High-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ studied by positron annihilation

S. J. Wang,* S. V. Naidu, S. C. Sharma,† D. K. De, D. Y. Jeong, and T. D. Black
Center for Positron Studies, Department of Physics, The University of Texas at Arlington, Arlington, Texas 76019

S. Krichene and J. R. Reynolds
Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019

J. M. Owens‡
Center for Advanced Electron Devices and Systems, The University of Texas at Arlington, Arlington, Texas 76019

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We have measured the positron-lifetime and the Doppler-broadening spectra in the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ as a function of temperature between 77 and 295 K. Positron-lifetime and Doppler-broadening data show new features in the superconducting phase. These results are interpreted in terms of positron localization in lattice distortions and positron surface states.

Since the recent discovery of high-T_c superconducting materials[1,2] there has been remarkable activity in the preparation and characterization of such materials and in the investigation of the possible theoretical models for understanding the mechanism(s) of superconductivity at such high temperatures. A number of high-T_c Y-Ba-Cu-O superconductors with transition temperature about 90 K have been studied by different experimental techniques[3] including positron annihilation.[4,5] A superconducting transition temperature of 155 K has also been reported in $YBa_2Cu_3F_2O_y$ in which fluorine seems to play a critical role in achieving such a high T_c.[6] On the theoretical side, the Bardeen-Cooper-Schrieffer, resonating-valence bond and other theories are being investigated in order to understand high-T_c superconductors.[7–9] However, the mechanism responsible for the high-T_c superconductivity remains unclear.

It is of considerable interest to understand the electronic structure and the role of defects, particularly close to T_c, in these oxides. Positron-annihilation techniques are known to probe changes in electron density and momentum, especially as materials undergo phase transitions.[10] In addition, they are highly sensitive to lattice defects in materials. The sensitivity of the positron-annihilation techniques to the superconducting transition has recently been shown by Jean *et al.*,[5] who observed an on-set increase in the positron-lifetime and Doppler-broadening S parameter at T_c in the high-temperature superconductor $YBa_2Cu_3O_{6+\delta}$. In order to investigate further the use of positron annihilation in the study of high-T_c superconductivity, we have measured the positron-lifetime and the Doppler-broadening spectra as functions of temperature in the superconductor $YBa_2Cu_3O_{7-\delta}$. Here we present the results of these measurements which show new features in the lifetime data in the superconducting phase of the material. They should provide additional tests for the theoretical models that are being advanced in order to understand high-T_c superconductors.

The $YBa_2Cu_3O_{7-\delta}$ ceramic samples were prepared by the solid-state reaction of 99.99% Y_2O_3, 99.999% $BaCO_3$, and 99.999% CuO powders. They were mixed stoichiometrically and ground. The powder mixture was calcined for 24 h at 1220 K in an atmosphere of oxygen flowing at a relatively low rate. The calcined material was reground and pressed into disks of 2 cm diameter and 0.18 cm thickness. These disks were sintered for 16 h at 1250 K in continuously flowing oxygen. The resistivity versus temperature data were obtained by using the standard four-point technique with current densities of $\sim$20 mA/cm^2 above T_c and up to $\sim$450 mA/cm^2 below T_c. The positron lifetime spectra were measured by using a fast-fast lifetime spectrometer having a full width at half maximum of $\sim$0.330 ns for the ^{60}Co prompt resolution data. These spectra were measured first for temperatures increasing from 77 to 295 K (heating cycle), second for temperatures decreasing from 135 to 77 K (cooling cycle), and finally for temperatures increasing from 175 to 295 K. The lifetime spectra were analyzed for two lifetime components by using the standard computer program[11,12] POSITRONFIT EXTENDED and for the mean lifetimes by calculating the centroids of the spectra. The Doppler broadening of the annihilation γ rays were measured by a digitally stabilized high-purity Ge detector spectrometer with an energy resolution of about 1.2 keV at 570 keV and analyzed for the S parameter. The temperature of the samples was controlled with an accuracy of $\pm$1 K by using an Oxford cryostat in which the sample remains in the atmosphere of nitrogen vapor during both the conductivity and positron-annihilation measurements.

