

Bismuth Valence in a $\text{Tl}_{0.7}\text{Bi}_{0.3}\text{Sr}_{1.6}\text{Ba}_{0.4}\text{CaCu}_2\text{O}_y$ Superconductor from X-Ray Photoemission Spectroscopy

R. ZALECKI^a, W.M. WOCH^a, M. KOWALIK^{a,b,*}, A. KOŁODZIEJCZYK^a
AND G. GRITZNER^c

^aDepartment of Solid State Physics, AGH University of Science and Technology, 30-059 Cracow, Poland

^bDepartment of Physics, Rzeszów University of Technology, 35-959 Rzeszów, Poland

^cInstitute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz
A-4040 Linz, Austria

The X-ray electron photoemission spectra of a $\text{Tl}_{0.7}\text{Bi}_{0.3}\text{Sr}_{1.6}\text{Ba}_{0.4}\text{CaCu}_2\text{O}_y$ superconductor were measured with Al K_α and Mg K_α radiation at room temperature. The Bi 4*f* spectrum was compared to the same spectra of $\text{Bi}_{1.75}\text{Pb}_{0.35}\text{Sr}_{1.9}\text{Ca}_{2.05}\text{Cu}_{3.05}\text{O}_y$ and $\text{Tl}_{0.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductors. In Bi,Pb-based superconductor only one type of Bi^{3+} ions is present. The Bi 4*f* spectrum in the Tl,Bi-superconductor consists of two contributions due to the different valences. The component from Bi^{5+} lines is in higher binding energy than from Bi^{3+} . The ratio of trivalent Bi^{3+} to pentavalent Bi^{5+} bismuth ions was calculated from decomposition of the spin-orbit split spectrum of the Bi 4*f* photoelectrons. The conclusion is that Bi is present in trivalent and in pentavalent form and the ratio of Bi^{3+} to Bi^{5+} is 1.87 ± 0.02 .

PACS numbers: 74.72.-h, 74.25.Jb, 79.60.-i

1. Introduction

Photoelectron spectroscopy is one of the important tools to probe electronic states. Difficulties in the interpretation of the *d*-electron photoemission in high-temperature superconductors (HTS) stems from the large correlation effect among 3*d* electrons and from the hybridisation of the metal *d*-electrons with the ligand *p*-electrons. It is already well-established that high-temperature superconductivity (HTS) is due to doping by holes as in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ or by electrons as in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$. In the former system the charge neutrality requires the conversion of Cu^{2+} to Cu^{3+} or the conversion of O^{2-} ($2p^6$) to O^{1-} ($2p^5$). This means an appearance of holes L^- in the oxygen 2*p* band (L^- indicates an oxygen ligand hole state) yielding the formally trivalent copper Cu^{3+} instead of the real Cu^{3+} ($3d^8$) states. It was shown that the superconductivity is determined by the formally trivalent copper Cu^{3+} with the $3d^9L^-$ electronic states. This is usually called “formally trivalent copper” because the extra electron missing with respect to divalent copper Cu^{2+} is taken from the oxygen 2*p* reservoir rather than from the Cu 3*d* reservoir [1, 2].

In the present paper the X-ray photoemission spectra (XPS) of the $\text{Tl}_{0.7}\text{Bi}_{0.3}\text{Sr}_{1.6}\text{Ba}_{0.4}\text{CaCu}_2\text{O}_y$ (Tl,Bi-1212), $(\text{Bi}_{1.75}\text{Pb}_{0.35})\text{Sr}_{1.9}\text{Ca}_{2.05}\text{Cu}_{3.05}\text{O}_y$ (Bi,Pb-2223)

and $\text{Tl}_{0.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_y$ (Tl,Pb-1223) superconductors were measured and analysed. Special attention was paid to the Bi 4*f* core-level spectra which showed double-peak structure. From analysis of the spectra we have proved that in the Tl,Bi-1212 superconductors Bi is present in trivalent but also in pentavalent form. The latter is a source of additional electrons missing with respect to trivalent bismuth which shall influence the superconducting properties of the material.

