

## Characterization of superconducting $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ phases with $^{57}\text{Fe}$ Mössbauer spectroscopy

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In order to study the dependence of superconductivity on sample preparation and the influence of cationic doping,  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$  samples were prepared using various sintering temperatures and nominal starting compositions. After each sintering the samples were characterized with x-ray-diffraction and magnetic-ac-susceptibility measurements. In all cases the corresponding  $^{57}\text{Fe}$ -doped samples were also made for Mössbauer measurements. The Mössbauer measurements usually show three quadrupole components arising from the different phases in the samples. The site assignment of  $^{57}\text{Fe}$  is discussed.

### I. INTRODUCTION

After the discovery of high- $T_c$  superconductivity at 40 K in the layered La-Ba-Cu-O system,<sup>1</sup> other perovskite-type cuprates have also been extensively studied in the search for materials with improved superconducting properties. Superconductivity above liquid-nitrogen temperature was soon observed in the 90-K orthorhombic phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,<sup>2</sup> which contains both the  $\text{CuO}_2$  planes and the Cu-O chains. The tetragonal, nonsuperconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  phase shows antiferromagnetic features, detectable, e.g., by Mössbauer spectroscopy.<sup>3</sup>

The bismuth based cuprate  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  was found to be superconducting below 10 K by Michel *et al.*<sup>4</sup> Superconductivity at temperatures as high as 110 K in the Bi-Sr-Ca-Cu-O system was first reported by Maeda *et al.*<sup>5</sup> and Chu *et al.*<sup>6</sup> Later, a series of superconducting phases  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ , whose structures do not contain Cu-O chains, has been reported.<sup>7</sup> There is a correspondence between the number of  $\text{CuO}_2$  planes in the unit cell and the index  $n$ ; the critical temperatures of the superconductivity of the different phases are 10 K (2:2:0:1 phase), 80 K (2:2:1:2), and 110 K (2:2:2:3), corresponding to  $n = 1, 2,$  and  $3,$  respectively. Mei *et al.*<sup>8</sup> carried out x-ray diffraction studies and found out that phase formation is sensitive to sintering temperatures. So far, the compound with the critical temperature of the superconductivity  $T_c = 110$  K has turned out to be difficult to prepare as a single phase.

Studies on the high- $T_c$  oxides and chemically substituted phases in these systems have revealed several important trends in their properties. It is generally believed that  $\text{CuO}_2$  planes are crucial for superconductivity and substitution of Cu by other elements in these planes within the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  phase leads to a drastic de-

crease in  $T_c$ . For a more complete understanding of the role of Cu in superconductivity it is of interest to study the influence of cationic doping within the bismuth-based cuprates. Doping with the  $^{57}\text{Fe}$  isotope enables the use of Mössbauer spectroscopy. As compared to the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound, few Mössbauer studies on the bismuth-based high- $T_c$  materials have been reported. In Refs. 9–11, as much as 20–100% of the Cu atoms has been reported to be substituted by natural Fe. By using enriched  $^{57}\text{Fe}$  isotope, significantly smaller amounts of iron substituent are needed.

In Ref. 9, the different quadrupolar components in  $^{57}\text{Fe}$  Mössbauer spectra of Bi-Sr-Ca-Cu-O samples were assumed to arise from different oxygen coordinations of the iron atoms. In spectra measured from samples made by replacing copper completely with natural iron in a 2:2:2:3 superconductor, iron at two sites and probably in the  $\text{Fe}^{4+}$  oxidation state, was detected. No magnetic splitting due to magnetic hyperfine interaction was found. Tarascon *et al.*<sup>12</sup> prepared Fe-doped samples and judged from x-ray diffraction data that Fe substituted Cu in the 2:2:0:1 phase. In measurements of samples prepared by substituting 50 at. % Cu by Fe, two quadrupolar components were detected. From this fact it was deduced that iron occupies two inequivalent sites. The isomer shift values indicated the  $\text{Fe}^{3+}$  oxidation state.<sup>11</sup>

The presence of different phases in the Bi-containing superconductors and the complexity of the crystal structure hamper the analysis of Mössbauer data. For the reliable identification of the different phases, comparative studies with other physical measurements are needed in addition to the careful control of the sample preparation. Here we report results of Mössbauer measurements of samples that were prepared using various nominal starting compositions and final sintering temperatures. In

most of the  $^{57}\text{Fe}$ -doped samples, the doping level was kept low (1 at. % of Cu) in order not to distort the crystal structure. To study the influence of the Fe content on the existence and on the crystal structures of the different superconducting phases, a series of  $^{57}\text{Fe}$ -doped samples was prepared with various iron concentrations (1–20 at. % of Cu). The samples were also studied with x-ray diffraction and magnetic ac susceptibility.