The resistance of the sample is shown as a function of temperature in Fig. 1. It drops by 5 orders of magnitude within about 10 K with T_c=87.5 K, taken as the midpoint of the transition. We show the temperature dependencies of the positron mean lifetime τ (Fig. 2), the S parameter (Fig. 3), the lifetime of the short-lived component τ_1 (Figs. 4 and 5), and the lifetime of the long-lived component τ_2 (Fig. 6). Both the positron-lifetime and Doppler-broadening spectra are sensitive to the high-T_c superconducting transition. The important features of these data can be summarized as follows: (1) There are abrupt changes in the lifetimes at certain temperatures in the superconducting transition region of the sample; (2)

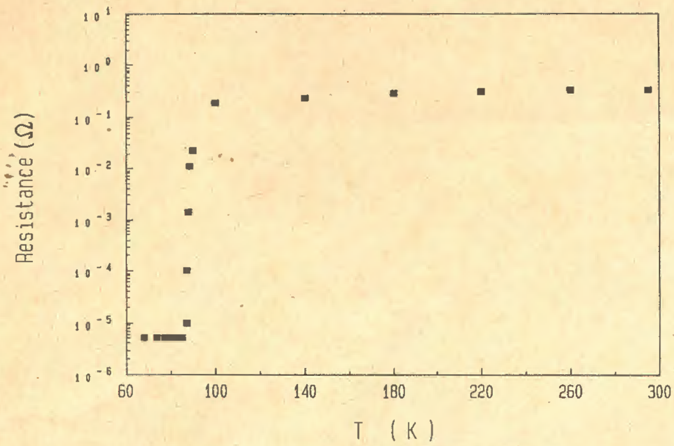

FIG. 1. Resistance of the $YBa_2Cu_3O_{7-\delta}$ sample vs temperature.

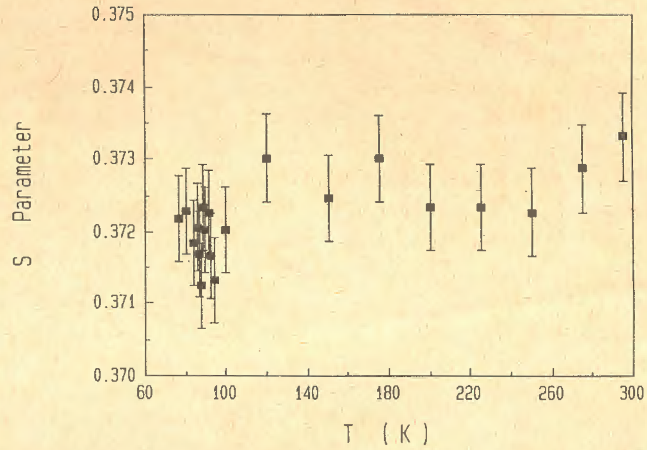

FIG. 3. Doppler-broadening line-shape parameter S as a function of temperature.

the mean lifetime increases rapidly from 0.257 ± 0.001 ns at 100 K to 0.268 ± 0.001 ns at 150 K, and then decreases slowly with temperature up to 295 K (Fig. 2); (3) the S parameter has a lower value in the superconducting phase compared to its value in the normal phase (Fig. 3). While decreasing the temperature, the S parameter begins to decrease a great deal before a significant reduction is seen in the resistance of the sample; (4) there are significant differences between the data taken during the heating and cooling cycles (Fig. 5); and (5) the lifetime data measured between 200 and 295 K show an aging effect (Fig. 4).

