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Positron annihilation measurements across the superconducting transition in $Y_1Ba_2Cu_3O_{7-x}$

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Abstract. Positron lifetime and Doppler broadened annihilation radiation lineshape measurements have been carried out in $Y_1Ba_2Cu_3O_{7-x}$ as a function of temperature in the range of 300 K to 58 K. The positron lifetime and the peak parameter of the annihilation radiation lineshape are observed to decrease on lowering the temperature without showing any discontinuous change across the superconducting transition temperature of 90 K as determined by susceptibility measurements. The variation of positron annihilation parameters with temperature in the superconducting state is significantly larger than that in the normal state. This is qualitatively explained in terms of the dimerization of oxygen ions in the superconducting state of $Y_1Ba_2Cu_3O_{7-x}$.

Keywords. Positron lifetime; Doppler-broadened lineshape; temperature dependence; YBCO; superconductivity.

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The recent discovery of high T_c in the oxide superconductors (Bednorz and Muller 1986; Wu *et al* 1987) has stimulated an enormous research activity to understand the superconductivity in these systems. Several experimental techniques have been used to obtain information on various aspects of the oxide superconductors such as their structure, electronic properties, phonon spectrum etc. Positron annihilation spectroscopy (PAS) is an established method to probe the electronic structure and defect properties of materials (Hautojarvi 1979; Brandt and Dupasquier 1983). The annihilation characteristics of a positron in a medium are determined by the overlap of the positron and electron wavefunctions. For example, the lifetime is determined by the electron density at the site of the positron while the angular correlation of annihilation photons and Doppler broadening of annihilation radiation lineshape (DBARL) are governed by the electron momentum distribution. Because of its sensitivity to electronic structure, PAS is expected to be useful in the study of superconducting transition. However previous positron annihilation experiments on lead and niobium alloys (Green and Madansky 1956; Briscoe *et al* 1966) did not indicate any change in the annihilation characteristics across the superconducting transition. This has been rationalised as arising due to the fact that the formation of Cooper pairs affects a small region near the Fermi surface whereas the annihilation characteristics of the positron are determined by both the valence and the core electrons. An increase in the smearing of the Fermi surface in the superconducting state of Nb_3Sn has been observed in two-photon angular correlation experiments (Faraci and Spaddoni 1969). In the present paper, we report the results of positron lifetime and Doppler-broadened

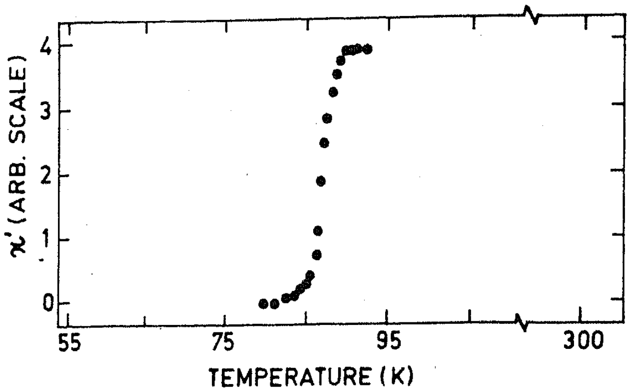

Figure 1. Variation of susceptibility with temperature indicating a sharp superconducting transition in YBCO. The onset temperature is 90 K and 90% of the sample becomes superconducting by 85 K.

lineshape measurements in $Y_1Ba_2Cu_3O_{7-x}$ (YBCO) across the superconducting transition in the temperature range of 300 K to 58 K.

Two identical pieces of YBCO samples were prepared by standard solid state reaction techniques starting from stoichiometric quantities of Y_2O_3, $BaCO_3$ and CuO. The final reaction product was pelletized and heat treated in flowing oxygen at 950° C for 2 hr, slow cooled (4–6 hr) to 380° C and maintained at that temperature for 35 hr before taking out of the furnace. X-ray measurements indicated the sample to be in the orthorhombic phase. The superconducting transition temperature was obtained by a double coil a.c. susceptibility apparatus operating at a frequency of 1·09 kHz. The results of a.c. susceptibility measurements, shown in figure 1, indicate a T_c onset of 90 K and 90% of the sample becomes superconducting by 85 K.

