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Positron annihilation in the high-temperature superconductor $YBa_2Cu_3O_{6+\delta}$

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Positron-annihilation lifetime and Doppler broadening energy spectra have been measured in high-temperature superconductors $YBa_2Cu_3O_{6+\delta}$ as a function of temperature between 10 and 293 K. The observed positron lifetime and Doppler broadening S parameter show an onset increase near the superconducting critical temperature ($T_c=90$ K). This variation does not exist in a similar nonsuperconducting sample that contains a saturated oxygen vacancy content. These results give evidence that the oxygen vacancy and electronic structure change play an important role for high-T_c superconductivity.

Recently, superconductivity above 90 K has been reported[1-4] in a series of samples with a composition of $ABa_2Cu_3O_{6+\delta}$, with A = Y, La, Nd, Sm, Eu, Gd, Ho, Er, and Lu. Although the metal-ion–oxide stoichiometry has been well established and the crystal structure of these compounds has been determined,[5] the mechanism of this high-T_c superconductivity is still unresolved. An enormous amount of activity has been devoted to search for phase transformation, electronic structure, phonon spectra, electronic density, and related physical parameters of such systems. X-ray[6] and neutron-diffraction results[5] do not find real crystalline structural phase transformations for these superconductors.

In this Rapid Communication, we report the first result using positron annihilation spectroscopy (PAS), which is known to be an especially sensitive probe[7] for determining the electronic structure and defect structure of solids, to study superconductivity of high-T_c systems. Two superconducting samples of $YBa_2Cu_3O_{6+\delta}$ ($\delta \sim 0.8$) were prepared independently at the University of British Columbia (UBC) and at the University of Houston (UH) by standard metallurgical procedures starting with high-purity Y_2O_3, $BaCO_3$, and CuO powders. The dc resistivity was measured in zero applied magnetic field and T_c was determined to be 88 and 90 K for the UBC and UH samples, respectively. A third sample with a stoichiometry ($\delta \sim 0$) was prepared by heating the superconducting sample with $\delta \sim 0.8$ (at UH) at 900 °C in vacuum. This sample is a nonsuperconducting compound with identical lattice parameters (tetrahedral symmetry) as the UH superconducting sample as determined by x-ray measurements but with low oxygen content (more perovskite vacancies). The single-phase crystals were pressed into two diskette samples (with a size 1–2 mm thickness and 5–10 mm diameter), which contain about 10% porous space.

50 μCi of a ^{22}NaCl positron source was either deposited on a thin Al foil (2.42 mg/cm^2) (for the UBC sample) or directly deposited on the surface of the materials (for UH samples). Two pieces of identical sample were sandwiched together with the positron source. The samples were attached to a cold head of a closed-cycle He refrigerator (Air Product). Three thermometers, an Fe-Au–Chromel thermocouple, a Pt resistor, and a Ge resistor, were employed to monitor the temperature (± 0.1 K) at the top, bottom, and side of the samples. The samples were under a vacuum of $<10^{-5}$ Torr during the experiments.

The positron lifetime measurements were performed by using a standard fast-fast coincident circuit to measure the time interval between the 1.28-MeV γ ray due to nuclear decay and the subsequent 0.511 MeV annihilation radiation. The lifetime resolution was found to be 260 ps from a ^{60}Co source. The actual resolution was determined to be a sum of two Gaussians with full width half maximum (FWHM) of 255 ps (80%) and 290 ps (20%), respectively, by using a computer analysis program RESOLUTION in the PATFIT package.[8] A source correction (10%) was made in the samples when a thin Al foil was used as a source supporter in the computer analysis by a method described elsewhere.[9] Each spectrum contains a total count of one million events. The Doppler broadening measurements were performed by measuring the energy spectra at 0.511 MeV annihilation radiation. A Ge(Li) solid detector (Ortec EG&G) with 1.5 keV resolution at 497 keV (15% efficiency) was employed to obtain Doppler broadening energy spectra. A ^{103}Ru radioisotope was used to monitor the detector resolution and electronic stability during the experiments. The energy spectra were processed and stabilized digitally using a method described elsewhere.[10] The Doppler broadening results were expressed as an S parameter which is taken as the ratio of the total counts of the central region of the 0.511 meV peak to the total counts of whole energy spectrum where the background has been subtracted. Detailed descriptions of positron lifetime and Doppler broadening spectroscopies can be found elsewhere.[11,12] Each series of experiments was performed from low to high temperatures and cycled three times. The results showed no hysteresis and good reproducibility in each cycle.

