Refinement by the Rietveld Method and Extended X-Ray Absorption Fine Structure of a 1,2,3-Type Ceramic Oxide containing Cobalt instead of Copper†

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The local structure around cobalt and yttrium ions in a 1,2,3-type ceramic oxide containing cobalt instead of copper, $YBa_{1.5}K_{0.5}Co_3O_8$, has been characterized by means of extended X-ray absorption fine structure spectroscopy. The crystal structure has been refined by Rietveld analysis of X-ray powder diffraction data. The refined structure is similar to that of the tetragonal form of $YBa_2Cu_3O_y$. The two independent cobalt ions have an octahedral and a five-co-ordinate environment of oxide ions, respectively. The potassium ions are located in the Ba^{2+} site.

Almost all of the ceramic high critical temperature (T_c) superconductors are mixed oxides containing copper ions.[1,2] A superconductor oxide, containing bismuth instead of copper, has been prepared only recently.[3] In all the copper-based mixed oxides superconductivity seems to be related to the presence of CuO_2 layers and of copper ions with different oxidation states. Partial substitution of Cu by other first-series transition metals in the so called 1,2,3-type superconductors $YBa_2Cu_{3-x}O_y$, for $x < 0.1$, resulted in a decrease in T_c,[4] although the tetragonal unit cell of the copper parent compound is preserved up to $x = 1$ for replacement by Fe or Co.[5] In the latter, a decrease of the c axis and an increase of the oxygen content ($y = 7.3$ when $x = 0.8$) was reported[6] when x increases. However, replacement of Cu for values of x larger than 1 resulted in the formation of a multiphase system.[5] On the other hand, some of us have recently reported[7] a ceramic mixed oxide of formula $Y(Ba,K)_2Co_3O_y$, having semiconducting behaviour. The chemical analysis and trial-and-error fitting of the experimental X-ray powder spectrum suggested a crystal structure close to that of the analogous copper 1,2,3 superconductor.

In order to confirm the above assignment, an extended X-ray absorption fine structure (EXAFS) analysis and refinement of the crystal structure by using the Rietveld method are now reported.

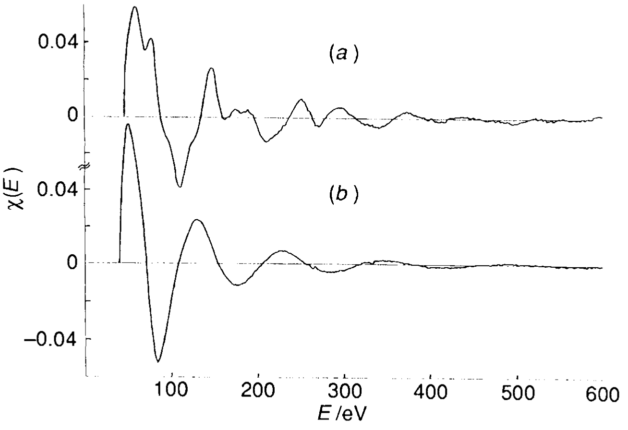

Fig. 1 EXAFS signals for cobalt ion in (*a*) $Y(Ba,K)_2Co_3O_y$ and (*b*) $Co(NO_3)_2{\cdot}6H_2O$

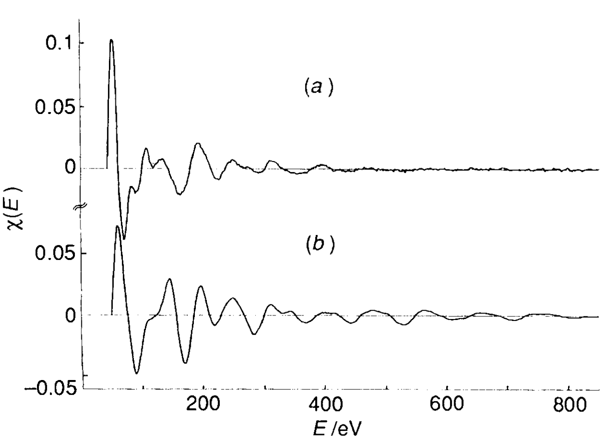

Fig. 2 EXAFS signals for yttrium ion in (*a*) $Y(Ba,K)_2Co_3O_y$ and (*b*) Y_2O_3

