Local electron density and vacancy properties for $YBa_2Cu_{3-x}Sn_xO_y$ $(x=0-1.5)$: A positron-lifetime study

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In this paper, we report positron lifetimes for $YBa_2Cu_{3-x}Sn_xO_y$ $(x=0-1.5)$. From these results, we calculate the local electron density n_e and vacancy concentration C_V as a function of Sn content. The results show a significant Sn-substitution dependence. At low x (≤ 0.4), n_e decreases as x increases while at high x (≥ 0.8) it reaches a constant value. For C_V, a large change occurs at x between 0.8 and 1.0 and corresponds to the known O-T phase transition. Positron experiments show that the structure of the Y 1:2:3 oxygen-deficient system is orthorhombic.

The superconducting properties of the $YBa_2Cu_3O_y$ system are known to be strongly dependent on its structure, electronic behavior, oxygen vacancies, and their ordering.[1-3] Extensive work has been done to study these properties. Elemental substitution is a very useful method from which many important results have been reported.[4-6] However, the mechanism of high-T_c superconductivity is still not completely understood. Positron-annihilation spectroscopy (PAS) can provide useful information about electronic properties, vacancies, and phase transitions and has been used to study high-T_c superconductivity.[7-10] In this paper, we present positron-lifetime results for a polycrystalline $YBa_2Cu_{3-x}Sn_xO_y$ system with a large Sn substitution. We have observed a very strong effect of Sn substitution on the calculated electron densities and vacancy concentration, and the O-T transition has been observed between $x=0.8$ and 1.0.

Samples of $YBa_2Cu_{3-x}Sn_xO_y$ ($x=0$, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.5) were prepared by the conventional solid-state reaction method.[6] The size of the sample was 13 mm diam and 1.5 mm thick. The resistance-temperature relationship was measured by the standard dc four-probe method with a voltmeter (type 181) resolution of 1×10^{-8} V. Lattice parameters were determined with the PGAKU-Max-YA rotating-target x-ray diffractometer (Cu-$K\alpha$). Positron-lifetime spectra were measured at constant temperature ($20\pm0.5\,°C$) by using the ORTEC-100U fast-fast coincident-lifetime spectrometer. The time resolution of the spectrometer was 220 ps as measured with the ^{60}Co radioisotope. Two pieces of identical samples were sandwiched together with a 10 μC ^{22}Na position source deposited on a thin Mylar foil (about 1.2 mg/cm^2 thickness). Each spectrum contained a total of 1×10^6 count. After subtracting background

and source contributions, the lifetime spectra were analyzed in two-lifetime components by using the program POSITRONFIT-EXTENDED where a source correction was made.

Experimental results of physical properties are listed in Table I, which includes T_c, oxygen content x, lattice parameters, and phase structure of the samples. It can be seen that T_c decreases while the oxygen content and x increase. For $x<0.4$, the samples are fairly good superconductors, while for $x>0.8$ the samples become nonsuperconducting. At the same time the samples become multiphase, as identified by Mössbauer and x-ray photoelectron spectroscopy (XPS) experiments.[6] Figures 1 and 2 show the positron-lifetime parameters, τ_1, τ_2, I_1 and mean lifetime τ_m as functions of the Sn content x. These positron-lifetime parameters show a significant Sn-substitution dependence. There are two large discontinuities at $x<0.1$ and in the range $0.8<x<1.0$ for τ_2 and I_1. τ_m and τ_1 show a smooth change below $x=0.4$ and

TABLE I. Physical parameters for $YBa_2Cu_{3-x}Sn_xO_y$ systems.