For the positron annihilation measurements, a 10 μCi ^{22}NaCl positron source deposited on a 2·5 μm Ni foil was sandwiched between two identical YBCO samples and the whole assembly was mounted on the cold finger of a metal cryostat. By pumping on liquid nitrogen and by using a small heater coil the temperature of the sample could be varied between 58 K and 100 K with a temperature stability of better than 1 K. Temperature measurements were carried out using a platinum resistance thermometer. Positron lifetime measurements were carried out using a fast-fast coincidence spectrometer having a time resolution of 300 ps FWHM. Lifetime measurements at various temperatures were carried out for a period of 4 hr resulting in ~20,000 coincidence counts at the peak of each lifetime spectrum. The lifetime spectra were analysed using the program due to Kirkegaard *et al* (1981) and it was found that the best fits ($\chi^2 < 1{\cdot}5$) were obtained for a single exponential decay component in addition to a component due to annihilations in the source foil ($\tau_s = 530$ psec, $I_s = 8\%$). The Doppler broadened annihilation radiation lineshape measurements were carried out using a high efficiency high resolution germanium detector having an energy resolution of 1·1 keV at 514 keV. The Doppler broadened spectra were analysed in terms of a peak parameter, I, defined as the ratio of counts in the central 11 channels (1 channel = 130 eV) to the total counts in 80 channels covering the entire photopeak. The I parameter provides an index of the relative fraction of annihilations with the low momentum valence electrons.

The variation of positron lifetime (τ) and the I parameter as a function of temperature are shown in figures 2 and 3 respectively. It is seen that both τ and I do not show

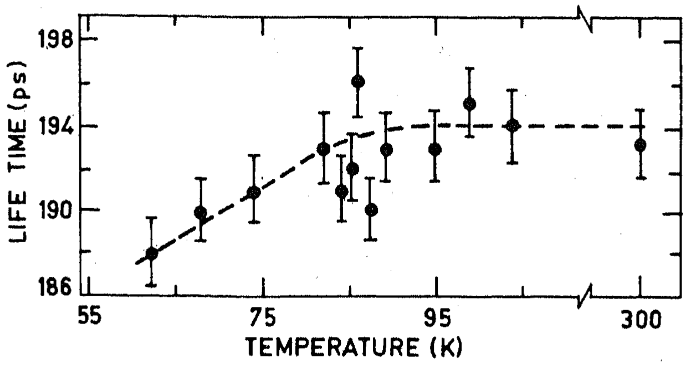

Figure 2. Variation of positron lifetime τ with temperature in YBCO.

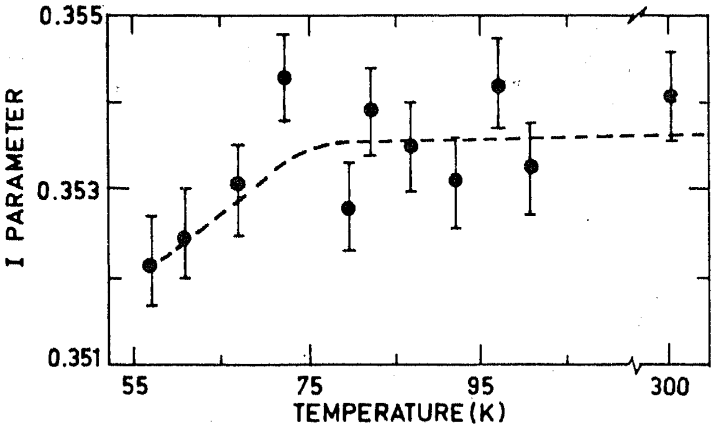

Figure 3. Variation of Doppler-broadened lineshape parameter I with temperature in YBCO.

much variation with temperature in the normal state. Further there is no discontinuous change in the annihilation parameters over the temperature range of 90 K to 85 K wherein the superconducting transition takes place (cf. figure 1). However, the variation of annihilation parameters with temperature in the superconducting state is distinctly larger than that in the normal state.

