JOURNAL OF SOLID STATE CHEMISTRY **115**, 514–520 (1995)

Magnetic Behavior of the "112" Type Substituted Cuprate $YBaCoCu_{1-x}Fe_xO_5$

L. Barbey, N. Nguyen, A. Ducouret, V. Caignaert, J. M. Grenèche,* and B. Raveau

Laboratoire CRISMAT, CNRS URA 1318-ISMRA, Université de Caen, Boulevard du Maréchal Juin, 14050 Caen Cedex, France; and
**Equipe de Physique de l'Etat Condensé, Laboratoire de Physique des Matériaux, UA 807 CNRS, Université du Maine, 72017 Le Mans Cedex, France*

Received April 25, 1994; in revised form July 8, 1994; accepted July 13, 1994

A new solid solution $YBaCoCu_{1-x}Fe_xO_{5+\delta}$ has been synthesized for $0.30 \leq x \leq 0.60$. The neutron diffraction study of the phase $YBaCoCu_{1-x}Fe_xO_5$ ($x = 0.50$) confirms that its nuclear structure is centric, i.e., belongs to the space group *P4/mmm*, which must be now considered as characteristic of the "112" structure, built up of double pyramidal layers of transition metal elements M(M = Fe, Co, Cu). The neutron diffraction spectra registered at 1.4 and 300 K show that the magnetic moments are antiferromagnetically coupled, lying in the (a, b) plane; the susceptibility measurements and Mössbauer spectroscopy data show for iron the only presence of Fe(III), a cationic disordering, and allow an intermediate spin configuration for Co(III) to be identified. For $x = 0.5$ the phase can then be formulated $YBaCo_{0.5}{}^{III}Co_{0.5}{}^{II}Cu_{0.5}{}^{II}Fe_{0.5}{}^{III}O_5$. © 1995 Academic Press, Inc.

INTRODUCTION

The study of the magnetic properties of iron and cobalt-substituted layered cuprates is of capital importance for understanding the relationships between magnetism and superconductivity in high T_C superconductors. In this respect, the "112" structure, first discovered for $YBaFeCuO_5$ (1), can be considered a school material owing to its simplicity. It consists indeed of corner-sharing CuO_5 and FeO_5 pyramids forming double layers interleaved with yttrium cations (Fig. 1). Several magnetic studies of this phase (2–6) reveal a rather complex behavior, characterized by an incommensurate magnetic structure below 200 K (6) and by the existence of two transition temperatures at 200 and 450 K respectively, with a 60° tilting of the spins with respect to **c**, in the 200–450 K temperature range. Moreover, the recent reinvestigation of this oxide (6) demonstrates that its nuclear structure is in fact characterized by the centrosymmetric space group *P4/mmm*, contrary to the previous results (5).

Studies of the cobalt-substituted cuprate $YBaCo_{2-x}Cu_xO_5$ have shown an identical centrosymmetric nuclear structure (8–12) but a different magnetic behavior (6, 8, 12). A mixed valency, Co(II) and Co(III), has been observed for cobalt (8) with an intermediate spin configuration $t_{2g}^5\, e_g^1$ for Co(III) and a spin orientation varying with temperature. Two domains are in fact evidenced; the first one, corresponding to $x \leq 0.75$, exhibits only one transition temperature T_N, with the spins lying in the (**a**, **b**) plane, i.e., in the $[Cu(Fe)O_2]_\infty$ layers. The second domain ($0.75 < x < 1$) exhibits two transition temperatures, labeled T_2 and T_3, with spins titled with respect to **c** for $T < T_2$, and parallel to **c** for $T_2 < T < T_3$.

No data are available as yet about the spin configuration and orientation in this structure when both elements, cobalt and iron, are simultaneously introduced on the copper sites. We report herein on the investigation of a new solid solution, $YBaCoCu_{1-x}Fe_xO_5$, whose magnetic properties are studied by neutron diffraction and Mössbauer spectroscopy.

EXPERIMENTAL

The oxides $YBaCoCu_{1-x}Fe_xO_{5+\delta}$ were prepared by reacting appropriate mixtures of Y_2O_3, CuO, $Co_3O_{4.2}$, Fe_2O_3, and $BaCO_3$. Powders were ground and calcined in air at 900°C for 24 hr in order to ensure decarbonation and were then heated at 1000°C for 1 day. They were quenched to room temperature in air. The oxygen content was determined by chemical analysis using back-titration with an Fe(II) solution.

