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POSITRON ANNIHILATION STUDY ON Y-Ba-Cu-O HIGH T_c SUPERCONDUCTORS

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A.G. Balogh, L. Liszkay, W. Puff, B. Molnár: Positron annihilation study on Y-Ba-Cu-O high T_c superconductors. KFKI-1987-49/E

ABSTRACT

First positron annihilation measurements are reported on high T_c superconductor $YBa_2Cu_3O_{7-x}$. The lifetime and Doppler broadening spectra show a slight but significant change about 240K suggesting a deviation from the normal structure far above 90K where the resistance falls to zero.

А.Г.Балог, Л.Лискаи, В.Пуф, Б.Молнар: Исследование аннигиляции позитронов в высокотемпературном сверхпроводящем веществе Y-Ba-Cu-O. KFKI-1987-49/E

АННОТАЦИЯ

Впревые в литературе опубликовываются результаты исследований аннигиляции позитронов в высокотемпературном сверхпроводящем веществе $YBa_2Cu_3O_{7-x}$. Наблюдаемые при 240К малые,но значимые изменения спектров времени жизни и доплеровского расширения обосновывают предположения о том, что отклонения от нормальной структуры появляются намного выше температуры 90 К, при которой сопротивление падает до нуля.

Balogh A.G., Liszkay L., Puff, W., Molnár B.: Pozitronannihilációs vizsgálatok magas hőmérsékletű Y-Ba-Cu-O szupravezetőn. KFKI-1987-49/E

KIVONAT

Pozitronannihilációs méréseket végeztünk - a szakirodalomban elsőként - magas hőmérsékletű $YBa_2Cu_3O_{7-x}$ szupravezető anyagon. Az élettartam és a Doppler spektrumok kismértékű, de szignifikáns változása 240 K környékén azt sugallja, hogy a szupravezető átmenet már jóval 90 K fölött, ahol az ellenállás értéke zérussá válik, megkezdődik.

First detailed positron annihilation measurements are reported on high T_c superconductor $YBa_2Cu_3O_{7-x}$. The lifetime and Doppler broadening spectra show a slight but significant change about 240 K suggesting a deviation from the normal structure far above 90 K where the resistance falls to zero.

The third generation of superconductors after some metals and alloys (T_c^{max}(Pb)≈7.22 K) and the A_3B intermetallic compounds [1,2] (where A=Nb,V;B=Si,Ge,Sn,Ga and T_c^{max}(Nb_3Ge)≈23.2 K), shows a transition temperature of about 90 K exceeding the liquid nitrogen temperature and making the technical utilization of the superconductors more attractive.

The BCS theory [3], which was one of the best developed theory in the physics, is not perfectly adequate for the new oxide ceramics, where the mean distance of the Cooper pairs is shorter, the interaction between the two electrons is stronger than earlier. Therefore beside the phonon-electron interaction new terms are necessary to describe satisfactorily the high temperature superconductivity of these compounds. After the first publications [4-6] it seems to be clear that the Cu-O planes/chains take place at the superconductivity and so far the O-vacancies and/or the charge state of the Cu atoms play an important role. While the positron annihilation method has a unique sensitivity for vacancy-like defects and reflects properly the change of the electron density it seemed to be straightforward to perform some positron annihilation measurement to clear up the properties of this new superconductors about the transition temperature.

Samples were prepared* from Y_2O_3, $BaCO_3$ and CuO by mixing and heating at 950 °C for 2h in air. After pressing into pellets at 7.5 t/cm^2 their were reheated to 1000 °C for 2h in oxygen flow for sintering and cooled down slowly during 3h.

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*Samples were prepared by Drs. B. Molnar, L. Bottyan and Mr. F. Gazdacska, Nucl. Phys. Dept., CRIP, Hungary

The temperature dependent resistivity measurements showed a transition temperature (T_c) of about 92 K [7]. The neutron diffraction measurements verified the orthorombic structure, which is typical for superconducting materials in the case of $x>6.5$ (mixed valence state) [8]. Cooling down to liquid nitrogen temperature the samples showed the Meissner effect holding a Co-Sm magnet of 45 mg in floating some 2 mm above the surface.

