PHYSICAL REVIEW B VOLUME 38, NUMBER 1 1 JULY 1988

Temperature dependence of the positron annihilation lifetime in single-crystal $YBa_2Cu_3O_7$

D. R. Harshman, L. F. Schneemeyer, and J. V. Waszczak
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Y. C. Jean,* M. J. Fluss, R. H. Howell, and A. L. Wachs
Lawrence Livermore National Laboratory, Livermore, California 94550
(Received 24 December 1987)

We report our measurements of the temperature dependence of the positron lifetime spectrum in single-crystal $YBa_2Cu_3O_7$. Contrary to earlier measurements in sintered powders, we observe only a single lifetime component τ for temperatures in the range $5 < T < 297$ K, exhibiting a constant value ($\tau \approx 176$ ps) above T_c and increasing monotonically below T_c to ≈ 187 ps at 5 K. Possible correlations with the superconducting gap, relaxation of the oxygen atoms, or a redistribution of the electrons are discussed.

Early speculations[1] concerning the behavior of the positron lifetime τ in conventional superconductors suggested that one should observe an increase in τ below the superconducting transition temperature T_c, due to a smearing of the Fermi surface. Subsequent experiments[2] aimed at measuring the temperature dependence of τ in Pb failed, however, to show any reproducible effect. The advent of the copper-oxide-based high-T_c superconductors[3,4] has revived interest in the positron as a probe of the superconducting state, particularly because of the comparatively large energy scales involved in such novel systems. There have been several studies of positron annihilation in the sintered high-T_c materials[5-8] yielding two general observations, albeit only qualitatively reproduced by different laboratories. The relevant observations are (a) two lifetime components: a short-lived component varying from lab to lab between ~ 50 and ~ 140 ps, and a longer component ranging from 190–230 ps; and (b) a discontinuous behavior in the temperature dependence of the long component, which is always accompanied with a significant slope change at T_c. The variability in the results reported to date are thought to be attributable to variations in the synthesis and processing of the sintered samples themselves. Moreover, some of the physical properties (critical current density, etc.) are known to be different for the sintered powder as opposed to the single-crystal material. Since positrons are sensitive probes of structural variations such as vacancies, dislocations, and grain boundaries,[9] it is important that similar experiments be done on high-quality single crystals. To this end we have carried out measurements on well-characterized single crystals of superconducting $YBa_2Cu_3O_7$.

The single-crystal samples of $YBa_2Cu_3O_7$ were grown from a partially melted CuO-BaO-Y_2O_3 mixture and annealed in oxygen (for a period of three weeks), as described previously.[10] The crystals grow as platelets with the a and b axes parallel to the growth faces and common cleavage planes, but with significant microtwinning in the a-b (basal) plane. The superconducting transition temperature for the crystals was measured using ac susceptibility, yielding a transition onset of ~ 95 K, with a 5-K width. No additional change in the ac susceptibility was observed in these samples. Measurements were also made using dc magnetization, indicating a transition at approximately 84 K, as is shown in Fig. 1. The apparent discrepancy in T_c measured by the two methods is not surprising since ac susceptibility is known to be more sensitive to skin effects. Four such crystals were used in the present study, each being ~ 0.1 mm thick and presenting a c-axis face with an area of $\sim 3 \times 2$ mm^2.

A positron source consisting of a dried, 1-mm-diam. deposition of ~ 50 μCi of $^{22}NaOC_2H_5$ on a Ni foil (~ 1.1 mg/cm^2) was sandwiched between the samples such that two crystals were stacked on either side of the foil. The estimated fraction of positrons stopped in the crystals was 99.4%.[11] The sample package was sealed in an Al cell under an ultrahigh-purity ^{4}He atmosphere. This assembly was cooled using a closed-cycle He refrigerator (Air Products) for temperatures above 10 K, and for temperatures below 10 K a helitran was used. The temperature of the

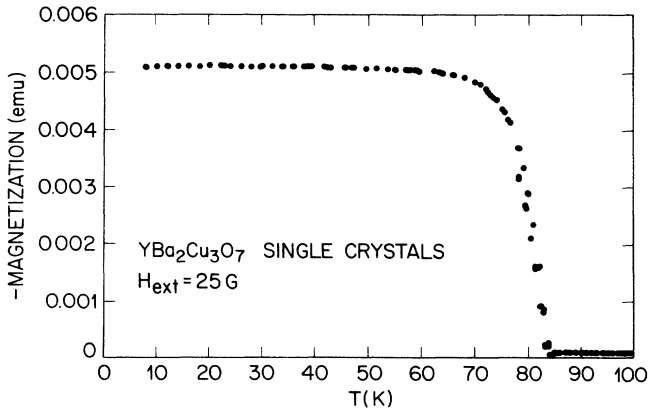

FIG. 1. dc magnetization measured ($H_{ext} = 25$ G) in field-cooled single-crystal $YBa_2Cu_3O_7$. The suppression in T_c (~ 84 K) is attributed to a slight oxygen deficiency.