No.	x	T_c (K)	Structure parameters a (Å)	b (Å)	c (Å)	Oxygen content (y)	Phase
1	0	91.4	3.887	3.819	11.700	6.93	single
2	0.05	90.5	3.875	3.824	11.651	7.15	single
3	0.1	90.0	3.872	3.824	11.642	7.28	single
4	0.2	89.2	3.881	3.832	11.661	7.34	single
5	0.4	86.8	3.875	3.827	11.641	7.30	multi
6	0.6	85.1	3.873	3.834	11.637	7.34	multi
7	0.8	82.0	3.872	3.842	11.631	7.40	multi
8	1.0	N/A	3.858	3.862	11.610	7.45	multi
9	1.2	N/A	3.860	3.868	11.615	7.45	multi
10	1.5	N/A	3.861	3.869	11.616	7.42	multi
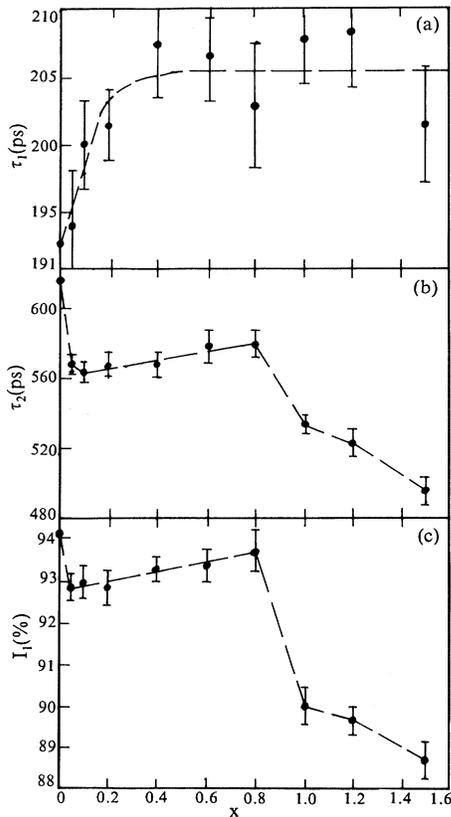
FIG. 1. Positron-lifetime parameters τ_1, τ_2, and I_1 as a function of Sn substitution x in $YBa_2Cu_{3-x}Sn_xO_y$ systems.

above $x=0.4$, a level of saturation. The structure of $YBa_2Cu_3O_y$ systems has been identified as an orthorhombic distorted, oxygen-deficient pervoskite. In polycrystalline samples, there are many types of defects, such as oxygen vacancies, grain boundaries, voids, twin boundaries, dislocations, etc., which may trap the positron. Therefore in the Sn-substituted Y 1:2:3 system, a two-state trapping model would be suitable for the interpretation of the positron results.[8] According to this model, two observed lifetime components are associated with annihilation at the defect and in the bulk state. We consider that
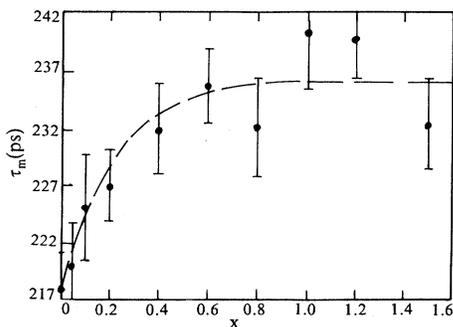
τ_1 is a weighted average of the lifetimes of free positrons and positrons in some shallow trap states and τ_2 contains mainly contributions from positron annihilation in open-volume defects, such as the oxygen vacancy discussed in Ref. 7. According to this model, we discuss the changes of the two lifetimes with Sn content. In Figs. 1 and 2 lifetime τ_1 has a similar change as τ_m with respect to x. The similarity is because τ_1 has a large intensity $(>85\%)$ and τ_m $(\tau_m = \tau_1 I_1 + \tau_2 I_2)$ is mainly determined by τ_1.

