Journal of Alloys and Compounds 323–324 (2001) 102–106

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Local structure around Fe and Cu ions in $PrBaFeCuO_{5+\delta}$

R. Castañer[a,]*, C. Prieto[b], R. Ramírez[c], F. Mompean[b], J.L. Martínez[b], M.J. Ruíz-Aragón[d], U. Amador[d]

[a]*Dep. de Ciencia y Tecnología de Materiales, Universidad Miguel Hernández, Avda. del Ferrocarril s/n, 03202-Elche, Spain*
[b]*Instituto de Ciencia de Materiales de Madrid, C.S.I.C. Cantoblanco, 28049-Madrid, Spain*
[c]*Dep. Física, Escuela Politécnica Superior, Universidad Carlos III de Madrid, Avda. Universidad, 30, 28911-Leganes, Spain*
[d]*Fac. Ciencias Expt. & Tecn. Universidad San Pablo, CEU, 28668-Madrid, Spain*

Abstract

XANES and EXAFS measurements has been performed in the 10–300 K temperature range in order to investigate the local order around the Fe and Cu ions in two samples with different oxygen stoichiometry: $PrBaCuFeO_{5.00}$ and $PrBaCuFeO_{5.25}$. XANES allows determining that extra-oxygen is coordinated to the Fe ions and is not coordinated to the Cu ions. EXAFS data have been analysed in order to obtain the temperature behaviour of the Debye–Waller factor related to the oxygen surrounding the Fe and Cu ions. Additionally, low temperature resistivity data are reported for both samples, they show a variable range hoping mechanism for the conductivity.

Keywords: High-T_C superconductors; EXAFS; NEXAFS; Electronic transport; Synchrotron radiation

1. Introduction

Within the ongoing investigation on the mechanism for the high T_C superconductivity, attention has been paid to the role of phonon excitations and localized vibrations in which oxygen ions are involved. Copper compounds with perovskite structure are structurally and electronically related to the high T_C superconductors. One interesting family is $RBaCuFeO_{5+\delta}$ (with R=rare earth and Y). This oxide consists of $[CuFeO_{10}]$ bilayers of corner sharing CuO_5 and FeO_5 square pyramids, as shown in Fig. 1. R^{3+} layers separate the $[CuFeO_{10}]$ bilayers and may accommodate the extra oxygen atoms of the oxidized sample, while the Ba^{2+} ions are located within the bilayer spacing, similar to the $YBa_2Cu_3O_{6+\delta}$ structure. In this paper we focused our attention on two family members corresponding to $\delta=0$ and 0.25, obtained when $R=Pr^{3+}$.

The magnetic response (neutron diffraction [1,2] and SQUID magnetometry [3]) of both compounds is different, since for $T<300$ K, the stoichiometric sample orders antiferromagnetically while the oxygen-rich remains paramagnetic in the whole range of temperatures studied. The magnetic susceptibility of that oxygen-rich sample presents an anomaly attributed to the freezing of the magnetic moments, at temperatures near 70 K. Prompted by this behaviour and given the natural presence of Fe ions in the samples, Mössbauer transmission spectroscopy was applied to study the local environment of the Fe ions in these samples [4]. Mössbauer experiments are in agreement with the susceptibility anomaly: at 70 K, the observed Mössbauer present a broad unresolved spectrum which could be originated from a relaxation of the hyperfine magnetic field due to a magnetic incipient transition.

The aim of this paper is to study carefully the local order around Fe ions in these two samples by XANES

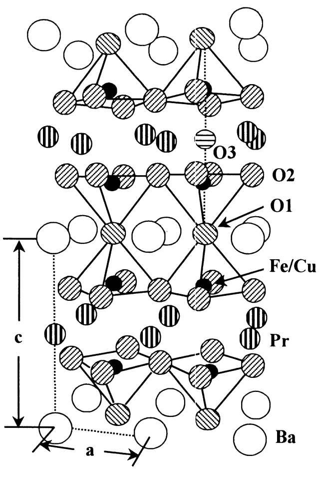

Fig. 1. Crystal structure of the $PrBaFeCuO_{5+\delta}$ compounds.

