Polarization dependence of EXAFS and XANES spectra of superconducting films on the basis of Y–Ba–Cu–O

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Abstract. Superconducting films of Y–Ba–Cu–O have been studied by EXAFS and XANES spectroscopy. Films of thickness 1000 Å obtained by laser sputtering onto sapphire substrates had T_c of about 90 K, ΔT_c of about 2 K and the $\bar{c}$ axis orientation normal to the substrate surface. The EXAFS and XANES spectra were measured in the region of Y and CuK edges at different orientations of the sample with respect to the polarization vector $\vec{E}$. The spectra were measured in the surface-sensitive total electron yield detection mode. The observed differences between the spectra are discussed and compared with theoretical calculations.

Keywords. Polarization dependence; EXAFS; XANES; Y–Ba–Cu–O.

1. Introduction

XANES and EXAFS spectroscopy are widely used in studies of new ceramic materials exhibiting high T_c superconductivity (Maeda *et al* 1987; Gygax *et al* 1987; Zhang *et al* 1988; Alp *et al* 1987; Antonioni *et al* 1987; Imazumi *et al* 1988). XANES can provide information about the charge state of atoms, while EXAFS enables us to determine not only the interatomic distances and coordination numbers but also the temperature dependence of the Debye–Waller factor for different pairs of atoms (Maeda *et al* 1987; Gygax *et al* 1987; Zhang *et al* 1988). Analysing the XANES data involves certain difficulties which may sometimes result in obtaining quite opposite conclusions from the same set of data. For example CuK–XANES has been interpreted to indicate the presence of Cu(+ 3) by Alp *et al* (1987) and Antonioni *et al* (1987) and a mixture of Cu(2 +) and Cu(1 +) by Imazumi *et al* (1988). The analysis of EXAFS data also involves some ambiguity. Thus, it has been shown that the Cu–O atomic pairs in the $\bar{a}\bar{b}$ plane in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic give a weak temperature dependence of the Debye–Waller factor (i.e. this bond is the most rigid in the system) without any anomalies (Zhang *et al* 1988). At the same time, for the Cu–O pairs whose oxygen atoms lie between the CuO_2 “layers” and CuO “chains” there was an anomalous increase of the Debye–Waller factor as the temperature was decreased below T_c (Maeda *et al* 1987). An anomalous increase of the Debye–Waller factor for the same atomic pairs has also been observed by Gygax *et al* (1987) at 170°K. On the basis of these two latter observations the role of the “soft mode” in the high T_c superconductivity mechanism is discussed in these studies. The complications in the analysis of the temperature behaviour of the Debye–Waller factor arise due to the presence in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system of several close Cu–O distances which are not resolved in the atomic radial distribution function. To determine the Debye–Waller factors for different Cu–O distances fitting procedures with a large number of fitting parameters are used which introduces a degree of ambiguity. Some of the problems in the analysis of the temperature dependence of the D–W factor in the Y–Ba–Cu–O system can be

avoided by employing the polarization dependence of EXAFS. There are two types of copper atoms present in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ —in the CuO “layers” and CuO “chains”. The copper atoms in the chains have an environment close to the planar-square one (at large oxygen content) and those in the “layers” have a pyramidal oxygen environment which can be considered as planar-square since the fifth top oxygen atom lies far away from the copper atom. A more informative polarization variant of CuK-XANES can be analysed on the basis of the available experimental (Kozugi *et al* 1984) and theoretical (Garg *et al* 1988; Kozugi *et al* 1984) data.

2. Experiment

Realization of the polarization methods requires monocrystalline objects of sufficiently large dimensions. The available single crystals were unstable even during a short storage time, forming various phases on their surfaces. The studies were performed on 1000 Å thick films of the composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared by laser-sputtering onto sapphire substrates (Varlamov *et al* 1988). The film parameters were as follows: $T_c = 90$ K, the transition width $\Delta T_c = 2^\circ\text{K}$, the critical current density was about 10^6 A/cm² at 78 K. According to the X-ray diffraction data, the $\bar{C}$ axis in such a film is oriented perpendicular to the substrate surface with no ordering in the $\bar{A}$ and $\bar{B}$ directions.

In the case of films, the use of transmission mode is impossible due to the presence of a massive substrate. The use of fluorescence method for such objects is also not optimal since the depth of penetration into a sample of X-rays with an energy of 8 keV is considerably greater than 1000 Å. To study the present film by EXAFS and XANES methods we made use of the most acceptable procedure based on total electron yield detection (Stohr *et al* 1979).

3. Discussion

Figure 1 shows CuK-XANES spectra of a high T_c superconducting film of the composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ obtained in total photoyield detection mode at different orientations of the polarization vector $\bar{E}$ with respect to axis $\bar{C}$. The same figure also shows a derivative of the absorption coefficient displaying more clearly the spectral features. The feature C following the main maximum of the spectrum has been ascribed by some authors to the presence in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ of +3 copper atoms (Alp *et al* 1987; Antonioni *et al* 1987), a conclusion based on the coincidence of the energy position of this band with that of the maximum in the spectrum of KCuO_2 which contains Cu(+3). This conclusion is supported by the absence of this feature in the first calculations for a cluster with two coordination spheres (Alp *et al* 1987). Garg *et al* calculated CuK-XANES for clusters involving 1,2,3,4 coordination spheres and only in the case of four coordination spheres was this feature reproduced. If the calculations are correct, it means that the feature under discussion is not associated with the presence of Cu(+3). In the same work polarization dependences of CuK-XANES have been calculated and it has been shown that feature C appears for Cu atoms in the chains at orientation $\bar{E} \perp \bar{c}$. Such dependence of feature C on orientation indeed appears in the experiment (figure 1) which confirms the correctness of the calculations

Figure 1. CuK-XANES spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film at different orientations of the sample with respect to the polarization vector $\vec{E}$.

