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Local structure around the Co cations in $YBa_2(Cu_{1-y}Co_y)_3O_{6+x}$ $(0<y\leq 0.06)$ determined by x-ray-absorption spectroscopy

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We studied the Cu substitution by Co in $YBa_2Cu_3O_{6+x}$. The samples have been analyzed by extended x-ray-absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) techniques in the oxidized and the reduced forms. We determined the Co cations average coordination and valence. Structural models for the arrangement around the cobalt atoms are proposed. The cobalt valence is 3^+ in both oxidized and reduced forms. XANES experiments showed that the coordination polyhedra around the cobalt cations are not centrosymmetrical. EXAFS spectra showed that the cobalt cations are displaced from the (000) position and are surrounded by 5 oxygen atoms (4 at 1.82 Å and 1 at 2.02 Å). Both the EXAFS and XANES show that the difference between these two sets of Co-O distances decreases for reduced compounds. This corresponds to a slight increase of the site symmetry. Tetrahedral, pyramidal, and highly distorted octahedral coordinations for the cobalt cations are proposed. They take into account all these results obtained for oxidized and reduced compounds. Our results corroborate the assumption that the Co cations in the $YBa_2(Cu_{1-y}Co_y)_3O_{6+x}$ compounds are in the intermediate spin state with a mixing of high-spin Co^{3+} in the tetrahedral site and low-spin Co^{3+} in the distorted octahedral site.

I. INTRODUCTION

Superconducting cuprates are oxides that contain two or more location sites of different size and by using the proper dopant, one can study the role and the influence of each site on the superconducting properties. Cation doping has been widely used to carry out such studies in $YBa_2Cu_3O_{6+x}$. Because doping with Fe, Co, Al, Ni, and Zn, which substitute for the Cu cations, has different effects on the superconducting properties, it can unveil the role of the two Cu sites, the planar Cu(2) or the square Cu(1) sites. To relate the structural perturbations induced by the cation doping with the superconducting properties one must determine the structure at the local level. This can be done only be combining as many techniques as possible, such as x-ray and neutron diffraction, electron microscopy and diffraction, and x-ray-absorption spectroscopy.

We report in this paper x-ray-absorption experiments at the Co K edge carried out to determine the local structure around the Co cations, starting from that obtained by diffraction techniques.[1] We aimed to determine the valence, the number of the nearest neighbors, and the Co-O distances for oxidized and reduced $YBa_2(Cu_{1-y}Co_y)_3O_{6+x}$ samples. More specifically we studied low-Co-substituted $(0<y\leq 0.06)$ samples in the oxidized and reduced forms. The sample preparation details, as well as neutron, electron diffraction, and microscopy results are described elsewhere.[1,2] The EXAFS and XANES spectra at the Co K edge were recorded at the EXAFS station D42 of the LURE in the fluorescence mode. In order to interpret the different features of the absorption spectra, EXAFS and XANES studies of model compounds, for which the coordinations, the nature of the chemical bondings, and the site symmetries are well established, were investigated.

II. EXAFS STUDIES

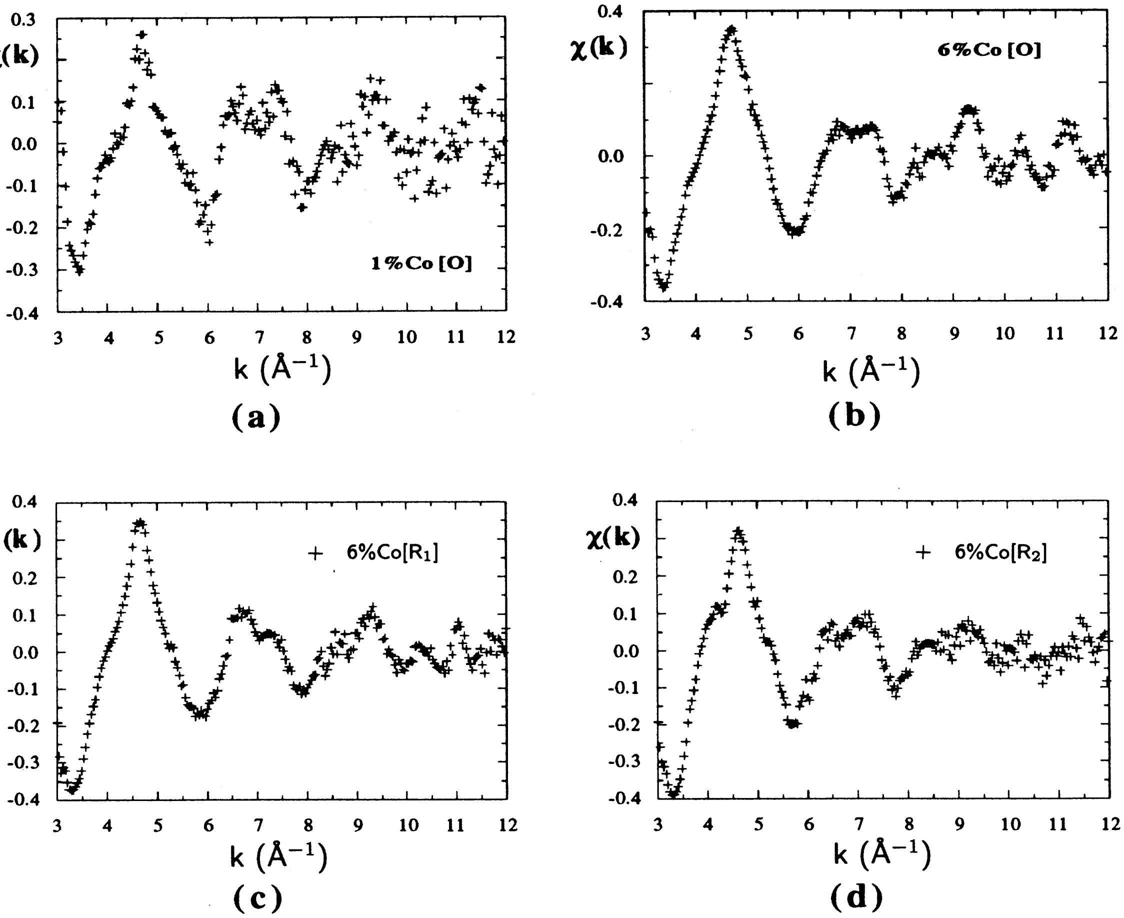
A. Experiment

The EXAFS spectra were measured at the Co K edge for four samples of two different Co dopings, $y=0.01$ and $y=0.06$. Only the oxidized form was investigated for the former concentration, whereas for the latter one, the oxidized form and two reduced forms were investigated. Hereafter 1:2:3-Co$_y$ followed by $[O]$ refers to the oxidized form $YBa_2(Cu_{1-y}Co_y)_3O_{6+y}$ and followed by either $[R_1]$ or $[R_2]$ refers to one of the reduced forms. Powders of 1:2:3-Co$_y$ samples were synthesized from stoichiometric mixtures of $BaCO_3$, Y_2O_3, CuO, and Co_3O_4 heated twice at 930 °C for 15 h. For the oxidized compounds $[O]$, a third firing at 930 °C for 10 h in an oxygen atmosphere was carried out, followed by a rapid cooling to 600 °C. Then the samples were cooled slowly (50 °C/h) to 300 °C where they were kept for 5 h. The reduced samples were heated in a flux of nitrogen, the temperature was increased slowly (50 °C/h) up to 700 or 830 °C; as the oxygen partial pressure over the sample remains low, the final oxygen stoichiometry depended essentially on the maximum temperature reached during the cycle. Thermal treatment $[R_1]$ refers to an oxidized sample heat treated at 700 °C in an inert atmosphere for one hour, while $[R_2]$ refers to an oxidized sample heat treated at 800–830 °C in an inert atmosphere for 20 h. Thermogravimetry measurements on 1:2:3-$Co_{0.06}$ show a variation of the number of oxygen atoms $\Delta x=0.60$ from $[O]$ to $[R_1]$ and $\Delta x=0.78$ from $[O]$ to $[R_2]$. For oxidized samples, as found by ac susceptibility measurements, the superconducting transition decreases with increasing y and disappears when the samples are reduced. For example, the T_c onset for 1:2:3-$Co_{0.06}[O]$ was 65 K. The lattice parameters were refined from x-ray powder patterns using 20 reflections and a Si standard. 1:2:3-$Co_{0.01}[O]$ is still orthorhombic ($a=3.8259$ Å, $b=3.8843$ Å, $c=11.6718$ Å) whereas 1:2:3-$Co_{0.06}[O]$ is tetragonal ($a=3.8674$ Å, $c=11.6785$ Å) as well as the reduced samples. The reduction process causes a significant increase of the c parameter ($a=3.8673$ Å, $c=11.781$ Å for 1:2:3-$Co_{0.06}[R_1]$).

Because all compounds investigated contained low Co concentrations, the fluorescence mode was used to collect spectra which were recorded between 7600 and 8400 eV with a 2 eV step. The EXAFS signals together with the corresponding Fourier transforms for the four samples are shown in Figs. 1(a)–(d) and 2(a)–2(d). Data were analyzed using the usual method of Fourier filtering with an EXAFS analysis package.[3] The mathematical functions used for the least-squares fit of the atomiclike absorption were 4th or 5th degree polynomials. The pre-edge spectrum was described by a linear function.

