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Physics Letters A 321 (2004) 376–380
PHYSICS LETTERS A
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Studies of coincidence Doppler broadening of the electron–positron annihilation radiation in the single crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductor

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Received 11 November 2003; accepted 29 November 2003

Communicated by V.M. Agranovich

Abstract

Background suppressed Doppler broadening spectroscopy using a two detector coincidence technique of the electron–positron annihilation γ-radiation has been employed on single crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ high T_c superconductor. The spectra at different sample temperatures have been compared with the room temperature spectrum by constructing ratio-curve. The results indicate an effective shift of oxygen ions towards the Bi–O plane from the Cu–O plane just above the superconducting transition temperature.

PACS: 74.72.Hs; 78.70.Bj

Keywords: Bi-based cuprate superconductors; Positron annihilation technique

Positron annihilation techniques are well-known nuclear solid-state techniques [1,2] used to study the electronic structure, defect properties, electron density distributions and the electron momentum distributions in materials. Among these techniques, Doppler broadened electron–positron annihilation γ-radiation (DBEPAR) measurements are very useful to probe the electron momentum distributions in materials. In the DBEPAR measurement technique positron from a radioactive (^{22}Na) source is thermalized inside the material and annihilate with an electron emitting two oppositely directed 511 keV γ-rays [2]. Depending upon the momentum of the electron (p) these 511 keV γ-rays are Doppler shifted by an amount $\pm\Delta E$ in the laboratory frame, where

$$\Delta E = p_L c/2,$$

p_L is the component of the electron momentum, p, along the measurement direction. Measuring these Doppler shifts by a high resolution HPGe detector one can measure the electron momentum distribu-

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doi:10.1016/j.physleta.2003.11.062

tions inside a material. In the conventional one detector Doppler broadening experiment, the peak to background ratio of the photo-peak of the 511 keV annihilated γ-rays is typically $\sim 30:1$. Thus the conventional one detector Doppler broadening experiment is restricted to probe the average distribution of the lower momentum region of the electrons in a material. The peak to background ratio can be improved by more than two orders of magnitude by use of the two detector coincidence Doppler broadening technique [3]. Using this technique one can measure the contributions of the core and the valence electron momentum in the Doppler broadening spectrum.

After the discovery of high temperature superconductor different experimental techniques, including the positron annihilation techniques [4–10] have been employed to understand the mechanism of the high temperature superconductivity (HTSC). The main aim of positron annihilation probing on HTSC is to study the superconductivity induced changes in the electron density distributions and in the electron momentum distributions. Employing positron annihilation techniques it may not be possible to probe directly the "superconducting electrons". But from the variations of the temperature dependent positron annihilation parameters (both lifetime and DBEPAR line shape parameters) it has been concluded that at or near the superconducting transition temperature there occurs some structural changes [8–11] which may be linked with the mechanism of high temperature superconductivity.

Presently we are reporting the results of the coincidence Doppler broadening of the electron–positron annihilation radiation (CDBEPAR) experiment on high quality single crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) HTSC sample. The high peak to background ratio for the measured spectra helps us to determine the accurate variations of electron momentums of different atomic sites present in this highly anisotropic crystal structured material [12] due to the superconducting transition.

The $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals were grown by the traveling-solvent floating-zone technique [13]. Optically smooth surfaced high quality cleaved single crystals ($3 \times 5 \times 0.15$ mm^3) were used for the present CDBEPAR experiment. The superconducting transition temperature T_c of these samples [14] is 91 K.

The two detector coincidence technique [3] has been used to achieve the higher peak to background ratio in the measured $N(E)$ vs. E spectrum under the Doppler broadened 511 keV photo-peak. A HPGe detector (efficiency 13%) having energy resolution of 1.1 keV for the 514 keV γ-ray line of ^{85}Sr with 6 μs shaping time constant in the spectroscopy amplifier and a $2'' \times 2''$ NaI(Tl) crystal coupled to a RCA 8850 photomultiplier tube have been placed oppositely (with an angle 180°) for the purpose of coincidence measurement.

About 10 μCi of ^{22}NaCl has been deposited directly on the *a–b* surface of one of the single crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ HTSC samples and then covered with another identical sample. Adoption of this procedure completely eliminates annihilation of positrons in the source cover and its contribution to the CDBEPAR spectrum. Source-sample sandwich has been placed inside a vibration free helium cryogenerator (APD Cryogenics Inc., model number DMX-20) for maintaining the sample at temperatures in the range 300 to 30 K. We have chosen a vibration free helium cryogenerator to reduce the possibility of the distortion of the CDBEPAR spectrum. The system temperature has been controlled by a temperature controller (Scientific Instruments Inc. 9620-1) with ± 0.5 K temperature stability.