Experimental

Preparation of the Sample.—The samples of $Y(Ba,K)_2Co_3O_y$ used for EXAFS and crystallographic measurements were prepared with the procedure previously reported.[7]

EXAFS Measurement.—The EXAFS spectra were recorded in the transmission mode at room temperature at the EXAFS-I station installed on the DCI storage ring (Orsay, France) working at 1.85 GeV, 250 mA, using a Si (331) channel-cut monochromator in the energy ranges 7500–8350 and 16 750–17 800 eV for Co and Y edges, respectively, with $\Delta E = 2$ eV. Each point was measured for 1.5 s. Given amounts of Y_2O_3[8] and $Co(NO_3)_2{\cdot}6H_2O$,[9] used as reference compounds, and of $Y(Ba,K)_2Co_3O_y$ were carefully deposited on Millipore membranes in order to obtain a very homogeneous film with a total absorption $\mu x = 2$ after edge jump. Two samples were

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

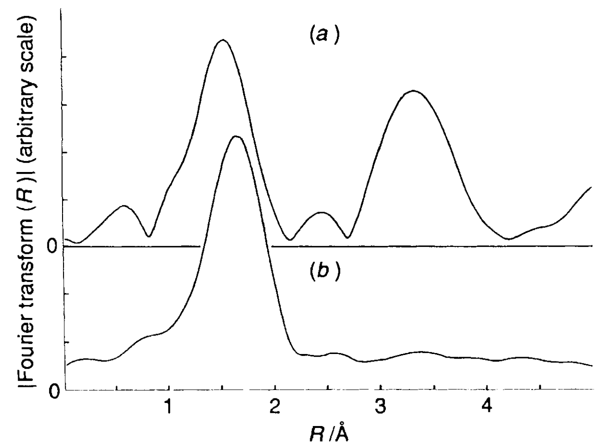

Fig. 3 Moduli of the Fourier transform of cobalt signals of (*a*) $Y(Ba,K)_2Co_3O_y$ and (*b*) $Co(NO_3)_2{\cdot}6H_2O$

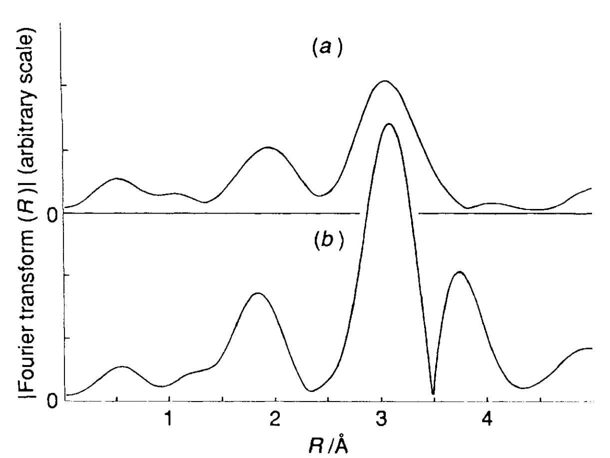

Fig. 4 Moduli of the Fourier transform of yttrium signals of (*a*) $Y(Ba,K)_2Co_3O_y$ and (*b*) Y_2O_3

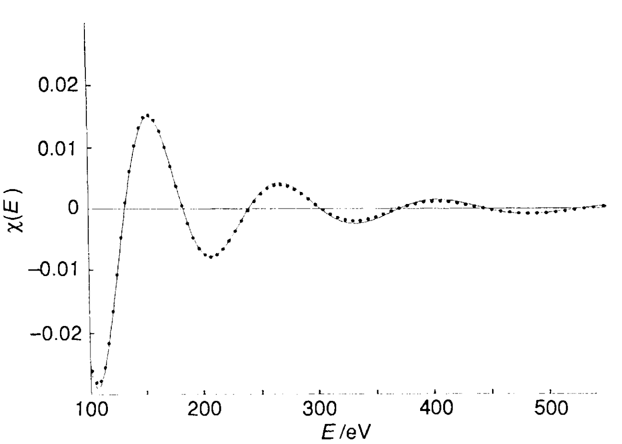

Fig. 5 Experimental signals of the first filtered peak of $Y(Ba,K)_2Co_3O_y$ (cobalt edge, · · ·) and fit (——)

