ACAP curve. Using the PDAPER program we were able to reconstruct the momentum distribution densities $\rho(\boldsymbol{p})$ from ACAP curves taking into account the actual resolution of the annihilation set-up and using the statistical regularisation method [4].

3. Results and discussion

In figure 1 we present the temperature dependence of the annihilation parameters. The full circles correspond to annealing the sample in vacuum (sample 1); the open circles correspond to annealing the sample in air (sample 2).

Within the range of T_c between 80 and 130 K we observed no essential changes in the values of the annihilation parameters.

It should be noted that, in studies of positron annihilation in classical superconductors, nothing unusual has been observed in the variation in positron annihilation parameters at the transition point, in contrast to the theoretical predictions [5]. The measurements made on high-T_c superconductors by several workers have shown that the S-parameter [6] and the positron lifetime spectra [7] change in the vicinity of T_c. However, these results are somewhat contradictory and do not agree with one another.

The experimental data obtained in another study [8] enables us to conclude that, within the accuracy of measurements, no changes occur in the annihilation parameters with transitions of the high-T_c ceramics to the superconducting state. Consequently, it is very unlikely that there are changes in the electron density of the studied ceramics or any phase transitions within this temperature range.

Figure 2 shows the momentum distribution densities reconstructed for sample 2 in the superconducting ($T = 80\ K < T_c$) and in the non-superconducting ($T = 293\ K > T_c$) states. These distributions are identical. The main specific feature of the range $130\ K < T < 640\ K$ is the monotonic growth of the FWHM and W-parameters for both samples. This effect could be due either to the lowering of the positron capture efficiency into the surface or bulk defects of the ceramics, or to the influence of linear (bulk) expansion of the sample lattice, the existence of which has been confirmed by the data obtained in [9].

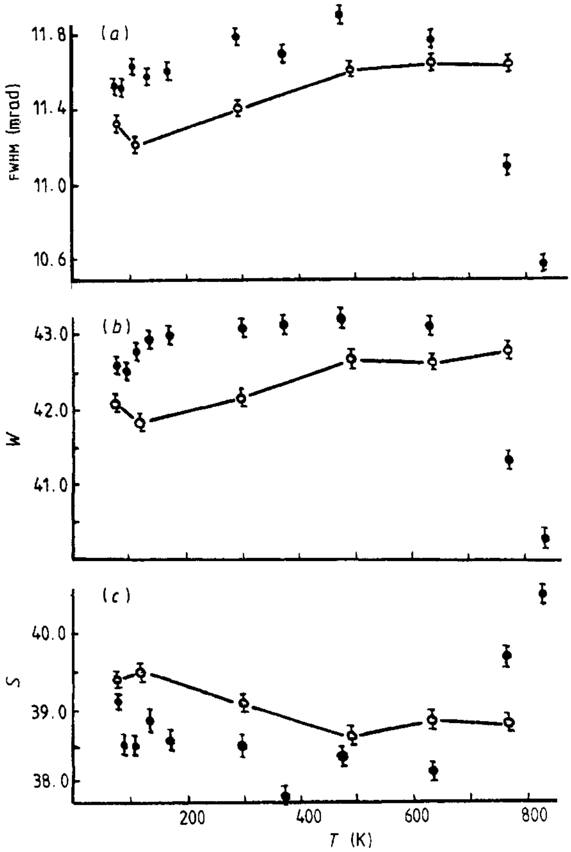

Figure 1. The dependences of (*a*) the FWHM, (*b*) the *W*-parameter and (*c*) the *S*-parameters on the temperature of the sample: ●, sample 1; ○, sample 2.

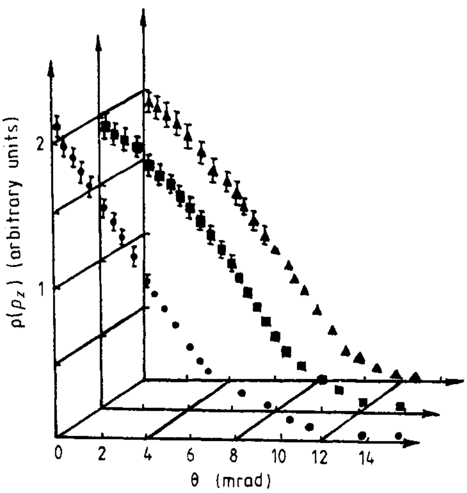

Figure 2. The momentum density distributions: ▲, $T = 80$ K $< T_c$; ■, $T = 130$ K $> T_c$; ●, $T = 740$ K.

