

J. Synchrotron Rad. (1999). **6**, 761–763

A structural model for the $\text{CaLaBaCu}_3\text{O}_7$ superconductor from a detailed EXAFS study

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The tetragonal bulk superconductor $\text{CaLaBaCu}_3\text{O}_7$ is obtained from $\text{YBa}_2\text{Cu}_3\text{O}_7$ by the replacement of Y by La and some of the Ba by Ca. Its detailed structure, particularly the cation site occupancy, is uncertain.

We have made EXAFS measurements on the edges of all four cations, Ba, Ca, Cu and La to determine the local environment of each and attempt to determine the site occupancies and to construct a possible structure, including local distortions.

Keywords: superconductors, structure, ordering

1. Introduction.

Substitution of lanthanum for yttrium and calcium for barium in the standard 123 superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) results in a tetragonal bulk superconductor $\text{CaLaBaCu}_3\text{O}_7$ (CLBO) which is isostructural with, and has essentially the same unit cell dimensions as, YBCO (de Leeuw, et al, 1988). The superconducting transition temperature of CLBO is about 80K (Carim, et al, 1988). The temperature and sharpness of the superconducting transition in CLBO depends on the cation stoichiometry, being highest and sharpest for cation ratios 1:1:1 (Carim, et al, 1988, Venkatesh, et al 1996). This has been attributed to a possible ordering of cations to form a supercell.

Although the basic structure of CLBO is clearly similar to that of YBCO there is little information on the occupancy of the various cation sites. EXAFS is ideal for determining the local structure around each cation by measuring the spectrum on an absorption edge of each. We can hence determine the cation site occupancies: these may be expected to strongly affect the superconducting behaviour owing to the differing charges on the cations. We also build up a picture of the local distortions around the cations: recent work (Attfield, et al, 1998) suggests that these strongly influence the transition temperature. We may also be able to construct a full description of the unit cell.

2. Experimental Method.

The compounds were prepared from high purity CaCO_3 , BaCO_3 , La_2O_3 and CuO by the usual solid state reaction process in a microprocessor-controlled furnace. Details of preparation methods and an analysis of the dependence of the transition temperature on composition are presented elsewhere (Venkatesh, et al, 1996). For EXAFS experiments, the pellets were finely ground, mixed with boron nitride and lightly pressed into thin cardboard sample mounts fitted with Sellotape windows.

EXAFS data were obtained at room temperature on station 7.1 of the Daresbury SRS. Beam currents during data

taking were about 200mA. Station 7.1 has a silicon (111) monochromator: harmonic rejection was achieved using a 50% detune. Standard transmission geometry was used. The edges measured were the Ca K, Cu K, Ba L_3 and La L_1 (the La L_3 edge is overlapped by the Ba L_1 edge). A useful data range out to $k = 13 \text{ \AA}^{-1}$ was achieved for the K edges, the L edges being limited to $k = 9 \text{ \AA}^{-1}$ by the presence of other L edges.

The EXAFS data were calibrated and background-subtracted using standard Daresbury software and analyzed using the Daresbury program EXCURV92. Single-scattering fast curved wave theory (Gurman, et al, 1984) was used throughout, with multiple scattering being included for the Cu-Cu coordination. Scattering parameters were calculated within the program using a complex, energy-dependent Hedin-Lundqvist potential. In all cases the raw background-subtracted data was fitted, with no further noise-reduction or glitch-removal attempted (see Fig 1): we believe that the use of raw data gives a better level of analysis, with no danger of introducing further artefacts.

3. EXAFS Results.

The results of the EXAFS analysis are shown in Table 1, which gives the fitted values of the bond lengths R, the partial coordinations N and the mean square variations in distance σ^2 for the cation-oxygen and cation-copper coordinations. Quoted errors are $\pm 2\sigma$ (95% confidence). All the shells given in Table 1 decreased the fit index significantly and all are therefore significant: in particular, the split Ca-O and La-O shells are required by the fit, whereas no significant improvement in fit index was obtained by splitting the Ba-O shell. No other coordinations could be completely fitted reliably, although the cation-cation coordinations representing the a and b cell axes usually fitted to about 3.9Å. In particular, no significant improvement in fit was obtained by including the axial Cu-O coordinations.

