An X-ray spectral study of the influence on the electronic structure of high T_c superconductors of the parameters determining the superconducting transition temperature

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Abstract. CuL_α and OK_α X-ray fluorescence spectra, corresponding to the $\text{Cu}3d\text{-Cu}2p$ and $\text{O}2p\text{-O}1s$ transitions, and XANES and EXAFS spectra (CuK , YK , BiL , PbL) have been obtained for the following series of samples: (i) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 < \delta < 0.8$), (ii) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0 < x < 0.3$) and (iii) $\text{Bi}_2(\text{Sr}, \text{Ca})_{n+1}\text{Cu}_n\text{O}_{2n+4}$ ($n = 1, 2, 3$), $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_2\text{Cu}_3\text{O}_y$. A correlation has been found between the decrease in the superconducting transition temperature (T_c) with variation in the stoichiometric parameters δ and x in series (i) and (ii), and the shift of the maximum in their CuL_α spectra and the relative increase in the number of occupied states $\text{Cu}3d$ in the upper part of the valence band. The changes in the distribution of the $\text{Cu}3d$ and $\text{O}2p$ densities and in the spectral parameters of the samples are discussed.

Keywords. X-ray spectra; electronic structure; superconducting transition temperature.

1. Introduction

It is known that the superconducting transition temperature of single-phase high- T_c superconductors can be changed by changing the corresponding stoichiometric coefficients. In this connection it appears useful to undertake an X-ray spectral study of the effect of such parameters on the electronic structure and the structural characteristics of high T_c superconductors.

2. Experimental

X-ray fluorescence spectra were measured on a "Stearate" spectrometer. The crystal-analyser was a RbAP single-crystal focussed according to the Johann scheme with a Rowland circle radius of 250 mm. The half-width was 3.7 and 1.7 eV for uncorrected CuL_α spectra of metallic copper and uncorrected OK_α spectra of MgO , respectively.

3. Results and discussion

The temperature dependence of $R(T)/R(300)$ has been obtained for the studied series of samples. Analogous dependences are given in Sawada *et al* (1987), Tarascon *et al* (1987), Somasundaram *et al* (1988), Erenburg *et al* (1988) and Tallon and Buckley (1989).

3.1 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 < \delta < 0.8$) system

As can be seen from a comparison of the data in figures 1 and 2, the changes in spectra with the variation in δ from 0.1 to 0.7 are substantial for OK_α and less pronounced for CuL_α [6,7]. For the analysis of small changes in such spectral shapes it has been proposed to study the difference spectra which are obtained by point-by-point subtraction of the spectra for all samples from the spectrum of the starting sample. In subtraction, the spectra were normalized according to the equality of the areas under the curves. The analysis of the difference spectrum ΔCuL_α has shown that the characteristic shape and amplitude of its features are mainly determined by small shifts of the maxima of the CuL_α spectra ($\lesssim 0.1$ eV) towards shorter waves relative to the initial sample with $\delta = 0.1$ (figure 3).

It should be noted that some increase in the relative intensity in the high-energy side of the difference spectra is probably due to a transfer of electrons to the copper atoms upon the loss of oxygen by the sample. This result is in agreement with the appearance in CuK spectra of a long-wave maximum, characteristic of the spectra of monovalent copper, as δ was increased. Such changes in the CuK spectra have been found by Oyanagy *et al* (1988) and are confirmed by the results of the present work.

Figure 4 shows the difference spectra OK_α for samples. As can be seen from the comparison of these spectra with the results of theoretical calculations (Mattheiss and Hawann 1987), the shape of the difference spectra corresponds to the energy dependence of the density of states for $\text{O}(x)$ (chain oxygen).

It can be seen from figure 4 that the main maxima of the difference spectra ΔOK_α ($\text{O}(x)$ oxygen) are shifted relative to the maximum of the OK_α spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ by an amount of the order of 0.2–0.4 eV towards shorter waves, which

Figure 1. X-ray fluorescence spectra CuL_α for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples: 1. $\delta = 0.1$; 2. $\delta = 0.3$; 3. $\delta = 0.5$; 4. $\delta = 0.7$; 5. $\delta = 0.7$.

Figure 2. X-ray fluorescence spectra OK_{α} for $YBa_2Cu_3O_{7-\delta}$ samples: 1. $\delta = 0.1$; 2. $\delta = 0.3$; 3. $\delta = 0.5$; 4. $\delta = 0.6$; 5. $\delta = 0.7$; 6. $\delta = 0.7$.

Figure 3. Difference spectra $\Delta ICuL_{\alpha}$ ($CuL_{\alpha}YBa_2Cu_3O_{7-\delta} - CuL_{\alpha}YBa_2Cu_3O_{6.9}$): 1. $\delta = 0.3$; 2. $\delta = 0.5$; 3. $\delta = 0.7$; 4. $\delta = 0.7$. At the bottom is shown the maximum of CuL_{α} spectrum of the starting sample with $\delta = 0.1$.

Figure 4. Difference spectra ΔOK_{α} ($OK_{\alpha} YBa_2Cu_3O_{6.9} - OK_{\alpha} YBa_2Cu_3O_{7-\delta}$) 1. $\delta = 0.3$; 2. $\delta = 0.5$; 3. $\delta = 0.7$. At the bottom is shown the maximum of OK_{α} spectrum of the starting sample with $\delta = 0.1$.

may be a result of a deepening of the $1s$ level and a lower negative charge for $O(x)$ and, hence, of a smaller binding energy for this oxygen.

