# Structural instability in the Bi(Pb)-Sr-Ca-Cu-O superconductor between 80 and 300 K studied by positron annihilation

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# Structural instability in the Bi(Pb)–Sr–Ca–Cu–O superconductor between 80 and 300 K studied by positron annihilation

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**Abstract.** We have measured the positron lifetime as a function of temperature from 80 to 300 K for the Bi(Pb)–Sr–Ca–Cu–O superconductor (the Bi(Pb)2:2:2:3 phase). We have observed that the positron lifetime results display three narrow valleys near 120, 140 and 160 K and two wide valleys near 240 and 270 K. The anomaly in the positron lifetime indicates the structural instability of the Bi2:2:2:3 superconductor in the normal state, which may be caused by structural changes, such as the softening of the lattice, or the motion of vacancies in Bi–O layers. We have also carried out positron lifetime measurements as a function of temperature from 80 to 180 K in the Bi2:2:1:2 superconductor; on comparison with the results for the Bi(Pb)2:2:2:3 system, we found that adding Pb impurities can stabilize the Bi2:2:2:3 phase.

## 1. Introduction

Investigation of the structural instability of high-$T_c$ superconductors is a very important subject today. Different physical probes [1,2], such as ultrasonic measurement, x-ray diffraction, specific heat and infrared absorption have been employed. These studies will be helpful in the understanding of the superconducting mechanism in cuprate superconductors.

Positron annihilation spectroscopy is an established experimental method for an electronic structure and defect study of solids. A number of positron experiments [3] have indicated that positron annihilation parameters are sensitive to the structural instabilities around and above $T_c$ in high-$T_c$ superconductors. In previous experiments, samples have often been Bi-based 2:2:1:2 phase or mixed-phase superconductors. In this paper, we present new results of positron lifetime measurements as a function of temperature from 80 to 300 K for Bi(Pb)–Sr–Ca–Cu–O (Bi2:2:2:3) superconductors and discuss the effect of adding Pb impurities.

## 2. Experiments

The $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{8+\delta}$ sintered samples used in the experiments were prepared by solid state reaction in air starting with mixing the appropriate amounts

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of high-purity $Bi_2O_3$, PbO, $SrCO_3$, $CaCO_3$ and CuO powders. The samples were pressed into two discs of 15 mm diameter and 1.5 mm thickness. The superconducting transition temperature $T_c$ was determined to be 109.6 K.

Positron lifetime measurements were carried out using a fast–fast coincidence spectrometer; the time resolution was determined to be 245 ps using a $^{60}$Co source. A 30 $\mu$Ci $^{22}$Na positron source was deposited on a 2 $\mu$m Ni foil and sandwiched between two pieces of identical samples. For the temperature experiment, the sample was attached to the cold head of a liquid-nitrogen cryostat with automatic control of the temperature to better than ±0.2 K over the operating range from 80 to 300 K. The experiment was performed from low to high temperature and repeated. The temperature interval is 4–5 K. Each spectrum contained $10^6$ counts and was analysed using the PATFIT program [4].

## 3. Results and discussion

We measured the positron lifetime spectra as a function of temperature from 80 to 300 K for the Bi(Pb)2:2:2:3 system. The results were best fitted to two exponential components with a variance of fit of less than 1.10 after subtracting a positron source correction (7%) for the 2 $\mu$m Ni foils. Using the experimental results and trapping model, the bulk lifetime $\tau_b$ $(= (I_1/\tau_1 + I_2/\tau_2)^{-1})$ was evaluated to be about 210 ps, which is a little less than the theoretically calculated value of 228 ps for Bi2:2:1:2 [5]. In our experiment, the lifetime $\tau_1$ of the short-lived component and the bulk lifetime $\tau_b$ *are not sensitive to changes in the temperature; the lifetime component* $\tau_1$ is about 197 ps with $I_1 \simeq 82\%$. The second lifetime component $\tau_2$ can be attributed to positron annihilation in the region of lower electron density, e.g. the defect and imperfection regions of crystals. This lifetime component $\tau_2$ is very sensitive to the change in electron density distribution in the sample.

### 3.1. *Structural instability*

The results of the positron lifetime $\tau_2$ as a function of temperature from 80 to 300 K are shown in figure 1; figure 2 presents detailed information about the variation in $\tau_2$ with temperature from 80 to 180 K.