sample was controlled and monitored to an accuracy of ± 0.1 K using a silicon diode. The positron lifetime measurements were performed using a standard fast-fast coincidence circuit, incorporating two BaF_2 scintillators mounted on XP2020Q photomultipliers, to measure the time interval between the 1.28-MeV nuclear gamma and the subsequent 0.511-MeV annihilation radiation. A similar positron lifetime spectrometer is described elsewhere.[12] The resolution function of the apparatus was adequately represented by the sum of two Gaussians with widths (full width at half maximum) of 230 ps (90%) and 310 ps (10%) by fitting the known ^{207}Bi metastable state lifetime (186 ps) using the cascade radiation lines at 0.569 and 1.064 MeV. The lifetime spectra were analyzed using the PATFIT program.[13] Apart from a source correction (4.6%, with a lifetime of 0.410 ns) all the data reported here on the single-crystal material exhibited only a single lifetime with a χ^2 per degree of freedom of 1.00 ± 0.06. Attempts made to fit the data assuming two or three lifetimes yielded unphysical and/or unstable results.

The fitted lifetime data for single-crystal $YBa_2Cu_3O_7$ are plotted as a function of temperature in Fig. 2. Each experimental data point is deduced from a time spectrum containing approximately one million events, collected in a period of about 1.5 h. The data were collected using the temperature sequences 10 to 250 K, 50 to 15 K, and 5 to 297 K, yielding no evidence for thermal hysteresis. The open symbols correspond to measurements taken on increasing temperature and the filled symbols are associated with the decreasing temperature sequences. Note that above T_c, τ is approximately constant with a linear fit (assuming zero slope) giving 176 ps, and increases approximately monotonically with decreasing temperature below T_c to 187 ps at 5 K.

In contrast to the single crystals, all of the existing sintered powder data[5-8] exhibit (ignoring the source and positronium components) two lifetimes, a short- and a long-lived component. An appropriate interpretation of these data may be found by invoking the two-state trapping model[14] in which positrons, initially in a state $|b\rangle$ with intrinsic annihilation lifetime τ_b, become trapped in a second state $|a\rangle$ with lifetime τ_a. The lifetime τ_b, assuming this model is

$$\tau_b = \frac{1}{I_1\lambda_1 + I_2\lambda_2}, \tag{1}$$

where λ_1, I_1, and λ_2, I_2 are the observed positron annihilation rates and intensities, corresponding (for the case at hand) to the short- and long-lived components, respectively. The τ_b deduced from the earlier sintered $YBa_2Cu_3O_{6.8}$ data[5] are shown as a function of temperature in Fig. 3. The temperature-independent behavior of τ_b may be interpreted as a verification of the positron trapping model in this system. In a pure single-crystal metal, where state $|a\rangle$ represents the positron trapping at a thermally generated vacancy, state $|b\rangle$ corresponds to a delocalized positron Bloch state and τ_b is the bulk lifetime. The difference in the value of τ obtained in single-crystal $YBa_2Cu_3O_7$ ($176 < \tau < 187$ ps), as opposed to the τ_b sintered $YBa_2Cu_3O_{6.8}$ ($\tau_b \approx 167$ ps) and $YBa_2Cu_3O_{6.0}$ ($\tau_b \approx 180$ ps), suggests that the electronic structure where the positron wave function is distributed is different for the different materials and oxygen stoichiometries. It has been noted in previous work[5] that the lifetime component presumably associated with O(1) vacancies ($\tau_2 \sim 220$ ps) in sintered $YBa_2Cu_3O_{6.8}$ responds to the superconductivity below T_c, indicating that the localized wave function of the trapped positron is also strongly coupled to the electronic structure changes associated with the superconductivity.

