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Superconductivity without dependence on valence electron density in Zn doped YBCO systems*

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This paper reports that the $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ ($x = 0-0.4$) samples are researched by means of x-ray diffraction, calculations of binding energy, the positron experiments and variations of oxygen content. The results of simulated calculations, positron experiments and variations of oxygen content support the existence of cluster effect. Moreover, it is concluded that the cluster effect is an important factor on suppression of high-T_c cuprate superconductivity and the T_c does not depend on the density of valence electron directly.

Keywords: YBCO, simulated calculations, positron annihilation, cluster effect
PACC: 7410, 7165, 3120C, 3640B

1. Introduction

'The high-T_c superconductivity is on the list of the most profound physics problems ...'.[1] In order to search and comprehend such a problem, scholars have suggested many new theories and experimental technologies.[2−4] Especially, elemental substitution is an important means,[5−8] for example, copper is replaced by magnetic or nonmagnetic elements. According to the traditional theory of magnetic break-pair, the nonmagnetic ions doped into superconductors will suppress less the superconductivity than magnetic ions. However, Zn^{2+} doped in YBCO, a kind of nonmagnetic ion, suppresses forcefully the superconductivity. At present, most researchers believe that the superconducting phenomenon occurs on CuO_2 planes,[9−11] where Zn^{2+} ions substitute for Cu(2) sites. Hence, Zn doping will suppress noticeably the superconductivity.[12,13] Some scholars suggested that Zn doping destroys the background of antiferromagnetism on CuO_2 planes,[14] however, this proposal is still one of viewpoints of magnetic break-pair. Besides, what cause induces the transition temperature T_c such that it falls faster and faster with the increase of substituted concentration[15−19] and so on? Many queries are still unclear, and therefore, further investigations of theories and experiments are necessary in Zn doped YBCO.

In order to realize the distribution of Zn ions, we calculate the total defect energy and average binding energy inside a cluster by Islam's method,[20] the simulated results reveal the possibility of cluster effect. When the doped concentration increases, Zn ions combine into different clusters on CuO_2 planes and tend to form seven ions cluster as Double Square. Afterwards, we use positron annihilation technique (PAT) to probe the change of electron structure as Zn substitutes for Cu in YBCO. PAT plays an important role in investigation of such condensed matters as semiconductors, metal materials and high-T_c cuprates.[21−24] Some positron studies exhibit the properties of normal and superconducting states, such as the Fermi surface, O–T transition and the carrier concentration.[25−28] In recent years, Jean and Li *et al* reported many important results from positron experiments and theories concerning high-T_c superconducting mechanism.[15−18,27−29] In the present article, we will report the systematical investigation concerning $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ ($x = 0.0-0.4$) samples. The results of positron experiments and variations of oxygen content support the existence of cluster effect. Moreover, it is reasoned that cluster effects suppress the cuprate superconductivity as an important factor and the T_c variations do not depend on the density of va-

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lence electron directly.

2. Experiments

Samples of $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ ($x = 0 - 0.4$) were prepared by the same method in Ref.[12]. Due to the sensitivity of the PAT experiments, all samples were sintered in the same conditions in order to reduce the dispersion of the experimental results. The superconducting transition temperature T_c was measured by the standard DC four-probe method with a voltage resolution of 10^{-7}V (HP3457A). The crystal structures of samples were analysed by powder x-ray diffraction (XRD) (Cu Kα) using the D/max-BX-ray diffractometer. The positron lifetime spectra were measured by the ORTEC-100U fast-fast coincidence lifetime spectrometer. Two pieces of identical samples ($\Phi 13 \times 3$ mm) were sandwiched together with a 10-μC22 Na positron source deposited on a thin Mylar foil (about 1.2 mg/cm^2 thickness). We apply Pilot-U plastic flicker sensor, which was measured by ^{60}Co and showed the excellent time resolution over 220 ps. Each spectrum contains more than 1×10^6 counts to guarantee the sufficient statistic precision. After subtracting background and source contributions, the lifetime spectra were fitted with two-lifetime components by POSITRON-FIT-EXTENDED program with the best fit ($\chi^2 = 1.0-1.1$). The positron lifetime spectra of all samples were measured at the identical environment temperature (283 ± 1K), and the results were repeatable. Table 1 lists the main experimental results of Zn doped systems, including T_c, lattice parameters, positron annihilation parameters etc.