Table 1 EXAFS fit results

	Atom pair	
Parameter	Y–O	Co–O
N	7.5 ± 0.5	5.2 ± 0.3
R/Å	2.42 ± 0.1	1.89 ± 0.1
$\Delta\sigma$/Å	0.06 ± 0.01	0.02 ± 0.005
E/eV	17 030	7720
ΔE/eV	2.0 ± 1.0	2.0 ± 0.5

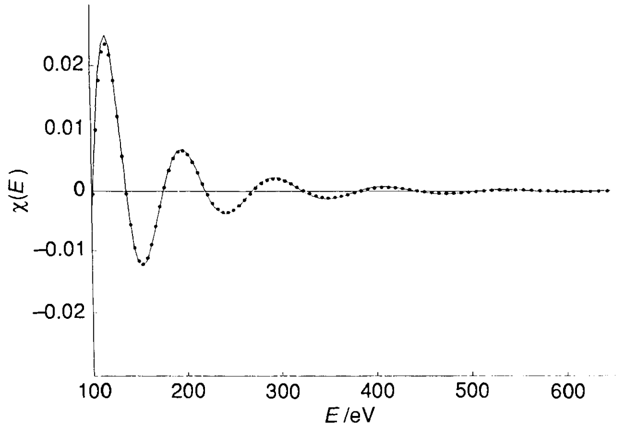

Fig. 6 Experimental signal of the first filtered peak of $Y(Ba,K)_2Co_3O_y$ (yttrium edge, · · ·) and the calculated fit (——)

prepared for each specimen and each sample was measured three times.

Analysis of the EXAFS data was carried out according to standard procedures.[10] Fig. 1 shows the EXAFS spectra for Co in $Y(Ba,K)_2Co_3O_y$ (*a*) and for the reference compound $Co(NO_3)_2{\cdot}6H_2O$ (*b*), while Fig. 2 shows the spectra for Y in $Y(Ba,K)_2Co_3O_y$ (*a*) and Y_2O_3 (*b*), respectively. The K^3-multiplied data were Fourier-transformed in the energy ranges 46–600 and 64–830 eV for the signals of Co and Y respectively, after application of a Kaiser window. Moduli of these results for Co and Y in $Y(Ba,K)_2Co_3O_y$ and in the reference compounds are reported in Figs. 3 and 4.

Only the first peak present in the Fourier transform was analysed as Co–O and Y–O interactions. Amplitude and phase functions for these atomic pairs were derived experimentally from the reference materials, using the structural bond distances Co–O (× 6) of 2.02 Å reported for $Co(NO_3)_2{\cdot}6H_2O$ and Y–O (× 6) of 2.296 Å found in Y_2O_3 as the average of three independent Y–O distances. The factor $\exp(-2\sigma^2k^2)$ was convoluted with the experimental amplitude. The functions were separately calculated for all the collected spectra of the reference materials. The reliability of these functions was checked by transferring them to each spectrum of the same material through a least-squares fitting. To take into account any approximation in chemical transfer of amplitude and phase functions, a variation of E_0 was introduced for the fit; E_0 was determined as the inflection point of the edge jump. The values of these functions were transferred to the spectra of $Y(Ba,K)_2Co_3O_y$. The fits are reported in Figs. 5 and 6, and the values obtained are listed in Table 1.

Analysis of the X-Ray Powder Profile.—Powder X-ray diffraction data were recorded at room temperature with an Ital Structures goniometer with θ–2θ geometry, equipped with step-scan attachment, proportional counter, and Soller slits. Nickel-filtered Cu-Kα radiation was employed with a divergence aperture of 0.3° and receiving aperture of 0.05°. The diffraction profile was recorded in the range $20 \leqslant 2\theta \leqslant 110°$ with a stepwidth of 0.02° and count time per step of 13 s.

