RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 7 1 SEPTEMBER 1988

Effect of microstructure on positron-annihilation parameters in $YBa_2Cu_3O_7$

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(Received 18 May 1988)

The temperature dependence of positron Doppler line shape has been measured for several samples of $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$). Two distinct temperature dependences have been observed. In one case the line-shape parameter S increases by $\approx 0.5\%$ between 15 and 100 K, remains constant between 100 and 230 K, and then decreases by $\approx 0.25\%$ between 230 and 290 K. In the second case, S remains constant between 20 and 100 K, decreases by $\approx 1\%$ between 100 and 200 K, and then remains constant up to 290 K. Room-temperature positron-lifetime measurements also reveal distinct differences between samples. An explanation of these differences based on microstructural differences observed by transmission electron microscopy is suggested.

Since Jean *et al.*[1] reported a discontinuous change in positron-annihilation parameters at the superconducting transition temperature (T_c) of $YBa_2Cu_3O_{6.8}$, a variety of authors[2-5] have reported similar transitions in polycrystalline samples of $YBa_2Cu_3O_{7-x}$ ($x = 0.0$–0.4). Both the line-shape parameter S and the positron lifetime were found to decrease at and below T_c. More recently, Harshman *et al.*[6] reported the opposite trend in single-crystal $YBa_2Cu_3O_7$. Thus far, the observed effects have been explained on the basis that the positron state[2] in $YBa_2Cu_3O_7$ is associated with the unoccupied crystallographic sites in the a-b planes containing the Cu-O chains. Theoretical calculations[3] indicate the state to be delocalized along the chains of unoccupied oxygen sites in the a-b plane containing the Cu-O chain. Here, we present positron data for polycrystalline materials, which support this hypothesis and indicate, albeit indirectly, that positron behavior in $YBa_2Cu_3O_7$ may depend critically on the twin density of the material studied.

The temperature dependence of positron annihilation characteristics were monitored using the Doppler line-shape parameter S defined[7] as

$$S = \int_{-a}^{+a} N(E)dE \Big/ \int_{-\infty}^{+\infty} N(E)dE \,, \qquad (1)$$

where $N(E)$ is the Doppler line and the limits $(-a, +a)$ of the restricted integral define a small energy range (511 ± 1.76 keV) about the peak of $N(E)$. Evidently, S depends upon the chosen energy interval, however, provided the interval is held constant, observed variations in S represent real changes in $N(E)$. Positron lifetime measurements were made at room temperature only using a lifetime spectrometer which had a timing resolution of 165 ± 3 ps full width at half maximum (FWHM) (with ≈ 30-ps exponential slope sides) and was gain stabilized.

Superconducting samples of $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$) with T_c's given in Table I were prepared from oxide and carbonate powders using previously described methods.[8,9] To ensure consistency of the preparatory technique, a great deal of care was taken during sample preparation. However, the nature of the manual grinding and mixing technique and variation in furnance temperature (± 10°C) inevitably resulted in samples with varying physical characteristics. Oxygen concentrations were not independently determined but known variations of lattice parameters with oxygen content[10] led to an estimate $|x| \leq 0.1$ in $YBa_2Cu_3O_{7-x}$. Sample densities were estimated to be $85\% \pm 5\%$ of the theoretical bulk density. The superconducting transition temperatures given in Table I were determined from ac susceptibility measurements. Optical microscopy revealed that all samples had grain sizes in the range 30 to 50 μm. Lattice parameters determined using x-ray diffraction are given in Table II.

Numerical analysis of positron lifetime spectra, each of which contained $\approx 1.5 \times 10^6$ counts, was completed with a curve-fitting computer program similar to that of Hall, Goland, and Snead.[11] Here, the spectrometer resolution function (SRF) was represented as an exponentially slope-sided Gaussian. Fitting was completed with the exponential slope sides of the SRF and the source lifetime ($\tau_s = 376$ ps) fixed. In this way, statistically significant fits were achieved, i.e., the variances of fits were ≤ 1.15. Parameters which were spectrometer constants (e.g., SRF

TABLE I. Superconducting transition temperatures and final heat treatments for samples (A, B, C, and D) of $YBa_2Cu_3O_7$.