3.2 $La_{2-x}Sr_xCuO_4$ ($0 < x < 0.3$) system

Analysis of the spectra for this series of samples (figure 5) indicates an increase in the relative amount of occupied $Cu3d$ states in the upper part of the valence band on going from samples with $0.1 < x < 0.3$ to samples with lower values of x . On going from La_2CuO_4 to samples with $x = 0.04, 0.1, 0.15$ there was a shift in the CuL_{α} maximum by about 0.1 eV towards higher energies, and by about 0.3 eV on going to samples with $x = 0.2, 0.3$, also towards higher energies. This allows us to interpret the observed shifts as an increase in the binding energy of the $2p$ levels for a portion of copper atoms and an increase in their effective positive charge. One can hardly expect that there will be substantial changes in the distribution of the $Cu3d$ electronic density since the first coordination sphere is not involved (in contrast to what occurs in $YBa_2Cu_3O_{7-\delta}$ with variation in δ).

Now it can be said that there is a correlation between the decrease in T_c and the relative amount of the occupied $Cu3d$ states in the upper part of the valence band (~ 4 eV from the CuL_{α} maximum) for both series of the samples as well as between the decrease in T_c and the decrease in the binding energy of the $Cu2p$ levels for the series $La_{2-x}Sr_xCuO_4$.

3.3 $Bi_2(Sr, Ca)_{n+1}Cu_nO_{2n+4}$ ($n = 1, 2, 3$), $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_y$ systems

For the ceramic sample of the composition $Bi_2(Sr, Ca)_{n+1}Cu_nO_{2n+4}$ T_c has been found to depend on the number of CuO_2 layers (Tallon and Buckley 1989). The maximum temperature of about 107 K has been achieved for a three-layer structure ($n = 3$).

Figure 5. Difference spectra $\Delta \text{CuL}_{\alpha}$ ($\text{CuL}_{\alpha} \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 - \text{CuL}_{\alpha} \text{La}_2\text{CuO}_4$) 1. $x = 0.04$; 2. $x = 0.1$; 3. $x = 0.15$; 4. $x = 0.2$; 5. $x = 0.3$.

Figure 6. Oscillation part $\chi(k)$ and radial distribution functions from BiL_{III} and PbL_{III} EXAFS spectra in $\text{Bi}_{2-x}\text{Pb}_x(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_y$.

Attempts to synthesize the three-layer structure gave only 15% of this phase, and single-phase samples could be obtained only by substitution of a portion of Bi atoms by Pb (Tallon and Buckley 1989).

In the fluorescence CuL_{α} spectra of the Bi systems measured by us there were no

noticeable changes (changes with respect to the ordinate were $< 2\%$) with (i) substitution of a portion of Bi atoms by Pb; (ii) quenching into liquid nitrogen from 850°C ; (iii) the change in n , i.e. there are no noticeable changes in the charge state of copper atoms and the Cu3d electronic density distribution with the change in the parameters of Bi systems.

It is not clear at present what is the role of Pb atoms in the formation of a stable three-layer structure. An unambiguous determination of the differences in the positions of Pb and Bi atoms in the lattice by X-ray diffraction methods presents difficulties because of the lack of good-quality single crystals.

To establish the nearest environment of the Pb and Bi atoms we have measured EXAFS spectra in the region of L_{III} absorption edges of a Bi and Pb sample of the composition $\text{Bi}_{2-x}\text{Pb}_x(\text{Sr, Ca})_4\text{Cu}_3\text{O}_y$ (where $x \sim 0.3$). The interval of the obtained data was limited to $9 \text{ \AA}^{-1}$ due to the interfering effects of other elements. Figure 6 shows the oscillating portion of the absorption coefficient and the atomic radial distribution functions for samples a, b, c obtained in different syntheses. All samples are superconducting at 107 K. Although the short interval of the data does not allow one to obtain a good resolution of the atomic radial distribution function, it is evident that the nearest environments of Pb and Bi in these samples are substantially different. Similar differences are clearly seen in $\chi(K)$. In all the samples the Pb atoms show a strongly pronounced sphere at about $3 \text{ \AA}$ which may be due either to a strong ordering in this coordination sphere or to a large coordination number. It follows from the obtained data that Pb atoms in these samples are not statistically distributed among the Bi sites but have a special arrangement. Establishing of the exact positions of Pb atoms requires further study.

References

- Erenburg S B, Khudoroshko G F, Asanov I P, Bessergenev V G, Gromilov S A and Mazalov L N 1988 *Abstracts of papers of the XXV All-Union Conference on the Low-Temperature Physics, Leningrad* p. 131
 Kurmayev E Z, Nefedov V I and Finkelstein L D 1988 *J. Mod. Phys.* **2** 393
 Mattheiss L F and Hawann D R 1987 *Solid State Commun.* **63** 395
 Mazalov L N et al 1988 *Izv. SO AN SSSR Ser. Khim* 39
 Oyanagy H et al 1982 *Physica C* **153** 1982
 Sawada H et al 1987 *Jap. J. Appl. Phys.* **26** L1054
 Somasundaram P, Nanjundaswamy K S, Umarji A M and Rao C N R 1988 *Mater. Res. Bull.* **23** 1139
 Tallon J L and Buckley R G 1989 *Physica C* **158** 247
 Tarascon J M et al 1987 *Science* **235** 1373