Journal of Univ of Sci and Tech Beijing
1997, Vol 4, No 1:54

Strong Localization Effect of Oxygen Deficiency on Carriers in Tl Based Superconductors

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(Received 1996-02-24)

Abstract: Investigation on the effect of Fe-doped Tl-1223 superconductors has been carried out by the simultaneous measurements of the spectra of positron annihilation lifetime and Doppler broadening of position annihilation, together with the measurement of Hall coefficient. The results of samples with different doping level show that the occupation of Fe atoms on Cu sites results in a linear decrement of superconducting transition temperature. The electron concentration in Cu-O layer has been enhanced by Fe doping. The difference in valence between Fe^{3+} and Cu^{2+} induces extra oxygen into the lattice and forms the extra oxygen defects. This Fe dopant leads to a strong localization of the electrons in the Cu-O layer. So the decrement of the concentration of the itinerant electrons results in a decline of the superconducting transition temperature.

Key words: positron annihilation, Tl based superconductors, oxygen defect

The structural defects in oxide superconductors and the arrangement of the defects strongly affect the superconducting properties. Due to the short coherence length of the cuprate superconductors, any small structural change in the Cu-O layers, which induced by various doping would results in an effect on their superconducting properties[1,2]. The impurity of 3d elements in the oxide superconductors changes the structure and configuration of the Cu-O layer as well as the effective valence of the Cu-O layer. The structural defect induced by doping will also change the carries concentration and the antiferromagnetic exchange interaction[3]. It is important to study the roles of the impurity of 3d elements on the superconducting properties, especially, the localization of the itinerant electrons in the Cu-O layers. In this paper, we report our results of the effect of Fe impurity on the extra oxygen defect of Tl-based superconductors studied by Hall effect measurement and positron annihilation technique.

1 Experiments

Samples with nominal composition $(Tl_{0.5}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2(Cu_{1-x}Fe_x)_3O_{9+y}$ (x=0.0, 0.01, 0.02, 0.03, 0.04, 0.05) were prepared by an ordinary solid-state reaction method. Appropriate amounts of $SrCO_3$, $BaCO_3$, CuO and $CaCO_3$ were mixed with an agate mortar and calcined at 890 ℃ for 24 h to form (Sr, Ba)-Ca-Cu-O as parent phase. The calcined powders were mixed with Tl_2O_3, PbO and Fe_2O_3 by a agate mortar again and were pressed into pellets (ϕ15 mm × 2 mm), and sintered at 940 ℃ for 10 h in oxygen. Finally the furnace cooled.

All samples were characterized by X-ray diffraction, AC magnetic susceptibility and DC resistivity measurements. The powder X-ray diffraction pattern for Cu K_α radiation were measured by a Rigaku rotating anode X-ray diffractometor of D/Max-RB. As a measure of the diamagnetic susceptibility, mutual inductance of bulk samples were measured using an AC Hartshow bridge. Resistivity measurements were accomplished utilized an ordinary four-probe method. The measuring current was 10 mA. The Hall coefficient was measured by an ordinary Hall coefficientometor. The measuring current was 100 mA, a 2T magnetic field was used.

For the samples with various Fe contents, the lifetime spectrum and Doppler-broadened radiation spectrum are simultaneously measured. A ^{22}Na source with an activity of about 3×10^4 Bq is deposited on Capton foils, it is confined in the center of the samples. The lifetime spectra are obtained in an ORTEC fast-fast coincidence system using a BaF_2 detector with timing resolution of 220 ps. The Doppler-broadened line-shape measurements are carried out using a Canberra intrinsic germanium detector with an energy resolution of 1.4 keV at the 497 keV radiation from ^{103}Ru. The resolution of the positron annihilation spectrometers are better than 220 ps. Total counts for each spectrum is about 10^6. The measurement is repeated for three times, and results are with high repeatability.

2 Results and discussions

2.1 Transport properties measurement

The X-ray diffraction spectra of different Tl-1223 samples with various Fe doping have no obvious difference. The main diffraction peaks can be indexed on the basis of the tetragonal unit cell with $a \approx 0.384$ nm and $c \approx 1.534$ nm, except some small peaks from minority phase ($BaPbO_2$). For low doping density ($x < 5\%$), no obvious changes of crystal structure or structural phase transition were observed.