4. Discussion.

The cation-oxygen distances determined by EXAFS are very similar to those found in many simple compounds. It appears that these distances are fixed by the cation, rather than by the requirements of crystal symmetry. The presence of multiple cation-oxygen distances for Ca and La shows that these cations cannot occupy single, symmetric cell positions. We have to sort out the possible atomic positions from the data.

For Ba, the EXAFS clearly shows a single, well-defined environment essentially identical to that in YBCO. The high value of the mean square deviation σ^2 found for this shell is due to the fact that it is probably due to three unresolved contributions, as occurs in YBCO. If the Ba environment is that found in YBCO then a contribution of about $100.10^{-4} \text{ \AA}^2$ in σ^2 is due to this static disorder. For Cu, we obtain an average of the environments of the Cu(I) and Cu(II) sites. The absence of any significant contribution from the axial oxygen atoms (at distances significantly different from the in-plane Cu-O distances) suggests that the positions of these are highly variable. However, the Cu-O in-layer coordination is well-defined, with a small value of σ^2 .

In order to understand the Ca and La environments we use the coordination numbers and the distances, especially the root mean square distances. The latter give mean cell parameters. The coordination numbers and distances cannot be fitted by assuming single site occupancy for Ca and La, even if we assume a distorted site. The RMS distances, and the very similar total oxygen coordinations, may both be fitted reasonably well by assuming that 25-50% Ca occupies a distorted Y site, the rest being on the Ba site, with the La filling the remaining sites. A roughly 50/50 site occupation gives a good fit and we assume

Table 1. EXAFS fits: cation coordinations in CLBO

Cation	N	Type	R Å	σ^2 (10^{-4}Å^2)	N	Type	R Å	σ^2 (10^{-4}Å^2)
Ba	11.5 ± 1.4	O	2.82 ± 0.02	120 ± 30	7 ± 5	Cu	3.47 ± 0.05	110 ± 80
Ca	1.8 ± 0.4	O	2.10 ± 0.05	25 ± 30	4 ± 3	Cu	3.05 ± 0.05	150 ± 100
Ca	3.7 ± 0.8	O	2.35 ± 0.02	20 ± 15	6 ± 4	Cu	3.61 ± 0.05	170 ± 80
Ca	3.7 ± 1.2	O	3.02 ± 0.02	40 ± 40				
Cu	3.8 ± 0.4	O	1.92 ± 0.02	60 ± 10	3.8 ± 0.4	Cu	3.92 ± 0.05	30 ± 10
La	8.7 ± 1.8	O	2.53 ± 0.02	70 ± 40	10 ± 6	Cu	3.31 ± 0.05	80 ± 50
La	4.3 ± 2.8	O	3.15 ± 0.05	35 ± 50				

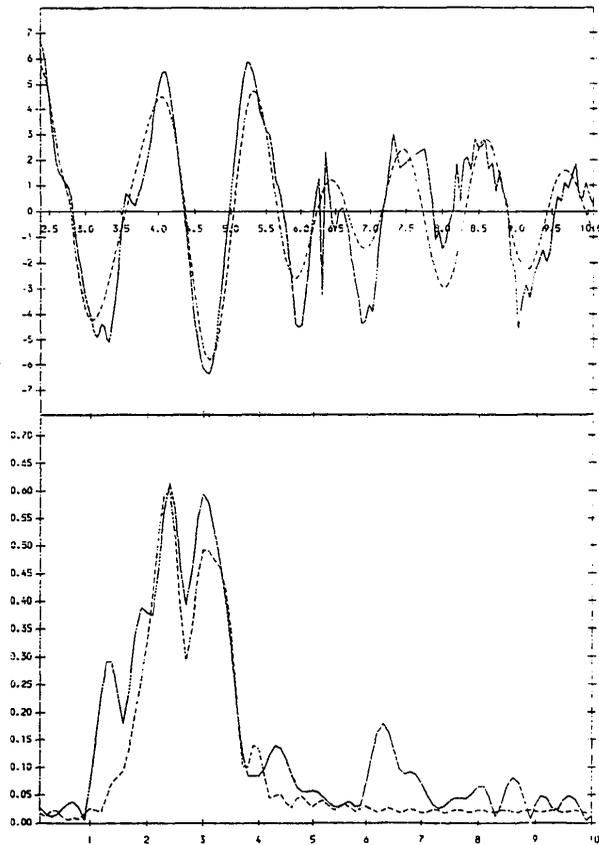


Fig 1. EXAFS spectra and their Fourier transforms: experiment (solid line) and fits (dashed line) for the calcium K edge from CLBO.

