Temperature dependence of the positron annihilation parameters in $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O_y$ and $Bi_2CaSr_2Cu_2O_y$ superconductors

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We report the results of temperature dependence of S-parameter and lifetime (τ) measurements on the normal and superconducting states of $Bi_2CaSr_2Cu_2O_y$ (Bi-2:1:2:2) and $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O_y$ (Bi-2:2:2:3) superconductors. A decrease of the S parameter as well as τ below T_c is seen for both compounds. These observations are interpreted qualitatively considering a reported positron-density-distribution calculation and invoking the local charge-transfer process from CuO_2 to Bi-O planes at the onset of the superconducting transition. The possible influence of sample preparation conditions and structural changes on the temperature dependencies of the positron annihilation parameters across T_c is also discussed.

INTRODUCTION

Positron annihilation spectroscopy (PAS) has long been recognized as an excellent microscopic probe for the electronic structure of solids.[1,2] It comes as no surprise, therefore, that a large number of investigations have been carried out in the ceramic high-temperature superconductors using this technique to probe the nature of the superconducting transition as well as to investigate the presence or absence of a Fermi surface. It is now well established that the lifetime (τ) and the Doppler-broadened annihilation line-shape (DBALS) parameter (S) show fluctuations at T_c which are intimately associated with the phenomenon of high-temperature superconductivity. For example, a decrease in τ and S is seen[3] for sintered $YBa_2Cu_3O_7$ (YBCO) compounds with the exception of one report on a single crystal, showing an increase[4] below T_c. Similarly, temperature dependencies of the positron annihilation parameters have been reported for superconducting Tl-Ca-Ba-Cu-O,[5,6] $YBa_2Cu_4O_8$,[7] Nd-Ce-Cu-O,[8] and Bi-Ca-Sr-Cu-O.[9-12] However, systems other than YBCO have been studied less extensively, and particularly in Bi-Ca-Sr-Cu-O the reports are few and conflicting in terms of the temperature dependence of positron annihilation characteristics across T_c. While Sundar *et al.*[9] have not observed any change in τ below T_c for $Bi_2CaSr_2Cu_2O_y$ (Bi-2:1:2:2) and mixed phase $Bi_2CaSr_2Cu_2O_y + Bi_2Ca_2Sr_2Cu_3O_y$ [Bi-(2:1:2:2 +2:2:2:3)], recent reports by Zhang *et al.*[10] and Wang *et al.*[11] show a discontinuous change in τ and S, respectively, below T_c for the latter compound, similar to the observations reported from this laboratory in terms of a shape parameter T_B.[12] In addition, a consensus is yet to emerge on what exactly is (are) the reason(s) for the observed increase and/or decrease of τ and S below T_c in all the superconductors. A notable attempt in this direction has been made by Jean *et al.*,[3] who provide an explanation taking into account the disposition of the positron density distribution (PDD) with respect to the CuO_2 plane and invoking a charge-transfer process between the CuO_2 plane and the O-Cu(1)-O chain in superconducting YBCO. The extension of this concept to Bi-Ca-Sr-Cu-O superconductors requires rationalization of discrepancies in the temperature dependences of τ and S vis-à-vis the theoretically calculated PDD. Therefore, further experimental and theoretical investigations are necessary in Bi-Ca-Sr-Cu-O superconductors. In the present work, we report the temperature dependence of S across T_c as well as lifetime measurements in the normal (300 K) and superconducting (15 K) states of the Bi-2:1:2:2 and Bi-2:2:2:3 superconductors. The observations are discussed in the light of the reported PDD calculation.

EXPERIMENTAL

Samples with nominal composition $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O_y$ (Bi-2:2:2:3) were prepared by the usual solid-state reaction, involving calcination followed by sintering at 850 °C. Resistivity measurements showed the T_c for Bi-2:2:2:3 to be 106 K ($R=0$) [Fig. 1(a)] and x-ray diffraction showed the compounds to be single phase. The $Bi_2CaSr_2Cu_2O_y$ (Bi-2:1:2:2) compound, prepared likewise, was seen to have a $T_c=53$ K ($R=0$) and x-ray diffraction measurement showed it to be single phase, except for a small impurity phase, which is responsible for the broader transition width in the resistivity curve seen in Fig. 1(b).