Fig. 1(a) shows that the superconducting transition temperatures decrease linearly from 122 to 85 K as the Fe content x increasing from 0 to 0.05. The observed superconducting transition width also increases with the increasing of Fe doping. This linear relationship between the transition temperature T_{CO} and the Fe content x reflects the structural and intrinsic physical properties of this system. The replacement of trivalent Fe ion for bivalent copper ion directly destroys the perfection of Cu-O layer, which reduces the carrier density due to $3d$-$2p$ hybridization. It is also possible that trivalent Fe ion enters the lattice after absorbing extra oxygen, bringing structural defects and distortion. These defects and distortion are possibly point defects. However, because of the small coherence length of oxide-superconductors, the local binding effect of small size structural defects on the Cu-O layers would be very important on the superconducting properties.

The measurements of Hall coefficient show that, similar to Tl-2223 phase[4], the carriers in Tl-1223 phase are also as hole type. The Hall coefficient of $(Tl_{0.5}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2(Cu_{1-x}Fe_x)_3O_{9+y}$ (x=0), R_H= 3.35×10^{-9} m^3/C, which is close to the reported value for Tl-2223 phase.

Fig. 1(b) shows that the Hall coefficient monotonously increases with enhanced doping level of Fe. Since the Hall carrier concentration have the relation of $n_H=(1/R_H) \cdot e$, it can be seen that the Hall carriers concentration decreases with increasing doping level of Fe, showing the decrement of transition temperature T_{CO} depending on carrier concentration. It is thus suggested that the decrement of carrier concentration due to Fe doping is one of the key factors which cause the decline of superconductivity of this system.

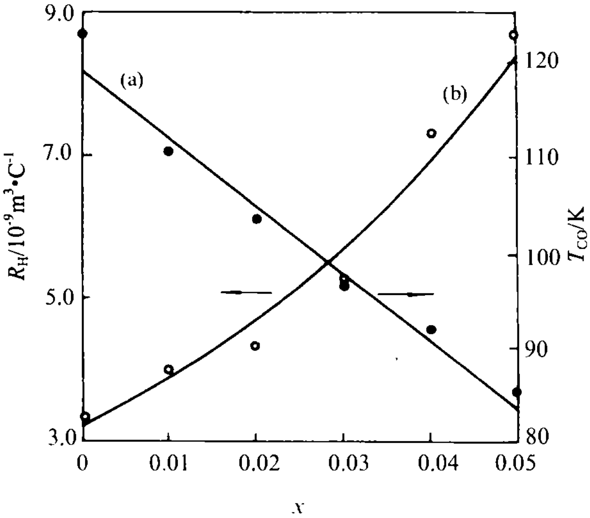

Fig.1 Superconducting transition temperature T_{CO} and Hall coefficient R_H vs Fe content x for $(Tl_{0.5}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2(Cu_{1-x}Fe_x)_3O_{9+y}$

2.2 Positron annihilation characteristics of Tl-2223 phase

(1) The positron lifetime spectra

The interpretation of positron lifetime spectra is based on so called two level trapping model as often used in the literature. The oxide superconductors are oxygen deficient layered perovskites. Their superconductivity is realized by introducing proper amount of carriers into the antiferromagnetie insulators via doping. There are different kinds of defects in oxide superconductors, for example, the disorder of Sr in $La_{2-x}Sr_xCuO_4$, the oxygen deficiency in Y-system superconductors and the incommensurable modulating structure in Bi-O layer for Bi-system superconductors. Therefore various positron lifetimes must exist in oxide superconductors. For simplicity, in this work we only use a two level trapping model[5,6].

D. Singh et al used a LAPW (the general potential lineared augmented plane wave) method to calculate the positron density distribution (PDD) in different oxide-superconductors[7]. Their result shows that positron annihilation prefers to be close to Cu-O layer in Tl-2212 superconductors.

C. S. Sundar, et al[8] also calculated the positron density distribution in Tl-2212 and Tl-2223 superconductors and also showed that PDD is concentrated between Cu-O layer and Ca layer. Considering the similarity of the structures it can be thought that the PDD in Tl-1223 is the same as in Tl-2223. In the lifetime spectra the short lifetime τ_1, which has a higher percentage presents the main annihilation characterization of positrons in Cu-O layers. The longer lifetime τ_2 shows means effect of the structural defects and other trapping states.