The EXAFS signals were normalized by using the Lengeler-Eisenberger procedure.[4] Because of the low concentration of Co, the EXAFS spectra corresponding to the samples 1:2:3-$Co_{0.01}[O]$, 1:2:3-$Co_{0.06}[R_1]$, and 1:2:3-$Co_{0.06}[R_2]$ were not exploitable beyond 11 $Å^{-1}$. In order to be able to compare the Fourier transforms, shown in Fig. 2, all of them were calculated with a k^3 weighting scheme and a Kaiser cutoff window limiting the k space between $k_{\min}=3$ $Å^{-1}$ and $k_{\max}=11$ $Å^{-1}$ (Ref. 5).

Structural parameters were refined by a nonlinear least-squares fitting procedure, using the CERN minimization package MINUIT,[6] which includes simplex and gradient algorithms. The minimized function is $F=\sum(k\chi_{\exp}-k\chi_{\mathrm{th}})^2$ and the agreement factor is taken as



(a) (b) (c) (d)

FIG. 1. EXAFS signal at the Co K edge for the four compounds $YBa_2(Cu_{1-y}Co_y)_3O_{6+x}$ (a) $y=0.01[O]$, (b) $y=0.06[O]$, (c) $y=0.06[R_1]$, (d) $y=0.06[R_2]$; (1:2:3-Co_y followed by $[O]$ refers to the oxidized form $YBa_2(Cu_{1-y}Co_y)_3O_{6+x}$ and followed by either $[R_1]$ or $[R_2]$ refers to one of the reduced forms).

$\rho = F_{\min} / \sum k\chi^2_{\exp}$, where the theoretical EXAFS function $k\chi_{\mathrm{th}}$ is the standard formula. We did not use the weighted minimization function since it was impossible to estimate correctly the error bars from our experimental data. However, as recommended by the international workshop on standards and criteria in x-ray-absorption spectroscopy,[7] only variations of the fitted parameters leading to a variation of the agreement factor greater than $2\rho_{\min}$ are meaningful. In all the fits, we took care of the maximum allowed number of free parameters, $N_{\mathrm{free}} = N_{\mathrm{ind}} - 1 = (2\Delta k \Delta R / \pi) - 1$, where Δk and ΔR are the k- and R-space bandwidths.

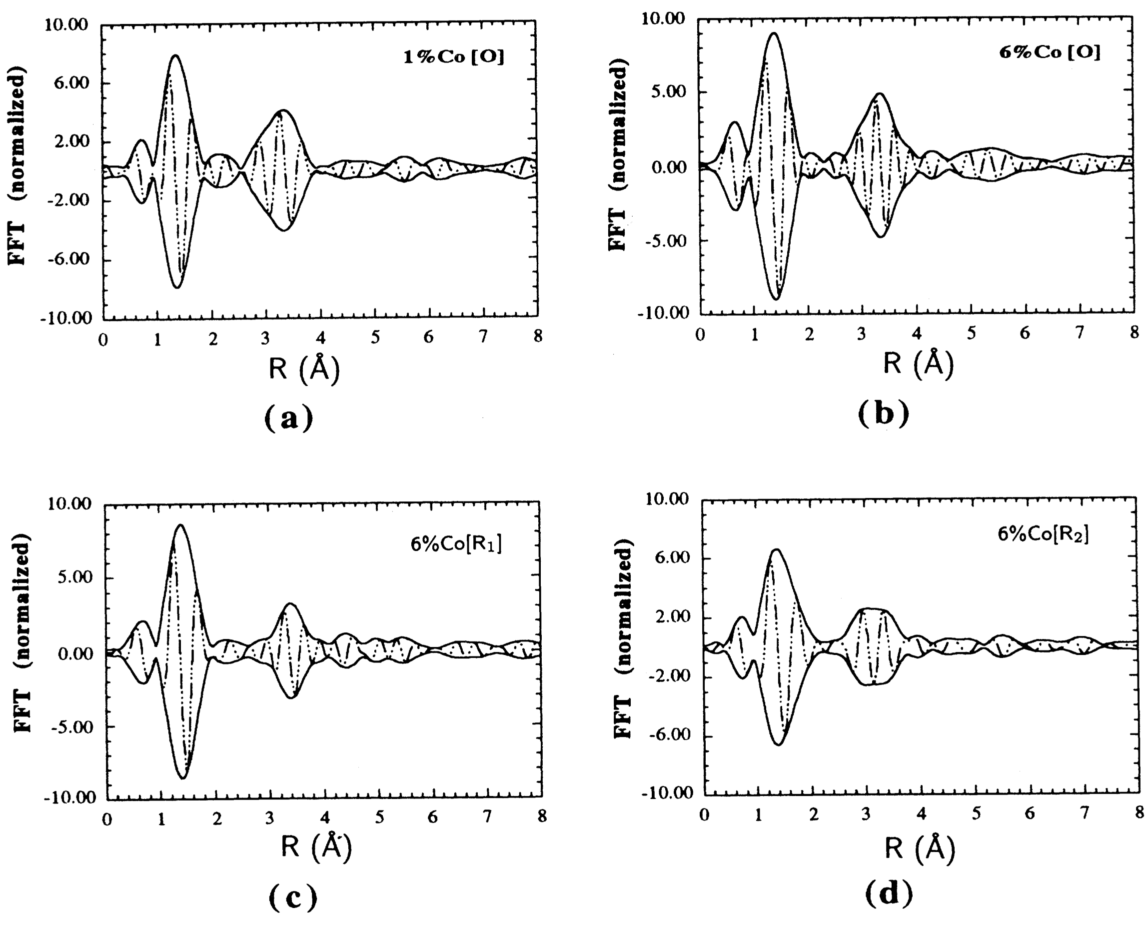
B. Cobalt cation coordination in the oxidized samples

1. 1:2:3-Co$_{0.06}$[O]

It can be seen in Fig. 1(b) that the signal-to-noise ratio of the EXAFS spectrum is good up to 12 Å^{-1}. The Fourier transform evidences the narrow and well resolved Co-O peak. The cutoff window is placed between 1.00 and 1.85 Å. The number of independent parameters is equal to 5. There is no evidence from the extracted phase that the Co-O peak is comprised of two unresolved peaks.

During the refinements we always used the same experimental terms for the phase and amplitude, namely those extracted for the Fe-O bond in $FePO_4$ with a slight theoretical correction to account for Co instead of Fe as the probed atom. The transferability of these terms was tested for the model compound Co_3O_4. For the 1:2:3-$Co_{0.06}$[O] compound the refined values for the number of oxygen atoms in the first shell (N_1), the Co-O distance (R_1), the energy shift (ΔE_1) and the Debye Waller factor ($\Delta\sigma_1$) are 3.9, 1.82 Å, −1.9 eV, and 0.04 Å^2, respectively. The agreement factor ($\rho = 6 \times 10^{-3}$) was satisfactory. There exists an energy shift of $\Delta E_1 = -1.9$ eV which coincides with the shift used for the analysis of the standard compound Co_3O_4 when the refinement is carried out with only one distance Co-O. A two-peak refinement was then tried for 1:2:3-$Co_{0.06}$[O], since it is likely that the Co coordination is greater than 4, the total oxygen stoichiometry being greater than O_7 as indicated by neutron diffraction.[8,1]

After several cycles of refinement where N_1 and N_2, R_1, and R_2 were varied, we obtained the fit shown in Fig. 3 which yielded the following values: $N_1 = 4.0$,



(a)
(b)
(c)
(d)

FIG. 2. Fourier transform (radial distribution function) of the EXAFS signal for the four compounds $YBa_2(Cu_{1-y}Co_y)_3O_{6+x}$, (a) $y = 0.01[O]$, (b) $y = 0.06[O]$, (c) $y = 0.06[R_1]$, (d) $y = 0.06[R_2]$. The calculations are carried out between $k_{\min} = 3$ and $k_{\max} = 11$ Å^{-1} with a Kaiser cutoff window ($\tau = 2,5$). Fourier transforms are normalized by $\delta k / \sqrt{\pi}$, where $\delta k = 0.04$ Å (Ref. 7).

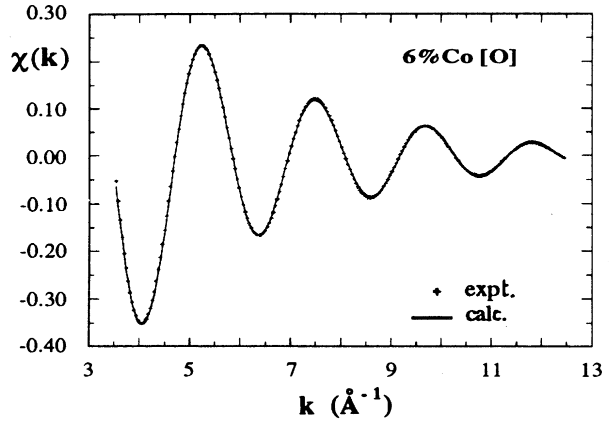


FIG. 3. The best two-shell fit of the Co-O distances for the 1:2:3-$Co_{0.06}$ [O] compound. Limits of the Fourier transform: 3 $Å^{-1}$ and 12 $Å^{-1}$.

$N_2=1.0$, $\Delta\sigma_1=\Delta\sigma_2=0.02$ $Å^2$, $R_1=1.82$ Å, and $R_2=2.02$ Å. The agreement factor ($\rho=6.3\times10^{-4}$) is ten times smaller than that obtained with one shell and the $\Delta\sigma$ values decrease. The best fit for the Fourier transform obtained with a cutoff window extending between 3 and 11 $Å^{-1}$ gives identical results to those obtained with a window extending between 3 and 12 $Å^{-1}$. It can be concluded that the Co cations in the sample 1:2:3-$Co_{0.06}$ [O] are on the average surrounded by five oxygen atoms of which four are at 1.82 Å and one at 2.02 Å. The average 1.86 Å value is somewhat short and much smaller than $a/2=1.9334$ Å.