(Garg *et al* 1988). The same work also predicted a long-wave shift of the spectrum at orientation $\vec{E} \parallel \vec{c}$ which has been reproduced in experiment (figure 1).

A series of features at the absorption edge extending to the main maximum can be analysed on the basis of calculations in Bair and Goddard (1980) and the polarization experiment on planar-square complexes of copper (Kozugi *et al* 1984). It has been shown in these studies that in addition to the $1s-4p$ transition, that forms the main maximum, there also appear $1s-4p$ transitions accompanied by charge transfer from ligands to the absorbing atom (shake down satellites). The satellites are shifted by 6–8 eV towards longer waves relative to the main transitions. The most intense satellites are observed for the $1s-4p_\pi$ transitions (i.e. for the orientation of the polarization vector perpendicular to the plane of the complex). The $1s-4p_\pi$ transition is shifted by about 5 eV towards longer waves relative to the $1s-4p_\sigma$ transition.

Analysis of the polarization dependence of CuK-XANES in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is complicated by the fact that (i) the CuO_4 squares in CuO_2 “layers” and CuO “chains” are mutually perpendicular and (ii) in the films under study there are no ordering in the A and B directions. Nevertheless, some restrictions on the allowed transitions may be inferred. It is clear that for the $\vec{E} \parallel \vec{c}$ orientation there are $1s-4p_\pi$ transitions for the copper atoms in the layers and $1s-4p_\sigma$ transitions for the copper atoms in the chains (with the corresponding shakedown processes). For the orientation $\vec{E} \perp \vec{c}$ there are $1s-4p_\sigma$ transitions for the copper atoms in the “layers” and all the $1s-4p_{\sigma,\pi}$ transitions in the chains with an angle averaging.

The long-wave shift of the absorption edge for $\vec{E} \parallel \vec{c}$ can be explained by the fact that the $1s-4p_\pi$ transitions (shifted by 5 eV towards longer waves relative to $1s-4p_\sigma$) (Kozugi *et al* 1984) appear in this case only for the copper atoms in the “layers”. For the

orientation $\bar{E} \perp \bar{c}$ the $1s-4p_\pi$ transitions are present only for the copper atoms in the "chains" the number of which per unit cell is one half that of the copper atoms in the "layers". In addition, the weight of the transitions due to these atoms is still more decreased, by a factor of two, due to the averaging over the angle.

In the $\bar{E} \perp \bar{c}$ spectrum the most long-wave structure (features a, b, e) must be depressed because of the forbiddenness of the $1s-4p_\pi$ + shakedown process for the copper atoms in the layers which is allowed only for copper atoms in the "chains" and is depressed by the averaging over the angle. Such a picture is observed in the experimental spectrum (figure 1): the feature e at $\bar{E} \perp \bar{c}$ is shifted towards longer waves as compared with feature a for $\bar{E} \parallel \bar{c}$. The spectral features at shorter waves (c, d) for $\bar{E} \parallel \bar{c}$ are $1s-4p_\pi$ transitions for copper atoms in the "layers" and $1s-4p_\sigma$ for copper atoms in the "chains", respectively.

In the $E \perp c$ spectra there appears feature e which is $1s-4p_\pi$ transition + shakedown for copper atoms in "chains", feature f which is $1s-4p_\pi$ transition for copper atoms in "chains" and $1s-4p_\pi$ for copper atoms in "layers", g is $1s-4p_\sigma$ transition for copper atoms in "chains". Thus, in the spectra there appear features a, b, e, which are shakedown satellites, c, f, which are $1s-4p_\pi$ transitions and d, g which are $1s-4p_\sigma$ transitions.

For obtaining a clearer picture it is necessary to perform experiments on films of the composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in which the "chains" are destroyed and the atoms become linearly coordinated with respect to oxygen. In this case at different orientations there will appear $1s-4p_\sigma$ or $1s-4p_\pi$ transitions without mixing.

Figure 2. Atomic radial distribution function obtained by processing CuK-EXAFS spectrum of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film at the $\bar{E} \perp \bar{c}$ orientation of the sample with respect to the polarization vector $\bar{E}$.

Figure 3. Atomic radial distribution function obtained by processing CuK-EXAFS spectra of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample.

It was possible to accumulate a statistics in the region of CuK-absorption edge for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high T_c superconducting film for $\vec{E} \perp \vec{c}$ which was sufficiently large to be processed. The atomic radial distribution function obtained in the processing of this spectrum is shown in figure 2. For comparison, in figure 3 is given the radial function for a polycrystalline sample. It can be seen from comparison that, as expected, the contributions from the coordination spheres of Y and Ba atoms are suppressed and there is no contribution from the oxygen atoms connecting the "layers" with "chains". Similar changes in the atomic radial distribution function have been obtained for $\vec{E} \parallel \vec{c}$ where the contributions from the Y, Ba, Cu atoms are depressed and there appear only oxygen atoms connecting the layers and the chains.

4. Conclusion

It has been shown that polarization variants of EXAFS and XANES allow us to obtain additional information on high T_c materials. In the study of a monocrystalline film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ the dependence on the orientation of the sample with respect to the polarization vector has been established for feature C in CuK-XANES spectrum which confirms the calculations and refutes the presence of Cu(+ 3). The observed shift of the absorption edge at $\vec{E} \parallel \vec{c}$ is in agreement with the existing ideas about the nature of the polarization dependence of XANES in the square-planar-square complexes of copper. The study of polarization dependence enables us to ascribe a series of features in XANES spectra to the specific transitions and shakedown satellites.

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