The purity of the materials was examined by X-ray powder diffraction using Cu*Kα* radiation. Their nuclear and magnetic structures were studied by neutron powder diffraction. Spectra were recorded at 1.4 and 300 K respectively using the multicounter diffractomers G 41 and 3T2 of Saclay.

RESULTS AND DISCUSSION

Chemical Synthesis of the Solid Solution $YBaCoCu_{1-x}Fe_xO_5$

The existence of the two isotypic phases $YBaFeCuO_5$ (1–6) and $YBaCo_{2-x}Cu_xO_5$ (7–12) with $0 \leq x \leq 1$, suggests

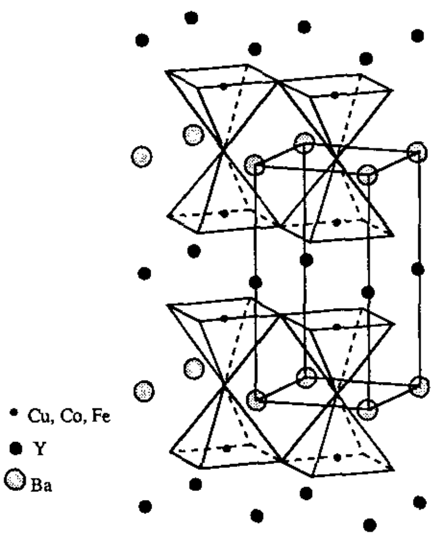

FIG. 1. The "112" type structure of $YBaFeCuO_5$.

the possibility of a large homogeneity range for the "112" structure in the system Y–Ba–Cu–Fe–Co–O. Nevertheless different attempts to substitute cobalt either for iron or for copper in $YBaFeCuO_5$ were unsuccessful: for both compositions $YBaFe_{1-x}Co_xCuO_5$ and $YBaFeCu_{1-x}Co_xO_5$ multiphasic samples have always been obtained. On the contrary, the substitution of iron for copper in the phase $YBaCoCuO_5$ allows a pure phase $YBaCoCu_{1-x}Fe_xO_5$ to be isolated with $0.30 \leq x \leq 0.60$.

This solid solution is isotypic with the 112-type structure of $YBaFeCuO_5$, so that the parameters of its tetragonal cell (Table 1) are directly related to the a_p parameter of the perovskite in the following way: $a \approx a_p$ and $c \approx 2a_p$. Note that the oxygen content (Table 1) of these quenched samples is close to the ideal stoichiometric "O_5" composition.

Neutron Diffraction Study

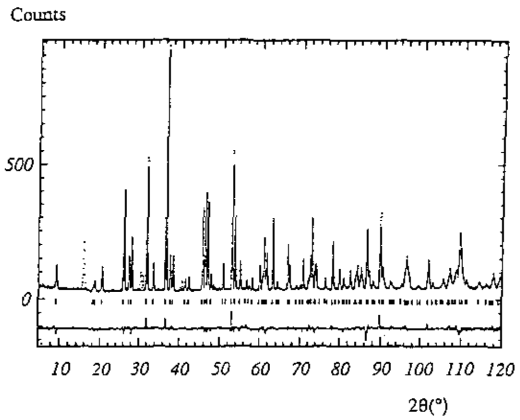

FIG. 2. Observed and calculated neutron profiles for $YBaCoCu_{0.5}Fe_{0.5}O_5$ at 300 K.

Taking into account the rather narrow homogeneity range of this solid solution, the study of the nuclear and magnetic structure was performed on the intermediate composition $YBaCoCu_{0.5}Fe_{0.5}O_5$ ($x = 0.50$). A preliminary X-ray diffraction determination was first carried out using the DBW program (13). The resulting atomic positions were then introduced as initial positions for the refinement of the structure from powder neutron diffraction data collected on the 3T2 diffractometer at 300 K. The neutron wavelength was of 1.2268 Å and the 2θ angle ranged from 5° to 120°.