2. *1:2:3-$Co_{0.01}$ [O]*

As shown in Fig. 1(a) the signal-to-noise ratio of the EXAFS spectrum for the 1:2:3-$Co_{0.01}$ [O] is small, which is due to the very low Co concentration corresponding to 230 ppm. A two-shell fit was carried out. The cutoff window for the radial distribution extended between 0.89 and 1.85 Å. The number of independent parameters was 5 and the starting values for R_1 and R_2 were those found for 1:2:3-$Co_{0.06}$ [O]. Several cycles of refinement yielded the following parameters: $N_1=3.3$, $N_2=1.15$, $R_1=1.82$ Å, and $R_2=2.04$ Å. The energy shifts ΔE_1 and ΔE_2 were fixed at -0.7 eV, which corresponds to the difference between E_0 (7720.4 eV) for 1:2:3-$Co_{0.06}$ [O] and E_0 (7721.1 eV) for 1:2:3-$Co_{0.01}$ [O]. The agreement factor ($\rho=5.5\times10^{-3}$) was quite satisfactory. The coordination number of the first shell, N_1, for 1:2:3-$Co_{0.01}$ [O] is smaller than that of 1:2:3-$Co_{0.06}$ [O] while N_2 is almost the same for both compounds. The interatomic distances are identical.

When the Fourier transform is carried out between 3 and 12 $Å^{-1}$, as shown by the dotted line in Fig. 4, the principal peak is flanked by a secondary peak centered at 2.4 Å. If the cutoff window is placed between 0.89 and 2.38 Å and a three-shell refinement is carried out, the following values are obtained: $N_1=3.4$, $N_2=1.5$, $N_3=1.25$, $R_1=1.83$ Å, $R_2=2.09$ Å, $R_3=2.40$ Å, and $\Delta E_1=\Delta E_2=\Delta E_3=-0.8$ eV. This fit seems correct; however, the peak corresponding to the 2.40 Å distance disappears when the Fourier transform is carried out between 3 and 11 $Å^{-1}$ or between 3 and 9.8 $Å^{-1}$ (see Fig. 4). The existence of such a distance was reported by Bridges *et al.*,[9] who studied the EXAFS spectra at the Co K edge of Co-substituted $YBa_2Cu_3O_{6+x}$ samples in the oxidized form. Nevertheless such a peak does not appear in the data of any other compounds we have studied. Moreover, our simulations showed that this is not only due to the background. Its intensity is too strong to be due to the cutoff oscillations. Since this peak is only present in the Fourier transform under particular conditions, we think that it has no structural meaning and it is due to constructive interferences between the signals and the oscillations associated with the cutoff. It can be concluded that the 2.40 Å distance does not exist in our samples.

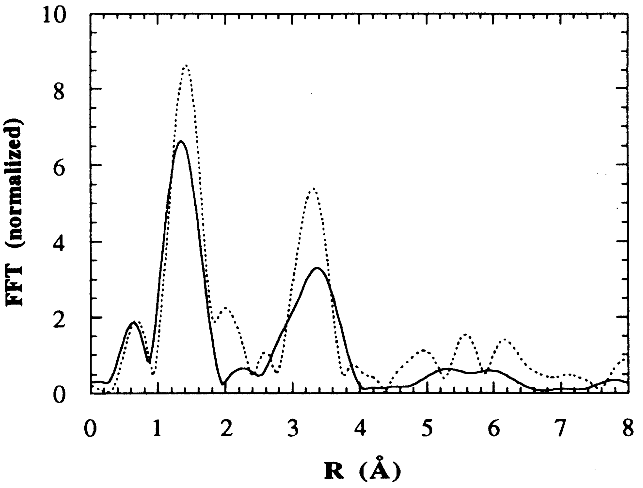


FIG. 4. Fourier transform of the EXAFS signal for the 1:2:3-$Co_{0.01}$ [O] compound carried out with a Kaiser cutoff window ($\tau=2,5$). (a) Continuous line: between 3 and 10 $Å^{-1}$. (b) Dotted line: between 3 and 12 $Å^{-1}$.

C. Cobalt coordination in the reduced samples

1. *1:2:3-$Co_{0.06}$ [R_1]*

Figure 1(c) shows the EXAFS spectrum for this compound, which is well defined up to $k=11$ $Å^{-1}$ and has a satisfactory signal-to-noise ratio. The corresponding Fourier transform (Fig. 2) exhibits a single Co-O peak which is broader and less intense than the Co-O peak of the 1:2:3-$Co_{0.06}$ [O] compound. The cutoff window extended between 0.89 and 1.92 Å. The number of independent parameters was 5. From the first refinement it was clear that there existed two Co-O distances very similar to those obtained for 1:2:3-$Co_{0.06}$ [O]. With $\Delta E_1=\Delta E_2=0$ and $\sigma_1=\sigma_2=0.02$ $Å^2$, the refined values for N_1, N_2, R_1, and R_2 were 3.8, 1.2, 1.85 Å, and 2.05 Å, respectively. The agreement factor ($\rho=5.2\times10^{-3}$) was satisfactory. The comparison of these results with those obtained for 1:2:3-$Co_{0.06}$ [O] reveals that the number of oxygen atoms in the first shell decreased ($4\Longrightarrow3.8$) while that in the second increased ($1\Longrightarrow1.2$), but the total number remained the same at 5 and the average distance increased slightly (1.86⟹1.90 Å).

2. 1:2:3-$Co_{0.06}$[R_2]

The Fourier transform of the EXAFS signal [Fig. 2(d)] exhibits an asymmetric Co-O peak extending up to 2.24 Å. Its maximum is smaller than that of the Co-O peak for 1:2:3-$Co_{0.06}$[O]; the beating between the two shells leads to this decrease which indicates that the difference between N_1 and N_2 is smaller. A Fourier transform calculated between 3 and 12 $Å^{-1}$ revealed the secondary peak more clearly. The cutoff window was between 1.0 and 2.24 Å and the number of independent parameters was equal to 6. The structural parameters are slightly different from those obtained for the compounds 1:2:3-$Co_{0.06}$[O] and 1:2:3-$Co_{0.06}$[R_1]. With $\Delta E_1=\Delta E_2=0$ and $\sigma_1=\sigma_2=0.02$ Å^2, the refined values for N_1, N_2, R_1, and R_2 were 3.1, 1.6, 1.845 Å, and 2.01 Å, respectively. The agreement factor was $\rho=2.1\times10^{-3}$. With respect to the results obtained for 1:2:3-$Co_{0.06}$[R_1], the number of the oxygen atoms in the first shell is smaller (3.8⟹3.1), whereas that in the second shell is larger (1.2⟹1.6). The average distance is 1.90 Å which is the same as that found for 1:2:3-$Co_{0.06}$[R_1].

D. The second-nearest-neighbor coordination sphere

Multiple scattering and the absence of standard compounds from which the phases and the amplitudes of the various Co-Ba, Co-Cu, and Co-Co pairs could be deduced, makes difficult a quantitative study of the second-nearest-neighbor coordination sphere. Furthermore, it is likely that linear coordinations such as Co-O-Cu/Co(1) exist in the basal plane, in which case the forward scattering is enhanced by the presence of the oxygen atom. However, it is possible to extract some information about the changes in the cation-cation distances.

The neutron diffraction results of 1:2:3-$Co_{0.06}$[O] showed that the coordination of the second-nearest neighbors around the Co cations comprises eight Ba at 3.494 Å and four Cu/Co(1) at 3.867 Å (Ref. 10). If one assumes that the Co(1) cations are at (000), the Fourier transform should contain two peaks separated by about 0.3–0.4 Å, corresponding to the Co(1)-Ba and Co(1)-Cu/Co(1) pairs, the difference between these distances being large enough to get two resolved peaks. However, as can be seen from Fig. 2(b), there is only one peak in the Fourier transform between 2.63 and 4.06 Å and moreover, its shape is rather complicated. The number of independent parameters is equal to eight. The theoretical phases and amplitudes calculated by McKale et al.[11] for the pairs Co/Ba, Co/Cu, and Co/Co have been used. We are perfectly aware of the inaccuracy of these parameters, especially the amplitudes. Therefore only gross features can be derived from the EXAFS analysis, such as approximate distances and variation from one sample to another. Since the values for the Co/Cu and Co/Co pairs are very similar, the refinements have been carried out by taking into account only the values corresponding to the Cu/Co pair which is good enough according to the previous remark.

The first two-shell refinement showed that the amplitude of the EXAFS signal corresponding to the second-nearest neighbors was small. The number of Ba and Cu/Co neighbors obtained from the fit was much smaller than the values, 8 and 4 respectively, quoted above. The same behavior is obtained at the Cu K edge for the undoped 1:2:3 reduced samples[12,13] and at the Co K edge for the Co-doped 1:2:3 samples.[9] The hypothesis that the Co cations are located at (000) does not allow even a qualitative adjustment of the phases. The results, $R_1=3.58$ Å, $R_2=3.52$ Å, suggest a distance Co(1)-Ba (3.58 Å) larger than the average distance (3.49 Å) determined from diffraction experiments, whereas the distance Co(1)-Cu/Co(1) (3.52 Å) is much smaller than the average one (3.87 Å) determined by the same technique. This could be taken as an indication that the Co cations are somewhat displaced from the (000) position. Since the a parameter increases with Co doping, two different Co(1)-Cu/Co(1) distances should exist in the structure. We tried to improve the fit by introducing a third Co(1)-Cu/Co(1) distance at about 4 Å which could explain the shoulder on the large distance side. The final parameters of this refinement were $R_1=3.58$ Å, $R_2=3.52$ Å, $R_3=4.17$ Å. For this refinement the parameters $\Delta E_1=\Delta E_2=\Delta E_3=6$ eV, and $\sigma_1=\sigma_2=\sigma_3=0.02$ were fixed at the values obtained in the previous one. Figure 5 shows the best fit for the three-shell refinement. Obviously the agreement factor improved to $\rho=7.1\times10^{-3}$ from $\rho=1.6\times10^{-2}$. The N parameters are weakly correlated with the R parameters. For example, if N_1, N_2, and N_3 are fixed at the theoretical values, the refined values of R_1, R_2, and R_3 are identical to those quoted above. The value of R_3 may correspond to the Co(1)-Cu(2) distance. Nevertheless, the existence of a short value of R_2 requires the correlated existence of a longer Co(1)-Cu/Co(1) distance such as R_3.