Table 2. Root mean square cation distances and cell sizes in CLBO.

Cation	RMS distance	cation z shift	RMS distance	cation z shift	Cell height
	cation-oxygen	oxygen $\Delta z/c$	cation-copper	copper $\Delta z/c$	$\Delta z/c$
YBCO: Y	2.40	0.12	3.20	0.145	0.29
YBCO: Ba	2.87	0.20, 0.00	3.43	0.175	0.35
Ba	2.82	0.20, 0.00	3.43	0.175	0.35
Ca all	2.60		3.34		0.32
Ca Y site	2.60	0.09, 0.20	3.34	0.11, 0.20	0.32
Ca Ba site	2.70	0.11, 0.21, 0.05	3.34	0.11, 0.20	0.32
La all	2.75		3.31		0.32
La Y site	2.52	0.14	3.31	0.16	0.32
La Ba site	2.84	0.14, 0.21, 0.0?	3.31	0.13, 0.20	0.32

this to be the case for simplicity, although it is probable that a small majority of the Ca atoms occupy the Ba site. With this assumption we have Ca-O distances of 2.35Å and 3.02Å on the Ba site and 2.10Å and 3.02Å on the Y site. For both sites, Ca-Cu is 3.05Å and 3.61Å. For La, we have La-O at 2.52Å and 3.15Å for the Ba site and 2.52Å for the Y site. La-Cu = 3.31Å for both sites. Thus La occupies an undistorted Y site and a distorted Ba site, whilst both Ca sites are distorted. The differing bond lengths may be fitted by assuming that Ca and La do not occupy symmetric positions. If we assume largely undistorted Cu layers, then the Ca-O and Ca-Cu distances can be accommodated on both sites by shifting the Ca atom by 0.6Å from the centre of its cell along one of the cube axes: the oxygen coordination suggests that this shift is in the z direction. La is found to be centred on its site, but one of the oxygen layers neighbouring the Ba site must then move. In all cases, distortion of the oxygen layers, by moving oxygen atoms away from the symmetry positions, is required in order to match cells in neighbouring columns. These motions need to be up to 0.5Å. The layer positions relative to the cations, derived from the bond lengths noted above, are also given on Table 2: the modulus sign arises since we do not know which layer is which, until we try to assemble a unit cell.

The results of this analysis, with all its assumptions, are that the Cu layers move only slightly (up to 0.2Å) from their positions in YBCO and are only slightly distorted, but that the oxygen layers move by up to 1.0Å and are probably much more distorted. This model accounts for the lack of any signal from the axial Cu-O distances. (The in-plane Cu-O distances are much less affected due to trigonometric effects.)

The structure obtained for CLBO is similar to that of YBCO, being a stack of three roughly cubical cells defined by the Cu layers. In order to get the c axis length, each stack must contain a Ba atom. Thus we have a structure Ba - La/Ca - Ca/La with the fully ordered Ba-La-Ca structure (similar to that proposed by Carim, et al (1988)) just excluded by the coordination numbers. The Ca and La cations do not occupy symmetric sites and it is also necessary for the oxygen atoms to be pulled away from their symmetric cube edge positions in order to meet the bond length requirements of these cations.

5. Conclusions.

Our EXAFS data have provided detailed information on interatomic distances in CLBO, and rather less reliable information on cation coordinations. From this data we have been able to suggest a possible structure for this material and obtained a rough idea of the cation site occupancy.

This study provides an example of the strengths and weaknesses of EXAFS: the detailed local information combined with the lack of long-range information.

6. References.

- Attfield, J.P., Kharlanov, A.L. and McAllister, J.A. (1998) *Nature* 394, 157-159.
Carim, A.H., de Jong, A.F. and de Leeuw, D.M. (1988) *Phys. Rev. B* 38, 7009-7012.
de Leeuw, D.M., Mutsaers, C.A.H., van Hal, H.A.M., Verweij, H., Carim, A.H. and Smoorenburg, H.C. (1988) *Physica C* 156, 126-131.
Gurman, S.J., Binsted, N. and Ross, I. (1984) *J. Phys. C* 17, 143-152.
Venkatesh, S., Srivastava, P., Saini, N.L., Dwivedi, G.L. and Garg, K.B. (1996) *Phys. Stat. Sol. A* 158, 545-552.

(Received 10 August 1998; accepted 5 January 1999)