2. Samples and experiments

Polycrystalline pellets of the Tl,Bi-1212, Tl,Pb-1223 and Bi,Pb-2223 superconductors were prepared by solid-state reaction following a procedure described elsewhere [3–5]. The superconducting transition temperatures T_c were 102.5 K, 118 K and 103 K, respectively. They were determined from the temperature dependences of dispersive and absorption part of ac susceptibility for Tl,Bi-1212 and of resistance for Tl,Pb-1223 and Bi,Pb-2223 with the overall accuracy ± 0.1 K [3–7]. The oxygen stoichiometry of the Tl,Bi-1212 superconductor was $y \approx 7$ [3].

We employed an X-ray and ultraviolet photoemission spectrometer equipped with dual Al K_α and Mg K_α X-ray sources with a typical resolution of 0.85 eV and with a high intensity UV source with an energy resolution of about 50 meV. The spectrometer was calibrated using the Ag Fermi edge, the Ag $3d_{5/2}$ line and the Cu $2p_{3/2}$

* corresponding author; e-mail: mkowalik@prz.edu.pl

white line to which the binding energies 0 eV, 368.3 eV and 932.7 eV were assigned, respectively. To avoid surface degradation all the experiments were performed under vacuum better than 10^{-9} mbar. To get the most representative spectra the sample surfaces were scrapped *ex situ* with a diamond file. Next they were heated up to 300 °C *in situ* during pumping, cleaned by Ar ion gun and heated once more. The intensity of the carbon C 1s peak at about 285 eV was as a test for possible contamination of the surface. The C 1s signal due to carbonate impurities was rather small for all samples. The XPS were measured at room temperature.

3. X-ray photoemission results and their analysis

The full energy scan spectra at room temperature with the Al K_{α} radiation are shown in Fig. 1 and with the Mg K_{α} radiation in Fig. 2 with the indicated important photoemission lines. In Fig. 1 the spectrum of the investigated Tl-based superconductor is compared to the previously measured spectrum of Bi-based superconductor [7] in order to reveal the difference of intensity of the relevant Bi 4*f* lines. We found out that the spin-orbit split spectrum of the Bi 4*f* electrons was enough intensive and resolved for further analysis (see the inset of Fig. 1). In Fig. 2 the spectrum of the investigated compound is compared to the Pb-substituted thallium superconductor without bismuth content in order to prove that there is no contribution to the Bi 4*f* line from core-level lines of other constituent elements (see the inset of Fig. 2).

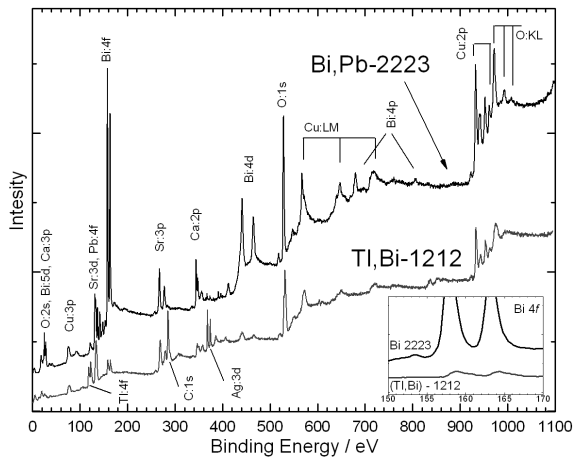


Fig. 1. XPS Al K_{α} of Tl,Bi-1212 sample in comparison to Bi,Pb-2223 sample [6] with the core-level lines as indicated. Inset shows the enlarged Bi 4*f* lines.

We found out that the spin-orbit split spectrum of the Bi 4*f* electrons is enough intensive for the analysis (cf. the inset of Fig. 1 and Fig. 2).