In addition to a large reduction of the total signal, the ratio $N_1/(N_2+N_3)$ is equal to 0.6, which is much smaller than the theoretical value of 1.3. The increase of N_2+N_3 with respect to N_1 is probably due to the existence in the

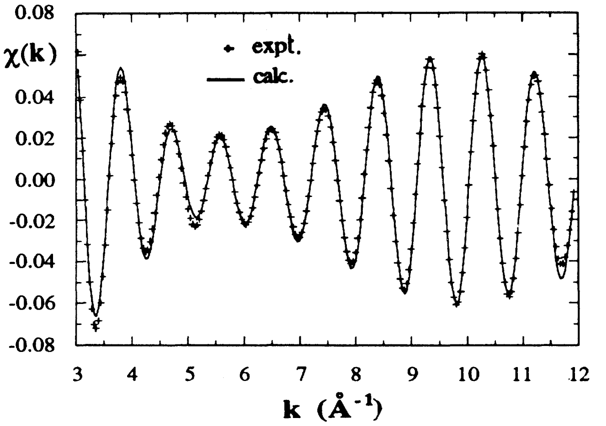


FIG. 5. The best three-shell fit of the EXAFS signal for the second-nearest neighbors corresponding to the 1:2:3-$Co_{0.06}$[O] compound.

compound of a focusing path, such as the linear coordination Co(1)-O(4)-Co/Cu(1), which enhances the forward scattering. Using single scattering theory on shells involving multiple scattering leads to an apparent shortening of the distances.[14] For example, Michalowicz[15] found that the Co-N distance determined by a standard analysis of EXAFS for $K_3Co(CN)_6$ leads to a value 0.13 Å shorter than that determined by diffraction techniques, if one does not take into account focusing effects.

Even though the EXAFS signal of 1:2:3-$Co_{0.06}$ [R_1] is weaker than that of 1:2:3-$Co_{0.06}$ [O], the shapes of the peak [see Fig. 2(c)] corresponding to the second-nearest neighbors for the two compounds are qualitatively very similar. On the contrary, the Fourier transform for the 1:2:3-$Co_{0.06}$ [R_2] compound shows that the peak corresponding to the second-nearest neighbors has a different shape from those of the [O] and [R_1] counterparts. It suggests that two distinct cation-cation peaks exist in the [R_2] compound. This is similar in a way to the results obtained at the CuK edge for the undoped 1:2:3 compound.[12] This could indicate that the Co cations are less displaced in the [R_2] compound than in the [O] and [R_1] ones.

The displacement of the Co cations from (000) would explain the large isotropic thermal parameter obtained by neutron diffraction for the Co/Cu(1) site. Dunlap *et al.*,[16] who studied the structure of the oxidized $YBa_2(Cu_{1-y}Fe_y)_3O_{6+x}$, showed that the R factor of their structural refinements decreased if the Fe cations were displaced along the [110] direction; for $y=0.05$ the displacement was of the order of 0.3 Å.

As determined by EXAFS the Co(1)-Ba distances are larger than the Cu(1)-Ba ones. This is in agreement with the unit cell volume increase. Since for the compounds 1:2:3-$Co_{0.06}$ there are 18% of Co cations in the Cu(1) plane, the average distance calculated from the EXAFS results is equal to $0.18\times3.58+0.82\times3.47=3.49$ Å, which fits exactly what has been found by neutron diffraction for this composition.[10]

E. Discussion

The structural parameters for the four compounds are given in Table I. The first coordination shell comprises two distances, one corresponding to relatively short ones, 1.80–1.85 Å, and the other to longer distances, 2.00–2.05 Å. The number of short distances is always larger than that of the long ones. Our distances are nearly the same than those found by Yang *et al.*[17] in oxidized 1:2:3-Co [O] compounds. Contrary to what has been reported by Bridges *et al.*[9] in our data there is no evidence for the long distance at 2.4 Å. All EXAFS studies of the 1:2:3-Fe compounds do not mention the existence of such a distance.[13,18,19].

TABLE I. Structural parameters obtained for Co-O distances obtained for the four 1:2:3-Co compounds studied.

	$y=0.01$ [O]	$y=0.06$ [O]	$y=0.06$ [R_1]	$y=0.06$ [R_2]
N_1	3.3	4.	3.8	3.1
R_1 (Å)	1.82	1.82	1.85	1.845
N_2	1.15	1	1.2	1.6
R_2 (Å)	2.04	2.02	2.05	2.01
N_1+N_2	4.45	5	5	4.7
$\bar{R}$ (Å)	1.87	1.86	1.90	1.90
$\bar{v}$	2.9	3.4	3.1	2.9

The values for the various Co-O distances calculated from the ionic radii reported by Shannon[20] indicate that in our compounds the formal charge of the Co cations should be between 3^+ and 4^+. The formal charge can also be calculated from the Co-O distances by using the Brown and Altermatt formula.[21] The values r_0 for high-spin and low-spin Co^{3+} are obtained from the structures of Co_2O_3 which can exist with the Co cations in the two-spin state.[22] The two values are 1.71 and 1.64 Å for high and low spin, respectively. The formal valence $\bar{v}$, reported in Table I, were calculated using $r_0=1.71$ Å. The assumption of the high-spin state is based on the magnetic susceptibility results and on those of neutron diffraction.[8,23,24] At ambient temperature the 1:2:3-$Co_{0.06}$[O] compound has been found to be paramagnetic.[25] The magnetic moment by susceptibility measurements was found to be $3.2\mu_B$ (Ref. 8), which corresponds to about 60% of that of Co^{3+} in the high-spin state ($5.4\mu_B$) (Ref. 26). This seems to indicate that the formal valence of the Co cations is closer to 3^+ with an intermediate spin state. The formal valence calculated from the interatomic distances in the 1:2:3-$Co_{0.06}$[O] compound is larger than 3^+. This could be explained by the presence in this compound of Co^{4+} and/or Co^{3+} cations in the low-spin state. This discussion will be developed further in the XANES studies section.

If one takes into consideration the distribution of the Cu(1)-O distances in the undoped 1:2:3[O] compound, 1.864 Å×2 and 1.942 Å×2, it is surprising that the Co cations are found to be surrounded by more than two oxygen atoms at short distances. Moreover, these distances, which are shorter than the average, result in a significant increase of the a parameter.[1] This increase is probably linked to the increase of the Ba-O(1) distance which compensates the additional charge coming onto the O(1) atoms from the Co^{3+} cations.

The number of oxygen atoms of the first shell increases slightly with increasing doping. The same was observed for the Fe doping.[18] On the other hand, the total coordination number and the value of the distances do not vary with the heat treatment [R_1] under inert atmosphere at 700 °C. For the [R_2] treatment, the number of short distances decreases and that of the long distances increases.

The EXAFS study of the second-nearest-neighbor coordination sphere shows clearly the existence of two separate distances Co(1)-Co/Cu(1) indicating that the Co cations are displaced from (000) by a few tenths of an angstrom. This value decreases appreciably for the [R_2] compound.

III. XANES STUDIES

A. Experimental

In order to determine the formal valence and the geometrical configuration of the Co coordinations,

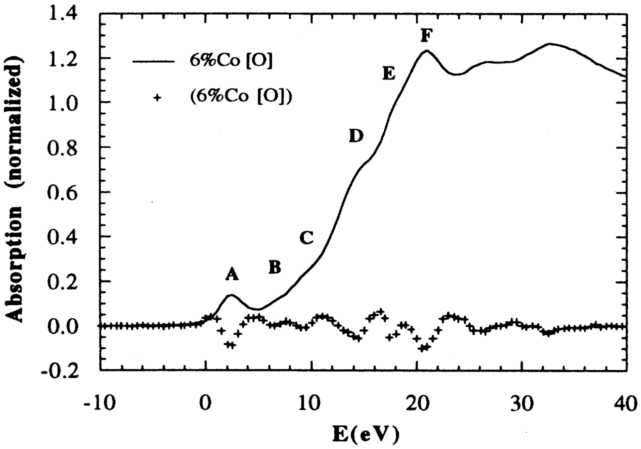


FIG. 6. (a) XANES spectrum at the Co K edge for the 1:2:3-$Co_{0.06}[O]$ compound. The normalization corresponds to $E=7753$ eV. The second-derivative curve (b) shows the existence of six structures (A–F).

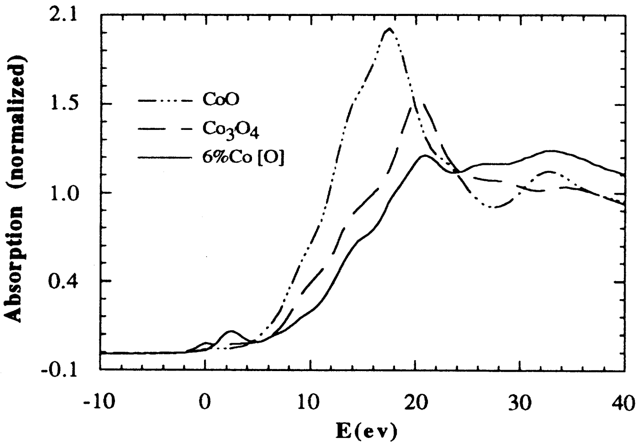


FIG. 7. Comparison of the absorption spectra at the Co K edge for the compounds 1:2:3-$Co_{0.06}[O]$, CoO, and Co_3O_4.

