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Positron annihilation study on Y-Ba-Cu-O high-T_c superconductors

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Detailed positron annihilation measurements are reported on high-T_c superconductors $YBa_2Cu_3O_{7-x}$. The lifetime and Doppler-broadening spectra show a significant change at about 240 K indicating a structural change in the sample far above 90 K where the resistance falls to zero. An analysis of the lifetime spectra shows positron trapping without any sign of saturation, indicating low specific trapping rates. On this basis, the charge states of Cu-O structures and a possible local charge decomposition are discussed.

The third generation of superconductors after certain metals and alloys [$T_c^{max}(Pb) \approx 7.22$ K] and the A_3B intermetallic compounds[1,2] [where A=Nb, V; B=Si, Ge, Sn, Ga, and $T_c^{max}(Nb_3Ge) \approx 23.2$ K], shows a transition temperature of about 90 K, exceeding the liquid-nitrogen temperature and making the technical utilization of the superconductors more attractive.

The BCS theory,[3] which is one of the best developed theories in physics, has not proved very successful for the new oxide ceramics, where the mean distance of the Cooper pairs is shorter and the interaction between two electrons is stronger than earlier. In spite of a great deal of work performed recently, the mechanism of high-T_c superconductivity is not completely understood.

After the first publications[4-6] it seems clear that the Cu-O planes and/or chains take part in superconductivity and so far the O vacancies and charge state of the Cu atoms play an important role. While the positrons have a unique sensitivity for vacancylike defects and properly reflect the change of the electron density it seems straightforward to perform the positron annihilation measurements to clear up some physical properties of these new superconductors between T_c and room temperature (RT).

$YBa_2Cu_3O_{7-x}$ ($x \sim 0.2$) samples were prepared using a standard procedure described in detail in Ref. 7. The sample preparation was checked by temperature-dependent resistivity measurements and a transition temperature of 91 K was found. Neutron-diffraction measurements verified the orthorhombic structure, which is typical for superconducting materials for $x > 6.5$, while x-ray powder diffraction showed at least 95% pure superconducting (SC) phase in the sample.[7] The density of the samples was about 80% of the theoretical value. Upon cooling down to liquid-nitrogen temperature the samples showed the Meissner effect holding a Co-Sm magnet of 45 mg floating some 2 mm above the surface.

On two pairs of $YBa_2Cu_3O_{7-x}$ samples positron lifetime and Doppler-broadening measurements were performed between RT and about 80 K. Because of the partly unexpected effect at 240 K the measurements were repeated after some time on the original (A) and on a second sample pair (B), which was produced very similar to A. (The parameters of sample B were T_c=92 K, pure SC phase $\geq 96\%$, density $\sim 82\%$ of the theoretical value.) Lifetime spectra were measured with a spectrometer having a time resolution of 270 ps full width at half maximum. Each spectrum contained at least 6×10^6 counts accumulated over a 20-h period. The positron source was rather strong, 35 μCi of ^{22}NaCl, and was deposited on a 5-μm-thick Al foil. The source correction was determined to consist of a 251-ps component with 6.6% intensity and a 450-ps component amounting to 2.0%. Numerical analysis was performed by the computer program described in Ref. 8.

The solid-state detector, applied for the Doppler-broadening measurements, was a HP-Ge coaxial detector with an energy resolution of 1.18 keV at the 497-keV ^{103}Ru γ line. The spectrometer was digitally stabilized (zero and gain) using ^{7}Be and ^{207}Bi, and spectra were accumulated to about 8×10^6 counts in the annihilation spectrum.

The lifetime and Doppler-broadening measurements were repeated several times by cooling down and heating up the samples between RT and 80 K. The small change (1%–2%) in the mean lifetime and in the S parameter of Doppler-broadening measurements is significant and reproducible each time the temperature of 240 K is passed (see Table I). The size of the superconducting crystallites is typically about a few μm,[9-11] which is large enough to avoid the positrons to escape if they already thermalized there. The small change of the positron parameters indicates that the average electron density does not vary drastically at the transition.

A possible transition of Y-Ba-Cu-O samples near to

TABLE I. Temperature dependence of S and $\bar{\tau}$ parameters.

Temperature range (K)	S	$\bar{\tau}$ (ps)
80–240	0.417 (±0.001)	185.5 (±1)
250–RT	0.413 (±0.001)	180.3 (±1)

240 K was reported recently, in agreement with our observation, by several workers.[11–15] It is unlikely that a superconducting transition would be possible at this elevated temperature as it was proposed by Ref. 11. The sharp change of all parameters may indicate some structural transition, maybe a second phase, as was also suggested by Refs. 13 and 14. The question why a series of publications on good quality samples detected this transition while other measurements did not find any change between T_c and RT is not completely understood. Maybe the interaction between the samples and water or water vapor[16] is responsible for these discrepancies. To clear up this point new experiments with careful water protection are necessary.