The reconstructed momentum distribution densities $\rho(p_z)$ are almost constant within the whole temperature range. In the temperature range 640 K $< T <$ 840 K the annealing experiments give essentially different dependences of annihilation parameters for

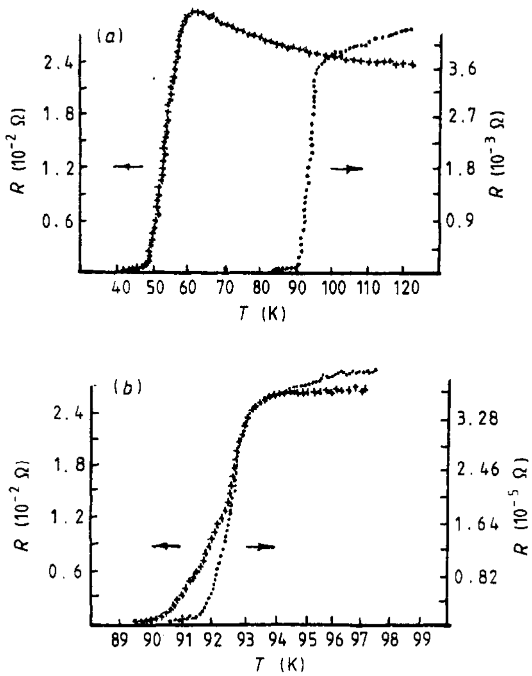

Figure 3. The temperature dependence of the electrical resistance: (*a*) sample 1; (*b*) sample 2.

annealing in air and in vacuum. For sample 1, one observes noticeable narrowing of the ACAP spectra. The momentum distribution density $\rho(p_z)$ also becomes substantially different (see figure 2, full circles).

The same is true for the superconducting properties of sample 1; they become essentially different after the sample has been annealed in vacuum at $T = 765$ K. The critical transition temperature is lowered to $T_c = 52$ K; the transition width increases to $\Delta T_c = 5$ K. The temperature dependence of the electrical resistance changes from being metal-like to being of a semiconductor type (figure 3(*a*)). For sample 2 which had been annealed in air, there are no noticeable changes either in the values of annihilation parameters or in the momentum distribution density $\rho(p_z)$ of annihilating e^+–e^- pairs. There are also no changes in the superconducting properties of this sample (in T_c and ΔT_c). The temperature dependence of electrical resistance has initially a metal-like form (see figure 3(*b*)). At the same time, one observes an increase in the electrical resistance of the sample at 293 K.

Thus the different behaviours of annihilation parameters are completely determined by the annealing conditions. At 840 K the oxygen content is reduced by about 2% [10], which results in the transformation of the orthorhombic phase of the sample to the tetragonal phase. All the observed changes are apparently due to the different types of defect which appear in the grains during this transition. According to x-ray structure analysis data, such a transition occurs at around 700 K. In this case, one observes a sharp increase (about 1%) in the elementary-cell volume [9].

The phase transition inside a grain is apparently not an instantaneous process; it begins at about 630 K and ends at around 840 K. As the necessary conditions are created inside the grain, microcrystals (regions) of the new tetragonal phase are formed together with the corresponding interphase boundaries containing defects. Dislocations, vacant

