PHYSICAL REVIEW B VOLUME 58, NUMBER 22 1 DECEMBER 1998-II

Probing $(Bi_{0.92}Pb_{0.17})_2Sr_{1.91}Ca_{2.03}Cu_{3.06}O_{10+\delta}$ superconductors from 30 to 300 K by positron-lifetime measurements

D. Sanyal and D. Banerjee
Department of Physics, University of Calcutta, 92 Acharya Prafulla Chandra Road, Calcutta 700009, India

Udayan De*
Variable Energy Cyclotron Centre, 1/AF Bidhan Nagar, Calcutta 700064, India

(Received 24 December 1997; revised manuscript received 24 July 1988)

The present measurement of positron annihilation lifetimes for the high-T_c superconductor $(Bi_{0.92}Pb_{0.17})_2Sr_{1.91}Ca_{2.03}Cu_{3.06}O_{10+\delta}$ or (Bi,Pb)-2223, as a function of temperature, has been inspired by our recent DBPARL (Doppler-broadened positron annihilation radiation line shape) finding of a step and minima in the region around $T_c(R=0)=104$ K, in the variation with temperature, of the fraction of low momentum electrons at the annihilation sites. The positron annihilation lifetime in the superconductor probes the number density of electrons at the annihilation sites. The present work observes a reduction of lifetime components in the T_c region. Significant changes in the lifetime components in other temperature regions have also been observed and discussed. [S0163-1829(98)05745-2]

I. INTRODUCTION

The positron annihilation technique has been applied[1] to find out whether superconducting pairing in momentum space affects the number density of electrons (as probed by the positron lifetime) and their momentum distribution (as probed by the Doppler-broadening parameter *S*) since the 1950s for various conventional superconductors.[2] The effort has been continued for the past 12 years for various high-temperature superconductors (HTSC's).[1,3] No measurable change in these positron annihilation parameters across the superconducting critical temperature, T_c, was detected for conventional superconductors like A-15 compounds. However, for high-T_c superconductors the ratio[1] Δ/ϵ_F, where 2Δ is the superconducting energy gap, and ϵ_F is the Fermi energy, is much higher to favor[1–4] a relatively larger fraction of charge carriers forming pairs on cooling below T_c. As a result, relatively larger and hence measurable change, $\delta\tau$, in positron lifetime, τ, in HTSC's has been expected[1] due to the superconducting transition:

$$\frac{\delta\tau}{\tau}\sim\left(\frac{\Delta}{\epsilon_F}\right)^2\ln\left(\frac{\epsilon_F}{\Delta}\right).$$

Similar change has been expected due to the superconducting transition in the Doppler-broadened positron annihilation radiation line shape or DBPARL parameter, *S*, in HTSC samples. Here *S* represents the fraction of suitably defined[5–7] low momentum electrons among the electrons annihilating with the probing positrons. Many groups,[1,3] including ours, reported a steplike increase or decrease of τ component/s and *S* at T_c, with some contradictions, and more than one explanation have been suggested.

Our recent DBPARL experiments[5–7] on (Bi,Pb)-2223 and Bi-2212 samples, however, repeatedly showed a new additional feature in the *S* versus *T* graphs, a minimum or two minima in the T_c region. It may be added that such a narrow minimum can be missed in readings at large intervals of temperature. This may explain previous reports of steplike changes[1,3] without any minimum. We found[5] two minima (at 99 K and 104 K) in the *S* -parameter of (Bi,Pb)-2223 having T_c $(R=0)=104$ K, in addition to the above-mentioned step at T_c. Such minima, in the T_c region, in the fraction of low momentum electrons[5–7] among the annihilating electrons, call for a careful measurement across T_c also of the lifetime, τ, that probes the density of electrons at the annihilation sites.