A large number of reflections are indexed in the tetragonal cell ($a_N \approx a_p$ and $c_N \approx 2a_p$) using the two possible space groups: $P4/mmm$ and $P4mm$. Whatever the choice of the space group, some extra peaks cannot be indexed in this unit cell. They correspond to an antiferromagnetic ordering as will be seen from the susceptibility measurements and Mössbauer spectra. So, in a first step, we have excluded these extra reflections in the refinement of the nuclear structure. The first Rietveld refinement (Fig. 2) performed in the space group $P4/mmm$, with the transition elements located in the ($2h$) position, lead to a low value of the reliability factor ($R_I = 0.06$). Similar calculations, carried out in the noncentrosymmetric space group

TABLE 1

Tetragonal Lattice Parameters Determined by X-Ray Diffraction and Oxygen Content of $YBaCoCu_{1-x}Fe_xO_{5+\delta}$ Phases Prepared in Various Atmospheres

	x	a (Å)	c (Å)	V (Å^3)	Oxygen content (±0.02)
Quenched samples	0.3	3.8802(1)	7.5616(2)	113.85	4.98
	0.5	3.8863(1)	7.5624(2)	114.22	5.00
	0.6	3.8856(1)	7.5698(2)	114.29	5.03
Oxygen annealed samples	0.3	3.8763(1)	7.5694(3)	113.73	5.01
	0.5	3.8758(1)	7.5816(2)	113.89	5.16
	0.6	3.8765(1)	7.5875(2)	114.02	5.23

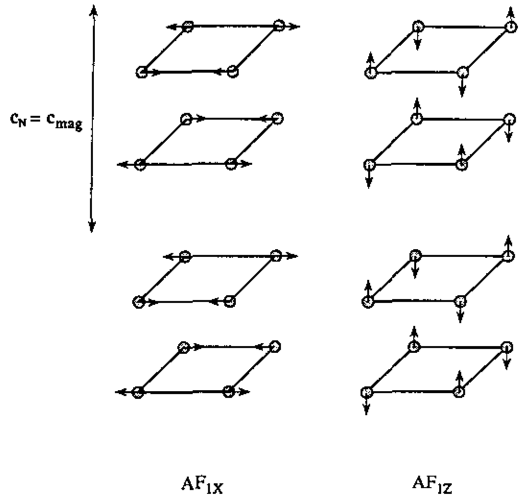

FIG. 3. Magnetic models corresponding to the $(h/2, k/2, l)$ conditions observed by neutron diffraction for the $YBaCoCu_{0.5}Fe_{0.5}O_5$ compound. Note: in the figure, the spin orientations in the (**a**, **b**) plane (model AF_{1X}) of the tetragonal structure have been arbitrarily fixed along the **a** axis.

$P4mm$, lead to significantly higher values of the reliability factor ($R_I \geq 0.09$), whatever the envisaged ordering of the cations over the two (1b) sites: (1/2 1/2 0.27) and (1/2 1/2 0.73). This result confirms that the structure is better described in the $P4/mmm$ group, in agreement with the previous works on $YBaFeCuO_5$ (6) and $YBaCoCuO_5$ (12) compounds.

At this stage, in order to study the magnetic structure of $YBaCoCu_{0.5}Fe_{0.5}O_5$, we have used simultaneously the neutron diffraction spectra obtained on G41 (λ = 2.426 Å) and 3T2 at 1.4 and 300 K respectively. The superlattice peaks due to the magnetic ordering correspond to $h/2$, $k/2$, l with h and k odd. These h, k, l conditions and the symmetry of the nuclear cell evidence a magnetic cell characterized by a superstructure along **a** and **b**, i.e., with the parameters $a_{mag} = a_N\sqrt{2}$ and $c_{mag} = c_N$.

TABLE 2
Neutron Refined Structural Parameters of $YBaCoCu_{0.5}Fe_{0.5}O_5$ at 1.4 K

Atom	Site	x	y	z	Occupancy
Y	1b	0	0	0.5	1
Ba	1a	0	0	0	1
Co, Cu, Fe	2h	0.5	0.5	0.2652(4)	2
O(1)	4i	0.5	0.0	0.3123(3)	4
O(2)	1d	0.5	0.5	0.0	1

Note. R_p = 0.11, R_{wp} = 0.12, R_e = 0.02, R_N = 0.045, R_M = 0.048. Nuclear cell: a = 3.8785(2) Å; c = 7.5441(4) Å; magnetic cell: a = 5.4853(3) Å; c = 15.0890(7) Å; space group: $P4/mmm$; magnetic moment μ_x = 5.28 (1) μ_B