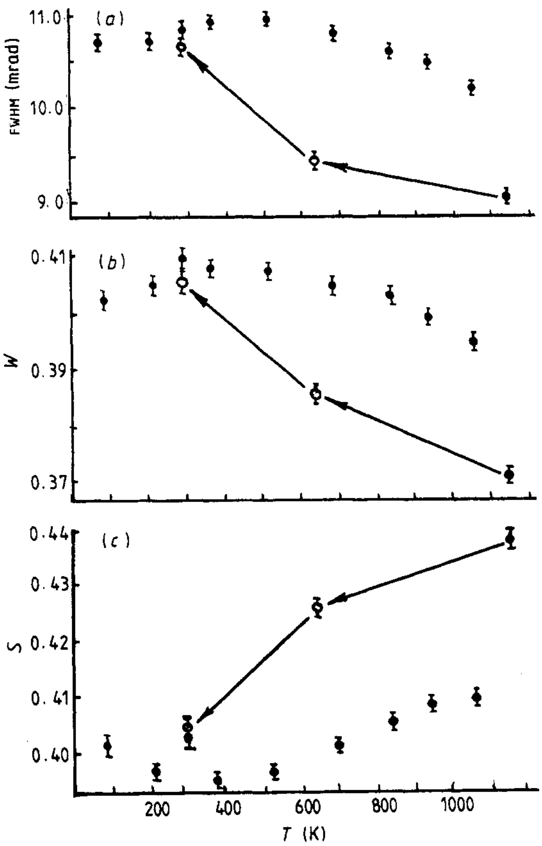

Figure 4. The dependences of (*a*) the FWHM, (*b*) the *W*-parameter and (*c*) the *S*-parameter on the temperature of the sample: ●, temperature increase; ○, temperature decrease.

loops, small voids, etc, can also form. It is the creation of these positron capture centres that results in the observed narrowing of the ACAP spectra to 10.5 mrad.

The second series of experiments was carried out with sample 1 which was annealed in vacuum at 765 K in the previous series and had much worse superconducting properties (see figure 3(*a*)). The measured dependences (figure 4) have a characteristic slope at intermediate temperatures, between 80 and 530 K. At maximum annealing temperatures a substantial narrowing of the FWHM to 9.05 mrad occurs and a corresponding sharp change in the *S*- and *W*-parameters.

The measurements made as the sample was cooled (the backward curve) at 740 and 293 K show that, in the positron annihilation method, there is almost complete restoration of the values of annihilation parameters.

The sharp changes in the values of the annihilation parameters and in the $\rho(p_z)$ distribution at $T > 930$ K are apparently due to several reasons: on the one hand, the oxygen losses become greater than 7% [10], the phase with composition $YBa_2Cu_3O_7$ breaks up, and possibly other phases are formed; on the other hand, we have intensively progressing processes of defect formation, which are mostly complicated (two and three dimensional). At maximum temperature, some of the defects are annealed with simultaneous enlargement of the bulk defects, i.e. of voids which under certain thermodynamical conditions can capture oxygen atoms. The narrow component observed in the ACAP spectra can just appear owing to the annihilation of positrons captured by the gas-filled voids, i.e. from the positronium or pseudo-positronium states.

After going through this cycle of measurements the sample completely lost its superconducting properties and was covered by many large cracks. This enabled us to conclude that the cooling of the sample was not slow enough and resulted in the formation of macrocracks, the disappearance of gas-filled voids, the creation and hardening of different types of point defect, dislocations, etc. This could have resulted in the 'restoration' of the annihilation parameters.

4. Conclusion

The results of this study have shown that the positron annihilation method is sensitive to different types of defect that appear in the Y–Ba–Cu–O ceramics during annealing. We discuss the possible mechanisms of defect formation during sample annealing in air and in vacuum and the influence of oxygen content on this process and on the conducting properties. Besides annihilating in defects, positrons also annihilate from e^+–$O^{-\eta}$ complexes localised in the Y–Ba–Cu–O lattice in the O(4) and O(5) positions (the position labels are those of [11]). On transition from the orthorhombic to the tetragonal phase a redistribution in the occupancy of different crystallographic positions of oxygen in the Y–Ba–Cu–O lattice occurs. This results in a change in the electronic structure in the O(4) and O(5) positions which, in turn, lowers the probability of positron annihilation from these positions. It also affects the momentum distribution densities $\rho(p_z)$ of annihilating e^+–e^- pairs.

At the same time, within the experimental error, no essential changes in the ACAP spectrum have been found in the vicinity of T_c which, however, does not rule out the possibility that finer effects exist.

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