From these, we calculated the relative electron density n_e and vacancy concentration C_V as a function of x (Ref. 11) (Fig. 3). It can be seen that for low Sn substitution, n_e rapidly decreases and then reaches a saturation value. According to the Mössbauer experiment by Zhang, Wang, and Zhang[6] for $x < 0.4$, Sn occupied the Cu(1) site. It is known that the Cu(1) atoms in the Cu-O chain have a Cu^{3+} valence state. Clayhold et al.[12] showed that in Cu(1) site substitution would introduce changes of electronic carrier concentration. Thus the apparent local electron density n_e obtained by positron experiments reflects a decrease of electronic carrier concentration or an increase of the hole carrier concentration as x increases. This is consistent with the recent experiments of Jean et al.[8] on positron annihilation in Zn- and Ga-doped Y 1:2:3 systems. According to Tokara et al.[13] and Mitzi et al.,[14] in the Y 1:2:3 system, there are two types of hole carriers: one is localized in the Cu-O chain and the other moves in the Cu-O plane. The former does not directly contribute to superconductivity and does not change T_c at low Sn substitution $(x < 0.4)$. For $x > 0.8$, n_e is almost unchanged or saturated which may show that positron annihilation gives only the local electron density (localized), and Sn substitution for Cu(1) reaches a saturation limit. For high X, Sn possibly occupies the Cu(2) site, i.e., in the Cu-O plane. For $x = 0.8-1.0$, the sample becomes nonsuperconducting. At the same time, C_V has a sudden increase although n_e is unchanged. Figure 4 shows the curves of lattice parameters a, b, and c vs x (the data were taken from Table I). It can clearly be seen that at $x = 0.8-1.0$, the structure changes from an orthorhombic to a tetragonal phase. This may be because Sn
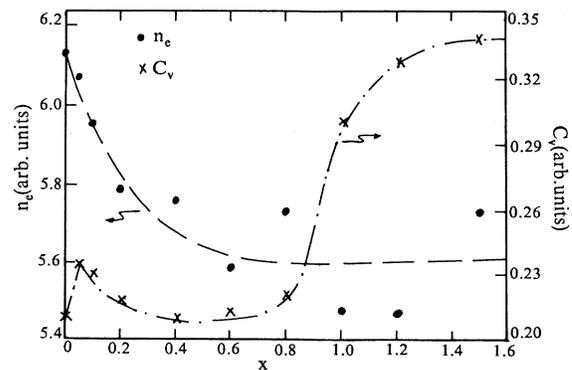

FIG. 2. Positron mean lifetime τ_m as a function of Sn substitution x in $YBa_2Cu_{3-x}Sn_xO_y$ systems.

FIG. 3. Local electronic density n_e and vacancy concentration C_V as a function of Sn-substitution content x in $YBa_2Cu_{3-x}Sn_xO_y$ systems.

occupies the Cu(1) and Cu(2) sites and O atoms occupy the O(5) site as the oxygen content increases. Along this structural transition, C_V shows a large anomalous change while n_e is unchanged. These data may be interpreted to indicate that the oxygen vacancy plans an important role in Y 1:2:3 phase structures but the local electronic structure is related to superconductivity. In the Y 1:2:3 system, a structural phase transition is not induced by electrons, but by vacancy-type defects. The data further show that polycrystalline Y 1:2:3 is an orthorhombic structure with defects. With further increase in oxygen vacancy concentration and Sn-substitution concentration, Sn atoms must enter the Cu-O plane and occupy the Cu(2) site. By the balance of Cu with other elements, a big change in the Cu oxidation state and an increase of oxygen vacancy concentration both occur.

In conclusion, we have measured the positron lifetime in the $YBa_2Cu_3O_y$ system with Sn substitution for Cu with a large doping concentration (from 0 to 1.5). The positron-lifetime results show a strong dependence on the amount of Sn doping. We have also calculated the local electronic density n_e and vacancy concentration C_V as a function of Sn-substitution content x. We have demonstrated that n_e mainly reflects the local electron density in the Cu-O chain as the Cu(1) site is substituted by Sn, and C_V mainly reflects the oxygen vacancy concentra-
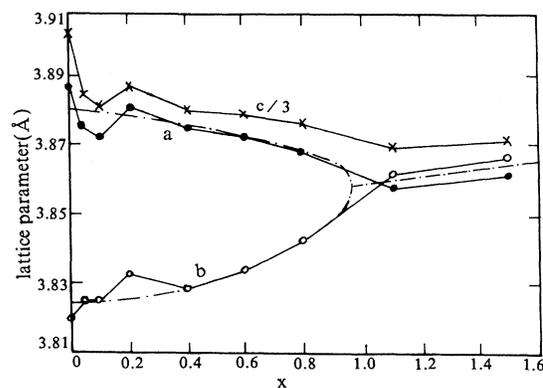

FIG. 4. Lattice parameters a, b, and c as a function of Sn-substitution content x in $YBa_2Cu_{3-x}Sn_xO_y$ systems.

tion. A change occurs in the Cu valence state in the Cu-O plane as the Cu(2) site is partly substituted by Sn. At the same time, n_e has an effect on high-T_c superconductivity but not on the O-T phase transition and C_V mainly determines the O-T phase transition. These observations may be explained by describing the Y 1:2:3 polycrystalline system as an orthorhombic structure with defects.

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