The existence of only one lifetime in the single-crystal data effectively precludes an interpretation of these data in terms of a multiple-state trapping model. However, it is not unreasonable to assume that the property being sampled by the positron in the case of the single-crystal material, as is evidenced by the increasing lifetime below T_c, is also sampled by positrons in the sintered powders. Theoretical estimates[15] of the positron wave function in $YBa_2Cu_3O_7$ suggests that the positron is preferentially located in the interstitial region near the Cu–O(1) chains, and would therefore be sensitive to electronic and bond-distance changes associated with the O(1) and O(4) sites. The difference in τ_b observed between the single-crystal

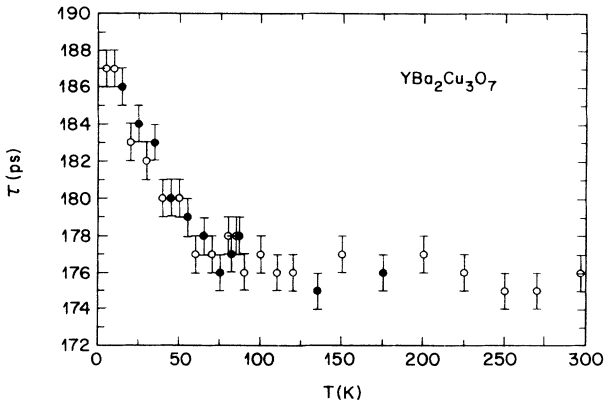

FIG. 2. The positron lifetime τ vs temperature in single-crystal $YBa_2Cu_3O_7$. The open circles correspond to data taken with increasing temperature, and the filled circles are associated with the decreasing temperature sequences.

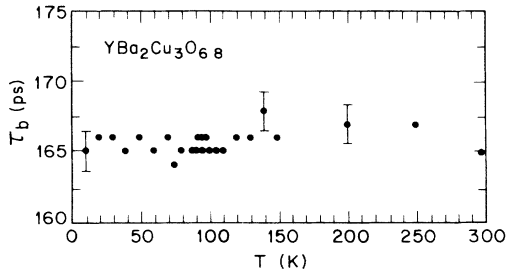

FIG. 3. The lifetime τ_b vs temperature, deduced from earlier results on sintered $YBa_2Cu_3O_{6.8}$ assuming the two-state trapping model of Eq. (1). The lifetime data are taken from Ref. 5, with an additional five new data points.

and sintered materials may imply that the low-temperature state of the positron seen in the single-crystal data is one from which the positron is easily removed, and its observation is dependent upon the degree of perfection of the crystalline structure over the diffusion length of the positron.

The electron density enhancement factor, which controls the annihilation rate $(1/\tau)$, is governed by the electron-positron Coulomb interaction. The Coulomb interaction is itself determined by the static dielectric function $\varepsilon(q,\omega=0)$ which, in the case of a conventional superconductor, is approximately[16]

$$\varepsilon(q,\omega=0)\approx\left[1+\frac{q_{\mathrm{TF}}^2[1-\frac{1}{2}(\Delta E(T)/E_F)^2]}{q^2}\right]. \quad (2)$$

Here, q_{TF} is the Thomas-Fermi momentum, which specifies the strength and range of the effective Coulomb screening potential, E_F is the Fermi energy, and $\Delta E(T)$ is the superconducting energy gap. According to the Bardeen-Cooper-Schrieffer theory, $\Delta E(T)$ has a temperature dependence (for T just below T_c) defined as

$$\Delta E(T)\approx 1.76\Delta E(0)(1-T/T_c)^{1/2} \quad (3)$$

and flattens off at $T\sim T_c/2$. Here, $\Delta E(0)$ is the gap width at 0 K. Incorporating Eq. (2) into the standard electron-density enhancement formalism[17] then results in a complicated equation involving the screened Coulomb interaction which enters as $[\Delta E(T)/E_F]^2$.[18] Thus, one would expect a corresponding change in τ of order $[\Delta E(T)/E_F]^2$. Note, however, that it is unclear how a gap varying with temperature according to Eq. (3) could account for the approximate linearity of the data (see Fig. 2) at temperatures well below T_c. Measurements[19] of the normal-state reflectivity and superconducting energy gap in single-crystal $YBa_2Cu_3O_7$ indicate a low-temperature gap of $2\Delta E(0)\sim 5$–$8\ kT_c$ (about 50–70 meV), which is at least an order of magnitude greater than in conventional superconductors. Unfortunately, E_F is not well determined for this material, making it difficult to estimate the quantitative effect of the variation in $\varepsilon(q,\omega=0)$ on the positron lifetime.