We assume that the shorter-lived component with a lifetime τ_1 results from annihilations in the grains of the sample. It is expected that these grains have a significant concentration of lattice defects, for example, oxygen vacancies and lattice distortions, which are believed to play an important role in high-T_c superconductivity. A large fraction of the positrons entering the grains should be trapped in these defects. The trapped positrons sample an electron density which is lower than the density seen by the free positrons. The time resolution of the spectrometer is not adequate to separate contributions to the τ_1 component from the trapped and free states. Therefore, τ_1 represents contributions from positrons annihilating from both the trapped and free states in the grain. The changes in τ and τ_1 in the vicinity of the transition temperature are striking. The changes seen in the lifetimes τ and τ_1 around 90 K suggest positron localization in regions of lower than average electron density (lattice distortions or other structural changes possibly related to superconductivity). It is interesting to note that these changes in the lifetime spectra occur within 10 K near T_c, which also happens to be the width of the superconducting transition in our sample. If positrons are localized by lattice distortions or structural changes related to superconductivity, as we infer from these data, then highly sensitive positron-annihilation techniques can be used to probe the mechanisms of high-T_c superconductivity.

There are marked differences between τ_1 values for the two sets of data obtained during the heating and cooling

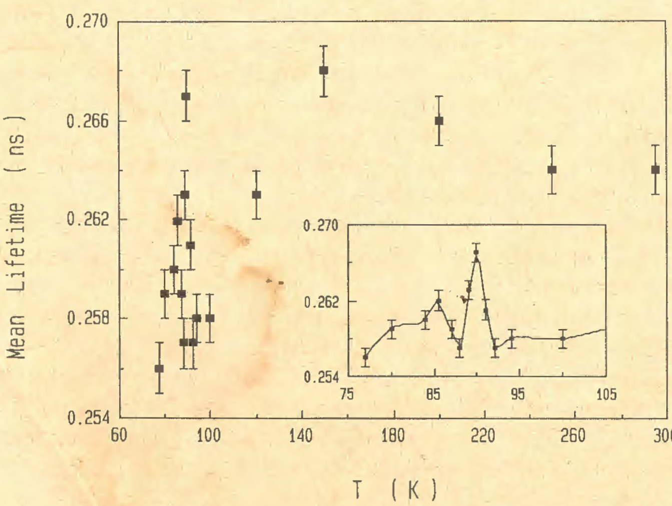

FIG. 2. Positron mean lifetime τ in $YBa_2Cu_3O_{7-\delta}$ as a function of temperature. The inset shows data on an expanded scale near T_c. The curve is hand drawn to aid the eye.

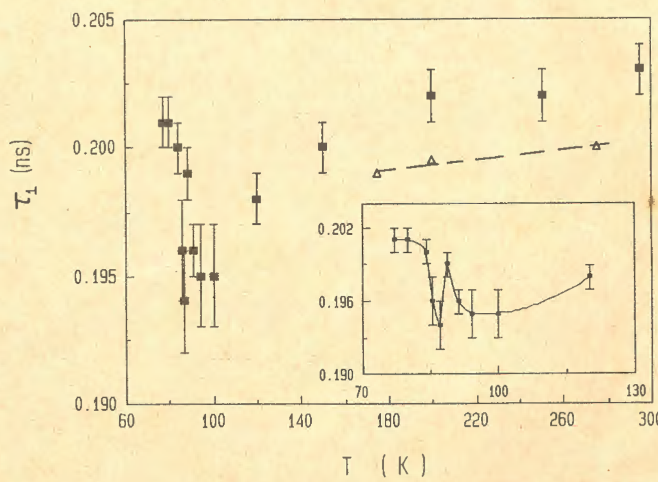

FIG. 4. Short lifetime τ_1 vs temperature for the $YBa_2Cu_3O_{7-\delta}$ sample. The inset shows data on an expanded scale near T_c. The dashed curve represents "delayed" data taken 40 h later.