Table 1. The experimental results of the relative physical parameters and positron lifetime in Zn doped $YBa_2Cu_3O_{7-\delta}$ systems.

Zn-x	T_c/K	a/nm	b/nm	τ_1/ps	τ_2/ps	I_1/%
0.00	92.0	0.381304	0.387826	195±3.9	573±22	91.2±1.76
0.02	90.2	0.381348	0.388043	195±3.9	541±22	87.3±1.74
0.04	88.0	0.381522	0.388261	189±3.8	561±22	86.2±1.72
0.08	83.1	0.381609	0.388348	182±3.6	554±22	86.6±1.73
0.10	72.3	0.381739	0.388696	184±3.7	551±22	87.8±1.74
0.12	66.3	0.381804	0.388783	189±3.8	556±22	87.9±1.74
0.20	44.6	0.381826	0.388696	184±3.7	528±21	86.4±1.72
0.30	37.4	0.381739	0.389130	185±3.7	557±22	87.7±1.75
0.40	15.7	0.381739	0.389217	182±3.6	553±22	86.7±1.73

3. Results and discussions

3.1. Simulated calculations

In order to understand the characteristics of cluster structure, we perform simulated calculations by using the energy minimization principle and framework of Born model, in which the effective pairwise potentials represent the interatomic forces in the following form:[20]

$$\Phi_{ij} = \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r_{ij}} + A_{ij} \exp\left\{-\frac{r_{ij}}{\rho_{ij}}\right\} - \frac{C_{ij}}{r_{ij}^6}, \qquad (1)$$

where Φ_{ij} is the effective potential between ion i and ion j; Z_i and Z_j are ion valences; r_{ij} is the distance between ion i and ion j; A_{ij}, C_{ij} and ρ_{ij} are the relative character constants. The first term is the long-range Coulomb interaction, the remaining terms represent the short-range interaction and the shielded revision. Because charge equilibrium determines the ion coordination characteristics in clusters, the clusters should be neutral in electricity. The neutral clusters may show several structures, two of which are illustrated as (a) and (b) on CuO_2 planes in Fig.1. Here (a) as

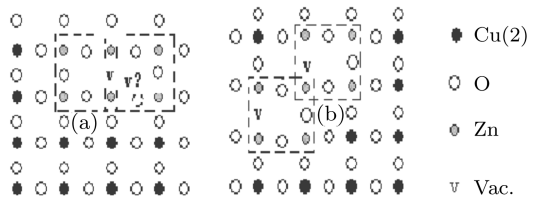


Fig.1. Zn doped ions enter Cu(2) sites on CuO_2 planes and combine into the ion clusters. (a) Hexamer, (b) Double Square, '?' indicates uncertainty.

Hexamer denotes six doped ions with two commonlateral squares, and (b) as double-square denotes

seven doped ions with two common-apical squares. On CuO_2 planes Cu ions are +2.25 valence, and doped Zn ions are +2, moreover holes exist on oxygen ions.[19,30] These two factors together make electrons lose, consequently, the oxygen ions have to decrease in order to keep the charge equilibrium. For example, in four doped ions cluster, every four Zn^{2+} ions may exclude an oxygen ion, which can be described as $\{4Zn^{2+} \rightarrow 4Cu^{2.25+}\text{–}O^{2-}\}$. Nevertheless, one Zn ion alone cannot exclude an oxygen ion. Hence, the binding energy of Zn^{2+} cluster is