---

*Corresponding author.

PII: S0925-8388(01)00983-5

(X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) techniques and to report the electrical characterization of both samples in order to give additional results about the role of the oxygen excess in that samples.

2. Experimental

Samples were prepared from the 'nitrates method' and their purity tested by X-ray diffraction on a Siemens D-5000 apparatus [1].

X-ray absorption experiments were carried out at the XAS-13 beamline at DCI storage ring (Orsay) with electron beam energy of 1.85 GeV and an average current of 250 mA. Data were collected by using a fixed exit monochromator with two flat Si (311) crystals; detection was made by using two ion chambers with air fill gas. Energy resolution was estimated to be about 2 eV by the Cu foil 3d near edge feature. The energy calibration was monitored using the Cu foil sample; it was taken as 8991 eV at the first maximum above the edge. In order to assure an appropriate energy calibration Cu and Fe foils were measured before and after to perform the corresponding Cu and Fe K-edges sample spectra, respectively.

We have performed EXAFS and XANES measurements in the 10–300 K temperature range in order to investigate the local order around the Fe and Cu ions in two samples with different oxygen stoichiometry [1]: $PrBaCuFeO_{5.00}$ and $PrBaCuFeO_{5.25}$. Data has been analysed, using a standard procedure, in order to obtain the temperature behaviour of the Debye–Waller factor of the oxygen surrounding the Fe and Cu ions. Special attention has been paid to the normalization of the XANES spectra. After the pre-edge background subtraction, data have been normalized to a value far enough from the absorption edge and that coincides with a zero of the EXAFS signal.

Resistivity measurements have been performed in a temperature range from liquid nitrogen to room temperature by using an electrometer Keithley 617 as a constant voltage source in order to prevent non-linear effects, and by recording the intensity passing through the sample (the typical applied voltage was 1 V).

3. Results and discussion

From XANES spectroscopy, information can be obtained regarding the electronic ground state. Changes of the threshold energy can also give information about the differences in the electronic configurations of the ground state and about the formal valence of the absorber atom. On the other hand, comparison between XANES spectra of compounds with different stoichiometries has been extensively used in high T_C Cu-superconductors [5] and also in their isomorphous Ni-compounds [6]. On these studies, it has been determined the oxygen stoichiometry influence in the metal ion valence and in their short-range order.

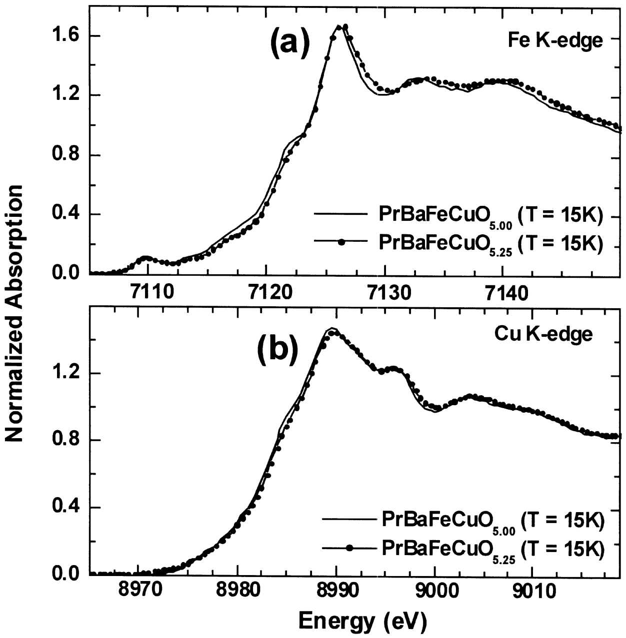

Fig. 2. Comparison of the XANES spectra at two different temperatures. Normalization has been performed at the inflexion point near 50 eV above the absorption edge in order to not perturb the characteristic features. (a) Fe K-edge; (b) Cu K-edge.