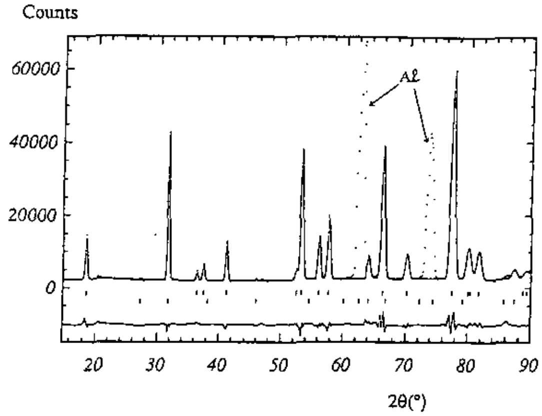

FIG. 4. Final profile refinement of $YBaCoCu_{0.5}Fe_{0.5}O_5$ at 1.4 K.

They also imply an antiparallel orientation of the spins in the (**a**, **b**) plane and an antiferromagnetic coupling between two successive layers along **c**. Two models can then be proposed, denoted AF_{1X} and AF_{1Z} (Fig. 3).

The refinements performed by the "FULLPROF" program (14) with the spins directed along the **c** axis (model AF_{1Z}) give a poor magnetic reliability factor (R_M), whereas a better fit is obtained assuming magnetic moments lying in the (**a**, **b**) plane (model AF_{1X}). The corresponding R_M factor is indeed lowered to 0.048, for the structural data listed in Table 2, leading to a quite acceptable profile fit at 1.4 K (Fig. 4). The interatomic distances (Table 3) are close to those generally observed for such oxides. The refined moment is 5.28 μ_B.

The inverse molar magnetic susceptibility (Fig. 5a) of $YBaCoCu_{1-x}Fe_xO_5$ ($0.3 \leq x \leq 0.6$) compounds reveals a minimum around 430 ± 5 K which corresponds to the antiferromagnetic–paramagnetic transition.

Mössbauer Spectroscopy Study

Mössbauer spectra for the $YBaCoCu_{0.5}Fe_{0.5}O_5$ powder sample collected at 500, 300, and 4 K are displayed in Fig. 6. The spectra at 4 and 300 K show an antiferromagnetic ordering, consistent with the susceptibility measurements. For these spectra, one observes a very small frac-

TABLE 3
Interatomic Distances for $YBaCoCu_{0.5}Fe_{0.5}O_5$ at 1.4 K

Bond	d (Å)
Y–O(1)	2.402(2) × 8
Ba–O(2)	2.742 × 4
Co, Cu, Fe–O(1)	1.972(1) × 4
Co, Cu, Fe–O(2)	1.996(3) × 1

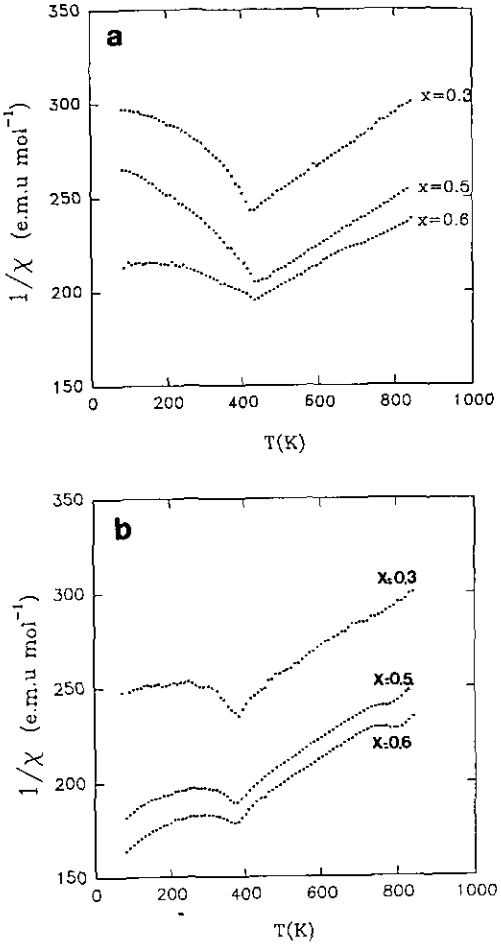

FIG. 5. Reciprocal molar magnetic susceptibility versus temperature of $YBaCoCu_{1-x}Fe_xO_5$ quenched samples (a) and oxygen annealed samples (b) ($0.3 \leq x \leq 0.6$).

tion (≤3%) of a paramagnetic iron contribution which can be attributed to some small paramagnetic particles of an iron oxide impurity; otherwise three sextets are necessary to obtain a correct fit (Table 4). The refined values of the isomer shifts IS, quadrupole lineshifts 2ε, absolute value of the quadrupole splitting QS, hyperfine fields H_f, and relative intensities are given in Table 4.