In view of the above-mentioned expectation, the degree to which such minima/maxima and/or step have been observed in earlier positron lifetime measurements on Bi-based 2223 HTSC is reviewed briefly. Such a step in lifetime data can be presumed to be less prominent in Bi-HTSC than in Y-HTSC on the basis of presently available *S*-parameter results. Such minima observed[8] (with a resolution of 270 ps) in mixed (Bi-2212 and Bi-2223) phase samples by Zhang *et al.* in the T_c regions of the 2223 as well as 2212 phase appear to have been ignored due to the possible unreliability of data on mixed phases. Zhang *et al.* noted that the earliest work[9] had concluded no observable effect on τ and *S* in mixed 2212-2223 samples, without presenting any data. An observable effect of the superconducting transition on *S* versus *T* has already been reported[5–7] for Bi-2212 and (Bi,Pb)-2223. Tang *et al.*[10] report (with a resolution of 245 ps) three narrow valleys near 120 K, 140 K, and 160 K and two wide valleys near 240 K and 270 K in their τ_2 versus temperature graph, where τ_2 is longer of the two short components τ_1 and τ_2. This result has neither been clearly explained nor verified. They found τ_1 and the bulk lifetime, τ_B, to be less sensitive to temperature. However, indications of minima in lifetime data in some cases[11] appear to have been ignored. Tang *et al.*[10] concentrated on the higher temperature region, and none of the above is a detailed measurement on single phase samples. Therefore, there is a clear need for high-resolution lifetime measurement, with readings at a closer interval of temperature, on single phase (Bi,Pb)-2223. This has been carried out in the present work.

Here we report our positron annihilation lifetime measurements with a resolution of 190 ps down to 30 K on the same pair of (Bi,Pb)-2223 samples as were used[5] in our S versus T measurements. Our lifetime spectrum, $N(t)$ versus t, is seen to consist of more than one lifetime component, τ_i.

It is known that lifetime components will correspond to individual characteristic lifetimes of the components, if the sample is a mixture of noninteracting components. However, if the sample is a single-component substance, element, or compound, with a characteristic Bloch lifetime, a detection of two or more lifetime components indicates the presence of one or more trapping site/s (Ref. 12) or other physical processes such as positronium states. In this investigation, the longest component, τ_3, can be identified[13] to be due to positronium (Ps) formation and ortho-Ps to para-Ps conversion. The simple two-state trapping model assumes annihilation from positron traps and the Bloch state (also called annihilation in the bulk). The lifetime for annihilation from the positron trap turns out to be τ_2. The lifetime for annihilation from the Bloch state, called τ_B, and that is supposed to probe the intrinsic properties of the material, can be easily shown to be given by the equation

$$\tau_B = \frac{(I_1 + I_2)}{\left(\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}\right)}.$$

So, in this trapping model, τ_B and τ_2 are the physically significant quantities, with τ_2 resulting from annihilation in regions of lower electron density. Such regions have been presumed to be vacancies or vacancy complexes in general, and unoccupied lattice sites[4,14] or oxygen vacancies[15,16] for various HTSC. Other positrons have been assumed, from simple rate calculations,[16] to annihilate mostly from oxygen valence electrons. However, the concept of a unique Bloch state, the concept of the traps being populated by positrons via the Bloch state only and not directly,[17] and hence the applicability of the above-mentioned model may be questioned, as some of the different parts of the complex HTSC structure are somewhat noninteracting. So results are given also in terms of mean lifetime, $\bar{\tau}$, without resorting to any particular model.

II. EXPERIMENTAL OUTLINE

An appropriate mixture of the oxides/carbonate has been repeatedly ground, pelletized, and fired until x-ray diffraction showed[13] only the lines characteristic of the (Bi,Pb)-2223 phase. The superconducting critical temperature, T_c, of this sample has been determined as 104 ± 0.2 K by electrical resistivity measurement[5,7] (standard four-probe method) and confirmed by ac magnetic susceptibility measurement.[5,6] A 10μCi ^{22}Na source, enclosed between two 2 mg/cm^2 nickel foils, has been sandwiched between two identical and plane-faced 6 mm×4 mm×0.8 mm pellets of the above-mentioned (Bi,Pb)-2223. The positron annihilation lifetimes have been measured with a fast-slow coincidence assembly. The detectors are 25-mm-diam×25-mm-long cylindrical BaF$_2$ scintillators coupled to Philips XP2020Q photomultiplier tubes. The resolving time [full width at half maximum (FWHM)], measured with a ^{60}Co source and with the windows of the slow channels of the fast-slow coincidence assembly set to select pulses corresponding to 300 keV to 550 keV in one channel and 700 keV to 1320 keV in the other, is 190 ps. The source-sample sandwich has been mounted inside a vibration-free He cryogenerator (APD Cryogenics Inc., model no. DMX-20). Good thermal contact between the cold head of the cryogenerator and the sample has been ensured by using indium foil. The temperature of the system has been controlled by a temperature controller (Scientific Instruments Inc. 9620-1). For each temperature a total of $\sim 10^6$ coincidence counts have been recorded with 8000:1 peak to random ratio. The recorded $N(t)$ versus t data have been analyzed by the PATFIT-88 computer program[18] with necessary source correction.

