Local Charge-Density Change and Superconductivity: A Positron Study

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The temperature dependence between 10 and 300 K of the positron lifetime was measured in the high-temperature superconductors $YBa_2(Cu_{1-x}M_x)_3O_{6+\delta}$, where M = Zn and Ga with x = 0.0 to 0.07 and $\delta > 0.8$. In the undoped and Ga-doped samples, the positron lifetime in the Bloch state, τ_b, was observed to decrease below T_c. In the Zn-doped samples, a dramatic x-dependent temperature variation of τ_b was observed: from a decrease of τ_b below T_c for $x = 0.01$ to an increase of τ_b for $x > 0.02$. These new experimental results are interpreted in terms of a change in the local charge density of high-T_c oxides associated with the superconducting transition.

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Currently there exists no universally accepted mechanism[1] for the explanation of experimental observations made on superconductors[2,3] with T_c above 30 K. In addition to the well-known phonon-mediated mechanism in terms of which the conventional low-T_c (i.e., < 30 K) superconductivity is understood, other proposed mechanisms fall into two groups, namely, spin mediated and charge mediated. In this respect, the positron-annihilation technique is particularly useful because[4] it probes the local charge- (either electrons or holes) density distribution in solids on which the superconducting properties may critically depend. Indeed, recent studies indicate that the annihilation characteristics exhibit a strong temperature dependence near and below T_c in the high-temperature superconductors,[5-14] whereas no such temperature dependence has been detected in the conventional low-T_c superconductors.[12] Two general types of behavior of positron lifetime have been observed in the oxide superconductors: The lifetime undergoes a rapid decrease[5-7] below T_c in $YBa_2Cu_3O_7$ (Y 1:2:3), whereas in $La_{1.85}Sr_{0.15}CuO_4$ (La 2:1:4) and $Tl_2Ca_2Ba_2Cu_3O_{10+\delta}$ (Tl 2:2:2:3), a large increase of lifetime is observed.[8,13] Several plausible explanations have been put forward[5-15] to understand the variation of annihilation parameters below T_c; for example, it has been attributed to a change in the electron density, electron-positron correlation,[15] and a change in the structure, such as the motion of O atoms.[7]

In spite of a large body of experimental results, in particular, in the Y 1:2:3 system, there is as yet no consensus on the explanation for the observed temperature dependence of annihilation parameters below T_c. For example, in Y 1:2:3, in addition to the observation of a decrease[5-7] in lifetime below T_c, there are reports of an increase in lifetime[9] and even of the absence[11] of temperature dependence of the lifetime below T_c. It is plausible[16] that the different temperature dependences are related to the disposition of positron density distribution (PDD) with respect to the CuO_2 layers which are believed to be responsible for superconductivity in these systems. The present investigation has been performed with a view to test this hypothesis. Experiments on the temperature dependence of the lifetime across T_c have been carried out in undoped and Zn- and Ga-doped Y 1:2:3. These results are discussed in the light of the calculated PDD, in particular, with respect to the CuO_2 layers and the Cu-O chains which are the dominant structural features of the Y 1:2:3 system. The present study shows that the temperature dependence of the lifetime is correlated with the PDD; a decrease in lifetime is observed if the positrons probe the chains and an increase in lifetime is observed if the positrons probe the CuO_2 layers. It is argued that the temperature dependence of the lifetime below T_c in both doped and undoped Y 1:2:3 is best understood if we invoke a new physics that there is a local charge transfer between the CuO_2 layers and the Cu-O chains as the materials become superconducting. In this respect, the present studies indicate that the Cu-O chains play an active role in the superconductivity of Y 1:2:3, a concept that has been used in many theoretical models of high-temperature superconductivity.[17]

Polycrystalline samples of $YBa_2(Cu_{1-x}M_x)_3O_{6+\delta}$ with M = Zn and Ga, x = 0.00, 0.01, 0.02, 0.05, and 0.07, and $\delta > 0.8$ were synthesized by solid-state reaction of appropriate amounts of Y_2O_3, $BaCO_3$, CuO, ZnO, and Ga_2O_3 in a fashion previously described.[3] The x-ray powder diffractions on all these samples showed a single

phase with the orthorhombic structure. The T_c's were determined magnetically and resistively to be 94 K in undoped Y 1:2:3, 25 K in the 7%-Zn-doped Y 1:2:3, and 76 K in the case of 7%-Ga-doped Y 1:2:3. The observed T_c versus doping concentration agrees well with previous results.[18] The transition widths in all cases are less than 2 K, indicating the good quality of the samples. In addition to measurements on polycrystalline samples, positron lifetimes were also measured on flux-grown[19] single crystals of $YBa_2Cu_3O_7$. The T_c was determined to be 92 K from dc magnetization measurements and the resistance vanished at 94 K with a narrow transition width of 0.5 K.