The isomer shift values of these sites show that iron is trivalent in this phase. The presence of several iron sites with hyperfine field values at 4 K ranging from 50 to 53 T shows that there are different magnetic interactions due to different local environments for the Fe(III) ion ($S = 5/2$). This feature corresponds to a disorder in the cationic sublattice which can also be observed in the paramagnetic Mössbauer results at high temperature (Fig. 6): the 500 K Mössbauer spectrum of this phase was indeed fitted either with two main components beside a small third component whose relative intensity is about 10% (Table 4) or with a quadrupole splitting distribution linearly correlated to IS (Fig. 7a). Note that the small amount of Fe(III) with a QS value of 1.1 mm/s can also be identified on the high QS tail of the distribution fit; it probably corresponds to an unidentified Fe(III) impurity and has already been observed in $YBaFeCuO_5$ (6). The mean value $\overline{QS}$ in the distribution, equal to 0.51 mm/s is slightly higher than that of $YBaFeCuO_5$ ($\overline{QS}$ = 0.2 mm/s); this corresponds to a less symmetric geometry of the FeO_5 pyramid for $YBaCoFe_{0.5}Cu_{0.5}O_5$ than for $YBaFeCuO_5$.

Taking into account the quadrupole shift value determined from the 4 K spectra and the quadrupole splitting QS observed in the 500 K spectra, one can estimate the orientation θ of the hyperfine field in the principal axes of the electric field gradient tensor (EFG) from the relationship $2\varepsilon = QS\,(3\cos^2\theta - 1)/2$: in this tetragonal compound, the EFG tensor is axial with its principal compo-

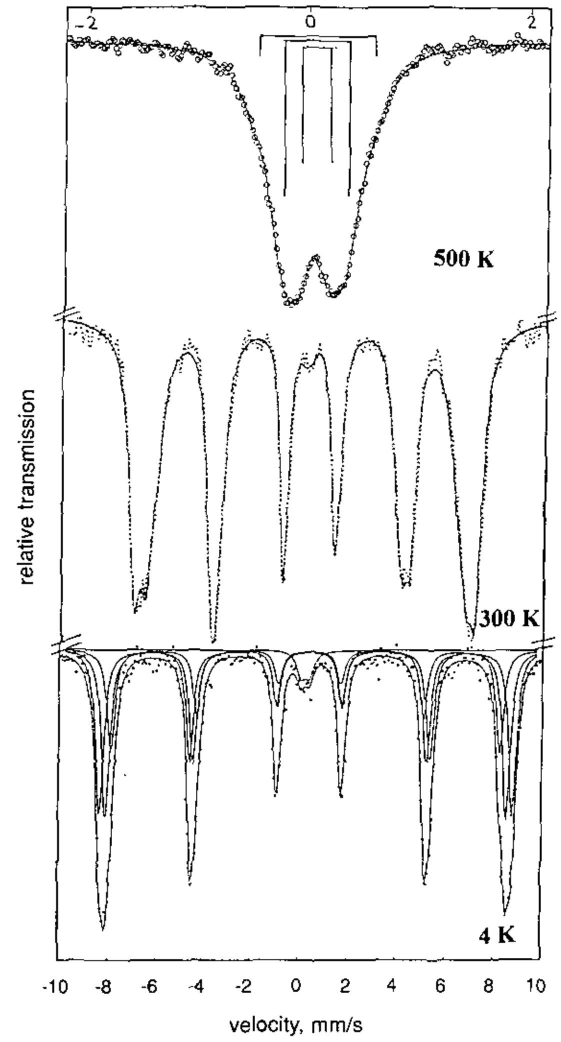

FIG. 6. Mössbauer powder spectra of $YBaCoCu_{0.5}Fe_{0.5}O_5$ at various temperatures.