The gap between the detectors and the source-sample sandwich has been kept at 30 cm. For each temperature $\sim 10^7$ coincidence counts have been recorded under the photo-peak of the 511 keV γ-ray at a rate of 110 counts per second. The energy per channel of the multichannel analyzer is kept at 79.6 eV. Background has been calculated from 607 to 615 keV energy range of the spectrum. The achieved peak to background ratio is obtained as $14000:1$. The system stability has been checked frequently during the progress of the experiment.

In the HTSC, superconductivity induced changes in the positron annihilation parameters at high momenta are very small $\sim 1\%$ [9]. To observe such a small change in the positron annihilation parameters we choose the room temperature (298 K) spectrum as a reference spectrum for the construction of the ratio-curve [15,16] at different temperatures. Ratio-curves at 14 different temperatures (252, 203, 178, 154, 135, 116, 107, 102, 98, 95, 92, 90, 65, and 30 K) have been constructed for the single crystalline Bi-2212 HTSC sample. Fig. 1 represents the ratio-curves at some selected temperature points ($T = 203$,

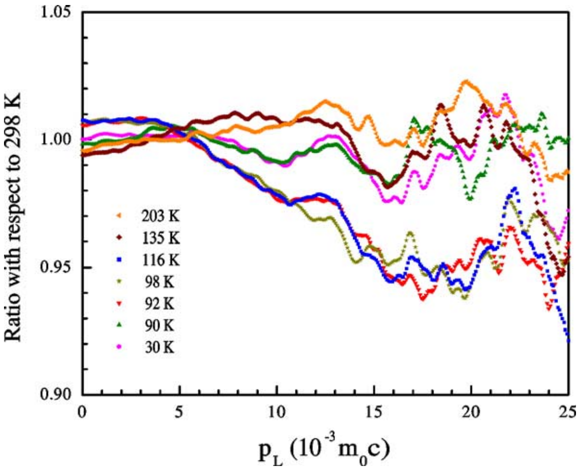

Fig. 1. Ratios of the experimental electron–positron momentum distributions at different sample temperatures to the electron–positron momentum distributions at the room temperature (298 K) for the single crystalline Bi-2212 HTSC.

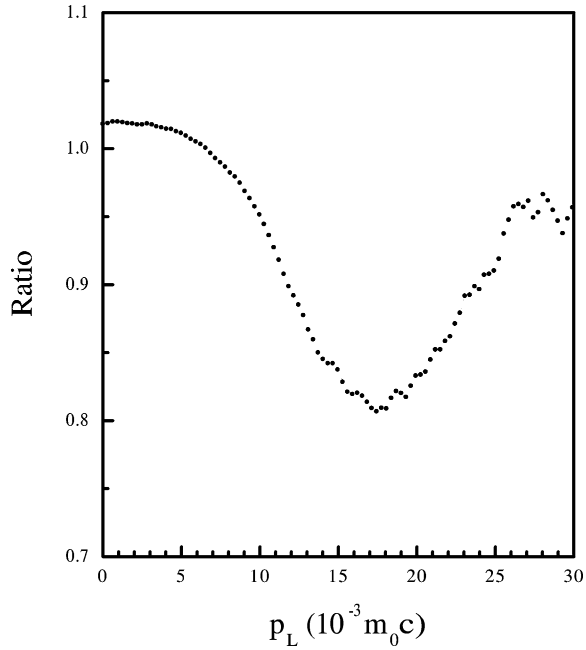

Fig. 2. Ratio of the experimental electron–positron momentum distributions for the nano-crystalline CuO powder to the electron–positron momentum distributions for the micro-crystalline CuO powder.

135, 116, 98, 92, 90, and 30 K). In between these temperature points, ratio-curves follow the same trend. It is clear from Fig. 1 that the ratio-curves for the temperature region 116 to 92 K have shown a dip in the momentum range $(10 < p_L < 25) \times 10^{-3}\ m_0c$. But below T_c (91 K) the dip in the ratio-curves disappears. Ghosh et al., have calculated and shown [17] that the annihilation of positrons with the 3d electrons of Cu atom is predominant in the momentum region $(15 < p_L < 40) \times 10^{-3}\ m_0c$.