From the variation in $\tau_2$, we have the following observations.

(1) The average value of $\tau_2$ between 80 and 180 K is about 305 ps and, from 180 to 300 K, the values of positron lifetime tend to increase.

(2) Above $T_c$, the positron lifetime data have three narrow valleys near 120, 140 and 160 K with a width of about 10 K (the differences from the average value are about 10 ps) and two wide valleys near 240 and 270 K with a width of about 25 K (the differences from the average value are about 20 ps).

The structural instability of high-$T_c$ superconductors has been extensively studied by various methods. The soft-mode-induced structural instability observed in the $La_{2-x}Sr_xCuO_4$ system was theoretically studied using an electron–phonon interaction model [6]. For the Bi2:2:1:2 superconductor, the anomalous behaviours near 120, 150 and 250 K have been reported in several experimental studies [2, 3]. For the Bi(Pb)2:2:2:3 sample, the structural instability near 140, 160 and 270 K was first observed in our positron lifetime measurements. Our experimental results show that the anomalous valleys are narrow in the low-temperature region and wide in the

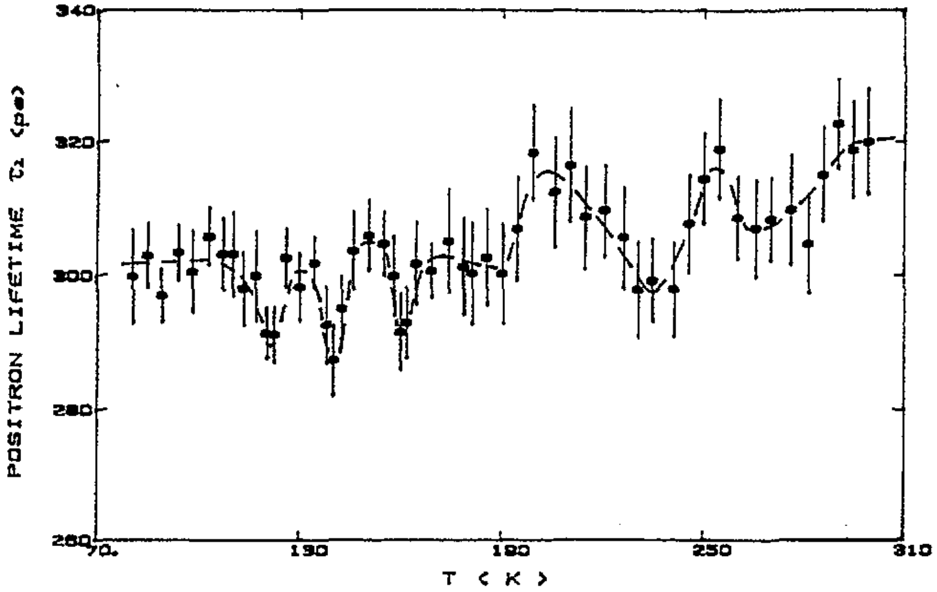

**Figure 1.** The temperature dependence of the positron lifetime $\tau_2$ from 80 to 300 K for the Bi(Pb)2:2:2:3 sample.