Special attention was paid to the Bi 4*f* core-level spectra which showed double-peak structure. They are shown in Figs. 3 and 4. For a quantitative analysis of the ratio $\text{Bi}^{3+}/\text{Bi}^{5+}$ in the Tl,Bi-1212 superconductor we have

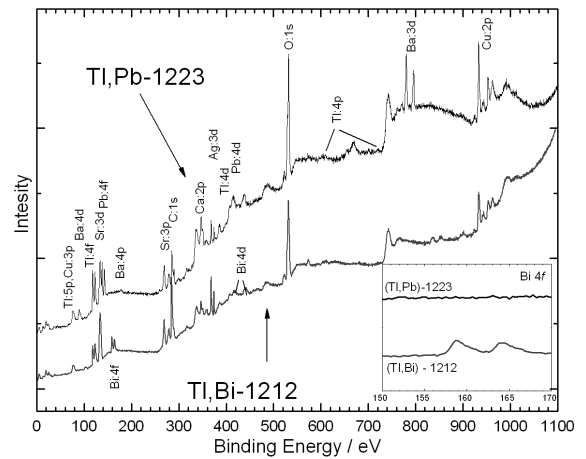


Fig. 2. XPS Mg K_{α} of Tl,Bi-1212 sample in comparison to Tl,Pb-2223 sample without Bi [6] with the core-level lines as indicated. Inset shows the enlarged Bi 4*f* lines.

measured the spectrum of the investigated compound separately with a very good statistics. The spectrum is shown in Fig. 3. The spectrum is compared with the Bi 4*f* spectrum of bismuth-rich superconductor Bi,Pb-2223 shown in Fig. 4.

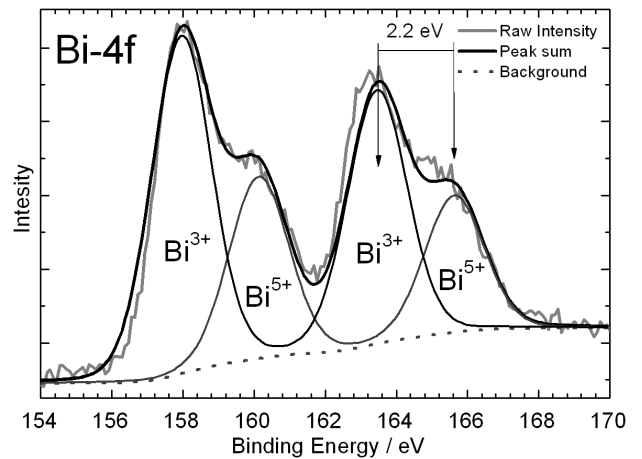


Fig. 3. Bi 4*f* spectrum in Tl,Bi-1212 sample together with the decomposition to two spin-split spectra corresponding to Bi^{3+} and Bi^{5+} contributions.

This spectrum is very symmetric in comparison to the Bi 4*f* spectrum in Tl,Bi-1212 sample. It means that only one valence of bismuth ions is present in Bi,Pb-2223.

The Bi 4*f* spectrum consists of two contributions due to the different valences. Bi is present in trivalent as in the Bi,Pb-2223 superconductor and in pentavalent form rather than in quaternary valence Bi^{4+} . This is because of the large separation 2.2 eV between the Bi^{3+} and Bi^{5+} lines in comparison to the typical separation about 1 eV or smaller seen by photoemission when unit difference in valence is observed for other ions. The component from