XANES spectra in the fluorescence mode at the Co K edge were measured between 7680 and 7780 eV and a 0.5 eV step. The following compounds were studied: 1:2:3-$Co_{0.01}[O]$, 1:2:3-$Co_{0.03}[O]$, 1:2:3-$Co_{0.06}[O]$, 1:2:3-$Co_{0.06}[R_1]$, 1:2:3-$Co_{0.01}[R_2]$, 1:2:3-$Co_{0.02}[R_2]$, 1:2:3-$Co_{0.03}[R_2]$, 1:2:3-$Co_{0.04}[R_2]$, and 1:2:3-$Co_{0.06}[R_2]$. The energy origin corresponds to the first inflection point ($E_0=7709$ eV) of the absorption spectrum for the Co metal and the spectrum has been normalized.

The XANES spectra for all values of x and y are qualitatively similar. Only small variations of the position and/or the intensities of the different features are visible in some cases. A relatively intense prepeak (10–20%) corresponding to the $1s \Longrightarrow 3d$ transition is always visible. The second-derivative curves around the edge reveal the existence of six features, labeled as A–F. Beyond F the features can have more than one origin and their interpretation is complicated (see Fig. 6).

B. Electronic structure

The position of the absorption edge is shifted towards high energies when the cation valence increases. The effect of the distance variation in the $1s$ energy level is an order of magnitude smaller than that due to the charge.[27,28] In general, because of the fine features of the absorption jump, it is difficult to determined precisely the position of the jump itself. Instead, the position of the pre-edge peak (when present) is a specific probe to determine the absorbant valence.

The XANES spectrum for the 1:2:3-$Co_{0.06}[O]$ compound together with those for CoO and Co_3O_4 is reported in Fig. 7. The Co^{2+} cation in tetrahedral coordination in Co_3O_4 is revealed by the presence of a pre-edge peak of low intensity at $E=-0.05$ eV and by the first change in slope at 9 eV of the absorption jump. In the structure of Co_3O_4, the Co^{3+} cations occupy octahedral sites, because of the center of symmetry of this coordination, the dipolar transitions $1s \Longrightarrow 3d$ are forbidden and no pre-edge peak is observed. However, a very weak peak is visible at 2.3 eV in the second-derivative curve in Fig. 8, which should correspond to the allowed quadripolar $1s \Longrightarrow 3d$ transition.

The pre-edge peak observed for 1:2:3-$Co_{0.06}[O]$ is shifted of 2.49 eV towards high energies with respect to the pre-edge peak for Co_3O_4 which is due to the tetrahedrally coordinated Co^{2+} cations. This shift, related to the $3d$ filling, is typical of a valence increase of about one valence unit (v.u.). This observation strongly indicates that the oxidation state of the Co cations in1:2:3-$Co_{0.06}[O]$ is 3^+. As shown below these results are corroborated by the value of the formal valence calculated from the interatomic distances obtained from the EXAFS data, by using the formula and the constants of Brown and Altermatt.[21]

No shift of the pre-edge peak has been observed in any of the compounds investigated by varying either the dopant concentration or the oxygen stoichiometry (see Figs. 11 and 12). This indicates that the Co formal valence is the same in all of them. The decrease in the formal valence of the Co cations, calculated from the interatomic distances shown in Table I, on going from 1:2:3-$Co_{0.06}[O]$ to 1:2:3-$Co_{0.06}[R_2]$ may be the result of a spin-state variation and not of a valence change.

C. Co-O distances

The EXAFS results show that for all the Co-doped samples the first-nearest-neighbor coordination sphere is comprised of two distances separated by 0.15 Å. According to the Natoli rule, XANES spectra exhibiting two features with the following equality must be obeyed:

$$(E_1-E_0)R_1^2=(E_2-E_0)R_2^2=C$$

where R_i (Å) is the cation–oxygen distance and E_i is the energy of the i transition.[29] The E_0 value, which corresponds to the energy origin, is determined experimentally from a nonbonding $1s \Longrightarrow 4p^*$ transition, that is, for an infinite R_i distance.[30] The Natoli rule states that a variation of the absorbant oxygen distance induces a displacement of the corresponding feature which reveals the position of cluster antibonding orbitals. This rule has to do with the Harrison approach which is valid in case of a large band such as the 4p of the 3d elements where the electron behaves like a free electron with a parabolic dispersion. E_0 is a constant only for those compounds in which both the electronic structures of the absorbant and the ligand are the same. Cartier *et al.*[31] observed that, for several metal porphyrins, where the transition elements are surrounded by a square of nitrogen atoms, the E_0 was situated at 4.6 eV for Fe^{2+}, 6.2 eV for Co^{2+}, and 6.4 eV for Cu^{2+} with respect to the quadripolar peak. The nonbonding $1s \Longrightarrow 4p^*$ transition for the Cu^{2+} cations in Nd_2CuO_4, where the Cu cations are surrounded by a square of oxygen atoms, is situated about 4.6 eV above the quadripolar peak.[30] The determination of E_0 is not always possible because a standard compound exhibiting the specific transition is not always available.

In the XANES spectrum of 1:2:3-Co$_{0.06}$[O], shown in Fig. 6, the maximum of the absorption jump comprises two features, one at 17.4 eV and the other at 20.6 eV, indicated as E and F, respectively. The position of the two peaks and the amount of separation between them, is the same for all spectra of the [O] compounds (see Fig. 11). On the other hand, on going from the [O] compounds to the [R_2] ones, the absolute and relative positions of the two peaks vary according to the interatomic distances (see Fig. 9). The second-derivative curves show that reduction shifts the F peak towards low energies which indicates an increase of the corresponding distance. As a first approximation the shift magnitude is proportional to the amount of reduction (see Fig. 10). The E peak is shifted, instead, towards high energies. It is reasonable to assume that the E and F features are due to the $1s \Longrightarrow 4p$ transitions corresponding to the long (2.02 Å) and short (1.82 Å) distances, respectively. If we could determine E_0, we would be able to verify the Natoli rule directly. However, indirectly, we can show that the rule is indeed verified.

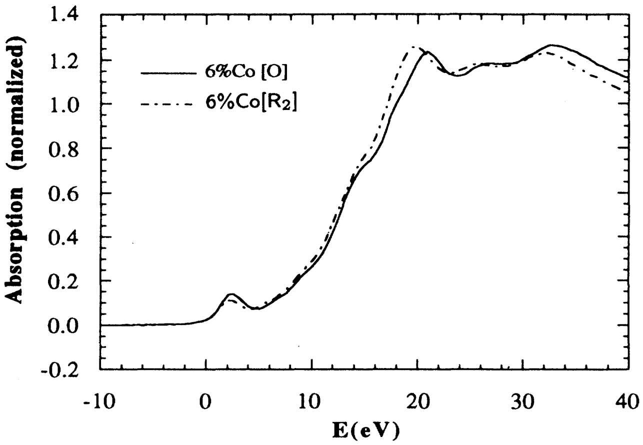


FIG. 9. Comparison of the CoK edges for the compounds 1:2:3-Co$_{0.06}$[O] and 1:2:3-Co$_{0.06}$[R_2]. The maximum F of the edge is displaced towards the low energies after the [R_2] heat treatment. This displacement is correlated with the lengthening of the Co-O distances.

The E_0 and C values for the 1:2:3-Co$_{0.06}$[O] compound can be calculated from the interatomic distances obtained from the EXAFS data ($R_2 = 2.02$ Å $\equiv E_E = 17.4$ eV and $R_1 = 1.82$ Å $\equiv E_F = 20.56$ eV). They are 3.7 eV and 56.0, respectively. The value for E_0 seems reasonable when compared with the values reported in the preceding paragraph. The C values for the standard compounds, Co_3O_4 and $ZnCo_2O_4$ (Ref. 32) in which the Co^{3+} cations are octahedrally coordinated, are very close to 56.0 (see Table II). The F features for Co_3O_4 and $ZnCo_2O_4$ correspond to the maximum of the white peak, that is, 20.05 and 19.9 eV, respectively. The values of C calculated with the Natoli formula and $E_0 = 3.7$ eV, for all compounds we investigated by EXAFS, are close to 56 (see Table II). Regardless of the doping concentration, the E and F features tend to be superimposed on going from [O] to [R_1] and to [R_2], which is in agreement with the EXAFS results.

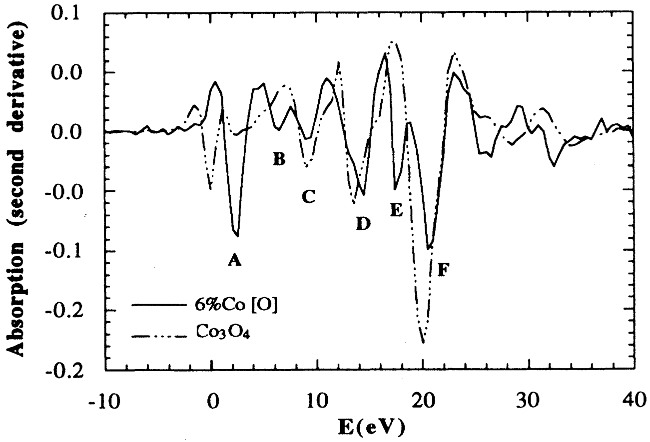


FIG. 8. Comparison of the second-derivative curves of the absorption spectra shown in Fig. 7 for the compounds 1:2:3-Co$_{0.06}$[O] and Co_3O_4.