Fig. 2 shows the XANES spectra of both samples taken at the Fe and Cu K-edges. Comparison is given at 15 K to avoid any temperature effect. It has not been obtained any variation with temperature of the normalized XANES spectrum. Nevertheless, there is a very important fact that should be commented on: the threshold part of the Cu K-edge spectrum is similar for both compounds, but the comparison of both samples at the Fe K-edge presents some subtle difference. Pre-peak at 7110 eV is the characteristic 1s a 3d transition and main absorption edge position and features at 7116, 7122, 7126, 7132 and 7139 eV are characteristic of a pyramidal iron environment. It can be easily observed that the spectra corresponding to the oxygen-rich sample present smaller features as it corresponds to a mixing of two iron environments (pyramidal and octahedral in this sample) whose XANES spectra do not have features at the same energy [7]. It should be noted here that (neutron or X-ray) diffraction techniques allow to determine the lattice position for the extra-oxygen [1,2,4] but, due to the substitutional disorder of the cation sub-lattice, these techniques are not capable to determine if the extra-oxygen is coordinated to the copper or to the iron because neither of these cations nor their coordinated oxygen's are ordered in the crystal. Nevertheless, by XANES data it can be concluded that most of the extra-oxygen in the $\delta=0.25$ sample is located at the iron first coordination sphere providing an octahedral environment for one half of the Fe ions. This fact gives a mixed environment for Fe ions for our studied sample and justifies the maximum $\delta=0.5$ that can enter in the $PrBaCuFeO_{5+\delta}$ structure [4] because it would correspond to an octahedral environment for all the Fe ions.

By using a PC computer program, developed by Bonnin et al. [8] a standard procedure has been used to analyze the spectra: $\chi(k)$ EXAFS signal has been obtained after background remotion by a cubic spline fitting polynomial. Fitting the EXAFS oscillation to the well-known expression has carried out a quantitative evaluation of the data [9]:

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} \times \exp(-2k^2\sigma_j^2)\exp(-\Gamma_j R_j/k) f_j(k) \sin[2kR_j + \Phi_j(k)] \quad (1)$$

Eq. (1) describes the EXAFS oscillations for a Gaussian distribution of N_j atoms at mean distances R_j around the absorbing atom considering single scattering and plane-wave approximation. σ_j is the Debye–Waller factor which is a measure of both the static and thermal displacement of atoms about a mean bond distance, $\phi_j(k) = 2\delta(k) + \gamma_j(k)$ is the phase shift, $\delta(k)$ and $\gamma_j(k)$ being the central and backscattering atom phase shifts, respectively. $f_j(k)$ is the magnitude of the backscattering amplitude of the jth-neighbour atom, k/Γ_j is a convolution of the mean free path of the photoelectron travelling from the absorbing atom to the backscatterer in the jth-shell and the lifetime of the core hole. Backscattering amplitudes and phases, and photoelectron mean free path have been calculated by the FEFF 6.01 code [10].

Fig. 3 shows the Fourier transform magnitude (FT) of the k^3-weighted EXAFS signal ($k^3\chi(k)$) obtained at the Fe K-edge. The FT is related to the Radial Distribution Function around the Fe^{3+} ions. For each sample, several temperature data have been plotted in order to illustrate the temperature evolution of the local order around Fe ions. In order to allow comparison between those temperatures the k-range of the $k^3\chi(k)$ function selected to perform the Fourier transform has been kept constant from 1.6 to 14.25 $Å^{-1}$. For both samples, the maximum at 1.5 Å is related with the first Fe coordination distance (first oxygen coordination shell) and the maximum at 3.2 Å is related to higher coordination shells (Fe–Cu, Fe–Fe, Fe–Pr and Fe–Ba).