Sample code	T_c (K) (midpoint)	ΔT_c (K)	Final heat treatment in O_2 gas[a]
A	91	4	48 h at 970 ± 10°C; 8 h at 700 ± 10°C
B	92	4	48 h at 975 ± 10°C; 8 h at 730 ± 10°C
C	91	4	48 h at 975 ± 10°C; 8 h at 700 ± 10°C
D	89	2	48 h at 985 ± 10°C; 8 h at 700 ± 10°C

[a]Followed by slow cooling to room temperature.

TABLE II. Lattice parameters for samples (*A*, *B*, *C*, and *D*) of $YBa_2Cu_3O_7$.

Sample code	Lattice parameters (Å) *a*	*b*	*c*	Comments
A	3.813 ± 0.002	3.888 ± 0.002	11.68 ± 0.01	
B	3.825 ± 0.002	3.884 ± 0.002	11.667 ± 0.005	No second phase present at the x-ray diffraction detection limit of 1% in all samples
C	3.813 ± 0.002	3.884 ± 0.002	11.683 ± 0.005	
D	3.815 ± 0.002	3.883 ± 0.002	11.682 ± 0.005	

TABLE III. Twinning characteristics for samples (*A*, *B*, *C*, and *D*) of $YBa_2Cu_3O_7$.

Sample code	Average (μm)	Twin widths minimum (μm)	Maximum (μm)	Total width measured (μm)	Line density of twins (μm^{-1})
A	0.094 ± 0.004	0.03	0.38	25.5	$10.64^{-0.47}_{+0.43}$
B	0.049 ± 0.002	0.01	0.27	19.3	$20.41^{+0.87}_{-0.80}$
C	0.170 ± 0.008	0.08	0.70	29.9	$5.88^{+0.25}_{-0.26}$
D	0.174 ± 0.008	0.07	0.79	44.9	$5.75^{+0.28}_{-0.25}$

TABLE IV. Positron lifetime parameters for samples (*A*, *B*, *C*, and *D*) of $YBa_2Cu_3O_7$.

Sample code	Room-temperature positron lifetime parameters τ_1 (ps)	τ_2 (ps)	I_2(%)	τ_B (ps)	Variances
A	72 ± 7	200 ± 2	92 ± 3	176	1.030
	101 ± 15	204 ± 3	84.4 ± 4	176	1.062
B	125 ± 8	190 ± 5	69.3 ± 6.6	164	1.006
	96 ± 6	182 ± 2	83.0 ± 2.0	158	1.062
C	163.8 ± 1	· · ·	0.0		0.967
	164.3 ± 1	· · ·	0.0		1.123
D	162 ± 1	· · ·	0.0		0.982
	161 ± 1	· · ·	0.0		0.995