TABLE 4

Refined Mössbauer Hyperfine Parameters of $YBaCoCu_{0.5}Fe_{0.5}O_{5+\delta}$ Compounds, at Various Temperatures

	Temperature										
	4 K				300 K				500 K		
	IS (mm/sec) ±0.02	2ε (mm/sec) ±0.02	H_f (T) ±5	% ±5	*IS* (mm/sec) ±0.02	2ε (mm/sec) ±0.02	H_f (T) ±5	% ±5	*IS* (mm/sec) ±0.02	*QS* (mm/sec) ±0.02	% ±5
Quenched compound	0.42	−0.20	531	37	0.31	−0.29	440	39	0.19	0.58	54
	0.41	−0.19	516	38	0.29	−0.18	413	38	0.18	0.26	39
	0.42	−0.25	501	22	0.29	−0.17	385	22			
	0.33	0.34[a]	—	3	0.29	0.24[a]	—	1	0.19	1.10[a]	7
Annealed compound	0.41	−0.17	517	33	0.31	−0.22	375	36	0.19	0.66	38
	0.41	−0.19	501	44	0.32	−0.16	334	63	0.19	0.29	51
	0.42	−0.23	482	20							
	−0.22	1.30[a]	—	3	−0.05	0.90[a]	—	1	0.18	1.06[a]	11

Note. % Relative intensity; Isomere shifts *IS* are referred to metallic iron at room temperature.

[a] Absolute value of the quadrupole splitting *QS*.

nent along the **c** axis. Assuming that *QS* is positive and is nearly thermal independent and using mean weighted values for 2ε and *QS* taking into account the relative intensities of the different sites, we have found for θ a value of 81° ± 7°. This result is in agreement with the neutron diffraction analysis showing that the magnetic moments are lying in the (**a**, **b**) plane. Note that this spin orientation can be correlated to a nearly regular configuration of the MO_5 pyramid (equatorial bonds at 1.4 K: $M\text{–}O_{(1)} = 1.972$ Å and axial bond $M\text{–}O_{(2)} = 1.996$ Å). This correlation has been mentioned in the previous work on $YBaCo_{2-x}Cu_xO_5$ (8) for $x \leq 0.75$.

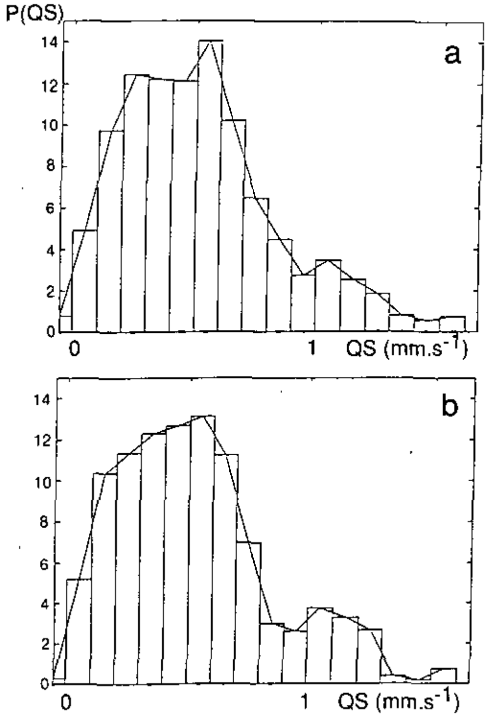

FIG. 7. P(QS) distribution corresponding to the 500 K Mössbauer spectra of (a) $YBaCoCu_{0.5}Fe_{0.5}O_5$ and (b) $YBaCoCu_{0.5}Fe_{0.5}O_{5.16}$.

If one takes into account the "O_5" stoichiometry and the mixed valency of cobalt Co(II)–Co(III) evidenced previously by XANES spectroscopy for $YBaCo_{2-x}Cu_xO_5$ (8), copper remaining in the divalent state, then, the formula $YBaCo_{0.5}{}^{III}Co_{0.5}{}^{II}Cu_{0.5}{}^{II}Fe_{0.5}{}^{III}O_5$ can be proposed in agreement with the Mössbauer results that imply for iron the only trivalent state. Taking this formula into consideration, the molar magnetic moment can be calculated and compared to the experimental one, deduced from neutron diffraction analysis (Table 5). For the calculated moment, we have distinguished three possible electronic configurations for Co(III) and used the following magnetic moments of Co(II), Cu(II), Fe(III), and Co(III) in high spin (hs), intermediate spin (is), and low spin (ls) state: $\mu Co_{hs}(II) = 3\ \mu_B$, $\mu Cu(II) = 1.1\ \mu_B$, $\mu Fe_{hs}(III) = 5\ \mu_B$, $\mu Co_{hs}(III) = 4\ \mu_B$, $\mu Co_{is}(III) = 2\ \mu_B$, and $\mu Co_{ls}(III) = 0\ \mu_B$. As in $YBaCo_{2-x}Cu_xO_5$, the intermediate spin state