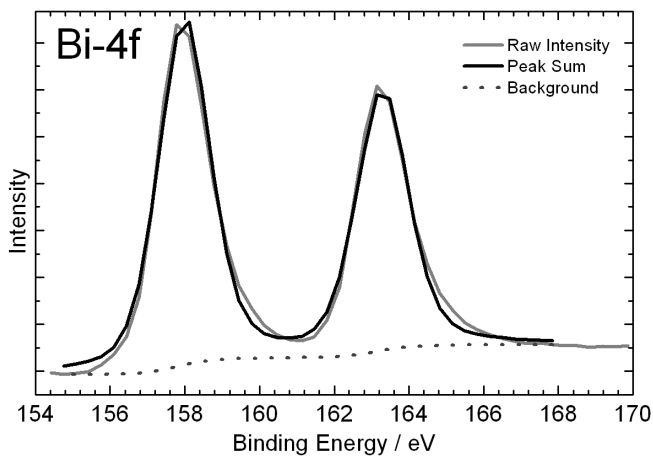


Fig. 4. Bi 4f spectrum in Bi,Pb-2223 sample together with the fitting to the one spin-split spectrum corresponding to Bi^{3+} contribution.

Bi^{5+} ions is in higher binding energy than from Bi^{3+} ions simply because kinetic energy of outgoing photoelectrons from Bi^{5+} ions is smaller due to their larger Coulomb attraction. Figure 3 shows the analysis. The most frequently used XPS Peak fitting program version 4.1 was used [8]. The program allows to keep constant intensity ratio of both spin-orbit split components as theoretically predicted 4:3 for Bi: $4f_{7/2}$ and $4f_{5/2}$ line, respectively. The spin-orbit split energy ΔE was about 5.4 eV, the same for all compounds during fitting procedure. The full-width half-maximum (FWHM) of each bismuth line was about 1.9 eV. The fit is reasonably good. As the result of the fit one can get the area under the peaks of Bi^{3+} and Bi^{5+} lines. The ratio of $Bi^{3+}/Bi^{5+} = 1.87 \pm 0.02$ was obtained as the ratio of the relevant areas.

4. Conclusions

1. From the X-ray electron photoemission spectra of the Tl,Bi-1212 superconductor the ratio of trivalent to pentavalent bismuth ions $Bi^{3+}/Bi^{5+} = 1.87 \pm 0.02$ was calculated from the quantitative analysis of the spin-orbit split spectrum of the Bi 4f photoelectrons.

2. The existence of about 35% of Bi ions in pentavalent form results in an increase of T_c to above 100 K in comparison to typical value of T_c about 80–90 K for 1221 thallium-based superconductors without Bi ions.
3. Our hypothesis is that the increase of T_c is most likely due to increase of oxygen electron holes because in pentavalent bismuth some part of electrons are missing with respect to trivalent bismuth. Thus, the density of oxygen-hole Cooper pairs increases and as a consequence also the transition temperature increases.

Acknowledgments

The samples were prepared in the frame of collaboration with the Professor G. Gritzner group from the Kepler University in Linz, Austria. Some measurements were performed at the Solid State Physics Department at the Jagiellonian University, Cracow in the frame of collaboration with the Professor A. Szytuła. This work was supported by the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Cracow, Poland.

References

- [1] For early review see A. Bianconi, in: *Proc. Taniguchi Int. Symp. Core Level Spectroscopy in Condensed System*, Eds. A. Kotani, J. Kanamori, Springer Verlag, Berlin 1989, p. 99.
- [2] For review see A. Bansil, *J. Phys. Chem. Solids* **52**, 1493 (1991) and in: K. Ueda, T. Moriya, Y. Takahashi, *J. Phys. Chem. Solids* **53**, 1515 (1992).
- [3] M. Mair, W. König, G. Gritzner, *Supercond. Sci. Technol.* **8**, 894 (1995).
- [4] W. König, G. Gritzner, P. Diko, J. Kováč, M. Timko, *J. Mater. Chem.* **5**, 879 (1995).
- [5] W. König, M. Mair, G. Gritzner, *J. Supercond.* **11**, 107 (1998).
- [6] R. Zalecki, A. Kołodziejczyk, W. Koenig, G. Gritzner, *Acta Phys. Pol. A* **98**, 513 (2000).
- [7] R.W.M. Kwok, *XPS Peak Fitting Program Version 4.1*, Department of Chemistry, The Chinese University of Hong Kong, <http://www.phy.cuhk.edu.hk/~surface/XPSPEAK>.