Positron-lifetime measurements were performed using a fast-fast coincidence spectrometer having a resolution of 260 ps, and the lifetime spectra were analyzed using the PATFIT program with source correction, both as previously described.[5,8] The lifetime spectra, measured at various temperatures between 300 and 10 K, were best fitted ($\chi^2 < 1.1$) with two and three components, respectively, for the undoped and doped samples. The long-lived component, having a lifetime between 1.8 and 2.5 ns with an intensity of about 0.3%, was found to be temperature independent. This component is attributed to[5] orthopositronium annihilation in the voids and intergrain spaces of the material and is not related to the superconductivity studied here. For the undoped samples, in addition to the long-lived component, there was a single component whose lifetime varied between 190 and 172 ps as the temperature was lowered. The doped samples were characterized by two short-lived components with τ_1 in the range of 90 to 200 ps (the intensity varied between 50% and 90%) and τ_2 in the range of 240 to 320 ps. The observed τ_2 are typical lifetimes for positron annihilation in the vacancies of oxide materials.[20] They are found to be temperature independent. In order to compare the temperature dependences in the undoped and various doped samples, we evaluate the positron lifetime in the Bloch state τ_b using the formula[4]

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

where I_1 and I_2 are the intensities corresponding to the annihilation modes with lifetimes τ_1 and τ_2, respectively. The variation of τ_b as a function of temperature in undoped and Zn- and Ga-doped Y 1:2:3 are shown in Figs. 1 and 2, respectively. From these results, we make the following observations:

(1) All the samples show a strong temperature dependence of τ_b for $T < T_c$ as compared to $T > T_c$. This can be seen clearly from the difference in the slope $d\tau_b/dT$ in the two temperature regimes.

(2) The lifetime in the normal state at 300 K decreases significantly with Zn doping; for example, a 7% Zn substitution leads to a decrease of 50 ps. Ga doping leads to an increase in τ_b.

(3) The temperature dependence of τ_b for $T < T_c$ is strongly influenced by doping. The decrease of τ_b for $T < T_c$, seen in undoped Y 1:2:3, reverses with increasing Zn concentration. On the other hand, in the case of Ga-doped Y 1:2:3, a decrease in lifetime is seen, analogous to the behavior in undoped Y 1:2:3. The magnitude of the lifetime difference between the superconducting state at 10 K and the normal state at 300 K, $\Delta\tau_b = \tau_S - \tau_N$, decreases with the increase of dopant concentration.

As a first step in understanding the variation in lifetime and its temperature dependence with doping, it is necessary to know the PDD in Y 1:2:3, in particular, the influence of doping, since the lifetime is determined by the overlap of the electron and positron densities.[4] There have been several[14,20,21] calculations of PDD in undoped Y 1:2:3. These calculations indicate that the maxima in the positron density distribution occur in the region between the Cu-O chains in the basal plane. In the present study, we have calculated the PDD for the case of undoped and Zn- and Ga-doped Y 1:2:3, following the

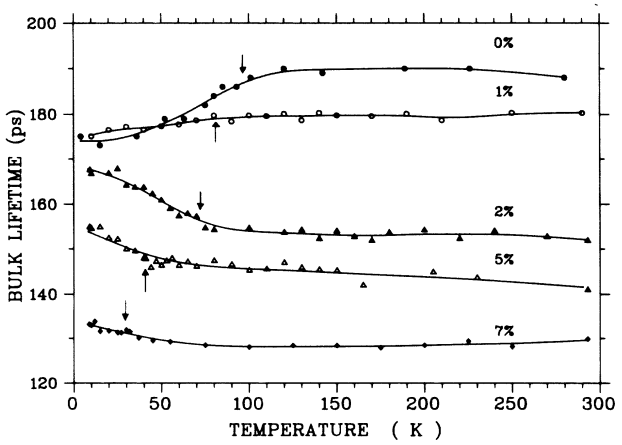

FIG. 1. τ_b vs T in undoped and Zn-doped Y 1:2:3. The arrows indicate T_c. Lines are drawn as a guide to the eye.