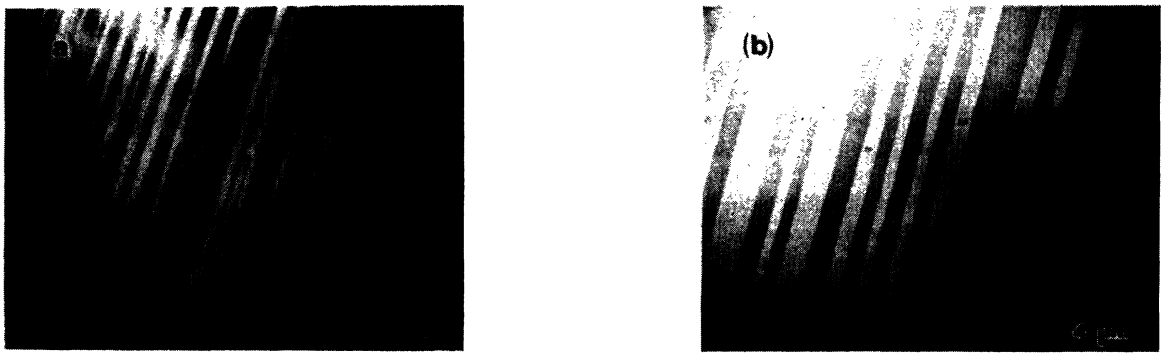

FIG. 1. Bright-field TEM images showing the crystal twins in $YBa_2Cu_3O_7$ samples; (a) sample *B* and (b) sample *D*.

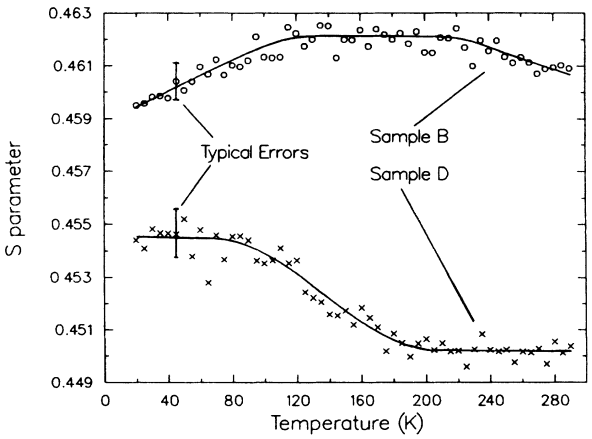

FIG. 2. Positron Doppler line-shape parameter S vs temperature for $YBa_2Cu_3O_7$ samples.

FWHM), but were fitted, were found to vary no more than ± 2 ps for all fits. Further, the source intensity, which was fitted in all cases, was found to vary less than $\pm 1\%$. Therefore, spectrometer stability was very good.

Transmission electron microscopy using a JEOL 100-C was performed on samples prepared from pieces of the samples used for positron annihilation measurements. Nine or ten different areas of each sample (A, B, C, and D) were photographed, in the bright-field mode, to produce images of the crystal twins. The photographs, typical examples of which are shown in Fig. 1, were taken with the crystal c direction parallel to the electron beam. Twin widths were measured manually and are given in Table III; here the average, widest and narrowest widths are tabulated with the total width of twins measured (i.e., the sum of the widths of the twins which were measured). Also, given in Table III are the twin densities which because area and volume densities are very difficult to measure are line densities (i.e., the number of twin boundaries per unit length perpendicular to the twin planes). It is quite evident that samples C and D have very similar average twin widths which are ≈ 1.9 and 3.5 times greater than those for samples A and B, respectively.

The Doppler line-shape parameter S as a function of temperature, is shown in Fig. 2 for two samples (B and D) of $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$). Evidently, the temperature dependence of the positron line-shape parameter S in $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$), shows considerable variations from sample to sample (Fig. 2). In sample B, S increases by $\approx 0.5\%$ between 15 and 100 K, remains constant between 100 and 230 K, and then decreases by $\approx 0.25\%$ between 230 and 290 K. In sample D, S remains constant between 20 and 90 K, decreases by $\approx 1\%$ between 90 and 190 K and then remains constant up to 290 K. Room-temperature positron lifetime parameters, from two independent measurements arrived at after source correction, for samples A, B, C, and D are given in Table IV. Also given in Table IV are the bulk lifetimes, calculated using the two-state trapping model,[7] for samples A and B which have two-component positron lifetime spectra.

A tentative explanation of the results presented here will now be explored. Samples A and D have similar superconducting transition (within 2 K) but very different temperature dependences of the positron Doppler line-shape parameter S. The lattice parameter, $a(=3.825)$, for sample B is larger than that (3.814) for all other samples (see Table II). However, this sample (B) has essentially the same temperature dependence of S as does sample A.[2] The only other significant differences, thus far observed, are the different twin widths.