$$E_{\rm bind} = E_{\rm b1}(4Zn^{2+} \rightarrow 4Cu^{2+} - O^{2-}) - 4E_{\rm b2}(Zn^{2+} \rightarrow Cu^{2.25+}) + E_{\rm b3}(O^{2-}), \quad (2)$$

where $E_{\rm b1}$, $E_{\rm b2}$ and $E_{\rm b3}$ are all represented by the formula of $E = \sum \Phi_{ij}$. The first term $E_{\rm b1}$ is the cluster total energy, $E_{\rm b2}$ is the binding energy that a Zn^{2+} substitutes for a $Cu^{2.25+}$ ion, and $E_{\rm b3}$ is the binding energy that an O^{2-} ion is lost. For Hexamer and Double Square, $E_{\rm bind}$ has similar formulation. The average binding energy of every doped ion is $E_{\rm mean} = E_{\rm bind}/N$, where N is the number of doped ions in a cluster. The calculation results are all listed in Table 2, in which the negative value of the binding energy indicates that the system is bound. It is well known, the larger average binding energy is, the more stable a cluster combines. Therefore, the doped ions should prefer to form the cluster with the largest average binding energy, that is, seven ions cluster.

Table 2. The total defect energy $E_{\rm b1}$ of Zn^{2+}—oxygen vacancies and the average binding energy $E_{\rm mean}$ of per ion on CuO_2 planes, here the negative value indicates the binding energy.

cluster structure	$E_{\rm b1}$/eV	$E_{\rm mean}$/(eV/ion)
dimer $\{2Zn^{2+} \rightarrow 2Cu^{2.25+}$ no $O^{2-}\}$	−31.15	−1.67
tetramer $\{4Zn^{2+} \rightarrow 4Cu^{2.25+} - O^{2-}\}$: collinear	−59.32	−1.49
tetramer$\{4Zn^{2+} \rightarrow 4Cu^{2.25+} - O^{2-}\}$: square	−60.91	−1.64
tetramer$\{4Zn^{2+} \rightarrow 4Cu^{2.25+} - O^{2-}\}$: zigzag	−59.03	−1.36
hexamer $\{6Zn^{2+} \rightarrow 6Cu^{2.25+} - 2O^{2-}\}$	−97.26	−1. 68
hexamer $\{6Zn^{2+} \rightarrow 6Cu^{2.25+} - O^{2-}\}$	−108.55	−1. 75
double square $\{7Zn^{2+} \rightarrow 7Cu^{2.25+} - 2O^{2}\}$	−122.97	−1. 78

3.2. XRD results and cuprate superconductivity

XRD results show that the undoped and low-doped Y-123 samples have the well single phase. As Zn doped concentration x increases, samples show slight impure phases at $x = 0.12$. By the least square method with powder XRD data, we calculate lattice parameter a and b, which increase slightly with the increase of x (Table 1), this is because Zn^{2+} radius (0.074 nm) is larger than Cu^{2+} radius (0.072 nm). However, O–T transition does not appear in $x = 0.0 - 0.4$, so Zn ions do not enter Cu(1) sites in Cu–O chains.[15−18,29,31] Generally, Zn doping should suppress strongly the superconductivity, which occurs since it is on CuO_2 planes. In fact, when $x = 0.0$, $T_{\rm c}$ is 92.0K, and at $x = 0.1$, $T_{\rm c}$ decreases to about 72.3K; for $x = 0.2$, $T_{\rm c}$ is 42.6K and $x = 0.4$, $T_{\rm c} = 15.7$K. Here the variation characteristics of $T_{\rm c}$ and the lattice parameters indicate that Zn ions enter mainly Cu(2) sites on CuO_2 planes, which is consistent with previous experimental results.[31−33]