Three positron lifetimes $\tau_1 \sim 139$ ps, $\tau_2 \sim 210$ ps, and $\tau_3 \sim 2.5$ ns were resolved from all obtained lifetime spectra with the variance of the fit less than 1.10. From these results we found that the intermediate positron lifetime (τ_2), the corresponding intensity (I_2) and S parameter show significant temperature dependence. The variations of τ_2, I_2, and S with temperature are plotted in Fig. 1. No significant temperature dependence was found in the short and long lifetimes, τ_1 and τ_3. The long lifetimes and the intensities were found to be 2.5 ± 0.6 ns and $0.34\% \pm 0.04\%$, respectively. The long-lived component is easily identified as ortho-positronium (triplet spin state) annihilation at the interfacial spaces or surfaces among crystals. Since τ_3 and I_3 were found to be the same values in all samples, they are neither from bulk nor from a vacancy, and not from a vacancy, and not related to superconductivity.

The structure of $YBa_2Cu_3O_{6+\delta}$ has been identified as an orthorhombic, distorted, oxygen-deficient perovskite.[5] Since the material contains many vacancies, it is reasonable to expect two positron lifetimes, one corresponding to annihilation in the interstitial region of the bulk and the other to the vacancies. The short lifetime τ_1 (139 ± 7 ps) is typical positron-annihilation lifetime in the interstitial region of bulk metal. The intermediate lifetime components, τ_2 and I_2, are attributed to positron annihilation at oxygen vacancies which are the most abundant trapping sites for positrons in the materials under study. A lifetime of 200 ps corresponds to the vacancy size of about 3.0 Å according to a reported correlation curve between void size and positron lifetime.[13] This is reasonable since the obtained size is about the expected size for an oxygen vacancy by taking the difference between the reported lattice parameters (3.8231 and 3.8864 Å) on the tetrahedral Cu-O plane and the radius of Cu ion for this structure.[5] This assignment is further supported by comparing the I_2 results between the nonsuperconducting and superconducting samples from UH (see Fig. 2). The known difference between these two samples is that the oxygen-vacancy concentration in the nonsuperconducting sample ($\delta \sim 0$) is greater than in the superconducting sample ($\delta \sim 0.8$) by 8.9%. As shown in Fig. 2, the intensity of the intermediate lifetime I_2 is larger by $8\% \pm 2\%$ in the nonsuperconductor than in the superconductor.

It is interesting to observe a significant change of τ_2 and S parameter at $T_c \approx 90$ K in both UBC and UH superconducting samples (see Figs. 1 and 2), while no such change is observed in the nonsuperconducting sample (see Fig. 2). Several attempts using positron-annihilation spectroscopy to study superconductivities of metals[14-17]

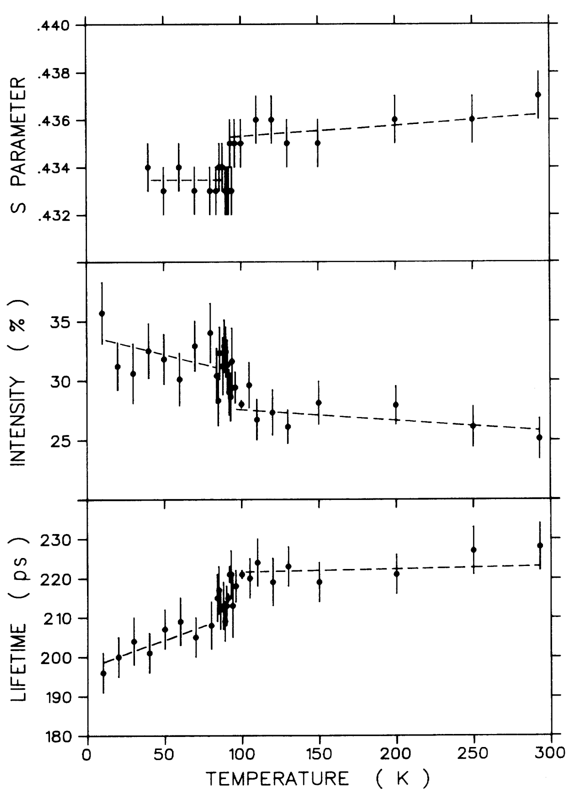

FIG. 1. S parameter, positron lifetime (τ_2), and intensity (I_2) vs temperature in an $YBa_2Cu_3O_{6+\delta}$ superconductor (from UBC). The dashed lines represent the best two-line fits for the data. Results of τ_1 (139 ± 7 ps), τ_3(2.5 ± 0.6 ns), and I_3 do not change with temperature.