To characterize the dip in the momentum range $(10 < p_L < 25) \times 10^{-3}\ m_0c$ we have studied the CuO powder separately by employing CDBEPAR technique. It has been reported that reducing the grain size (< 100 nm) of some metal oxides, e.g., CuO, ZnO, etc., by ball mill grinder one can introduce cation vacancies in the grain surfaces [18,19]. Wang et al. [18] show that in the surface of the nano-crystalline CuO the atomic ratio of Cu and O (calculated on the basis of Cu_{2p} and O_{1s} XPS spectra) is approximately equal to 3 : 4. In case of metal oxides having the grain size of the order of micro-meter positrons mostly annihilate at the bulk of the material which is more or less stoichiometric. But in the nano-crystalline metal oxides (grain size less than 100 nm) a significant amount of positrons annihilate at the grain surfaces, which are non-stoichiometric, making it possible to probe the cation vacancies. Thus we have ball milled 99.99% pure CuO powder (grain size ~ 1 μm) to achieve the grain size less than 100 nm and constructed the ratio-curve (from the CDBEPAR spectrum) for CuO nano-crystalline sample with respect to CuO micro-crystalline sample. The ratio-curve (depicted in Fig. 2) shows a broad minimum in the momentum range $(10 < p_L < 25) \times 10^{-3}\ m_0c$. This clearly indicates that in the CuO one can expect a minimum in the momentum range $(10 < p_L < 25) \times 10^{-3}\ m_0c$ when the system contains more cation vacancies and hence the positrons are less annihilating with the 3d electrons of the Cu ion. Similarly the dip observed in the ratio-curves for the Bi-2212 HTSC at temperatures between 116 and 92 K (see Fig. 1) can be interpreted as showing that less positrons annihilate with 3d electrons of the Cu ions.

We define two area-parameters: R_O and R_{Cu}. R_O is the total area under the ratio-curve of Fig. 1 from 0 to $5 \times 10^{-3}\ m_0c$, this is a good measure of the fraction of positrons annihilating with the 2p electrons of the

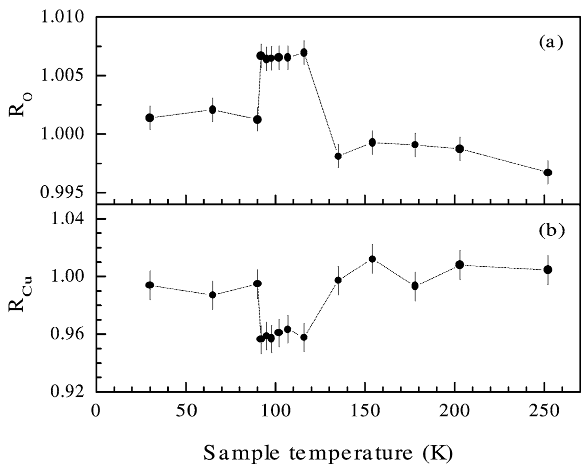

Fig. 3. Variation of the area-parameters (a) R_O and (b) R_{Cu} with sample temperatures for the single crystalline Bi-2212 HTSC.

oxygen ions. Similarly, R_{Cu} is the total area under the ratio-curve from 10×10^{-3} to 25×10^{-3} m_0c, which is a good measure of the fraction of positrons annihilating with the 3d electrons of the Cu ions. Fig. 3(a) and (b) represents the variation of R_O and R_{Cu}, respectively, with sample temperatures. It is clear from Fig. 3(a) and (b) that just above the superconducting transition temperature (116 to 92 K), positrons are more likely annihilating with the 2p electrons of the oxygen ions than with the 3d electrons of Cu ions. From the positron density distribution calculations for Bi-2212 system [6,20] it is expected that positrons are mainly probing the Bi–O plane and a small fraction is expected to probe the Cu–O plane. To explain the above observations we consider the possibility of an effective shift of the "apical oxygen" ions towards the Bi–O plane, so that the probability of positrons to be annihilated with the 2p electrons of the oxygen ions increases. This type of structural changes also results a decrease in the number of the 3d electrons in the Cu–O band, which in a way support the "charge transfer model" valid for these cuprate superconductors [21].

In conclusion, the less annihilation of the positrons with the 3d electrons of Cu ions and more annihilation with the 2p electrons of the O ions suggest a shift of the apical oxygen ion towards the Bi–O plane. Present analysis of the CDBEPAR spectrum by constructing the ratio-curve helps us to understand with higher certainty the variation of the DBEPAR line-shape parameter with temperature at or around the superconducting transition temperature for the high T_c cuprate superconductors.

Acknowledgements

We gratefully acknowledge Dr. A.K. Pradhan of the Norfolk State University, USA for supplying us single crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ HTSC sample and Dr. Alok Chakrabarti of the Variable Energy Cyclotron Centre, Kolkata 700064, India for valuable suggestions and encouragements. We thank Mr. M. Bettonte of the Dipartimento di Fisica, Università di Trento, Italy for technical suggestions during experiments.

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