Theoretical calculations[3] indicate the positron state in $YBa_2Cu_3O_7$ to be delocalized along the open crystallographic sites in the a-b plane containing the Cu-O chains. Thus, at high twin densities the positron will encounter many twin boundaries prior to annihilation. If the twin boundaries, the structure of which is at the present time uncertain, are relatively "open," i.e., oxygen deficient, the positron certainly would be trapped. Samples with low twin densities exhibit a single positron lifetime while those with a higher twin densities have two. Further the calculated bulk lifetimes for samples A and B are close to the measured lifetimes for samples C and D. However, even the room-temperature positron lifetime parameters are inconsistent here, in that if a simple trapping process occurs between the bulk and twin boundaries I_2 [the relative intensity of τ_2 (Table IV)] should be proportional to the twin density. Notwithstanding the fact that the line densities quoted in Table III are not necessarily proportional to volume, there could be any number of reasons for the observed discrepancies. The small differences between calculation bulk lifetimes for samples A and B and those measured for samples C and D may be due to the fact that a deep trap was assumed in the calculation while the temperature dependence of S in samples A and B suggest[3] a shallow trap.

With respect to the relationship between I_2 and the twin densities for samples A and B, very small variations in oxygen concentrations are probably important here. If the positron state is delocalized along the open crystallographic sites in the a-b plane containing the Cu-O chains the ordering of these sites will affect the localization length of the state. Thus, a variation in the value of x on the order of $x = \pm 0.01$ in $YBa_2Cu_3O_{7-x}$ may significantly affect positron localization length, which in turn, would affect the trapping rate at twin boundaries.

The following conclusions are evident from the results presented here. (i) The sample-to-sample variations in the positron annihilation parameter of polycrystalline $YBa_2Cu_3O_7$ are not confined to the relatively small differences previously reported.[1-3] (ii) The results reported for single-crystal $YBa_2Cu_3O_7$ (Ref. 6) are likely to be reproduced for low twin-density polycrystalline samples. (iii) The positron annihilation parameters for $YBa_2Cu_3O_7$ seem to depend critically on the twin densities of the samples studied. More work is required to clarify this situation.

The authors wish to thank Dr. P. Sperlazzo and Dr. I. Kanazawa for their contributions during the completion of this work. This work was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract No. DE-AC02-76CH00016.

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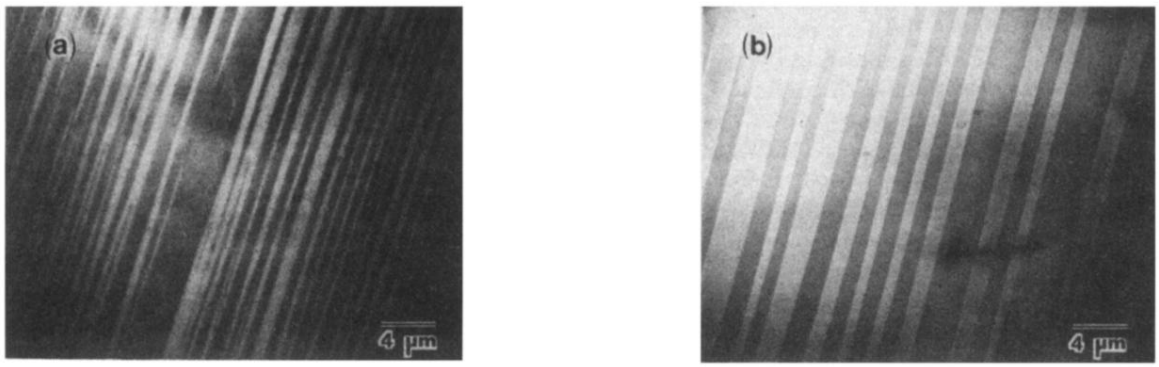

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