A reduction in the electron density sampled by the positron can also arise through a redistribution of electronic charge or a change in the positions of the atoms. Calculations[15] show that a slight outward relaxation of the O(4) site could explain the present single-crystal results. In a charge redistribution picture, the increase in τ observed in the single-crystal material below T_c would be related to a corresponding decrease in the electron density along the ordered vacancy (interstitial) region of the material. In comparison, the long-lived component in the sintered powders associated with positrons trapped at the oxygen vacancies in the Cu–O(1) chains[5] becomes shorter with decreasing temperature below T_c consistent with an increasing electron density at the O(1) trapping site. As was stated earlier, the τ_b deduced from the sintered powder data do not agree with that found for the single crystals, implying that the positron wave function is distributed differently in the two materials. Nevertheless, the data may suggest an electronic charge rearrangement or lattice relaxation leading to an increased electron density along the Cu–O(1) chains, with a corresponding decrease elsewhere in the crystal.

To summarize, we have measured the positron lifetime spectrum in single-crystal $YBa_2Cu_3O_7$. Only a single lifetime τ was observed throughout the temperature range studied; above T_c, τ was found to be relatively independent of temperature while increasing monotonically with decreasing temperature below T_c, suggesting a strong correlation with superconductivity. We have proposed three possible mechanisms to explain the data: one involving the superconducting gap, another based on a redistribution of charge, and a third associated with lattice relaxations. Further experimental and theoretical work is clearly required to understand the behavior of positrons in the high-T_c materials. Of particular relevance would be a systematic study of the annihilation lifetime and electron momentum distribution as a function of temperature and oxygen stoichiometry in single-crystal $YBa_2Cu_3O_{7-\delta}$. A comparative experimental study should also be conducted on the single-crystal $La_{2-x}Sr_xCuO_{4-\delta}$ series as well. Finally, beam experiments aimed at measuring the positron diffusion length in these materials should be performed.

The authors would like to thank L. W. Rupp for technical assistance. We also acknowledge helpful discussions with G. Aeppli, B. Batlogg, P. M. Platzman, A. Ruckenstein, and C. W. Chu. The work at Lawrence Livermore Laboratory is supported under the auspices of the U.S. Department of Energy, Contract No. W7405-ENG-48.

*Permanent address: University of Missouri, Kansas City, MO 64110.

[1]M. Dresden, Phys. Rev. **93**, 1413 (1954).

[2]R. Stump and H. E. Talley, Phys. Rev. **96**, 904 (1954); B. Green and L. Madensky, *ibid.* **102**, 1014 (1956); S. M. Shafroth and J. A. Marcus, *ibid.* **103**, 585 (1956).

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

[4]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (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, Z. J. Huang, and C. W. Chu, Phys. Rev. B **36**, 3994 (1987).

[6]S. G. Usmar, P. Sferlazzo, K. G. Lynn, and A. R. Moodenbaugh, Phys. Rev. B **36**, 8854 (1987).

[7]L. C. Smedskjaer, J. L. Routbort, B. K. Flandermeyer, S. J. Rothman, and D. G. Legnini, Phys. Rev. B **36**, 3903 (1987).

[8]L. Hoffman, A. A. Manuel, M. Peter, and E. Walker, Europhys. Lett. **6**, 61 (1988).

[9]See, for example, *Positron Solid State Physics,* edited by

W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

[10]L. F. Schneemeyer, J. V. Waszczak, T. Siegriest, R. B. van Dover, L. W. Rupp, B. Batlogg, R. J. Cava, and D. W. Murphy, Nature **238**, 601 (1987).

[11]D. M. Schrader, S. W. Chiu, H. Nakanishi, and S. Rochanakij, in *Positron Annihilation,* edited by P. C. Jain, R. M. Singru, and K. P. Gopinathan (World Scientific, Singapore, 1985), p. 822.

[12]H. Rajainmaki, Appl. Phys. A **42**, 205 (1987).

[13]P. Kirkegaard, M. Eldrup, O. E. Mogensen, and N. J. Pedersen, Comput. Phys. Commun. **23**, 307 (1981).

[14]Y. C. Jean and M. J. Fluss, J. Phys. C **17**, 2619 (1984); W. Brandt, in *Positron Annihilation,* edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967).

[15]P. Turchi *et al.* (unpublished).

[16]R. E. Prange, Phys. Rev. **129**, 2495 (1963).

[17]S. Kahana, Phys. Rev. **129**, 1622 (1963).

[18]A. Millis (private communication).

[19]Z. Schlesinger, R. T. Collins, D. L. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1958 (1987).