Initial cell and atom parameters as well as the tetragonal space group *P*4/*mmm* were assumed to be those proposed in a previous study.[7] Refinement was carried out on both structural and non-structural parameters with the the aid of a program written by Immirzi.[11] The *z* coordinates of Ba(K), Co(2), O(1) and O(2) together with all thermal parameters and the occupation factors of the Ba–K atom pair and of O(3) were refined. For the statistical variance of Ba and K, the only constraint imposed on their relative occupation factors was that their sum corresponded to a full occupancy.

Among non-structural parameters, the peak shapes were described by pseudo-Voigt functions where the Gaussian

Table 2 Refined non-structural parameters in the Rietveld analysis

Zero correction 2θ/°	0.046(1)
Profile function parameters	
n	0.51(2)
U	0.088(8)
V	−0.070(8)
W	0.025(2)
Preferred orientation G	0.026(7)
Background intensities (k counts) at nodes of the segmented line	
2θ/° = 20	0.100(1)
= 30	0.111(1)
= 40	0.125(1)
= 60	0.142(1)
= 80	0.150(1)
= 90	0.143(1)
= 100	0.110(1)
= 110	0.080(1)
Cell parameters (Å)	
$a = b$	3.846(2)
c	11.176(3)

Table 3 Refined structural parameters in the Rietveld analysis. OF = occupancy factor

Atom	x	y	z	B/°	OF
Y	0.5	0.5	0.5	0.10(1)	0.125
K	0.5	0.5	0.162(1)	0.50(6)	0.070(7)
Ba	0.5	0.5	0.162(1)	0.50(6)	0.180(7)
Co(1)	0.0	0.0	0.0	1.50(9)	0.125
Co(2)	0.0	0.0	0.344(2)	1.50(7)	0.25
O(1)	0.0	0.0	0.170(7)	1.5	0.25
O(2)	0.5	0.0	0.371(4)	1.5	0.5
O(3)	0.5	0.0	0.0	1.5	0.236(20)

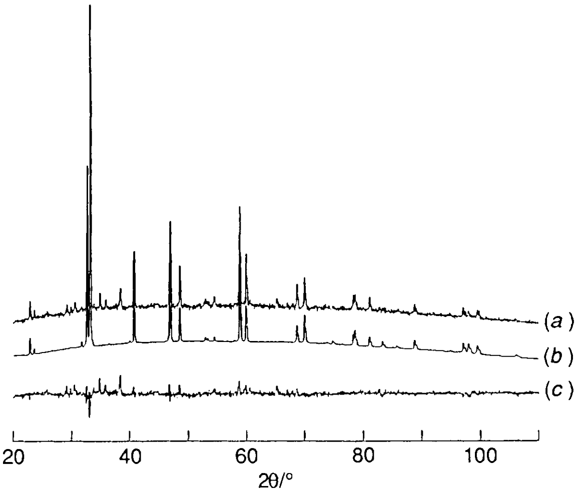

Fig. 7 Rietveld refinement patterns for $Y(Ba,K)_2Co_3O_y$. Comparison of the experimental (*a*) and calculated (*b*) profiles. The bottom line (*c*) represents the difference between the two profiles

Table 4 Comparison of the unit-cell parameters (Å) and of the interatomic distances (Å) in Cu–123 (tetragonal form) **I** * and Co–123, **II**

I			**II**	
$a = b$		3.8683(6)	$a = b$	3.846(2)
c		11.688(2)	c	11.176(3)
Ba–O(1)	(×4)	2.7586(8)	Ba(K)–O(1)	2.721(3)
Ba–O(2)	(×4)	2.945(2)	Ba(K)–O(2)	3.03(4)
Ba–O(3)	(×4)	2.9265(4)	Ba(K)–O(3)	2.641(8)
Y–O(2)	(×8)	2.404(1)	Y–O(2)	2.40(3)
Cu(1)–O(1)	(×2)	1.839(4)	Co(1)–O(1)	1.90(8)
Cu(1)–O(3)	(×4)	1.9341(3)	Co(1)–O(3)	1.923(1)
Cu(2)–O(1)		2.353(4)	Co(2)–O(1)	1.94(8)
Cu(2)–O(2)	(×4)	1.9472(4)	Co(2)–O(2)	1.95(8)
Ba–Y		3.6477(7)	Ba(K)–Y	3.78(1)
Ba–Cu(1)	(×4)	3.5079(4)	Ba(K)–Co(1)	3.267(6)
Ba–Cu(2)	(×4)	3.3856(5)	Ba(K)–Co(2)	3.40(2)
Y–Cu(2)	(×8)	3.1958(4)	Y–Co(2)	3.23(1)

* Data from ref. 12.