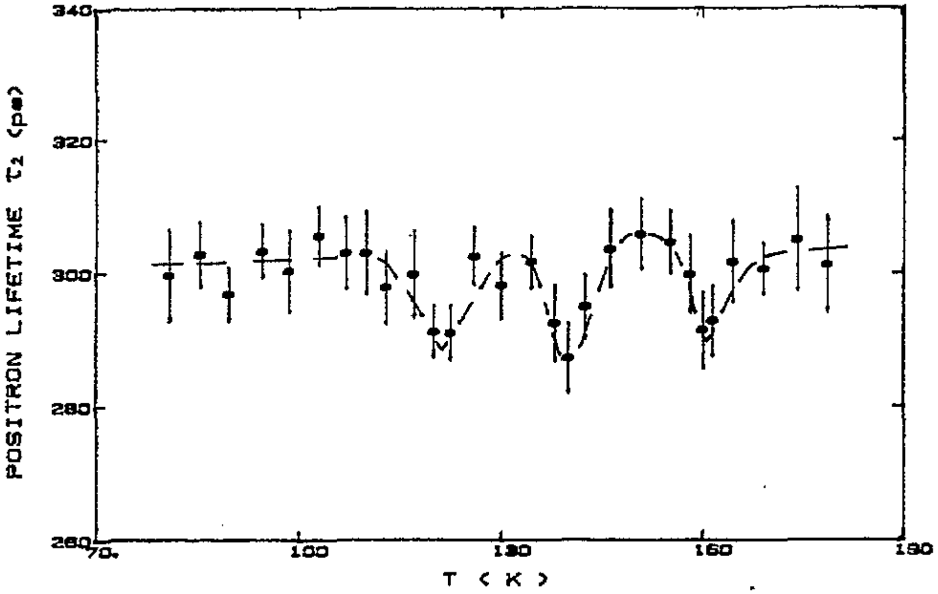

**Figure 2.** The temperature dependence of the positron lifetime $\tau_2$ from 80 to 180 K for the Bi(Pb)2:2:2:3 sample.

high-temperature region, which is consistent with the ultrasonic measurement results [2].

In order to understand our positron results we should know the sites where the positron annihilates. The positron lifetime $\tau$ is defined as an inverse of the overlap integral of the positron density $\rho_+$ and the electron density $\rho_-$:

$$1/\tau \simeq \pi r_e^2 c \int \rho_+(r)\rho_-(r)\,\mathrm{d}r^3.$$

The positron density distribution in the Bi2:2:1:2 system has been studied by McMullen *et al* [7]. The calculated results show that the positron density is greatest between the Bi–O planes and extends up towards the Cu–O plane; aside from the large Bi atom, the metal ion vacancies can bind positrons weakly, but oxygen defects cannot bind positrons; any experimental temperature dependence associated with trapping at point defects will arise from weak binding to the metal ion vacancies. We therefore suggest that the decrease in the positron lifetime $\tau_2$ is due to the increase in the electron density at Bi–O layers. The increase in the electron density may be caused by some structural instabilities, such as the motion of vacancies at Bi–O layers and the softening of the lattice which will change the average ion position at the Bi–O layer and consequently lead to changes in the electron density and metal ion vacancy binding.

### 3.2. *Effect of adding Pb impurities*

In order to study the effect of adding Pb impurities, we have also carried out positron lifetime measurements at room temperature and as a function of temperature from 80 to 180 K for the Bi2:2:1:2 superconductor sample. The positron lifetime results at room temperature are summarized in table 1.

**Table 1.** The $\tau_2$ and $\tau_b$ results for Bi(Pb)2:2:2:3 and Bi2:2:1:2 at room temperature.

| Sample | $\tau_2$ (ps) | $\tau_b$ (ps) |
|---|---|---|
| Bi(Pb)2:2:2:3 | 316 ± 12 | 209 ± 2 |
| Bi2:2:1:2 | 333 ± 8 | 230 ± 2 |

From table 1, a significant feature can be seen, namely the lifetime component $\tau_2$ and the bulk lifetime $\tau_b$ in the Bi(Pb)2:2:2:3 system are shorter than in the Bi2:2:1:2 system. As mentioned above, the calculated results [6] indicate that the positron density is greatest between the Bi–O planes, and the positron is largely localized in the vicinity of the metal ion vacancies, which may account for the relatively large lifetime change. In the Bi(Pb)2:2:2:3 superconductor, Pb atoms mainly occupy sites of Bi atoms at Bi–O layers, and the radius of Pb is larger than that of Bi; so adding Pb impurities will increase the positron annihilaton rate with core electrons, which can cause a decrease in positron lifetimes. This is also consistent with lifetime values reported for the pure metals Pb (214 ps) and Bi (248 ps) [7].

The results on the lifetime $\tau_2$ between 80 and 180 K for the Bi2:2:1:2 sample are shown in figure 3. These results are in close agreement with those of Sundar *et al* [5]. In their experiment, the positron lifetime $\tau_2$ was independent of temperature; we also cannot find valleys similar to those in figure 1 in the temperature range from 80 to 180 K. It is noteworthy that the variations in the lifetime $\tau_2$ for the Bi2:2:1:2 sample are more irregular than those for the Bi(Pb)2:2:2:3 sample, and the range of lifetimes $\tau_2$ for the Bi2:2:1:2 sample is about 40 ps, which is larger than that for the Bi2:2:2:3 sample between 80 and 180 K (in this case, the range of $\tau_2$ is about 20 ps). This is because the Bi-based superconductor has a complex modulated structure; the Bi2:2:1:2 sample is *not* a pure Bi2:2:1:2 phase superconductor but the Bi(Pb)2:2:2:3 sample is almost a pure Bi2:2:2:3 phase superconductor. Therefore, it is evident that adding Pb impurities can stabilize the 2:2:2:3 phase.