In principle, the evolution of the FT with temperature should be in such a way that FT decreases when temperature increases because of the thermal contribution to the Debye–Waller factor (σ); vibration acts in the same way as a statistical disorder of the atoms. It can be clearly observed that the FT peak at 3.2 Å decreases according to that rule for both samples. Nevertheless, the peak associated to Fe–O coordination presents a much more complicated behavior. For the stoichiometric sample, that peak nearly follows the thermal decrease, but the oxygen-rich sample presents a non-monotonous behavior that gives highest peaks in the 50–100 K temperature range.

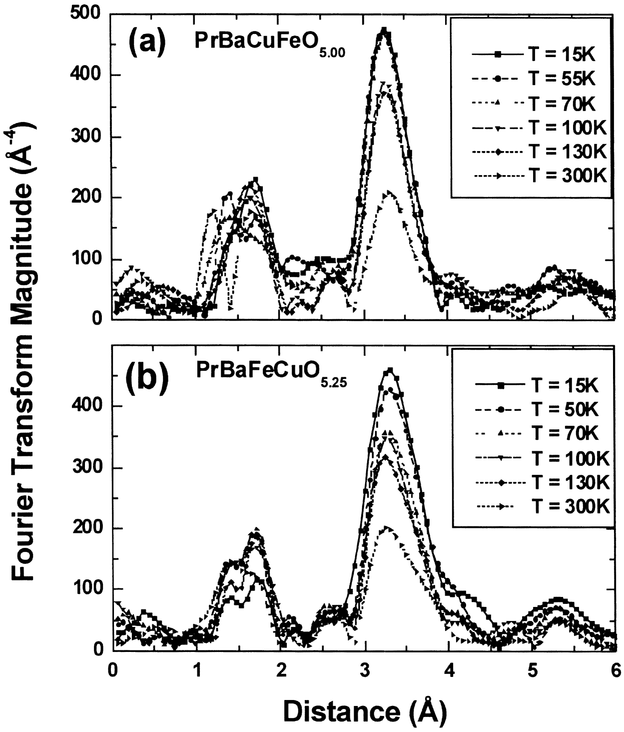

Fig. 3. Fourier transform magnitude of the k^3-weighted EXAFS signal. (a) Stoichiometric sample $PrBaFeCuO_{5.00}$; (b) oxygen-rich sample $PrBaFeCuO_{5.25}$.

In order to have a more precise idea about the oxygen vibration behavior we have fit the oxygen contribution to the EXAFS signal to obtain the temperature dependence of σ. By using the crystallographic data for a wide range of temperatures [2], distances and coordination number have been taken as known values and Debye–Waller factors as free parameters. Fit of the oxygen's peak have been performed by considering the three different crystallographic types of oxygen that surrounds iron ions: in both samples, the pyramidal Fe site is formed by the O_1 and O_2 (planar and apical atoms) and oxygen-rich sample has an additional O_3 that completes the octahedral environment. In Fig. 4 are given the crystallographic distances at helium liquid temperature and at room temperature, neutron diffraction provides a linear dependence with the temperature, but it should be noted that this thermal variation is really small compared to other compounds.

Fig. 4 shows the obtained temperature dependence of the Debye–Waller factor. Stoichiometric sample presents a standard behavior for both types of oxygen. Nevertheless, the oxygen-rich sample presents a very flat dependence of σ for O_1 and O_2 but σ for O_3 has larger values below 100 K showing an anomalous behavior. The bigger magnitude of the Debye–Waller value for the Fe–O_3 pair with respect