TABLE 5

Experimental and Calculated Molar Magnetic Moments at 1.4 K in $YBaCoCu_{0.5}Fe_{0.5}O_5$

μ_{exp} (μ_B)	μ_{cal} (μ_B) with Co_{hs}(III)	μ_{cal} (μ_B) with Co_{is}(III)	μ_{cal} (μ_B) with Co_{ls}(III)
5.28	6.5	5.5	4.5

of Co(III), with $t_{2g}^5 e_g^1$ configuration, has been confirmed by the good agreement between the experimental value and the corresponding calculated value.

Effect of Oxygen Annealing

This oxygen deficient perovskite suggests the possibility of intercalating additional oxygen at the level of the yttrium plane between two CuO_5 (or FeO_5 or CoO_5) pyramids (Fig. 1). Such a phenomenon has been observed in the "112" cobalt-substitued phase $YBaCo_{2-x}Cu_xO_{5+\delta}$ for which an excess oxygen δ has been evidenced (7–9) by annealing at low temperature in oxygen. Moreover, in $YBaCo_2O_{5+\delta}$ (9) this nonstoichiometry leads to the observation of crystallographic superstructures. For this reason, we have undertaken a study of the oxygen effect on the $YBaCoCu_{1-x}Fe_xO_5$ compounds.

By annealing the pure quenched samples in an oxygen flow at 450°C for 12 hr, we have obtained the corresponding oxygenated phases $YBaCoCu_{1-x}Fe_xO_{5+\delta}$. No superstructure was detected by X-ray diffraction, whatever the x and δ values. The cell parameters and oxygen content are given in Table 1. Note that the a parameter does not vary, whereas the c parameter and oxygen content increase as x increases.

Figure 5b shows the thermal evolution of the inverse molar magnetic susceptibility of these annealed samples ($x = 0.3, 0.5, 0.6$). One observes an undulation in the curves at high temperatures ($750 \leq T \leq 800$ K), probably due to oxygen loss at these temperatures, using helium as atmosphere. The Néel temperatures are lower than that observed for the quenched compounds ($T_N \approx 380 \pm 5$ K).

For the $x = 0.5$ composition, i.e., "$O_{5.16}$", we have performed a Mössbauer study at various temperatures. These spectra (Fig. 8) are similar to those of the stoichiometric sample and have been fitted in the same way, except for the spectrum at 300 K in which only two sextets have been evidenced (Table 4). Around the $\overline{QS}$ mean value, the distribution fit of the 500 K spectrum (Fig. 7b) is more settled down and the correlation between the IS and QS values is weaker than that of the quenched sample. This suggests that the local environment of iron is distributed in a more homogeneous way in the oxygenated sample than in the "O_5" phases.

CONCLUSION

This study shows the possible coexistence of iron, cobalt, and copper in the same "112" type matrix, but for a rather rich cobalt compound. It demonstrates once again that the nuclear structures of all the "112" compounds exhibit the *P4/mmm* group, and are characterized by a disorder of the transition elements in the pyramidal layers.

As for the oxides $YBaCo_{2-x}Cu_xO_5$, one observes an intermediate spin configuration of Co(III). Curiously, the simultaneous presence of copper, iron, and cobalt makes that the magnetic moments are lying antiferromagnetically in the (**a**, **b**) plane. The same orientation is also observed for cobalt rich compositions in $YBaCo_{2-x}Cu_xO_5$ (8), i.e., for $x \leq 0.75$, whereas for $YBaFeCuO_5$, the moments are titled with respect to the **c** axis (6).

As for the phases $YBaCo_{2-x}Cu_xO_{5+\delta}$, further neutron diffraction investigations are required to better understand the influence of oxygen annealing on the magnetic properties of this phase.