The experimentally measured spectra can be treated as two independent components τ_1 and τ_2. τ_1, τ_2 and their strength I_1, I_2 can be obtained by fitting the experimentally measured spectra. The mean life time τ_m is also a main parameter to characterize the properties of positron annihilation and is defined as:

$$\tau_m = I_1\tau_1 + I_2\tau_2 \tag{1}$$

Many investigations show that the value of mean lifetime has a general certainty, which is hardly affected by the detail of the lifetime spectra.

The PATFIT-88 program has been used to fit the room temperature lifetime spectra for samples with various Fe doping. Correction has been made for the annihilation in the source foil. Fig. 2 and Fig. 3 show the curves of τ_1 and I_1 versus Fe content x, and τ_2, I_2 versus x respectively.

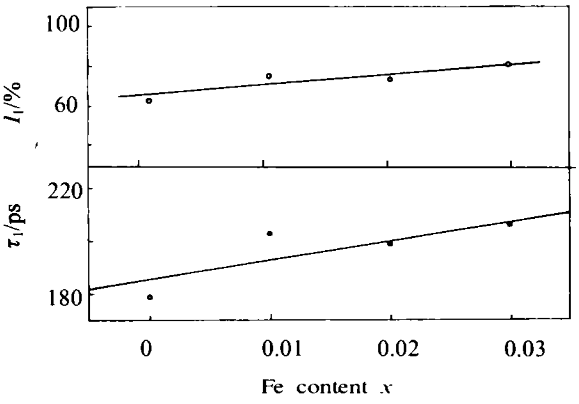

Fig.2 Short lifetime τ_1 and its intensity I_1 vs Fe content

It can be seen that the short lifetime τ_1 and its intensity I_1 almost linearly increase with increasing Fe content x. The increment of I_1 shows a increasing electron density in the Cu-O layer. The replacement of trivalent Fe ion for bivalence copper ion induces more electrons into the Cu-O layer. The increment of τ_1 reflects the enhance of the localization of the electrons which were induced into the Cu-O layer. The reason for this is that the trivalent Fe ions possibly absorb extra oxygen into the crystal lattice. This forms a oxygen deficiency and leads to the localization of electron.

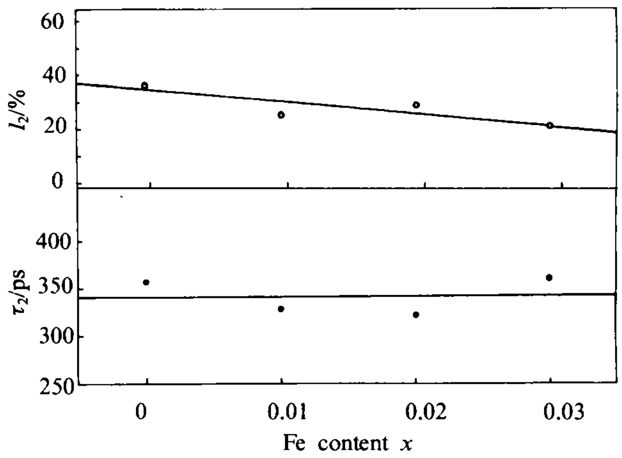

Fig.3 Long lifetime τ_2 and its intensity I_2 vs Fe content

The curve of the mean lifetime τ_m versus the Fe content x is shown in Fig. 4. The mean lifetime τ_m decreases with increasing x. This shows that the electron density in the Cu-O layer has been increased. However, these increased electrons are strongly localized by the extra oxygen deficiency. Therefore the carries density in the conducting layer has been reduced. This is consistent with the result of Hall coefficient measurements. The longer lifetime τ_2 has no obvious change with x because of the electrons induced by Fe doping are localized by extra oxygen.