cycles (Fig. 5). There is evidence of sample "deterioration" between these two cycles. A similar deterioration effect has been seen in the $La_{1.9}Ba_{0.1}CuO_4$ superconductor.[13] The temperature dependence of τ_1 at temperatures below 100 K seems to have smeared after the heating cycle. The temperature at which an abrupt increase in τ_1 occurs shifts to a lower value during the cooling cycle (this is consistent with a shift in T_c indicated by the resistance measured after the completion of the positron experiments). In addition, the two sets of lifetime spectra measured 40 h apart between 200 and 295 K are significantly different from each other: τ_1 decreases; however, τ_2 remains unchanged though the intensity I_2 increases, and consequently τ increases for the latter set (identified in Fig. 4 as the delayed set). This suggests an aging effect. Between 100 and 295 K, τ_1 increases almost exponentially with increasing temperature. Assuming that the temperature dependence of τ_1 between 100 and 295 K is due to the trapping of positrons in lattice defects and that τ_1 represents contributions from positions annihilating from the trapped and free states, an analysis of these data following the trapping model provides an Arrhenius plot with an activation energy of 0.07 ± 0.01 eV. Here we have also assumed that the lifetimes of the positrons annihilating from the "trapped" and "free" states are 0.203 and 0.194 ns, respectively. This energy is much too small in comparison with the values of vacancy-activation energies that are of the order of 1 eV in metals and alloys.[14] Considering this low value of the energy, the activation process is more likely associated with an order-disorder transition in the sample.

The temperature dependencies of the long lifetime and its intensity, shown in Fig. 6, also exhibit abrupt changes around T_c. For temperatures between 77 and 150 K, τ_2 values range between 0.45 and 0.57 ns. We attribute this component to the surface-state positron lifetime for the grains of the ceramic. This assignment is supported by the observations of the positron surface-state lifetimes of 0.58 ns for Al (Ref. 15) and 0.45 ns for graphite powders.[16] In order to see if there is a significant contribution from positronium annihilations to τ_2, we have analyzed the lifetime spectra for three components. The total numbers of counts under these spectra are not quite adequate to provide unconstrained three-component analyses with acceptable statistical errors in the parameters. We believe that the two-component analysis results are the most reliable. Nonetheless, the three-component analyses, in spite of producing relatively large errors in the shorter-lived components, show a long component with average lifetime $\tau_3 = 1.75$ ns and intensity $I_3 = 0.5 \pm 0.1\%$ between 77 and 150 K. The latter increases to $1.2 \pm 0.2\%$ around 200 K and remains at this high value up to 295 K. Therefore, there is no significant contribution to τ_2 from positronium annihilations between 77 and 150 K. Above 150 K, a high value of τ_2, reaching 0.860 ± 0.032 ns at 295 K, probably has contributions from both the positron surface state and positronium. A resolution of this issue requires accumulation of the lifetime spectra with much higher statistics and additional experiments utilizing, for example, positronium quenching.

In conclusion, we have presented positron-lifetime and Doppler-broadening data for the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$. The positron-lifetime data show hitherto unknown features in the superconducting phase of this sample. Both positron-lifetime and Doppler-broadening spectra are sensitive to the superconducting transition. These data suggest positron localization in some kind of lattice defects present in the superconductor. We plan future experiments to investigate this further.

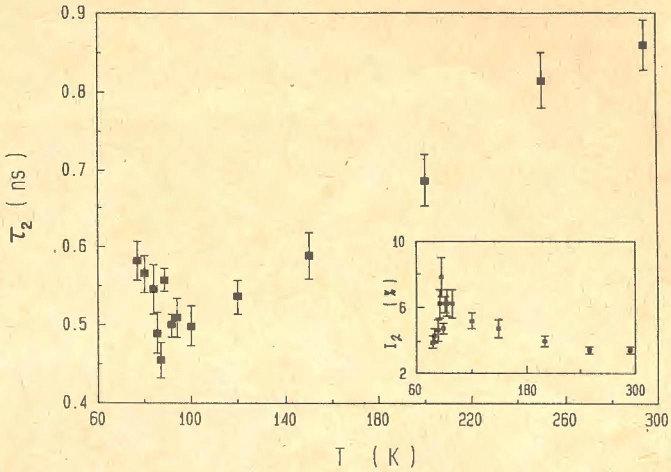

FIG. 6. Long lifetime τ_2 vs temperature for the $YBa_2Cu_3O_{7-\delta}$ sample. The inset shows temperature dependence of the relative intensity of this component.