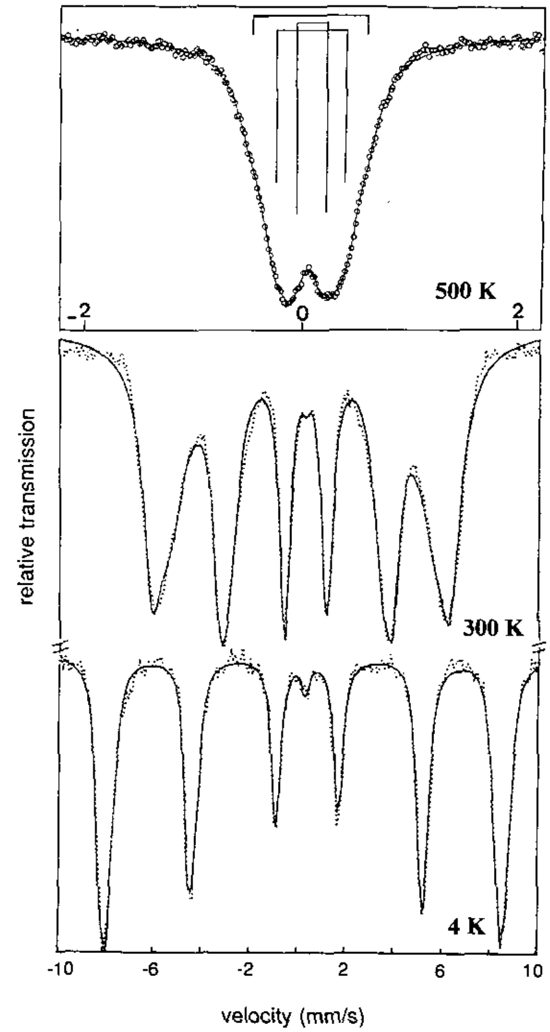

FIG. 8. Mössbauer powder spectra of $YBaCoCu_{0.5}Fe_{0.5}O_{5.16}$ compound at 4, 300, and 500 K.

REFERENCES

1. L. Er-Rakho, C. Michel, P. Lacorre, and B. Raveau, *J. Solid State Chem.* **73**, 531 (1988).
2. J. T. Vaughey and K. R. Poeppelmeier, *in* "Proceedings of the International Electronic Ceramics Conference," Special Publication

804, p. 419. National Institute of Standards and Technology, Washington DC, 1991.

3. C. Meyer, F. Hartmann-Boutron, Y. Gros, and P. Strobel, *Solid State Commun.* **76,** 163 (1990).
4. M. Pissas, C. Mitros, G. Kallias, V. Psycharis, D. Niarchos, A. Simopoulos, A. Kostikas, C. Christides, and K. Prassides, *Physica C* **185–189,** 553 (1991).
5. M. Pissas, C. Mitros, G. Kallias, V. Psycharis, A. Simopoulos, A. Kostikas, and D. Niarchos, *Physica C* **192,** 35 (1992).
6. V. Caignaert, I. Mirebeau, F. Bourée, N. Nguyen, A. Ducouret, J. M. Greneche, and B. Raveau, *J. Solid State Chem.,* to be published.
7. L. Barbey, N. Nguyen, V. Caignaert, M. Hervieu, and B. Raveau, *Mater. Res. Bull.* **27,** 295 (1992).
8. L. Barbey, N. Nguyen, V. Caignaert, F. Studer, and B. Raveau, *J. Solid State Chem.* **112,** 148 (1994).
9. W. Zhou, C. T. Lin, and W. Y. Liang, submitted for publication.
10. C. T. Lin, S. X. Li, W. Zhou, A. Mackenzie, and W. Y. Liang, *Physica C* **176,** 285 (1991).
11. M. Jacob, S. Hansen, and S. Sturefelt, *Microsc. Microanal. Microstruct.* **1,** 319 (1990).
12. Q. Huang, P. Karen, V. L. Karen, A. Kjeleshus, J. W. Lynn, A. D. Mighell, I. Natali Sora, N. Rosov, and A. Santoro, *J. Solid State Chem.* **108,** 80 (1994).
13. D. B. Wiles and R. A. Young, *J. Appl. Crystallogr.* **14,** 149 (1981).
14. J. Rodriguez-Carvajal *in* "Satellite Meeting on Powder Diffraction," Abstracts of the XVth Conference of the International Union of Crystallography, Toulouse, 1990, p. 127.