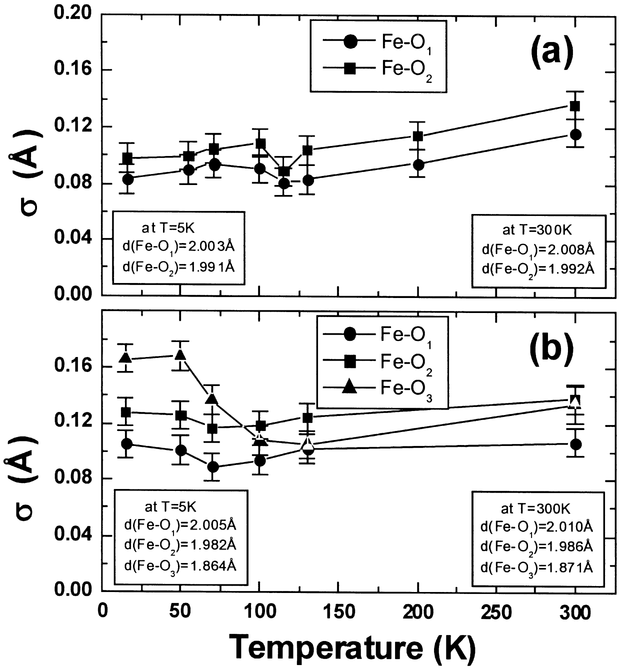

Fig. 4. Temperature dependence of the Debye–Waller factor obtained after a standard analysis of EXAFS data. Crystallographic distances taken from Ref. [2] are given at liquid helium and room temperatures.

to the others is in agreement with the smaller Fe–O_3 distance. This increase in σ is due to higher vibrational amplitude for the O_3 below 100 K. It seems to be the cause of the reported anomalous broad unresolved Mössbauer spectrum at these temperatures and support the idea that, below 100 K, in the oxygen-excess compound there is a magnetic incipient transition.

Additionally, the low temperature behavior of the electrical resistivity has been measured. The stoichiometric sample presents values of the resistivity that at room temperature are four orders of magnitude higher than the oxygen-rich one, this fact indicates that in the oxygen-rich sample the extra-oxygen is very important in the conduction mechanism. Resistivity data are given in Fig. 5. In the measured range of temperature, the oxygen-rich sample follows perfectly the expression $\rho = \rho_0 \exp(T_0/T)^{\nu}$ with $\nu = 1/2$. This is the expression for the general variable range hoping conduction mechanism [11,12]. Nevertheless, stoichiometric sample resistivity seems to follow the expression for the variable range hoping but with an exponent $\nu = 1/3$, which has been proposed for planar conduction [13]. That change in the exponent could be explained because conduction in the stochiometric sample is carried out by variable range hoping and carriers moves in the Fe/Cu–O planes; but when extra-oxygen are in the O_3 sites (apical oxygen of both octahedral belonging to different Fe/Cu–O planes), these Fe/Cu–O planes are connected and the two dimensional conduction becomes destroyed.