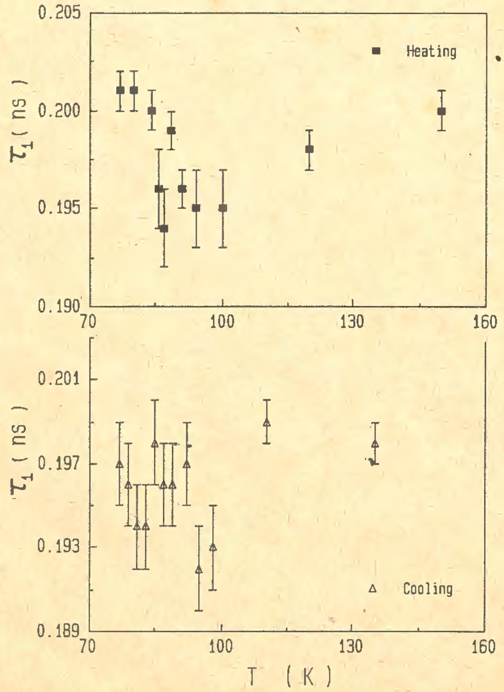

FIG. 5. Variations in τ_1 as a function of temperature between heating and cooling cycles.

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*Permanent address: Wuhan University, People's Republic of China.

†To whom all correspondence should be addressed.

‡Present address: Department of Electrical Engineering and Computer Science, Santa Clara University, Santa Clara, California.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. L. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[3]For a listing of papers on high-T_c superconductivity that were recently published in Phys. Rev. Lett. and Phys. Rev. B, see Phys. Rev. Lett. **58**, No. 20 (1987); **59**, No. 1 (1987).

[4]S. Ishibashi, A. Yamaguchi, Y. Suzuki, M. Doyama, H. Kumakura, and K. Togano, Jpn. J. Appl. Phys. **26**, 1688 (1987).

[5]Y. C. Jean, S. J. Wang, H. Nakanishi, W. N. Hardy, M. E. Hayden, R. F. Kiefl, R. L. Meng, P. H. Hor, J. Z. Huang, and C. W. Chu, Phys. Rev. B **36**, 3994 (1987).

[6]S. R. Ovshinsky, R. T. Young, D. D. Allred, G. DeMaggio, and G. A. Van der Leeden, Phys. Rev. Lett. **58**, 2579 (1987).

[7]P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).

[8]M. H. Cohen and D. H. Douglas, Phys. Rev. B **35**, 8720 (1987).

[9]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[10]S. C. Sharma, R. M. Johnson, and L. M. Diana, *Novel NDE Methods for Materials,* edited by B. B. Rath (The Metallurgical Society of AIME, Warrendale, PA, 1982), pp. 45–61, and references therein.

[11]S. C. Sharma, S. Berko, and W. K. Warburton, Phys. Lett. **58A**, 405 (1976).

[12]P. Kirkegaard and M. Eldrup, Comp. Phys. Commun. **1**, 401 (1974).

[13]E. F. Skelton, W. T. Elam, D. U. Gubser, S. H. Lawrence, M. S. Osofsky, L. E. Toth, and S. A. Wolf, Phys. Rev. B **35**, 7140 (1987).

[14]*Positrons in Solids,* Vol. 12 of *Topics in Current Physics,* edited by P. Hautojarvi (Springer-Verlag, New York, 1979), and references therein.

[15]K. G. Lynn, W. E. Frieze, and P. J. Schultz, Phys. Rev. Lett. **52**, 1137 (1984).

[16]Y. C. Jean, K. Venkateswaran, E. Parsai, and K. L. Cheng, Appl. Phys. **35A**, 169 (1984).