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Doppler-broadened positron annihilation studies in Y–Ba–Cu–O, Tl–Ca–Ba–Cu–O and Bi–Ca–Sr–Cu–O superconductors

P K PUJARI, T DATTA, SATYA PRAKASH, S B MANOHAR, I K GOPALAKRISHNAN, G M PHATAK, J V YAKHMI, P V P S S SASTRY and R M IYER
Chemical Group, Bhabha Atomic Research Centre, Bombay 400085, India

Abstract. Doppler-broadened annihilation radiation spectra have been measured as a function of temperature from 77 K to 300 K, for several high temperature oxide superconductors viz single-phase YBCO, single- and mixed-phase Tl–Ca–Ba–Cu–O and Bi–Ca–Sr–Cu–O compounds. The temperature-dependent parameters extracted respond to a change at the onset of superconducting transition. The observations point to involvement of oxygen valence electrons at the onset of superconducting transition. Also a possible structural change and/or increase in electron density at the oxygen vacancy/defect sites seem to accompany the transition. In addition, the parameters derived are seen to be sensitive to the presence of more than one superconducting phases in mixed phase samples.

Keywords. Positron annihilation; Doppler broadening.

1. Introduction

Since the discovery of high temperature oxide superconductors (Bednorz and Muller 1986), experiments using a wide range of techniques have been carried out to elucidate the mechanism of this phenomenon. Positron annihilation spectroscopy (PAS) technique is one of the powerful diagnostic tools in solid-state research as it can give information about the momentum distribution and local density of electrons besides being sensitive to the defects/vacancies present in the material. Investigations carried out by several researchers using positron annihilation technique in high temperature oxide superconductors (HTcSc) (Pujari *et al* 1989a and references therein) reveal a distinct correlation of line-shape parameters (S or I, S_{2D}, P_{2D}) and lifetime (τ) with the superconducting transition. No such changes at T_c were observed for conventional superconductors (Green and Madansky 1956), in contrast to the significant changes observed in the HTcSc. In this paper, we discuss the Doppler broadened positron annihilation (DBAR) data obtained for a number of samples of YBCO, Tl–Ca–Ba–Cu–O and Bi–Sr–Ca–Cu–O compounds, the details of which are given in table 1. The measurements were carried out in the temperature range of 77 K to 300 K. Since S might not provide unambiguous information regarding momentum distribution, a more sensitive analysis of the DBAR spectra were carried out.

2. Experimental

The preparation procedure and characterization of all the samples studied are given elsewhere (Pujari *et al* 1988, 1989a, b). A ^{64}Cu positron source in the form of a metal wire strand was sandwiched between identical pellets of the same material. The DBAR spectra were measured at temperatures between 77 K and 300 K using a 2 cc HPGe

Table 1. Compounds studied in the present work.