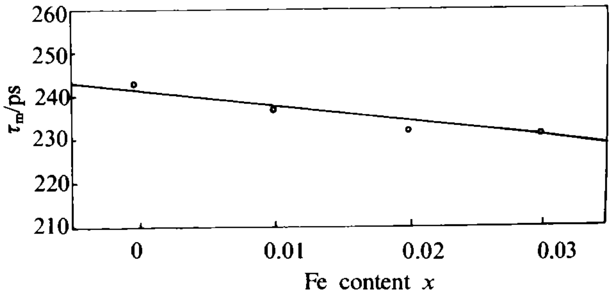

Fig.4 Mean lifetime τ_m vs Fe content x

(2) Doppler broadening

Typical parameters describing the line shape of the Doppler broadening spectrum are S, W and S/W. If the total area below the line in Fig. 5 is Δ and those of the shaded area are A, B and C respective--ly, the parameters can be then defined as:

$$\begin{cases} S = A / \Delta \\ W = (B + C) / \Delta \\ S / W = A / (B + C) \end{cases} \tag{2}$$

where, *S* is for the changes of low momentum electrons (conduction electrons), *W* for the high momentum electrons (inner-shell electrons), *S/W* for the overall changes of the annihilation rate of both electrons. Usually *S* value is chosen as about 0.5 for better statistics. The measured *S/W* values of all samples are shown in Fig. 6. It can be clearly seen that *S/W* value of Iron dopped samples are markedly lower than that without doping (x=0). This can be interpreted as the redistribution of the momentum density of the electrons due to Fe ions occupying the sites of Cu ions, which leads to a decrement of the density of conducting electrons and a increment of localized electrons, or the localization of conduction electrons

The room temperature positron annihilation spectra of $(Tl_{0.5}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2(Cu_{1-x}Fe_x)_3O_{9+y}$ shows that the occupation of Cu sites by a few Fe ions will increase the electron density of the conduction Cu-O layer and the extra oxygen will enhance the localization of the conduction electrons. These will eventually affect the band structure and the inter-layer coupling, leading to damage to the superconductivity of the material.

The increment of I_1 in Tl-1223 indicates the increment of electron density of Cu-O layer and the increment of τ_1 reflects the enhancement of the localization of such electrons. The decrease of the mean lifetime τ_m and the *S/W* value along with the increment of Fe composition x also show that the increasing of electron density is originated from low momentum electrons.

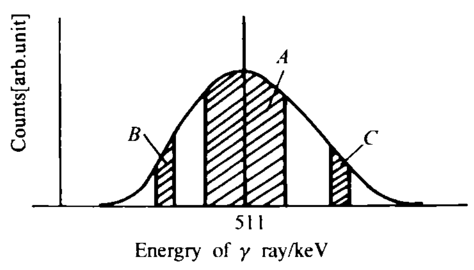

Fig.5 Definition of the parameters describing the line of the Dopper spectrum

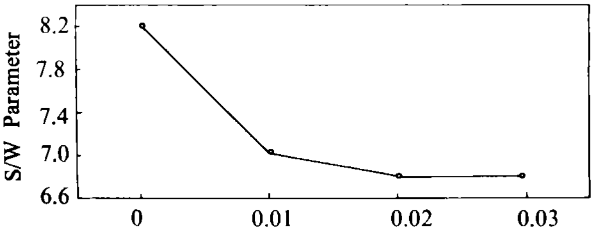

Fig.6 Parameter S/W vs Fe content x

The above results are consistent with the results of room temperature Mossbäuer spectra. The increasing of trivalent Fe ion doping level will enhance the interaction between high momentum d_{xy}, d_{yz} electrons and the π-bond of O^{2-} resulting in the decrease of *S/W* value. At the same time the weakening of the screen effect against inner-shell *S* electrons will reduce the isomer shift. The above effects will enhance the rigidity of the lattice and restrain possible softening, which might be one of the main reasons for its superconductivity being restrained.

4 Conclusion

The experimental results of Hall coefficient measurements and positron annihilation spectra of $(Tl_{0.5}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2(Cu_{1-x}Fe_x)_3O_{9+y}$ samples indicate that the occupation of a few Fe atoms on the sites of Cu not only damages the perfection of the CuO_2 plane but also reduces the superconducting transition temperatures. The doping of Fe impurity induces extra oxygen atoms into lattice and leads to a strong localized binding, resulting in a decrease of carrier concentration with increasing doping level. The increment of electron density of Cu-O layer and the enhancement of the localization of conductive electrons will affect its band structure and the inter-layer coupling and will eventually leads to the damage of its superconductivity.

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