III. OBSERVATIONS AND DISCUSSION

One- to four-component PATFIT-88 fittings have been carried out for each of the $N(t)$ versus t lifetime spectra over 30 K to 300 K to decide the best fit for each spectrum. In the region 300 K to 215 K the best fit has been obtained with a three-component fit indicating the presence at a low intensity of a very long third component (1.3 ns~1.5 ns). The two-component fit worked better for lower temperatures.

The longest lifetime component can be attributed to positronium formation[13] and subsequent ortho-Ps to para-Ps conversion, quite likely in voids or intergranular spaces of the sintered samples. The presently observed low intensity of 0.5% to 1.0% of τ_3 compares well with earlier findings.[8,13] While Sedov *et al.*[1] have considered the contribution of the superconducting transition to the positron annihilation parameters to be positronium-related, most of the earlier workers have not done any detailed study of τ_3 due to its low intensity and an apparently temperature-independent nature. Here we confirm that ignoring this third component, in cases where it is present even with a small intensity of the order of 1%, leads[13] to a significantly wrong estimate of the smaller components in the forced two-component fit. This is simply due to its large value. The fact that our lifetime spectra below 215 K show the best fit with two components implies that either ortho-Ps to para-Ps conversion or positronium formation is not favored in the present samples at lower temperatures. More experiments on other samples, such as our recent finding[19] that 300 K lifetime spectra for HTSC single crystals show only two components, are needed to explain this temperature dependence. Our incompletely understood but observed temperature dependence of τ_3 can be supported from earlier experiments on Y-123 pellets by Wang *et al.*[20] Although their positron lifetime data in Y-123 (with T_c of 87.5 K) are discussed on the basis of a two-component fit, they found the positronium-related contribution to τ_2 to become more prominent as the temperature increased towards 300 K. In fact, their three-component fit showed τ_3 of about 1750 ps to be significant (1.2%) down to 200 K.

Figure 1 shows the temperature dependence of (a) the S parameter[5] and (b) $\bar{\tau}$. The S parameter as well as $\bar{\tau}$ show the average effect of various positron annihilation processes in the solid, without resorting to any model or details of these processes. A decrease in the average positron lifetime, $\bar{\tau}$, is caused by an increase of electron density (at the annihilation sites) that should, in general, bring about a concomitant in-

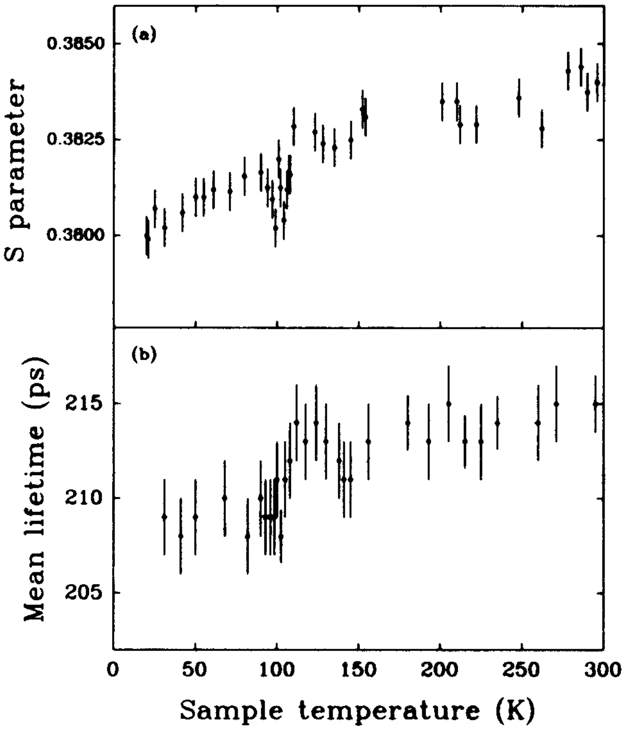

FIG. 1. Variation of (a) the DBPARL parameter, *S*, and (b) the mean positron lifetime, $\bar{\tau}$, with sample temperature for the sample (Bi,Pb)-2223.