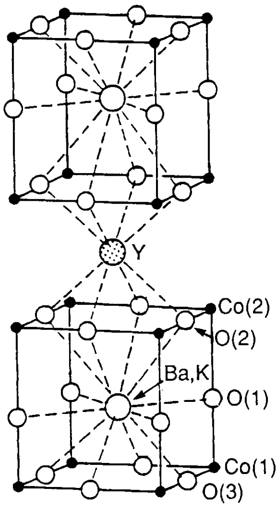

Fig. 8 Crystallographic model of $Y(Ba,K)_2Co_3O_y$ with the numbering scheme for the independent ions

contribution η was refined; half-height widths, as a function of 2θ, were described by the expression $H_k^2 = U[\tan(2\theta_k)]^2 + V[\tan(2\theta_k)] + W$. Preferred orientation was taken into account through the expression PO = exp(−Gα_k), where α_k is the angle between the scattering vector of the Kth reflection and the scattering vector of a fixed preferred orientation. The background line was reproduced by a segmented line whose nodes, arbitrarily chosen on the 2θ scale, could be refined on the intensity scale. Cell parameters together with a zero correction on the experimental 2θ scale were also refined.

The final crystallographic parameters are reported in Tables 2 and 3. The final R' value was 0.046, calculated on the whole experimental profile, while the artificial suppression of spurious peaks lowered this factor to 0.040. Fig. 7 shows the comparison of the calculated and experimental profile.

Results and Discussion

The EXAFS results are summarized in Table 1, where N is the number of O^{2-} ions at a distance R from Y and Co respectively. These data clearly show that the environment of the yttrium ions is formed by eight oxygen atoms in a cubic arrangement. The Y–O distance of 2.42 Å is in good agreement with that of 2.40(3) Å derived from X-ray analysis. The cobalt environment is well interpreted assuming an octahedral and a square-pyramidal geometry for two crystallographically independent cobalt ions in 1 : 2 ratio, respectively. The Co–O distance derived by EXAFS is 1.89(10) Å.

The results of the X-ray powder refinement confirm the structure previously proposed by the trial-and-error method shown in Fig. 8, together with the numbering scheme for the crystallographically independent ions. The occupancy of the oxygen atoms could be considered essentially complete, and the content of the unit cell may be formulated as $YBa_{1.44}K_{0.56}Cu_3O_{7.9}$ in agreement with the chemical analysis which showed that about 1/3 of the Ba^{2+} ions are replaced by K^+.[7] Atom Co(1) is approximately octahedral with Co(1)–O(1) and Co(1)–O(3) distances of 1.90(8) and 1.923(1) Å, respectively, while Co(2) is square pyramidal with basal Co(2)–O(2) and axial Co(2)–O(1) distances of 1.94(8) and 1.95(8) Å, respectively. These values compare well with those derived from EXAFS measurement (see above) within the experimental errors.

Finally, the Ba^{2+} and K^+ ions are co-ordinated by twelve oxide ions which occupy the vertices of a distorted cubo-octahedron: Ba,K–O(1), Ba,K–O(2) and Ba,K–O(3) are 2.721(3), 3.03(4) and 2.641(8) Å, respectively.

A comparison with distances found in the tetragonal form of $YBa_2Cu_3O_6$,[12] where the co-ordination around Cu(1) is digonal and that around Cu(2) is five-co-ordinate, is given in Table 4, together with the unit-cell parameters. The axial distance of the five-co-ordinate cobalt ions is about 0.4 Å shorter than that of the analogous copper ion. This difference is mainly responsible for the lengthening of the *c* axis in the copper compound as well as of the lengthening of the Ba,K–O(3) distances by *ca.* 0.3 Å (Table 4).

Attempts to elucidate by EXAFS the environment of the K^+ ions in the cobalt derivative and to prepare samples of $Y(Ba,K)_2Co_3O_y$ with a lower oxide content are in progress.

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