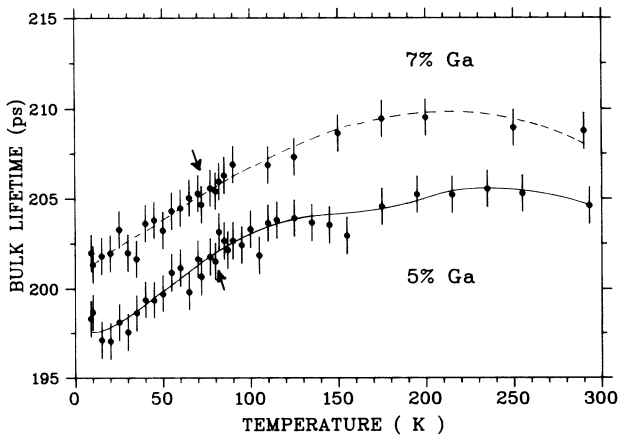

FIG. 2. τ_b vs T in Ga-doped Y 1:2:3. The arrows indicate T_c. Lines are drawn as a guide to the eye.

method discussed in Ref. 21, by solving the Schrödinger equation with the positron potential taken as a sum of the Hartree potential due to electrons and ions and the correlation potential in the local-density approximation. The calculations in doped Y 1:2:3 have been performed for a complete substitution by Zn at Cu(1), Cu(2), and Y sites and for the case of Ga replacing either of the Cu sites. In order to quantify the effect of doping on PDD, we have estimated the ratio of the maxima of the positron density in the Cu-O chains (ρ_{+C}) to the maxima in the CuO_2 layers (ρ_{+L}) for various substitutions. From a comparison of the ratio ρ_{+C}/ρ_{+L}, we find that for Zn substituting at Cu(2) and Y sites, the positron density in the CuO_2 layers increases as compared to undoped Y 1:2:3. With Ga substitution at the Cu(2) site, the maxima of the PDD is in the region between the Cu-O chains as in the case of undoped Y 1:2:3. The contour plots of the PDD for the case of Zn substitution at various sites in Y 1:2:3 are shown in Fig. 3. We have also calculated the PDD using the electron density obtained from the self-consistent orthogonalized-LCAO band-structure calculations[22] on Zn-doped Y 1:2:3. The PDD obtained from these calculations are in qualitative agreement with the results presented in Fig. 3.

With the known positron densities for various substitutions, we have calculated the lifetime by evaluating the overlap with the valence- and core-electron densities. The changes in lifetime with doping are calculated to be -3, $+2$, -8, -7, and $+6$ ps for the case of Zn doping at Cu(2), Cu(1), and Y sites, and Ga substituting at Cu(1) and Cu(2) sites, respectively. The calculated changes in lifetime are much smaller than what are observed experimentally (cf. Figs. 1 and 2). This suggests that in addition to the changes in PDD due to doping there must be a large change in the electron density due to doping. In order to know the change in electron density due to doping, we have made use of the correlation between T_c and the hole concentration that has been established[23] from the Hall and wet-chemistry studies on Y 1:2:3 with various dopants such as Zn and Ga. An increase in the mobile-hole concentration on the CuO_2 layers, as is seen[23] in Zn-doped Y 1:2:3, will result in an increase in the local electron density around the positron due to positron-hole anticorrelation[15] and this can account for the observed decrease in lifetime with Zn doping. By similar arguments, the decrease[23] in mobile-hole concentration in Ga-doped Y 1:2:3 will lead to an increase in lifetime. Using the measured T_c in the various doped samples in conjunction with the correlation[23] between T_c and the hole concentration, we have estimated the change in electron density due to Zn and Ga doping. Incorporating the change in electron density, the positron lifetime in the various doped samples was evaluated using the Brandt-Reinheimer formula,[4] which takes into account the enhancement of the electron density around the positron. The calculated lifetimes are found to reproduce very well the observed decrease in lifetime with Zn doping and the increase in lifetime with Ga doping.