After these experiments were completed, we became aware of other papers on positron annihilation studies on YBCO (Teng *et al* 1987; Jean *et al* 1987; Ishibashi *et al* 1987). Teng *et al* (1987) have observed an abnormal peak in the mean lifetime in a small temperature range of 90·5 K to 92·5 K in a YBCO sample having a T_c of 91·4 K. This abnormal behaviour has been tentatively attributed to the formation of positronium due to microscopic volume expansion caused by lattice relaxation at the transition temperature. This explanation seems untenable since there is no change in volume across the superconducting transition as is confirmed by X-ray and neutron diffraction experiments (Capponi *et al* 1987; Flukiger *et al* 1987). Jean *et al* (1987) did not observe any abnormal peak but a decrease in lifetime and the lineshape parameter at the superconducting transition temperature. Ishibashi *et al* (1987) observed a gradual decrease in the I parameter in the temperature range of 105 K to 70 K. Jean *et al* (1987) have explained the decrease in lifetime on lowering the temperature as arising due to the excess electrons in the superconducting state as is predicted by the excitonic-enhanced superconductivity model (Ching *et al* 1987). However, recently Anderson and Abrahams (1987) have cast doubts on the validity of the exciton-mediated mechanism for superconductivity in the oxide superconductors.

Comparing our results (see figures 2 and 3) with the above mentioned results we find that while our results are at complete variance with those reported by Teng *et al* (1987), there is a marked similarity with those of Jean *et al* (1987) and Ishibashi *et al* (1987). Though the reason for discrepancy with the results of Teng *et al* is not clearly understood it is felt that it may be related to the fact that the annealing conditions, porosity and grain size influence the positron annihilation characteristics in YBCO (Sundar *et al* 1987). In the following we try to explain the common features observed in the various positron annihilation experiments viz., the decrease in the annihilation parameters at low temperatures and their larger temperature dependence in the superconducting state.

In order to understand the positron annihilation results in YBCO it is necessary to have information about the site from which the positron annihilates. The superconducting phase in YBCO has been identified as having an oxygen defect-perovskite structure (Rao *et al* 1987; Cava *et al* 1987). From a knowledge of the lattice constants and the interatomic separations (Beech *et al* 1987) it can be inferred that the open regions in this structure, which are most likely to be preferred by the positron, are the oxygen vacancies in the basal Cu-O plane and the yttrium plane. A calculation of the potential felt by the positron, obtained from a superposition of atomic potentials, indicates that the most probable sites for the positron are the ordered vacancies in the basal Cu-O plane (Bharathi *et al* 1987).

As mentioned earlier, the positron lifetime (τ) is correlated to the electron density at the site of the positron, and the Doppler-broadened lineshape parameter I is related to the fraction of annihilations with the low momentum valence electrons. The decrease in τ on lowering the temperature can arise due to an increase in the electron density resulting from a decrease in the unit cell volume. The unit cell volume, obtained from neutron diffraction experiments (Capponi *et al* 1987), indicates a decrease by 0·6% in the temperature range of 300 K to 75 K and by an insignificant amount at lower temperatures. Thus the volume contraction on lowering the temperature cannot account for the 3% decrease in τ observed in the temperature range of 80 K to 58 K.

The observed large decrease in τ and I parameter below the superconducting transition temperature (see figures 2 and 3) coupled with the fact that no such temperature dependence is observed in the non-superconducting tetragonal phase (Jean *et al* 1987) indicates that the temperature dependence of positron annihilation parameters is intimately related to superconductivity in these systems. One plausible explanation for the temperature dependence of τ and I is the dimerization of oxygen ions which has been invoked to explain the photoemission data (Sarma *et al* 1987; Dauth *et al* 1987). The dimerisation of oxygen ions is consistent with the resonating valence bond model (Anderson *et al* 1987), wherein the oxygen-oxygen interaction is mediated by the Cu ions (Bhaskaran 1987). The coming together of oxygen ions in the superconducting state leads to an increase in the electron density at the site of the positron resulting in a decrease in lifetime. Further, the dimerization results in an increase in the overlap of the positron wavefunction with the core electrons of oxygen ions leading to a reduction in the fraction of annihilations with the low momentum valence electrons. This can explain the decrease in I parameter in the superconducting state. The gradual increase in the extent of dimerization as the temperature is lowered in the superconducting state can qualitatively account for the observed decrease in τ and I parameter in the temperature range of 80 K to 58 K. To substantiate the above mentioned physical picture, a first principles calculation of the positron wavefunction and its annihilation characteristics in YBCO is in progress.

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