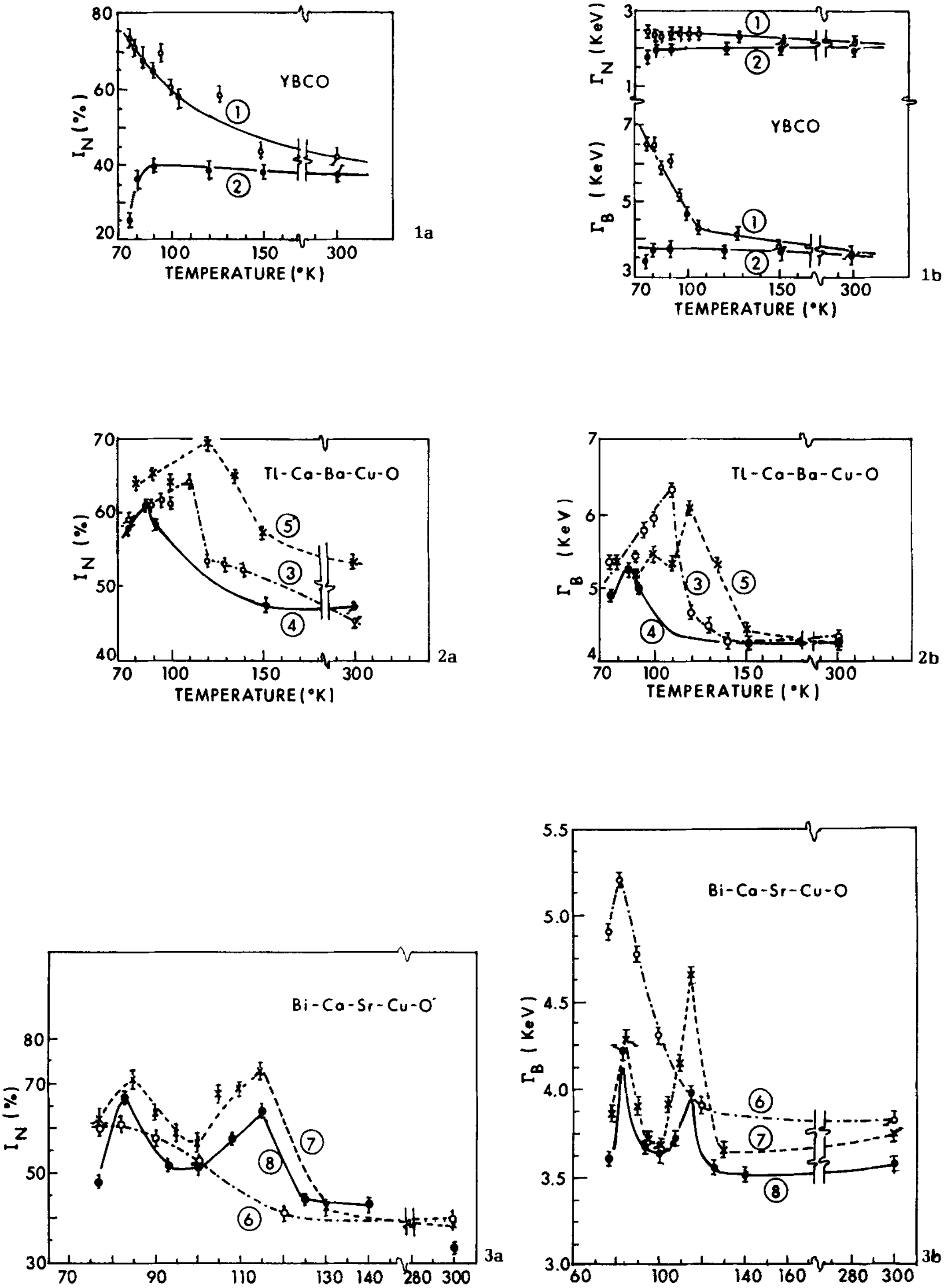
No.	Compound	Phase	T_c(K) ($R=0$)	Remarks
1	$YBa_2Cu_3O_{7-x}$	single 123	93	–
2	$YBa_2Cu_3O_{7-y}$	do	–	Semiconducting down to 77 K
3	$Tl_2CaBa_2Cu_2O_x$	single 2122	108	–
4	$Tl_2CaBa_2Cu_2O_x$	single 2122	95	Result of argon annealing of 3.
5	$Tl_2Ca_2Ba_2Cu_3O_x$	mixed 2122 + 2223	125	–
6	$Bi_2CaSr_2Cu_2O_x$	single 2122	85	–
7	$Bi_{1\cdot 6}(Pb)_{0\cdot 4}$ $Ca_2Sr_2Cu_3O_y$	mixed 2122 + 2223	110	–
8	$Bi_{1\cdot 6}(Pb)_{0\cdot 4}$ $Ca_2Sr_2Cu_3O_y$	mixed 2122 + 2223	85	Different T_c than 7 due to different heat-treatment schedule; having a significant drop at 110 K in resistivity.

detector system, coupled to a 4 K MCA with a resolution of 1·0 keV at 511·8 keV gamma line of ^{106}Ru. The observed spectra were deconvoluted off the detector resolution function to obtain the intrinsic momentum distribution using the standard gamma spectrum (511·8 keV) of ^{106}Ru. The intrinsic distributions were then resolved for components using PAACFIT program (Kirkegaard 1981) without any bias. The details of the experimental set-up and data analysis were reported earlier (Pujari *et al* 1988).

3. Results and discussion

The intrinsic spectra of all the samples, over the entire temperature range were subjected to PAACFIT analysis which yielded two gaussian components—a narrow and a broad component—without any bias about the intensity and width (FWHM) of the individual components and with a variance < 1. Any attempt at invoking a third component failed and the only temperature-dependent parameters were seen to be the intensity of the narrow component, I_N, and the width (FWHM) of the broad component, Γ_B. The variation of I_N and Γ_B as a function of temperature for all the samples are given in figures 1a to 3a and 1b to 3b respectively.

In view of the positrons annihilating from the bulk and the defect/vacancy sites in polycrystalline samples like ours, two components are expected as observed in the present case. The narrow and the broad components were identified to be originating from the defects/oxygen vacancy sites and bulk respectively. In other words, the narrow component is the signature of the positrons annihilating from the trapped state and the broad component primarily represents the momentum distribution of the oxygen valence electrons (Pujari *et al* 1988).



Figures 1–3. Variation of I_N and Γ_B as a function of temperature for different samples. **1a, 2a, 3a.** I_N vs temperature. **1b,** Γ_B and Γ_N vs temperature. **2b, 3b.** Γ_B vs temperature.

For brevity the salient features of our observations are outlined here with subsequent discussion: (i) Increase of the width (FWHM) of the broad component, Γ_B, at the onset of superconducting transition; (ii) Increase of the intensity of narrow component, I_N, at the onset of superconducting transition; (iii) Observation of double peak structure in $\Gamma_B(T)$ profile for mixed phase samples of Tl–2122 + 2223 and Bi–2122 + 2223; and the relative change of the magnitude of the derived parameters at the maxima, varying from sample to sample; (iv) Decrease of Γ_B and I_N below T_c for Tl and Bi compounds unlike in YBCO.