The good quality two-component analysis ($\chi^2=1.01$, typically) shows a detailed picture (Figs. 1 and 2). (Since the experimental results on samples A and B within the statistical error are identical, only the B series is shown in the figures.) The two lifetime components, observed in the whole temperature range, were attributed to the free and trapped positrons. Probably, O vacancies are responsible for the longer lifetime, the only known defects in the sample with high concentration which might be able to trap the positrons, as was also suggested in Ref. 17, where a correlation between the positron parameters (mean lifetime and S parameter) and the O concentration was also found. The two different sets of lifetime values, reported here under and over 240 K, are very similar to the values

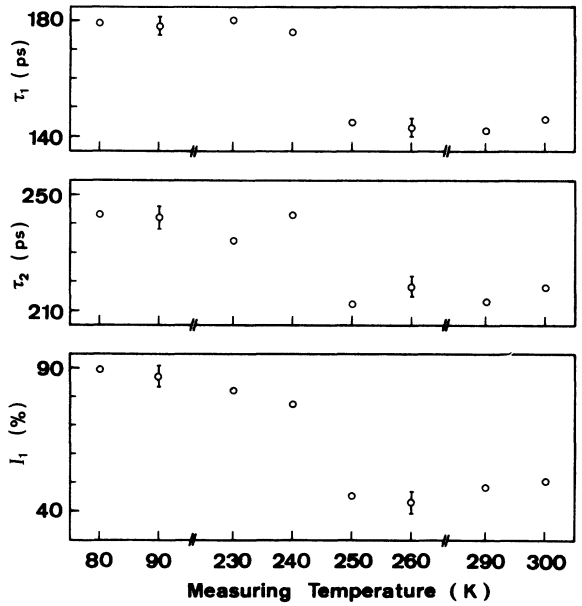

FIG. 1. Positron lifetime (τ_1, τ_2) and relative intensity (I_1) vs temperature.

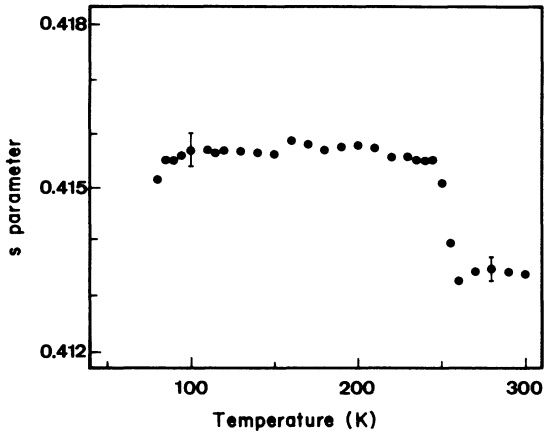

FIG. 2. S parameter of Doppler measurement vs temperature.

found by Refs. 17 and 18, respectively. The Ps component (third lifetime with typically 1–2 ns) with a very low intensity (0.34%) observed by Ref. 18 is probably the consequence of a lower sample density.

Although the oxygen deficiency of these materials is rather small ($x=0.1$–0.5) typically, depending on sample preparation,[19] it results in an O-vacancy concentration of about 10^{-1}–10^{-2}, typically some 2 orders of magnitude higher than the concentration of metallic vacancies near to the melting point. Therefore, for the lack of saturation a low specific trapping rate (δ_{1V}) could be responsible. Applying the two-state trapping model[20] one obtains

$$\delta_{1v}C_{1v}=I_{1v}(1/\tau_1-1/\tau_{1v}),$$

where δ_{1v} is the specific trapping rate and C_{1v} is the vacancy concentration. Using the measured values of the lifetime parameters ($\tau_1, \tau_{1v}, I_{1v}$) one gets the values for δ_{1v} of $10^{10}\,s^{-1}$ and $10^{11}\,s^{-1}$, in good agreement with Ref. 21 at $T<240$ K and $T>250$ K, respectively. These values are 4 orders of magnitude lower than for the most metals, indicating weak, maybe neutral, trapping centers.

It was shown by recent band-structure calculations[22,23] that the Cu(2)-O(2)-O(3) states (2D character) and the Cu(1)-O(1)-O(4) states (1D character) are highly decoupled. [Because of the almost empty antibonding and the almost full bonding bands O(4) belongs probably to the Cu(1)-O(1) chains creating Cu(1)-O(1)-O(4) ribbons.] On the other hand, it was reported by neutron-diffraction measurements[24] that most of the O vacancies arises from the O(1) sites, where the positrons are probably trapped. As a consequence, in agreement with Ref. 21, a local charge decomposition between O(1) and the neighboring Cu(1) atom is suggested. Such a type of charge transfer or local decomposition is supported by the strong correlation between Cu $3d$ and O $2p$ electrons along the metallic-like chains or ribbons, which makes the screening of O vacancies possible.[23] Recent EPR measurements[25–28] have shown that there are no unpaired electrons either in the normal or in the superconducting states. The observed EPR signals arise from impurities and not superconducting grains. As a consequence all processes which presume the presence of Cu^{2+} ions can be excluded. Assuming, as

it is generally accepted, that the Cu(1) sites are occupied by Cu^{3+} ions, one can write

$$Cu^{3+}+O^{2-}\rightarrow Cu^{1+}+O^{0}\rightarrow Cu^{1+}+O_{lv}^{0}+O\ (\text{free}),$$

creating neutral O vacancies which are able to trap positrons and explain the low specific trapping rate.

In conclusion, the positron annihilation measurements show a transition on the $YBa_2Cu_3O_{7-x}$ samples at about 240 K that probably has a structural origin. The weak but significant trapping indicates the presence of neutral trapping centers, probably O vacancies. A local decomposition model creating neutral O vacancies was proposed.

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