As shown in Fig. 1, the temperature dependence of the positron lifetime in undoped Y 1:2:3, a decrease in τ_b correlated with T_c, is consistent with the majority of reported results[5-7,14] in this system. Our calculated PDD in undoped Y 1:2:3, with the positron mainly probing the chains, also agree with the existing results.[14,20,21] The direct correlation between a change in lifetime and T_c, even though positrons probe the Cu-O chains, suggests that the chains are electronically active in the superconducting process. The decrease in lifetime below T_c implies an increase in electron density at the site of the positron, viz., the Cu-O chains. A simple physical picture to understand the decrease in lifetime below T_c is to invoke[24,25] that there is a local transfer of electron density between the layers and the chains in the superconducting state. Such a proposal can also account for the temperature dependence in the Zn- and Ga-doped systems if we take the PDD into account correctly. The calculated PDD shows that the weight of the positron density shifts

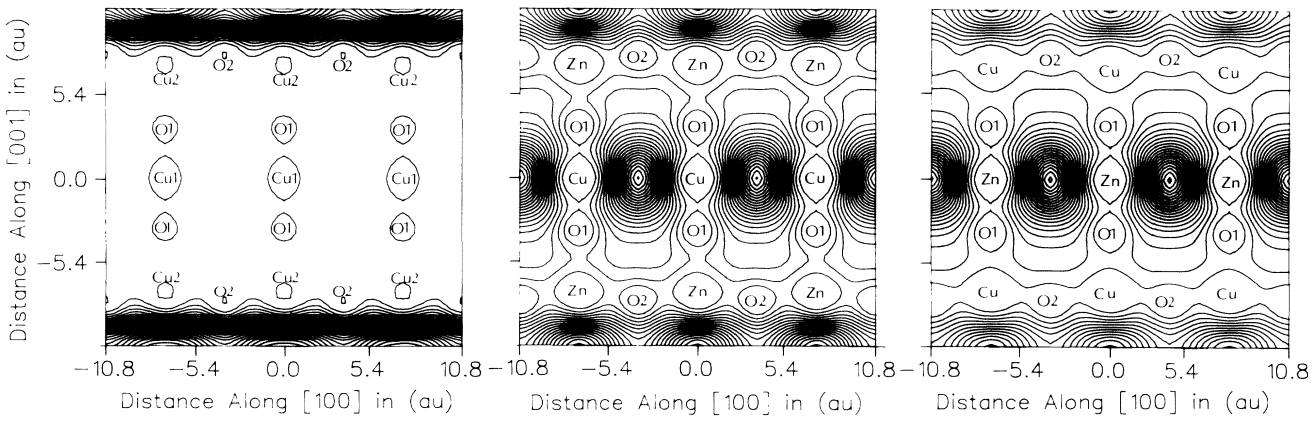

FIG. 3. The contour plot of the positron density distribution in Zn-doped Y 1:2:3 for the cases of Zn replacing Cu(1) (right), Cu(2) (center), and Y (left).

from the Cu-O chains to the CuO_2 layers due to Zn doping in Y 1:2:3. A transfer of electron density from the CuO_2 layers to the chains will in this case lead to a decrease in electron density at the site of the positron and this can account for the observed increase in lifetime below T_c. In the Ga-doped Y 1:2:3 system, the PDD is seen to be on the Cu-O chains and a decrease in lifetime is seen below T_c; once again this is consistent with the notion of electron-density transfer from the CuO_2 layers to the chains. In addition to providing an explanation for the direction of lifetime change, viz., an increase or decrease below T_c, the above-mentioned model can also account for the observed decrease of $\Delta\tau_b$ with doping. An electron transfer from the CuO_2 layer to the Cu-O chains in the superconducting state can be viewed as an increase in the charge state of Cu in the CuO_2 layers from 2+ to 3+. With the partial replacement of Cu by Zn or Ga, such a charge transfer can be expected to be suppressed, leading to a decrease in the magnitude of $\Delta\tau_b$ with the increased Zn and Ga doping of Y 1:2:3.

To summarize, the present investigation on the variation of lifetime in undoped and doped Y 1:2:3, coupled with the calculation of PDD, has established the correlation between the change in lifetime below T_c and the PDD. A decrease in lifetime is observed when the positrons probe the chains and an increase is observed if the positrons probe the CuO_2 layers. This correlation provides a consistent rationale for understanding the different temperature dependences observed in the earlier experiments[9,11] on Y 1:2:3, when we take the effect of the PDD due to the presence of impurities into account correctly. This correlation can also form the basis of understanding the observed[8,13] increase in lifetime below T_c in Tl 2:2:2:3 and La 2:1:4 systems where positrons probe the CuO_2 layers.[8,26] The present investigation further shows that the change in positron lifetime below T_c in the oxide superconductors can be intrinsically related to superconductivity. In this case the current positron study provides a new physics of a change of the local charge density associated with the superconducting transition in oxide high-T_c materials.

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