One of the common features seen in all the superconducting samples is the sharp increase of Γ_B at the onset of superconductivity (figures 1b, 2b, 3b). A measurement carried out on a semiconducting (down to 77 K) YBCO (no. 2, which was obtained by annealing the parent superconducting compound, no 1) does not show this change, and, hence this feature is intimately associated with the phenomenon of superconductivity (figure 1b). Since Γ_B primarily represents the momentum distribution of the oxygen valence electrons, the increase could be due to increased momentum of these electrons at the onset of superconductivity. The reason for such an increase, however, cannot be deduced from the present experiments. Nevertheless, our observation points to an electronic involvement of oxygen ion in the process of superconducting transition; also many spectroscopic evidence exists in the literature supporting this view (Emery 1987; Takahashi *et al* 1988).

The other interesting feature is the increase in I_N at the onset of superconductivity (figures 1a, 2a, 3a). Since the narrow component arises due to the positrons annihilating from the trapped state, this increase could be attributed to the increase in electron density at the vacancy/defect sites or a possible structural change leading to an increased number of trapping sites, at the onset of superconducting transition. However, since this increase is a common feature in all the three classes of oxide superconductors, and, since only YBCO has a greater number of oxygen vacancies, the second reason, namely, a possible structural change seems to be a more favourable proposition. Recently, sound velocity measurements carried out on YBCO also suggest an electronically-driven structural anomaly at the superconducting transition (Bishop *et al* 1987). In addition, the I_N values for 2223 + 2122 samples in Tl and Bi compounds are seen to be higher than their single phase counterpart (figures 2a and 3a; no. 5 vs 3 and 7 vs 6). The higher I_N values for mixed phase samples than the single phase ones could be due to the higher number of Cu–O and Ca–O planes ($n = 3$), which make available an increased number of trapping sites in the 2223 phase compared to the $n = 2$ in the 2122 single phase compounds.

The increase of Γ_B and I_N at the onset of superconductivity reaches a maximum value and decreases on further cooling below T_c in Tl and Bi compounds (figures 2, 3). This decrease below T_c is, however, not seen in YBCO at least down to 77 K, below which no measurements were carried out. In the 2122 single phase compounds of Tl and Bi oxide superconductors (nos. 3 and 6) these parameters reach a maxima at $\sim T_c$ and decrease monotonically on further cooling (figures 2, 3). However, for the mixed phase compounds (2122 + 2223) of Tl and Bi (nos. 5 and 7), there appears another peak on further cooling and results in a double peak profile of $\Gamma_B(T)$ (figures 2b, 3b). Since the mixed phase contains two phases, namely 2223 and 2122, the latter phase seems to be responsible for the second peak. These observations thus point to the fact that multiple superconducting phases, with different values of T_c's, should, in principle, give rise to separate peaks in Γ_B and I_N. A look at the Γ_B profile of the mixed phase compounds (nos. 5, 7 and 8 in figures 2b and 3b), in fact, reveals that the stronger peak in each case corresponds to the superconducting phase that yields the zero resistance. The single phase compound 2122 in both Tl and Bi superconductors (nos. 3 and 6) registered the largest peak Γ_B at the zero resistance temperature compared to their mixed phase counterparts (figures 2b and 3b). We believe that these observations are due to the presence of a larger volume fraction of the superconducting phase corresponding to the zero resistance temperature of the material. Argon annealing (which results in decrease of T_c and increase in transition width ΔT_c) of 2122 Tl compound, no. 3 resulting in no. 4, in fact, resulted in a reduction in the magnitude of the Γ_B peak (figure 2a).

The only dissimilarity in the Γ_B and I_N profiles is the decrease of these parameters below T_c for Tl and Bi systems which is not apparently seen in the YBCO system. The decrease of I_N below T_c for Tl and Bi systems is not known to us. Though we hesitate to speculate the reason behind the decrease of Γ_B below T_c, it has been pointed out by Broveto *et al* (1987) that the presence of a superconducting gap (2Δ, which has a temperature dependence) might result in a narrower momentum distribution and hence a decrease of Γ_B below T_c as

$$E'_F = E_F - \Delta, \tag{1}$$

$$\Delta(T) = 1{\cdot}76\,\Delta_0(1 - T/T_c)^{1/2}, \tag{2}$$

where E'_F and E_F are Fermi energy in the superconducting and normal state, Δ_0 is the superconducting gap at 0 K and T and T_c are temperature and transition temperature respectively. A similar conjecture is provided by Harshman *et al* (1988) to explain qualitatively the observed increase in τ below T_c in single crystal YBCO.

The whole discussion is based on the fact that the changes seen at T_c are a direct manifestation of the phenomenon of superconductivity. At present, discrepancies exist in positron annihilation research on these oxide superconductors as the behaviour of positrons in these oxides is yet to be completely understood. The exact reason(s) for the observed changes are therefore unknown.

4. Conclusion

In conclusion we suggest (i) involvement of oxygen valence electrons in the superconducting transition; (ii) possibly an increase in electron density at the vacancies/defects and/or a structural change is associated with the transition; (iii) positron annihilation studies can, in principle, pinpoint the existing superconducting phases in a mixed phase sample and (iv) a common mechanism governs the phenomenon of high T_c superconductivity in all the three types of oxide superconductors studied.

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