DBALS measurements were carried out using a 2-cc high-purity geranium (HPGe) detector with a resolution of 1.0 keV at the 511.8-keV γ line of ^{106}Ru. A ^{22}Na positron source, sandwiched between two pellets, was mounted on the cold head of an APD closed-cycle helium refrigerator and measurements were carried out from 300 to 15 K. Lifetime spectroscopy LTS measurements were

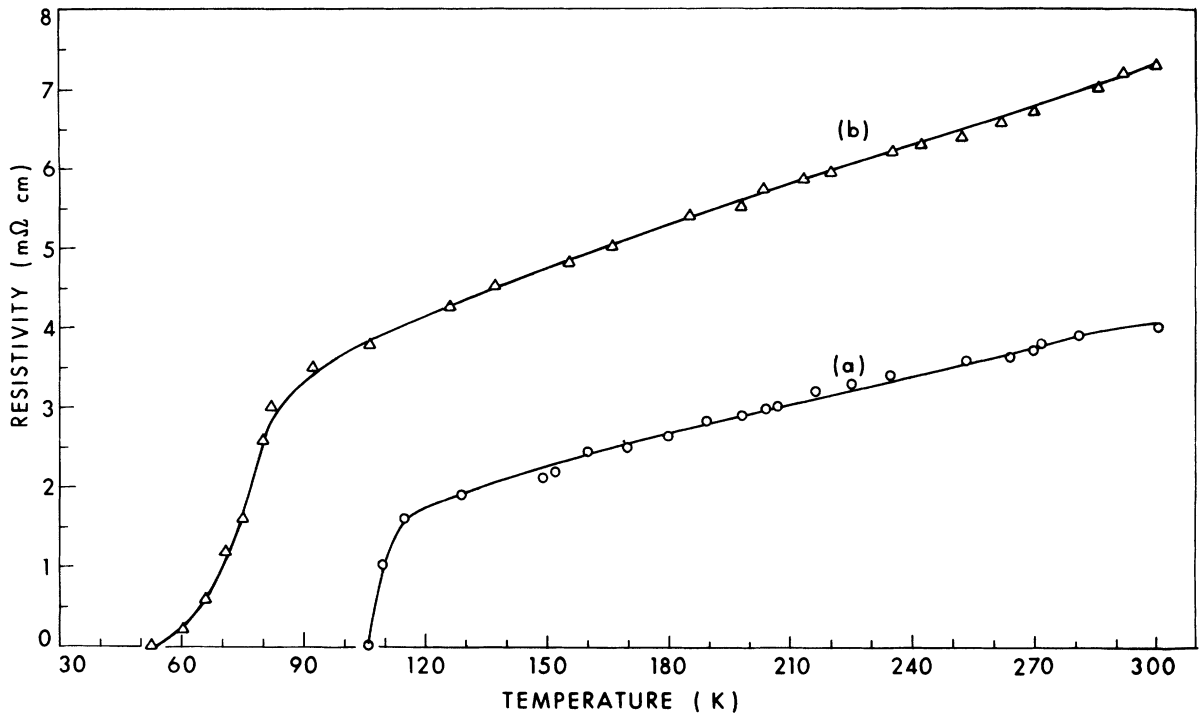

FIG. 1. Resistivity as a function of temperature for Bi-2:2:2:3 (a) and Bi-2:1:2:2 (b) superconductors.

carried out at 15 and 300 K using a fast-fast coincidence spectrometer with a time resolution of 250 ps. The response function as well as source contribution were determined using standard procedures as described elsewhere.[13] The lifetime spectra were analyzed using POSITRONFIT.[14]

RESULTS AND DISCUSSION

The lifetime analysis showed two components τ_1 and τ_2 after source correction. The average lifetime $\bar{\tau}$ and bulk lifetime τ_B were calculated using τ_1, τ_2, I_1, and I_2 as

$$\bar{\tau}=\tau_1 I_1+\tau_2 I_2 ,$$

$$\tau_B=(I_1/\tau_1+I_2/\tau_2)^{-1} ,$$

and are presented in Table I.