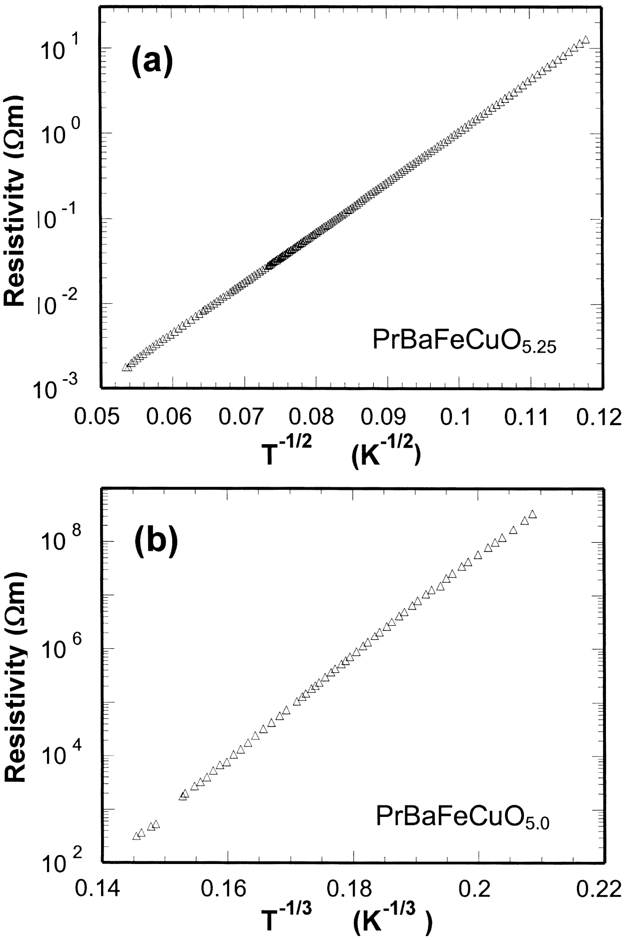

Fig. 5. Low temperature dependence of the resistivity of $PrBaFeCuO_{5.00}$ and $PrBaFeCuO_{5.25}$ compounds.

4. Conclusions

XANES and EXAFS spectroscopies have been performed to study the local order of Fe ions in $PrBaCuFeO_{5.00}$ and $PrBaCuFeO_{5.25}$ compounds. It has been found that extra-oxygen's are located in the first neighbourhood of iron giving an octahedral environment for one half of Fe ions. EXAFS analysis report an anomalous Debye–Waller factor for that extra-oxygen at temperatures below 125 K in agreement with the incipient magnetic transition detected by Mössbauer spectroscopy. Finally, a variable range hoping mechanism is observed for both samples, the obtained exponents of that expression seems to indicate that the $PrBaCuFeO_{5.25}$ sample presents a three dimensional transport behaviour and $PrBaCuFeO_{5.00}$ a bi-dimensional one.

Acknowledgements

We acknowledge the staff in charge of the DCI storage ring of LURE for beam time allocation, special thanks are given to Dr. A. Traverse for experimental assistance. We also thank A.W. Hewat from ILL for the graphic ‘xtal3d’ software package. This work has been partially supported by Spanish CICYT under contract MAT97/0725.

References

[1] M.J. Ruíz-Aragón, C. Rial, E. Morán, J.B. Torrance, N. Menéndez, J.B. Tornero, Solid State Ionics 63–65 (1993) 932.

[2] M.J. Ruíz-Aragón, U. Amador, E. Morán, N.H. Andersen, Physica C 235/240 (1994) 1609.

[3] M.J. Ruíz-Aragón, E. Morán, U. Amador, N. Menéndez, J.B. Tornero, Physica C 282/287 (1997) 1001.

[4] M. Pissas et al., Phys. Rev. B 55 (1997) 397.

[5] H. Tolentino, F. Baudelet, A. Fontaine, T. Gourieux, G. Krill, J.Y. Henry, J. Rossat-Mignon, Physica C 192 (1992) 115.

[6] M. Jiménez-Ruiz, C. Prieto, J.L. Martínez, J.M. Alonso, J. Solid State Chem. 140 (1998) 278.

[7] H. Maruyama, I. Harada, K. Kobayashi, H. Yamazaki, Physica B 208/209 (1995) 760.

[8] D. Bonnin, P. Kaiser, J. Desbarres, EXAFS PC-software, 8th Europhys. School on Chemical Physics, La Rabida, 1992.

[9] D.C. Koningsberger, R. Prins, X-ray Absorption Principles, Techniques of EXAFS, SEXAFS and XANES, Wiley, New York, 1988.

[10] J.J. Rehr, Jpn. J. Appl. Phys. 32 (1993) 8.

[11] N.F. Mott, Metal–Insulator Transitions, Taylor & Francis, London, 1990.

[12] A.L. Efros, B.I. Shklovskii, J. Phys. C: Solid State Phys. 8 (1975) L49.

[13] J.C. Bourgoin, G. Frossati, A. Ravex, D. Thoulouze, M. Vandorpe, B. Vaksmann, Phys. Status Solidi (A) 92 (1979) 585.