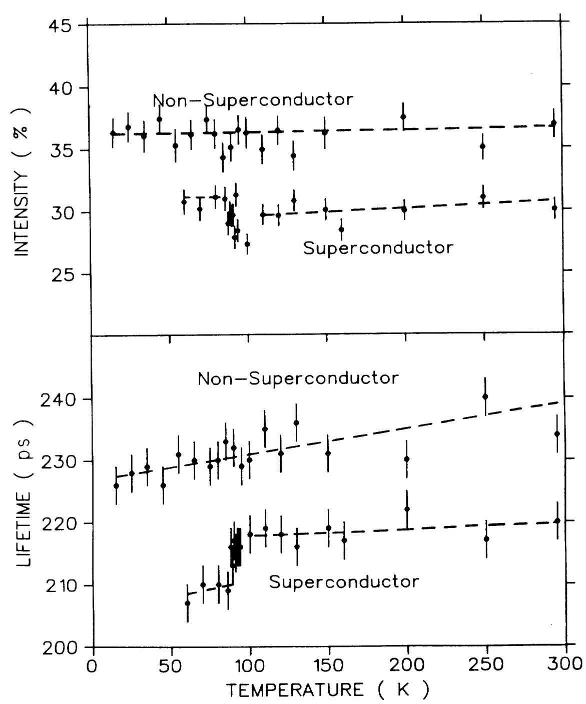

FIG. 2. Positron lifetime (τ_2) and intensity (I_2) vs temperature in an $YBa_2Cu_3O_{6+\delta}$ ($\delta \sim 0.8$) superconductor and in an $YBa_2Cu_3O_{6+\delta}$ ($\delta \sim 0$) nonsuperconductor (from UH). The dashed lines represent the best two-line and one-line fits for the superconducting and nonsuperconducting results, respectively. Results of τ_1(139 ± 7 ps), τ_3(2.5 ± 0.6 ns), and I_3 do not show temperature dependence.

and niobium alloys[18-21] have been made in the past. No significant changes in positron-annihilation characteristics, neither lifetimes nor electronic momentum distributions from angular correlation of positron-annihilation radiations have ever been confirmed. Speculation about the different behavior of positrons in normal and in superconducting states has been reported[22-24] based on the Bardeen-Cooper-Schrieffer (BCS) theory. Results of Figs. 1 and 2 show the first clear evidence of different positron behavior at a superconducting state from a normal state. A high annihilation rate below T_c shows that the electron density at the site where the positron annihilates is higher for the superconducting state than for the normal state. Recent theoretical results based on the excitonic enhanced superconducting mechanism[25] show that below T_c excess electrons are available in the excitonic superconducting composite state, but no such electrons exist above T_c. The existence of oxygen vacancy will raise up the Fermi level of $YBa_2Cu_3O_7$ and thus make the electronic structure more favorable for an excitonic enhanced superconducting mechanism. A significant change of S parameter below and above T_c is also observed in the superconductors (see Fig. 1). No such a change is observed in the nonsuperconductor. This result indicates that there is a change in electronic structure as the material changes from a superconducting state to a normal state for this high-T_c system. This implies that the high-T_c superconductivity is related to a change in the electronic state.

We notice that τ_2 increases with temperature in the superconducting state. The rate of the τ_2 increase with respect to temperature at low temperatures (<50 K) in the superconducting state was found to be relatively large, i.e., $(7.3\pm3.4)\times10^{-4}$ K^{-1}, which is about one order of magnitude larger than that in the normal state, as shown in Fig. 1. We also observe a sudden decrease of I_2 across T_c from the superconducting state to the normal state as shown in Figs. 1 and 2. A detailed account of these results will be presented in a full paper later.

From the results of positron-annihilation spectroscopies presented in this Rapid Communication, we conclude that (1) behavior of positrons and their annihilation characteristics are different in the superconducting state compared with the normal state of $YBa_2Cu_3O_{6+\delta}$; (2) the oxygen vacancy plays an important role in high-temperature superconductivity; (3) there is an electronic structure change below and above T_c; the electronic density near the oxygen vacancies is higher in the superconducting state than in the normal state, and the electron momentum distribution undergoes a change at T_c.

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