The room-temperature (300 K) τ_1, τ_2, and τ_B obtained for Bi-2:1:2:2 are 220 ps (75%), 377 ps (25%), and 245 ps, respectively, not very different from those reported by Sundar *et al.*,[9] i.e., 220 ps (85%), 360 ps (15%), and 233 ps. The difference in τ_B arises due to the fact that our sample contains a small amount of impurity phase. The τ_B for the single-phase Bi-2:2:2:3 is also seen to be lower (230 ps) as compared to the Bi-2:1:2:2 phase (245 ps), consistent with the observation in the Tl series[5] where the τ decreases with increasing number of CuO_2 planes. In the superconducting state (15 K), the τ_B values were 4 and 7 ps lower than the values at 300 K for Bi-2:2:2:3 and Bi-2:1:2:2 samples, respectively. The S parameter evaluated as a function of temperature in Bi-2:1:2:2 and Bi-2:2:2:3 is seen to decrease at the onset of superconductivity as shown in Fig. 2. The present observation is consistent with our earlier measurements[12] on Bi-2:1:2:2 and Bi-(2:1:2:2+2:2:2:3) in terms of a shape parameter T_B (full width at half maximum of the bulk electron momentum component), which was seen to increase at T_c. An increase in T_B i.e., an increase in the higher-momentum component in the Doppler curve, leads to a decrease in the S parameter. Therefore, in view of the present work and the literature data,[10-12] S and τ are seen to change at the onset of the superconducting transition in these compounds, although no such temperature dependence was observed by Sundar *et al.*[9]

TABLE I. Lifetime measurements on Bi superconductors.

Sample	τ_1 (ps)	τ_2 (ps)	$\bar{\tau}$ (ps)	τ_B (ps)
Bi-2:1:2:2	220 (75%)	377 (25%)	259	245
Bi-2:2:2:3	223 (93%)	396 (7%)	235	230

There are several possible reasons for the temperature dependency of S and τ parameters in high-T_c superconductors, such as changes in local electron density, changes in the momentum distribution of electrons due to a structural transition, the effect of the superconducting gap parameter, changes in electron-positron correlation, etc. In the light of the above, we have attempted to rationalize our observations in what follows in the framework of the proposal by Jean *et al.*[3] based on the disposition of positrons to CuO_2 plane and electron transfer away from this plane.

In order to understand the decrease of S below T_c, it is essential to consider the calculated PDD in Bi-based superconductors. A calculation by Sundar *et al.*[9] shows a maximum of the PDD in the region between the Bi-O

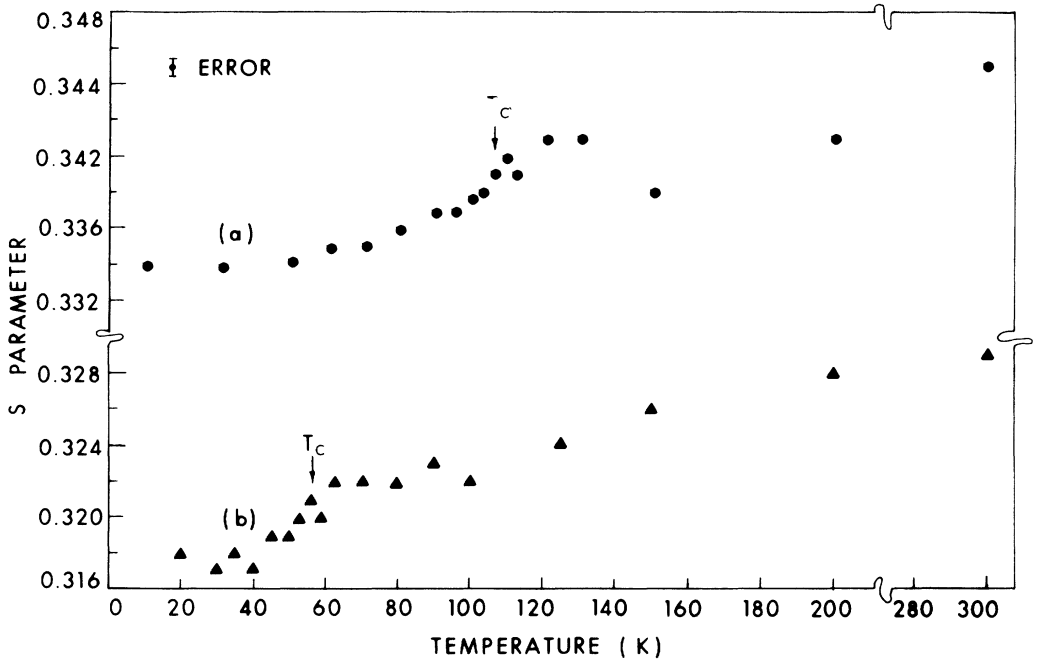

FIG. 2. Temperature dependence of S for Bi-2:2:2:3 (a) and Bi-2:1:2:2 (b) superconductors.