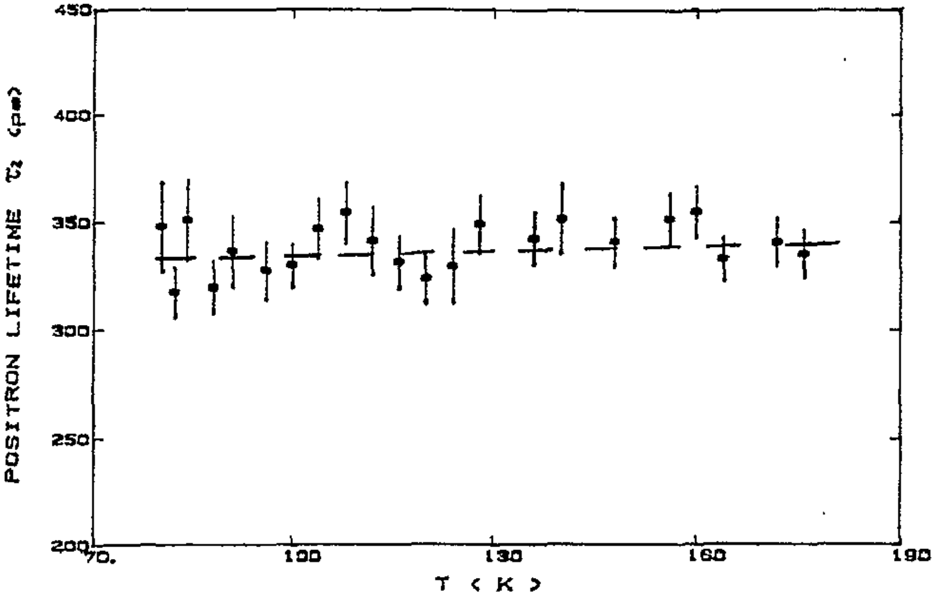

**Figure 3.** The temperature dependence of the positron lifetime $\tau_2$ from 80 to 180 K for the Bi2:2:1:2 sample.

Further positron lifetime measurements in a temperature range below 80 K are suggested so that more structural information on cuprate superconductors can be obtained.

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## References

[1] He Y S, Xiang J and Wang X 1989 *Progress in High Temperature Superconductivity* vol 22, ed Z X Zhao, G J Cui and R S Han (Singapore: World Scientific) p 332

[2] Wang Y N, Wu J, Zhu J S, Shen H M, Zhang J Z, Yan Y F and Zhao Z X 1989 *Progress in High Temperature Superconductivity* vol 22, ed Z X Zhao, G J Cui and R S Han (Singapore: World Scientific) p 426

[3] Wang S J, Naidu S V, Sharma S C, De D K, Jeong D Y, Black T D, Kirchene S, Reynolds J R and Owens J M 1988 *Phys. Rev.* B 37 603

Wang S J, Li X H, Chen Y L, Li S Q, Feng G H, Wang Z, Chen A and Li B R 1989 *Phys. Status Solidi* a **114** 273

Wang S J, Chen Y L, Li S Q, Feng G H, Wang Z and Chen L Q 1990 *Kexue Tongbao* **35** 1298 (in Chinese)

[4] Kirkegaad P and Eldrup M 1974 *Comput. Phys. Commun.* 7 401

[5] Sundar C S, Bharathi A, Ching W Y, Jean Y C, Hor P H, Meng R L, Huang Z J and Chu C W 1991 *Phys. Rev.* B **43** 13019

[6] Bussmann-Holder A, Migliori A, Fisk Z, Sarrao J L, Leisure R G and Cheong S W 1991 *Phys. Rev. Lett.* **67** 512

[7] McMullen T, Jena P, Khanna S N, Li Y and Jensen K O 1991 *Phys. Rev.* B **43** 10422

[8] Mackenzie I K 1983 *Positron Solid State Physics* ed W Brandt and A Dupasquier (Amsterdam: North-Holland) p 200