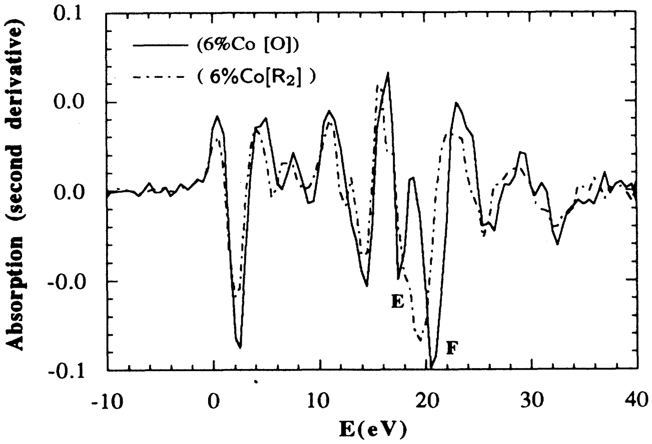


FIG. 10. Comparison of the second-derivative curves of the absorption spectra for the compounds 1:2:3-Co$_{0.06}$[O] and 1:2:3-Co$_{0.06}$[R_2].

TABLE II. C_E and C_F constants obtained for different Co^{3+} compounds. The energy $E_0=3.7$ eV is calculated with values R_1, R_2, E_E, and E_F of 1:2:3-$Co_{0.06}[O]$ compound.

	E_E (eV)	R_2 (Å)	E_F (eV)	R_1 (Å)	C_E	C_F	$100\lvert C-C_{E/F}\rvert/C$
$ZnCo_2O_4$[a]	b		19.9	1.89		57.9	3.4
Co_3O_4	b		20.06	1.89		58.4	4.4
$Co_{0.06}[O]$	17.4	2.02	20.56	1.82	56.0	56.0	0/0
$Co_{0.06}[R_1]$	17.46	2.05	20.3	1.84	57.8	56.2	3.3/0.4
$Co_{0.06}[R_2]$	c		19.56	1.85		54.9	1.9
$Co_{0.01}[O]$	18.07	2.04	21.06	1.82	59.6	57.5	6.5/2.7

[a] Reference 32.

[b] No peak.

[c] Peaks too close to be separated.

D. Pre-edge peak intensity

When the first-nearest-neighbor coordination polyhedron contains the center of symmetry, such as an octahedron or a square, the dipolar $1s \Longrightarrow 3d$ transition is forbidden as the $3d$ and $4p$ orbitals do not overlap. The quadripolar $1s \Longrightarrow 3d$ transition can give rise to a pre-edge peak, but its intensity is in general extremely weak. When the coordination polyhedron does not contain the center of symmetry, such as a distorted octahedron, a tetrahedron or a pyramid, the hybridization of the $3d$ and $4p$ orbitals becomes possible and the dipolar $1s \Longrightarrow 3d$ transition is allowed.[33-35] The pre-edge peak intensity is a function of the departure from a centrosymmetric coordination and of the overlapping between the $3d$ orbitals and the $2p$ of the oxygen atoms.[36,37]

Figure 11 shows that the pre-edge peak intensity is about the same for the 1:2:3-$Co_{0.03}[O]$ and 1:2:3-$Co_{0.06}[O]$ compounds, whereas that of the 1:2:3-$Co_{0.01}[O]$ is weaker. It also decreases on going from 1:2:3-$Co_{0.06}[O]$ to 1:2:3-$Co_{0.06}[R_2]$ (see Fig. 12). For all $[R_2]$ compounds the pre-edge peak intensity is the same. The presence of this strong pre-edge peak due to the $1s \Longrightarrow 3d$ transition strongly indicates that the coordination polyhedron of the Co cations is not centrosymmetrical. Therefore, a large fraction of the Co cations should not have the square or undistorted octahedral coordination. Our EXAFS results show that the coordination number of the Co cations increases from 4.5 to 5.0 on going from 1:2:3-$Co_{0.01}[O]$ to 1:2:3-$Co_{0.06}[O]$. The intensity of the pre-edge peak for the former is weaker than that of the latter. As the average Co-O distances are identical in both compounds, this decrease for 1:2:3-$Co_{0.01}[O]$ is probably due to a higher site symmetry. Yang *et al.*[18] carried out absorption experiments on the 1:2:3-Co$[O]$ compounds and found that the pre-edge peak intensity changes only slightly with Co content,[17] whereas for the 1:2:3-Fe$[O]$ compounds they found that the pre-edge peak intensity systematically increases when the doping concentration decreases.[18] These authors suggested that the coordination number of the Fe cations increases as a function of y. For the Co-doped compounds we did not observe the same relationship.

The continuous decrease of the pre-edge peak intensity on going from 1:2:3-$Co_{0.06}[O]$ to 1:2:3-$Co_{0.06}[R_2]$ could be the effect of two causes (Fig. 12). Both the EXAFS and XANES studies show that the difference between the two sets of Co-O distances for each compound tends to decrease, which is an indication of an increase of the site symmetry leading to a decrease of the pre-edge peak intensity. Less important should be the effect of the average Co-O distance increase with increasing reduction.

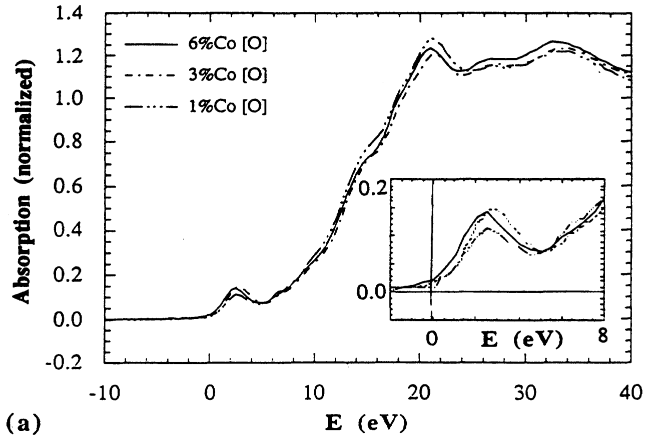


FIG. 11. Comparison of the Co K edges for the compounds 1:2:3-$Co_{0.01}[O]$, 1:2:3-$Co_{0.03}[O]$, and 1:2:3-$Co_{0.06}[O]$.

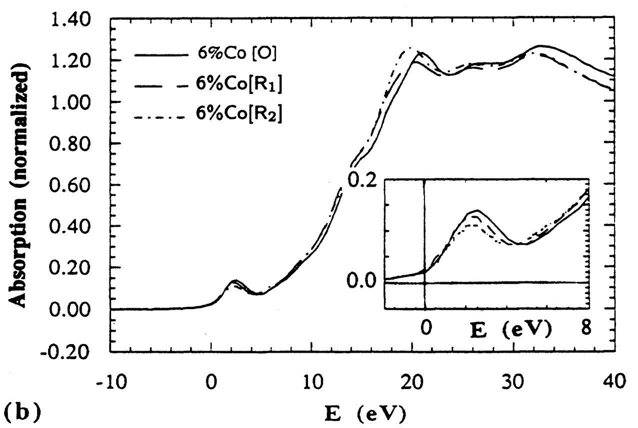


FIG. 12. Comparison of the Co K edges for the compounds 1:2:3-$Co_{0.06}[O]$, 1:2:3-$Co_{0.06}[R_1]$, and 1:2:3-$Co_{0.06}[R_2]$.

This leads to a decrease of the overlapping between the 3*d* orbitals and the 2*p* of the oxygen atoms and consequently to an additional decrease of the pre-edge peak intensity.[36]

E. Discussion

It can be deduced from the XANES spectra that in these compounds the Co oxidation state is 3^+ regardless of the dopant concentration and the oxygen stoichiometry. Moreover, there is no pre-edge feature corresponding to a Co^{2+} cation either in a tetrahedral or octahedral coordination. This means that the concentration of the Co^{2+} and Co^{4+} cations should be negligible. Our results are compatible with Co^{3+} in more than one coordination.

The presence of a strong pre-edge feature indicates that the Co sites are definitely noncentrosymmetric. Thus, the square coordination can be excluded. Furthermore, a large fraction of Co cations cannot have an undistorted octahedral coordination. The undistorted octahedral coordination would give rise to a well-defined *F* feature as in Co_3O_4 (Figs. 7 and 8), and the square coordination would produce a characteristic feature corresponding to the nonbonding $1s \Longrightarrow 4p^*$ transition. The departure from the centrosymmetric coordination decreases slightly on going from the $[O]$ to the $[R_2]$ compounds.

The two *E* and *F* structures appearing at the absorption edge, due to the $1s \Longrightarrow 4p$ transition, correspond to the two Co-O distances obtained from the EXAFS spectra. The variation of *E* and *F* positions is in agreement with the corresponding distance variation. The analysis of the XANES spectra confirms the existence of two shells, one at 1.80–1.85 Å and the other at 2.00–2.05 Å. It should be pointed out that the *E* and *F* positions are highly sensitive to the distance variations.

IV. MODELS FOR THE Co CATION COORDINATIONS

The Co cations occupy a noncentrosymmetric site and their average coordination number is 5. As stated above, it is very likely that the Co cations possess more than one coordination. This hypothesis is corroborated by the results obtained on the 1:2:3-Co and 1:2:3-Fe compounds by Mössbauer spectroscopy, indicating the presence of three cation species for the Cu(1) site.[38,39] The absorption spectra of the Fe compounds are very similar to those of the Co counterparts.