crease in electron momentum,[3] implying a decrease in *S*. This expected correlation between *S* and $\bar{\tau}$ with respect to their temperature dependence can be seen to be roughly satisfied by our results in Figs. 1(a) and 1(b) from two entirely different experiments. A sharp decrease of *S* and $\bar{\tau}$ on cooling across T_c is most notable among the similarities, which are, however, not quantitative. Hints of minima or maxima at temperatures between 125 K and 300 K in Fig. 1(b) can be better discussed in the next graphs. These minima or maxima need to be ignored and the average graph drawn to observe the effect, on $\bar{\tau}$, of lattice expansion only. Such a graph shows a steplike break at T_c. The slow increase of $\bar{\tau}$ with temperature for the 30 K to T_c segment as well as for the segment between T_c and 300 K is in agreement with the slight decrease in electron density due to lattice expansion.[5,21] The steplike decrease of $\bar{\tau}$ below T_c is less than that in Y-123, in agreement with positron density distribution calculation[3,8,22] arguments. There appears to be a minimum between 140 K and 150 K. Next, on cooling from 140 K towards T_c, $\bar{\tau}$ increases. But it shows a steep fall for $T<T_c$. So $\bar{\tau}$ shows a steplike decrease across $T_c=104$ K. This feature in the T_c region will be clearer in the τ_2 versus *T* figure.

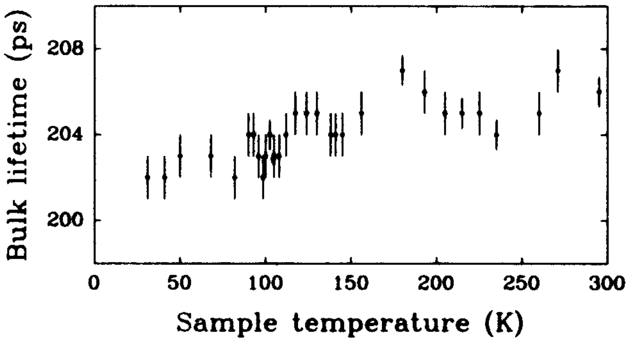

FIG. 2. Variation of the bulk lifetime, τ_B, with sample temperature for positron annihilation in (Bi,Pb)-2223.

Using the two-state trapping model, τ_B has been calculated, as already discussed, over the 30 K to 300 K range (Fig. 2). For example, τ_B at 295 K has been calculated to be 206 ps from the fitting results: $\tau_1=(193\pm2)$ ps and $\tau_2=(359\pm7)$ ps. Here τ_2/τ_B is 1.74 at 295 K and about 1.71 if averaged over 30 K to 295 K. These compare well with the room temperature values 1.55 and 2.34 calculated from Ref. 9 and Ref. 11, respectively. To estimate the effect on τ_B (Fig. 2) of lattice contraction due to cooling, one must draw an average graph ignoring structures such as the broad minimum between 200 and 270 K, as was done for Fig. 1. The graph is seen to have two branches—30 K to T_c and T_c to 300 K. The steplike change of τ_B at T_c can be seen to be smaller than in $\bar{\tau}$. In fact, the lowest temperature value of τ_B is seen to be only about 4 ps lower than the room-temperature value, as we observed in an earlier work.[3] One cannot consider the variations (within the error bars) in the T_c region, to be hints of minima or maxima in τ_B. These variations are certainly less convincing than the double minima in the *S* parameter for (Bi,Pb)-2223 pellets, Fig. 1(a), and Y-123 single crystals[23] and than the single minimum in Bi-2212 pellets.[7] Figure 3 (a) shows that between 30 K and 175 K the intensity of the intermediate component, I_2, decreases with lowering of temperature. This implies that the probability of positrons annihilating in the vacancylike traps decreases at lower temperatures. In Fig. 3(b), τ_2 has been plotted against temperature. The most prominent feature of this plot is a broad minimum at around 175 K. While the possible link of this 175 K minimum to the opening up of the recently discovered spin gap[24,25] will be investigated in a