On a pair of $YBa_2Cu_3O_{7-x}$ samples positron lifetime and Doppler broadening measurements were performed between RT and 80 K. Lifetime spectra were measured with a spectrometer having a time resolution of 270 ps full width at half maximum. Each spectrum contained $6x10^6$ counts accumulated over a 20h period. The positron source was rather strong, 35 µCi of $^{22}NaCl$, and was deposited on a 5 µm thick Al foil. The source correction was determined to consist of a 251 ps component with 6.6% intensity and a 450 ps component amounting to 2.0%. Numerical analysis was performed by the programme described in Ref. 9.

The solid state detector, applied for the Doppler broadening measurements, was a HP-Ge coaxial detector with an energy resolution of 1.18 keV at the 497 keV ^{103}Ru γ-line. The spectrometer was digitally stabilized (zero and gain) using ^{7}Be and ^{207}Bi, and spectra were accumulated to about $8x10^6$ counts in the annihilation spectrum.

Lifetime and Doppler broadening measurements were repeated several times by cooling down and heating up the samples between RT and 80 K. The small change (1-2%) in the mean lifetime and in the S parameter of the Doppler broadening measurements is significant and reproducible at each time passing by the temperature of 240 K. (See Table 1.) Both parameters (τ, S) are higher at low temperature. The size of the superconducting crystallites is typically about 1 µm [10,15,16] which is however large enough to avoid the positrons to escape if they already thermalized there. The small change of the positron parameters indicates that the average electron density doesn't vary drastically at the transition.

The good quality two-component analysis ($\chi^2 \approx 1.01$ typically) show a detailed picture. (Table 2.) It is not surprising that there are two strongly different components because these polycristaline compounds contain generally not only one phase.

We suggest that the drastical change in the first component (τ_1,I_1) correlates with the superconducting transition of the crystallites, while the second component arises from the other probably amorphous phase which separates the crystalline grains and comprises some 10% of the sample [15].

Although the oxigen deficiency of these kind of materials is rather small (x≃0.1-0.5 typically, depending on heat treatment [14]) it results an O-vacancy concentration of about 10^{-1}-10^{-2}. If these vacancies would trap the positrons we ought to see a saturation (the probability of thermal detrapping at this temperature is negligable), however it is not the case. The Cu-O planes contain Cu^{3+} and Cu^{2+} atoms with an average valence, which is changing from 2.33 (at x=7) to 1.67 (at x=6), [11,17] meaning in our case a ratio of about 30% Cu^{3+} and 70% Cu^{2+}. Most of the O-vacancies are probably localy positive consequently they are not attractive for the positrons. If there would be some change in the Cu^{3+}/Cu^{2+} ratio at the transition, it could be followed by a lattice relaxation and some of the positively charged O-vacancies could be filled up with electrons producing neutral or negatively charged O-vacancies which can trap the positrons. Although the coordination and the lattice structure are different it is stimulating that the 179 ps value of τ_1 at low temperature agrees very good with the vacency lifetime in pure Cu [12].

There is some contradiction in the literature and especially in the privat communications whether the transition temperature of about 240 K reported by more laboratories (see for example [13,16], is reliable or not. Our results show a significant and reversible change in the positron parameters about 240 K. If this change correlates with the superconducting transition, as we believe it, it would indicate that this transition takes place in some crystallites already at about 240 K, however this effect will be macroscopic only about 90 K, where the resistance fails to zero. On the other hand some structural change in the superconducting crystallites as a reason of the higher lifetime can not be excluded.

We hope that these first detailed positron annihilation results will stimulate further measurements on the high T_c superconductors. Angular correlation measurements would be fruitful in getting information about the distribution of electron density and the charge density at the Fermi level. Positron annihilation measurements depending on magnetic field could be check whether the expected change in T_c correlates with the jump in positron parameters.

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Table 1. Temperature dependence of S and τ parameters

Temp. range (K)	S	τ (ps)
80 - 240	0.417 (±0.001)	185.5 (±1)
250 - RT	0.413 (±0.001)	180.3 (±1)

Table 2. Results of two-component analysis of lifetime spectra vs. temperature

	RT	250 K	240 K	80 K
τ_1 (ps)	146 (±2)	143 (±2)	176 (±2)	179 (±2)
τ_2 (ps)	218 (±3)	218 (±3)	243 (±3)	243 (±3)
I_1 (%)	50.86 (±1.36)	43.04 (±1.18)	77.17 (±2.38)	89.62 (±2.36)

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