The results at the Co *K* edge are compatible with three types of coordinations: (i) a pyramidal site with three or four short Co(1)-O distances at 1.82 Å and one or two long ones at 2.02 Å; (ii) a mixing of a tetrahedral site with four short distances at 1.82 Å and of an octahedral site with four short distances at 1.82 Å and two long ones at 2.02 Å; (iii) a mixing of (i) and (ii). Other configurations could also exist, however, these three seem the simplest and most probable.

The fit of the peak corresponding to the second-nearest-neighbor coordination sphere shows clearly the existence of two separate distances Co(1)-Co/Cu(1), indicating a displacement of the Co cations from (000) by a few tenths of an angstrom. This displacement can occur in different ways.

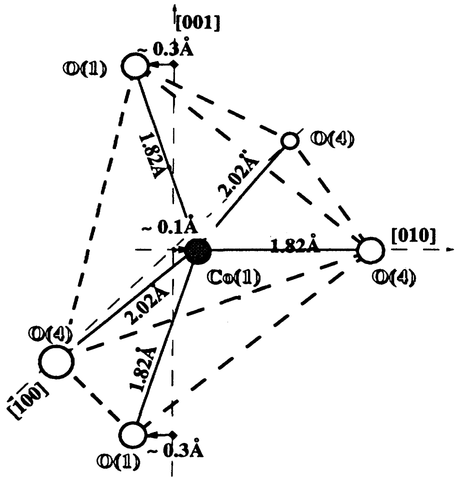


FIG. 13. Schematic model for the fivefold-coordinated Co site taking into account a cation displacement along the [100] direction, leading to three short distances and two long ones.

Let us consider now an isolated Co cation in the Cu(1) layer. Two of the short distances should be the two apical Co(1)-O(1) ones. The Co/Cu(1)-O(1) distances as determined by neutron diffraction run along the *c* axis. Their average decreases linearly with dopant concentration and the value extrapolated for $y = 0.33$ is Co(1)-O(1) = 1.77 Å [all the Cu(1) atoms are substituted by Co.][1,40] This value can be obtained in two ways, either by displacing the Co cation of 0.4 Å and in this case the projection of the 1.82 Å distance on the *c* axis is 1.77 Å, or by displacing both Co(1) and O(1) by a smaller amount, perpendicular to the *c* axis in opposite directions with respect to each other. This second case seems more probable and is illustrated in Figs. 13–16. As shown in Fig. 13, in order to accommodate three short distances, the Co cations move 0.1 Å either along the [100] or the [010] direction and the O1 atoms move 0.3 Å in the opposite direction. One short and two long distances should correspond to the Co(1)-O(4) distances, which are in the

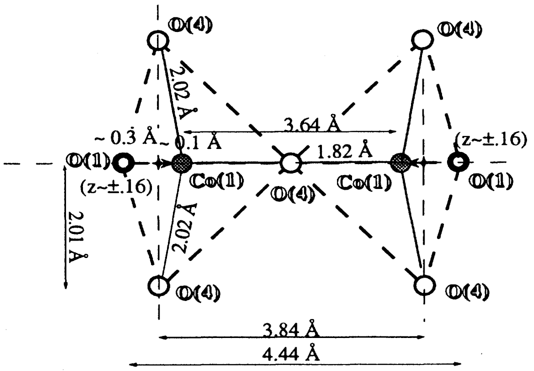


FIG. 14. [001] projection of two fivefold-coordinated Co sites forming a dimer. The cations are displaced along the [100] direction.

basal plane. These five oxygen atoms form a square-base pyramid. Such a configuration for the Co^{3+} cations has been found in $Sr_2Co_2O_5$ (Ref. 41). It could exist inside the orthorhombic domains where the Co cations do not break the square chains as well as in the fivefold-coordinated dimers $[Co(1)]_2$, as shown in Fig. 14. Note that in this model the Co(1)-Co(1) distance is 3.64 Å, which is close to the value obtained by EXAFS.

A simple way to obtain four short Co-O distances is to shift the Co cation along the [110] direction so as to have around it a tetrahedron formed by two O(1) and two O(4) [see Fig. 15(a)]. The projection of the Co(1)-O(1) distance on the [001] axis is 1.77 Å when both Co(1) and O(1) are shifted 0.2 Å in opposite directions perpendicular to [001]. These displacements result in an almost regular tetrahedron. This coordination was found in the recently reported $YSr_2CoCu_2O_7$ structure[42] where the Co cations substitute entirely for the Cu(1) cations. The fivefold and sixfold coordinations are obtained by filling one or two of the remaining O(4) sites [Fig. 15(b)]. Note that such coordination polyhedra are highly distorted. In this description the tetrahedron is the basic unit of the first shell at 1.82 Å. The projections along [001] of these three polyhedra are shown in Figs. 16(a)–16(c). The Cu/Co(1)-Co(1) distances found by EXAFS are more easily generated by the formation of $[Co(1)]_2$ dimers or small $[Co(1)]_n$ clusters for which the Co displacements add up to each other [Fig. 16(c)]. The values of the Co-Co/Cu(1) distances yielded by these models are 3.64, 3.72, and 4.0 Å, while the average lattice parameter remains unchanged at 3.87 Å.

At this stage it is difficult to state which coordination is dominant in these compounds and in what proportion. However, it should be pointed out that the average Co-O distance for the distorted octahedral coordination is exactly the same as the corresponding distance in Co_3O_4 in which the Co^{3+} cations are in the low-spin state. By using the Brown and Altermatt formula and the constant $r_0 = 1.64$ Å (Co^{3+} cations in the low-spin state), the

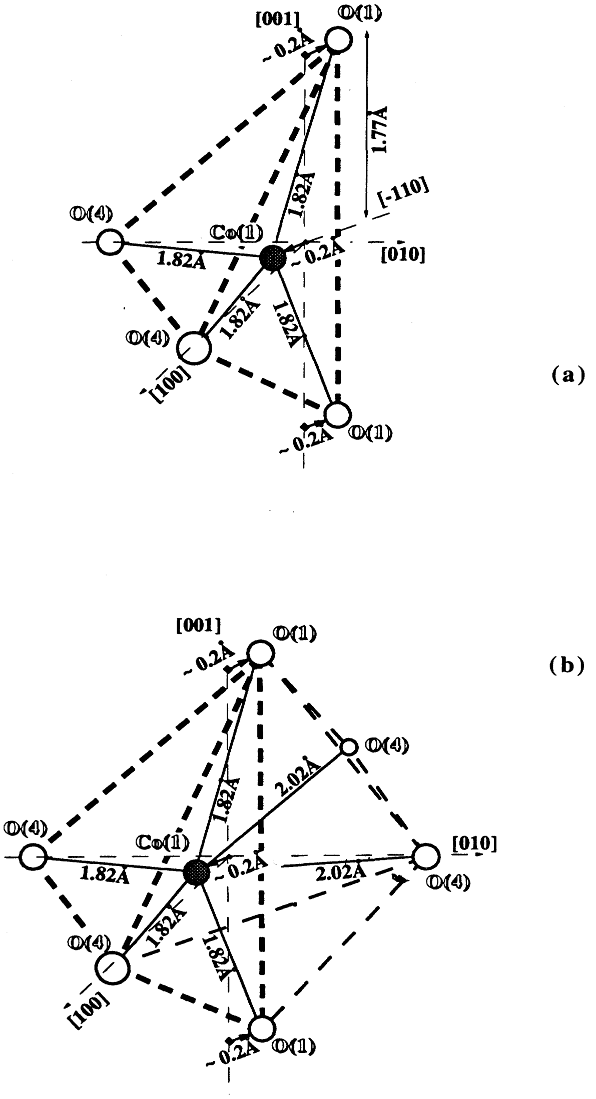


FIG. 15. Schematic models of two Co sites in which a cation displacement along the [110] direction is taken into account: (a) having a fourfold-coordination leading to four short distances, and (b) having a sixfold-coordination leading to four short distances and two long ones.

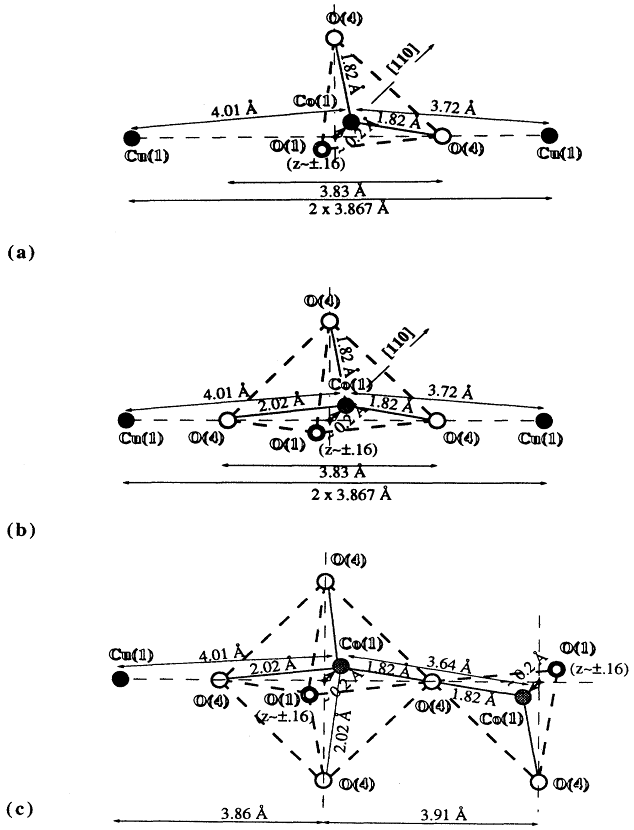


FIG. 16. [001] projection of the Co sites in which a cation displacement along the [110] direction is taken into account: (a) fourfold-coordinated, (b) fivefold-coordinated, and (c) sixfold- and fourfold-coordinated dimer.