layers, and the positron density in the CuO_2 planes is negligible. However, a calculation using the linearized augmented-plane-wave (LAPW) method by Singh *et al.*[15] shows that positron density is substantial in the CuO_2 planes (as well as in the Bi-O plane) if electron-positron correlation is taken into account. This homogeneous distribution of positron density is true for an idealized structure; but the actual material is known to be incommensurate with a fairly large modulation in the Bi-O layer. This modulation, among other things, is due to the presence of bismuth-rich and bismuth-deficient (vacant) regions with a periodicity. These vacant Bi regions attract positrons preferentially, and the positron density may still be a maximum in the Bi-O layer instead of the CuO_2 planes.[15] In other words, the PDD is greatly influenced by the superstructure and is mainly confined between the Bi-O layers. The Bi-O planes might be electronically active at the onset of superconductivity, resulting in the changes in the S and τ parameters across T_c. The involvement of the Bi-O layer in the mechanism of high-temperature superconductivity is well documented. For example, a band-structure calculation shows that, apart from the CuO_2-derived bands, the Fermi level also has contributions from the Bi-O-derived bands.[16] It is also known that the Bi-O plane acts like a charge reservoir and a charge-transfer process exists between CuO_2 and Bi-O layers.[17] The Bi-O layer seems functionally equivalent to the O-Cu(1)-O chain in YBCO. At the onset of superconductivity, a local electron transfer from CuO_2 to the Bi-O plane results in the generation of holes (charge carriers) in the CuO_2 plane and a concomitant increase in electron density in the Bi-O plane. This leads to a reduction in τ in the superconducting state, as observed. Under the electron-gas approximation,[2] an increase in electron density would lead to an increase in Fermi cutoff (momentum), reducing the area under the central low-momentum region of the Doppler curve. Therefore an increase in electron density would also decrease S at the onset of superconductivity, as seen in this work (Fig. 2).

The observation of Sundar *et al.*[9] seems contradictory to the present observation and literature data. They ascribed the temperature invariance of τ to the lack of positron density in the CuO_2 plane and at the apical oxygen atom. It was also shown by these authors[9] that τ in Bi-2:1:2:2 is dependent on heat treatment in oxygen atmosphere, because intercalation of excess oxygen in the region between Bi-O layers increases the effective valence of Bi. Therefore the involvement of the Bi-O plane in governing the positron annihilation parameters is corroborated. The superstructure in the Bi-O plane is affected by the heat-treatment conditions,[18] and in turn influences the PDD and consequently the temperature dependence of the S and τ parameters across T_c. It is interesting to note that different temperature dependencies of the S and τ parameters were seen in YBCO (Refs. 19,20) under different heat-treatment conditions, indicating a link between the heat-treatment conditions and the PDD.

A plausible reason for the observation of a temperature independence of τ could be a homogeneous PDD involving both the CuO_2 and Bi-O planes as expected in an idealized structure.[15] In case positrons sample both these planes with near-equal probabilities, increase in the S and τ parameters due to annihilation from the CuO_2 plane[3] might counterbalance the decrease in these parameters due to annihilation from the Bi-O plane, leading to near-constant $S(T)$ and $\tau(T)$ profiles. A probable cause for such a homogeneous PDD could also be the presence of

vacancies in the CuO_2 plane owing to Cu deficiency. Apart from the above reasons, the structural changes at the onset of superconductivity might also influence the temperature dependence of the S and τ parameters. In Bi-based superconductors such structural change is seen from the ^{17}O NMR response[21] as well as being expected from the change in the lattice parameter following electron transfer away from the CuO_2 plane (as seen in Tl superconductors[5]).

We conclude that the Bi-O plane is electronically active at the onset of superconductivity and probably performs a similar role to that of the O-Cu(1)-O chain in superconducting YBCO. The temperature dependence of the S parameter is explained taking into account the PDD and invoking a local electron-transfer process between the CuO_2 and Bi-O planes at the onset of superconductivity. The effects of heat-treatment conditions and structural changes on the temperature dependencies across T_c could be substantial. Further investigations with selective substitution in the CuO_2 and Bi-O planes may help confirm the explanations provided in this work.

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