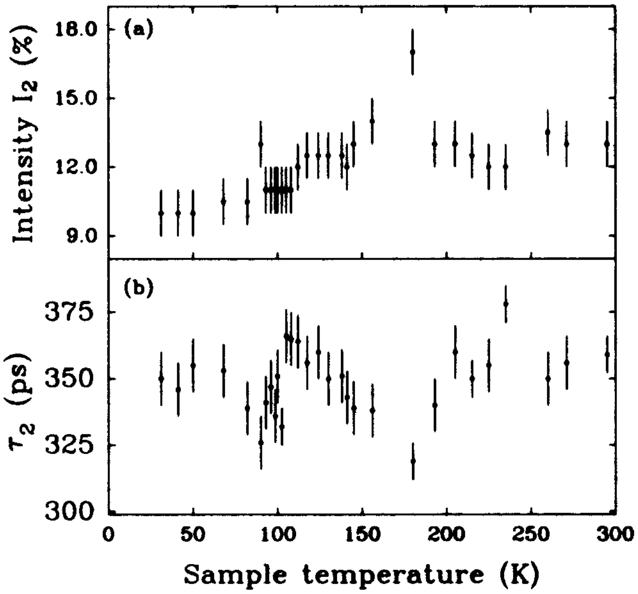

FIG. 3. Variation of the positron lifetime component τ_2, and its intensity, I_2, with sample temperature for (Bi,Pb)-2223 pellets in (b) and (a).

separate work, other possibilities such as positron trapping at defects due to certain lattice instabilities[10] cannot be ruled out. However, the large I_2 and small τ_2 at 175 K necessarily imply a larger number of smaller-sized traps (vacancylike defects). S parameter versus T graphs[5–7] for Bi-2212 and (Bi,Pb)-2223 also show significant variations in the temperature region between T_c and 300 K. Let it be pointed out that a few of the critically important data points of our graphs (at 230 K, 180 K, and 102.5 K, for example) have been taken twice, confirming the values presented in this work. Hints of a peak in τ_2 at around 235 K compare well with the anomaly reported near 240 K by at least four different groups, as reviewed by Manuel.[14] There is a rise of τ_2 on cooling towards T_c. But at $T \simeq T_c$ there is a steep fall in the lifetime component τ_2, as has been observed[5–7] in S versus T graphs in DBPARL experiments. Follow-up of this fall by one or two minimum/minima at lower temperatures is evident[5–7] in S versus T data but it is not so in τ_2 versus T data.

A number of neutron PDF (pair distribution function) experiments have indicated[25] a local structural response to a change in the electronic state, like the appearance of superconductivity and the opening of the pseudogap. Particular mention may be made of the complex maximum (Fig. 20 of Ref. 25) observed at the T_c region in Tl-2212 HTSC of the PDF peak-height at 3.4 Å. It concerns the pair correlation between in-plane, O(1), oxygen and apical, O(2), oxygen. The striking similarity of this variation to our complex minimum[5] in S is noteworthy. The lower value at or near T_c of τ_2 physically implies a higher exposure to electrons of positrons trapped mostly at O vacancies.[15,16] In Y-123, the tunneling frequency of apical oxygen between two possible sites shows a maximum (Fig. 23 of Ref. 25) at T_c. Such a phenomenon in (Bi,Pb)-2223 is probable in view of superconductivity-related lattice effects,[25] receiving increased attention in recent years. The decrease of τ_2 on cooling below T_c can be related either to such enhanced jumping of oxygen ions between the two sites or to electron transfer[15] from CuO_2 layers to BiO regions.[3,15] These explanations need to be worked out more precisely to understand the changes observed in the positron annihilation parameters across T_c.

The lifetime component τ_2 can be a sensitive probe for lattice instabilities, giving rise to sites with low electron density. In this context we recall the well known lattice instability[26] in A-15 compounds on cooling towards T_c and its arrest by the appearance of superconductivity. Such an instability causing the rise of τ_2 on cooling towards T_c and its arrest at T_c leading to the sharp fall of τ_2 somewhere between 105 K and 102.5 K may be possible in such high-T_c compounds.

IV. CONCLUSION

Certain minima and maxima in positron lifetime components for $T_c < T < 300$ K likely to be related to magnetic effects[5,25] or other lattice instabilities,[10] similar to those reported earlier for lifetime and S-parameter experiments, are confirmed. Their origin cannot be pinpointed without further clarifying experiments. More important is the steep fall in lifetime component τ_2 and mean lifetime $\overline{\tau}$ on cooling below T_c. This removes the confusion in the literature on whether the positron lifetime in (Bi,Pb)-2223 HTSC is affected by the superconducting transition. A drastic redistribution of electrons on cooling across the superconducting transition temperature has been clearly observed in the present work.

ACKNOWLEDGMENTS

One of us (D.S.) thanks the University Grants Commission, Government of India, for financial support. U.D. thanks the Humboldt Foundation, Germany, for a Leybold cryogenerator, used in characterizing the sample. The inspiring interest of Professor Bikash Sinha, Director, VECC in this work is gratefully acknowledged.

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*Author to whom correspondence should be addressed. Electronic mail: ude@veccal.ernet.in

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