charge of 3.17 v.u. is calculated from the Co-O distances found in 1:2:3-$\mathrm{Co}_{0.06}[O]$. Although high-spin state Co^{3+} in tetrahedral coordination is not a common configuration, several authors gave evidence for its existence.[32,43] The oxidation state of the Co1 cations in 1:2:3-$\mathrm{Co}_{0.06}[O]$, calculated for the tetrahedral coordination with $r_0=1.71$ Å (Co^{3+} in the high-spin state), is equal to 2.97 v.u. The calculated formal oxidation state for fivefold-coordinated Co cations, with four short distances and one long one, in the high-spin and low-spin state is 3.45 and 2.82 v.u.; with three short distances and two long ones, in the high-spin and low-spin state is 3.09 and 2.66 v.u., respectively. A possible model for 1:2:3-$\mathrm{Co}_{0.06}[O]$ would comprise a 50/50 mixing of tetrahedral and distorted octahedral coordinations. The calculated oxidation state would be 3.07 v.u. with an intermediate spin state. As stated above, magnetic susceptibility measurements showed that the Co cations possess a magnetic moment of $3.2\mu_B$ which is too low for a high-spin state for which the expected value would be $5.4\mu_B$. This corroborates the assumption that the Co cations in 1:2:3-Co compounds are in an intermediate spin state.

Our model contains primarily a nearly equal number of tetrahedral and distorted octahedral sites with a small amount of pyramidal sites for the Co cations. This is not in contradiction with the results found in $\mathrm{YSr_2CoCu_2O_7}$ (Ref. 42) where the Co cations are all in tetrahedral sites. The Co cations are smaller than the Cu cations and in the Co/Ba compounds an increase of the Co-O distance is needed in order to match the Ba-O distance. This increase is realized by an increase of the oxygen stoichiometry above O_7. The increase in stoichiometry induces an increase of the Co coordination and consequently an increase of the Co-O distance. Because the Sr cations are smaller than the Ba cations in the Co/Sr compound the Co-O distance in tetrahedral coordination match well the Sr-O distance and a stoichiometric compound such as $\mathrm{YSr_2CoCu_2O_7}$ can exist.

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[1] H. Renevier, thesis, Université J. Fourier, Grenoble, 1991.

[2] H. Renevier, J. L. Hodeau, T. Fournier, P. Strobel, M. Marezio, J. C. Martinez, and J. J. Préjean, J. Less-Common Met. **164-165**, 907 (1990).

[3] A. Michalowicz, in *Logiciels pour la Chimie* (Société Française de Chimie, Paris, 1991), p. 102.

[4] B. Lengeler and P. Eisenberger, Phys. Rev. B **21**, 4507 (1980).

[5] These Kaiser cutoff windows described by the formula $w(k)$:

$$w(k)=\frac{I_0\{\tau\sqrt{1-[(2k-k_{\max}-k_{\min})^2/(k_{\max}-k_{\min})]}\}}{I_0(\tau)},$$

where I_0 is the modified zero-order Bessel function, $\tau=2.5$ is a damping factor, chosen equal to 2.5.

[6] F. James and M. Roos (unpublished).

[7] F. W. Lytle, D. E. Sayers, and E. A. Stern, Physica B **158**, 701 (1989).

[8] J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).

[9] F. Bridges, J. B. Boyce, T. Claeson, T. H. Geballe, and J. M. Tarascon, Phys. Rev. B **39**, 11 603 (1989).

[10] R. Sonntag, D. Hohlwein, A. Hoser, W. Prandl, W. Schäfer, R. Kiemel, S. Kemmler-Sack, S. Lösch, M. Schlichenmaier, and A. W. Hewat, Physica C **159**, 141 (1989).

[11] A. G. McKale, G. S. Knapp, and S. K. Chan, Phys. Rev. B **33**, 841 (1986); A. G. McKale, S. K. Chan, B. W. Veal, A. P. Paulikas, and G. S. Knapp, J. Phys. (Paris) Colloq. **47**, C8-35 (1986).

[12] J. B. Boyce, F. Bridges, T. Claeson, and M. Nygren, Phys. Rev. B **39**, 6555 (1989).

[13] H. Oyanagi, H. Obara, H. Yamaguchi, K. Murata, H. Ihara, T. Matsushita, M. Tokumoto, Y. Nishihara, and Y. Kimura, J. Phys. Soc. Jpn. **58**, 2140 (1989).

[14] B. K. Teo, J. Am. Chem. Soc. **103**, 3990 (1981); J. J. Boland, S. E. Crane, and J. D. Baldeschwieler, *ibid.* **77**, 142 (1982).

[15] A. Michalowicz, thesis, Université de Paris, 1990.

[16] B. D. Dunlap, J. D. Jorgensen, C. Segre, A. E. Dwight, J. L. Matykiewicz, H. Lee, W. Peng, and C. W. Kimball, Physica C **158**, 397 (1989).

[17] C. Y. Yang, A. R. Moodenbaugh, Y. L. Wang, Youwen Xu, S. M. Heald, D. O. Welch, M. Suenaga, D. A. Fisher, and J. E. Penner-Hahn, Phys. Rev. B **42**, 2231 (1990).

[18] C. Y. Yang, S. M. Heald, J. M. Tranquada, Youwen Xu, Y. L. Wang, A. R. Moodenbaugh, D. O. Welch, and M. Suenaga, Phys. Rev. B **39**, 6681 (1989).

[19] A. Koizumi, H. Maeda, N. Bamba, H. Maruyama, E. Takayama-Muromachi, J. Shi, K. Shimizu, M. Mino, and H. Yamazaki, Jpn. J. App. Phys. **28**, L203 (1989).

[20] R. D. Shannon, Acta Crystallogr. Ser. A **32**, 751 (1976).

[21] I. D. Brown and D. Altermatt, Acta Crystallogr. Ser. B **41**, 244 (1985).

[22] J. Chenavas, J. C. Joubert, and M. Marezio, Solid State Commun. **9**, 1057 (1971).

[23] P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, D. A. Neumann, J. J. Rhyne, L. F. Schneemeyer, and J. W. Waszczak, Phys. Rev. B **38**, 9209 (1988).

[24] P. Zolliker, D. E. Cox, J. M. Tranquada, and G. Shirane, Phys. Rev. B **38**, 6575 (1988).

[25] P. F. Miceli, J. M. Tarascon, P. Barboux, L. H. Greene, B. G. Bagley, G. W. Hull, M. Giroud, J. J. Rhyne, and D. A. Neumann, Phys. Rev. B **39**, 12 375 (1989).

[26] N. W. Ashcroft and N. David Mermin, *Solid State Physics* (SCP, City, 1976), Chap. 31, p. 658.

[27] C. Mande and V. B. Sapre, in *Advances in X-ray Spectroscopy*, edited by C. Bonnelle and C. Mande (Pergamon, New York, 1983), Chap. 17, p. 287.

[28] C. Cartier, thesis, Université de Paris Sud, Orsay, 1988.

[29] C. R. Natoli, in *EXAFS and Near-edge Structures,* edited by A. Bianconi, L. Incoccia, and S. Stipcich, Springer Series on Chem. Phys. Vol. 27 (Springer, New York, 1983), p. 43.

[30] H. Tolentino, thesis, Université de Paris Sud, Orsay, 1990; H. Tolentino, M. Medarde, A. Fontaine, F. Baudelet, E. Dartyge, D. Guay, and G. Tourillon, Phys. Rev. B **45**, 8091

(1992).

[31] C. Cartier, thesis, Université Paris Sud, Orsay, 1988; C. Cartier, M. Momenteau, E. Dartyge, A. Fontaine, G. Tourillon, A. Michalowicz, and M. Verdaguer (unpublished).

[32] M. Lenglet, R. Guillamet, J. Dürr, D. Gryffroy, and R. E. Vandenberghe, Solid State Commun. **74**, 1035 (1990).

[33] R. G. Shulman, Y. Yafet, P. Eisenberger, and W. E. Blumberg, Proc. Nat. Acad. Sci. **73**, 1384 (1976).

[34] R. A. Bair and W. A. Goddard III, Phys. Rev. B **22**, 2767 (1980).

[35] A. L. Roe, D. J. Schneider, R. J. Mayer, J. W. Pyrz, J. Widom, and L. Que, Jr., J. Am. Chem. Soc. **106**, 1676 (1984).

[36] F. W. Kutzler, C. R. Natoli, D. K. Misemer, S. Doniach, and K. O. Hodgson, J. Chem. Phys. **73**, 3274 (1980).

[37] J. Wong, F. W. Messmer, and D. H. Maylotte, Phys. Rev. B **30**, 5596 (1984).

[38] M. G. Smith, J. B. Goodenough, A. Manthiram, R. D. Taylor, and H. Oesterreicher, Phys. Rev. B **46**, 3041 (1992).

[39] M. E. Lines and M. Eibschutz, Physica C **166**, 235 (1990).

[40] P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, F. J. Rotella, and J. D. Jorgensen, Phys. Rev. B **37**, 5932 (1988).

[41] J. C. Grenier, S. Ghodbane, G. Demazeau, M. Pouchard, and P. Hagenmuller, Mater. Res. Bull. **14**, 831 (1979).

[42] Q. Huang, R. J. Cava, A. Santoro, J. J. Krajewski, and W. F. Peck (unpublished).

[43] D. L. Wood and J. P. Reimeika, J. Chem. Phys. **46**, 3595 (1967); R. Krishnan, Phys. Status Solidi B **73**, K51 (1976).