3.3. Oxygen content variations

The inlet picture in Fig.2 shows the experimental results of oxygen content.[12] For little Zn doping, the oxygen content decreases slightly. With the increase of x, the oxygen content falls obviously. Such variation characteristics are consistent with the simulated calculations. According to the simulated results above, while a little Zn ions doping, the cluster does not yet form and Zn ions distribute randomly and individually. Although Zn^{2+} valence is lower than $Cu^{2.25+}$, the dispersed ions cannot extrude oxygen ions to achieve electric neutrality. Hence, there are hardly oxygen vacancies around Zn ions, accordingly, the oxygen content reduces a little. With the increase of x, Zn ions form clusters. Because Zn ions require less oxygen ions for coordination, the superfluous oxygen ions will be extruded from the clusters, therefore, oxygen vacancies would appear on CuO_2 planes, and then the oxygen content should descend noticeably. From the above analyses, we can conclude that cluster effect is indeed a factor that causes oxygen content to reduce

in Zn doped YBCO.

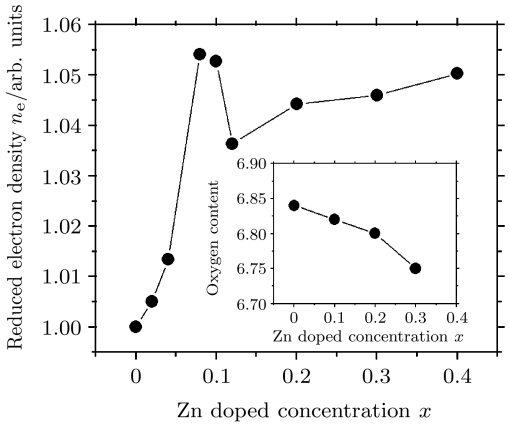


Fig.2. The reduced density of valence electron in Zn doped samples. The inlet picture indicates the oxygen content variation with x (Ref.[12]).

3.4. Positron experiments

Table 1 shows the PAT experimental results of Zn doped samples as well. We can see that the short lifetime τ_1 is 195ps at $x = 0.00$, then falls to the lowest value 182ps at $x = 0.08$, as x increases the τ_1 increases to 189ps and then reaches a saturation state. And the long lifetime τ_2 has the similar characteristics with τ_1. On the whole, the τ_1 and τ_2 show a falling trend. According to the model of two-state capture in condensed matters,[34] the process of positron annihilation is attributed to free-state annihilation and trapping-state annihilation. The positron lifetime is defined as the inverse of annihilation rate. The inverse of the former annihilation rate is the short lifetime parameter τ_1, the intensity I_1 denotes the proportion of free-state annihilation to total annihilation events. τ_1 reflects mainly the annihilation process in the perfect crystal lattices and can be used to detect the electron distribution of the inner microstructure. In addition, the inverse of the latter annihilation rate is the long lifetime τ_2, accordingly the intensity $I_2 = 1 - I_1$, τ_2 reflects mainly the process of positron captured in the imperfect areas inside the material, it can characterize the intrinsic structure and preparation quality of samples. If positrons annihilate in the imperfections, such as oxygen vacancy, twin boundary, dislocation, and cation vacancies, τ_2 will be larger, sometimes it is designated as τ_3, generally $\tau_3 > 800$ps.[35−37] Our samples do not contain τ_3 component, this indicates the credibility of the sample quality.

According to the characteristics of positron annihilation, local electron density $n_e = 1/(\pi r_o^2 c\tau_{bulk})$, where r_o is the classical electron radius, c is the velocity of light, and τ_{bulk} is the systematical lifetime parameter, it is defined as:

$$1/\tau_{bulk} = I_1/\tau_1 + I_2/\tau_2. \quad (3)$$

Some relational calculation results[38,39] show that about 90% positrons annihilate with the valence electrons, and only about 10% positrons annihilate with the electrons within the atomic kernel. These results indicate that the n_e amount is determined mainly by the valence electrons, so we may regard the density of valence electrons as the n_e without influence on the general conclusions. Figure 2 shows that the density of valence electrons changes with x. In a little Zn doping, the density ascends rapidly and then reaches maximum at $x = 0.08$. After the density shows a fluctuation and then keeps a high saturation, it can convincingly explain the rising of the density at the beginning. Nevertheless, these results cannot explain why the density shows the saturation phenomenon. In fact, in the beginning, while +2 valence ions enter CuO_2 planes, Zn^{2+} loses fewer electrons than $Cu^{2.25+}$, so the density rises. However, as x increases, the Zn ions begin to form clusters. As mentioned before, every four Zn^{2+} will extrude an O^- (including a hole) which carries away two valance electrons, so the density begins to fall. When the rising and falling of the density reach a balance, then the density tends to high saturation. As a result, the cluster effect influences obviously the variation characteristics of the density too.

3.5. Valence electron density and the T_c of cuprates

Figure 3 shows the relationship between the T_c of samples and the density of valence electrons. In the beginning stage, the density raises from 5.750 to 5.825, the T_c descends slightly. When the density exhibits sharp fluctuation, the T_c starts to drop sharply, namely, the T_c turning point occurs in the fluctuation region of the density, where the impure phases appear significantly. Then T_c seems to lose the association with the density, specifically, when T_c drops from 72.3K to 15.7K, the density only slightly increases. In fact, when x is a little, Zn ions enter the crystal lattice individually, Zn^{2+} loses fewer electrons than $Cu^{2.25+}$,

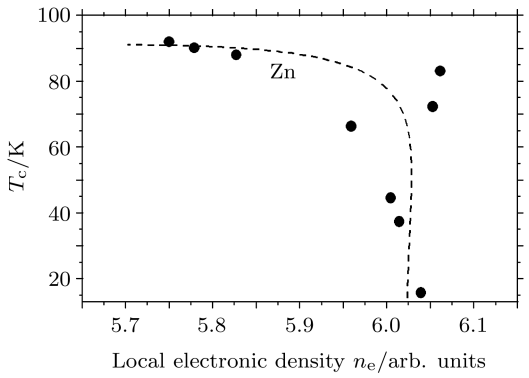


Fig.3. The relation between the density of valence electron and the T_c of cuprates.

so the density will increase. However, the T_c descends slightly with the increase of density, because the dispersed ions may not destroy the crystal lattice. While in the fluctuation region of the density, the T_c starts to drop sharply with the appearance of clusters. The stronger cluster effect will distort the structures of crystal lattice, which directly influence the pairing and transportation of carriers, and thus the superconductivity is suppressed markedly. Furthermore, with more and more clusters forming, not only the density reaches saturation, but also the pairing and transportation of carriers are badly influenced, thus, the T_c drops swiftly. On all accounts, when the density increases evidently, the T_c only alters slightly, on the contrary, while the T_c falls dramatically, the density hardly changes. As a result, we can conclude that the T_c has no direct relationship with the density. However, the cluster effect starts to strengthen gradually in the fluctuation region of the density, the T_c falls noticeably. Therefore, the cluster effect is an important factor that suppresses the cuprate superconductivity.

4. Conclusions

The high-T_c cuprates YBa_2Cu_{3-x} $Zn_xO_{7-\delta}$ ($x = 0.0-0.4$) have been analysed and studied systemically by means of XRD, positron annihilation technique, oxygen content and calculations of binding energy. XRD patterns indicate that the lattice parameters a and b of the samples increase slightly as the Zn concentration increases because Zn^{2+} radius is larger than Cu^{2+}. As the O–T transition does not appear, the Zn ions substitute mainly into Cu(2) sites. In conclusion, simulated calculations reveal that Zn ions tend to form seven ions cluster on CuO_2 planes, and the variations of oxygen content and positron experiments support the existence of cluster effect. Especially, it is reasoned that the cluster effect is an important factor on suppresses of high-T_c cuprate superconductivity and the T_c has no direct relationship with the density of valence electrons.

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