## II. EXPERIMENTAL

The  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  samples with the nominal starting compositions corresponding to  $n = 1, 2, 3$ , or 4 were synthesized by a direct reaction of a mixture of high-purity  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  in the temperature range 800–884 °C. A sample of a nonstoichiometric starting composition with a 4:3:3:4 ratio for Bi, Sr, Ca, and Cu was also prepared. All samples were first heated at 800 °C for 20 h and then ground. This procedure was repeated at subsequent temperatures of 825 °C (for 15 h), 850 °C (10 h), 870 °C (10 h), 877 °C (10 h), and finally at 884 °C (10 h). In order to increase the relative amount of the 110-K phase, the influence of a long heating period (100 h) was also investigated. For Mössbauer studies, in each case also a corresponding specimen containing  $^{57}\text{Fe}$  (1 at. % of Cu) was synthesized.  $^{57}\text{Fe}$  was added as metallic (95% enriched). Additionally, a series of Fe-doped 2:2:2:3 samples were prepared by replacing 1, 3, 5, 7, 10, 15, or 20 at. % of Cu by  $^{57}\text{Fe}$ .

The phase contents of the specimens with various nominal compositions were identified after each heat treatment using x-ray diffractometry (XRD). Because the crystal structures of the phases differ only slightly, high-resolution XRD measurements are needed to distinguish between the different bismuth phases. We used a Philips powder x-ray diffractometer model MPD 1880, equipped with a graphite secondary monochromator and a Cu tube.

Mössbauer measurements were performed at room temperature (RT) in the normal transmission geometry using a 20 mCi  $^{57}\text{Co}:Rh$  source. To improve the homogeneity of the samples, the superconducting material was mixed with resin. The thickness of our polycrystalline samples was approximately 20 mg/cm<sup>2</sup> (for the superconductor material).

The magnetic ac susceptibility of the samples was measured using a mutual inductance bridge where the basic circuit consists of two identical coils: a test frame and a compensator. The samples were magnetized by applying a sinusoidal field of 1.4 Oe at a frequency of 20 Hz. The apparatus is described in more detail in Ref. 3. The phases with different transition temperatures are revealed by the susceptibility measurement, but this method alone does not allow a very accurate phase identification. Ambiguity may arise, e.g., from shielding effects that hamper the observation of phases with lower  $T_c$  inside the superconducting inclusions (this effect is less pronounced in powder samples). The lowest-measurement temperature of our device is 20 K, and hence the 10-K transition could not be observed with this system.

In order to check the homogeneity of iron doping, two

samples containing 1 at. % of  $^{57}\text{Fe}$  were subjected to a secondary-ion-mass-spectroscopy (SIMS) analysis in a Cameca 3f instrument. The 20–40  $\mu\text{m}$  crystallites were imbedded in an indium foil and depth profiling with an  $\text{O}^-$  primary beam was performed on an area with a 13  $\mu\text{m}$  diam. The  $^{57}\text{Fe}$  and  $\text{CaOH}$  interference was overcome by energy filtering. The  $^{57}\text{Fe}$  signal was normalized to  $^{63}\text{Cu}$ .

## III. RESULTS

The phase contents of our samples were basically controlled by the initial nominal composition. The samples were prepared by using stoichiometric amounts of starting materials corresponding to the formula  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ , with various  $n$  values. According to XRD measurements, the main component in the samples with  $n = 1$  was the 2:2:0:1 (10-K) phase. In samples with  $n = 2, 3$ , and 4, the 10-K phase is clearly present but the most abundant phase is the 80-K phase. The 110-K phase was not obtained at sintering temperatures lower than 870 °C. The residual traces of the starting materials were negligible, e.g., the XRD peaks corresponding to  $\text{CuO}$  were barely noticeable. Other weak XRD peaks are possibly due to binary oxides, such as  $\text{CaCuO}_2$  and  $\text{Ca}_2\text{CuO}_3$ . The presence of these oxides can be understood by studying the nominal compositions. If the stoichiometry of the starting material is 2:2:2:3 (the nominal 110-K phase) and nevertheless the sintered material consists mainly of the 2:2:1:2 (80-K) phase, the excess of Ca and Cu forms oxides mentioned above.

The influence of nominal starting composition on the real part of magnetic ac susceptibility  $\chi'$  is shown in Figs. 1(a)–1(c). In the nondoped sample with  $n = 2$  no 110-K phase was detected after final heat treatment at 877 °C [Fig. 1(a)]. Judging by the susceptibility data, the 80-K phase was found to be rather insensitive to extra sinterings. For samples with  $n = 3$ , the magnetic ac susceptibility measurements showed characteristic superconductivity transitions for both the 110- and the 80-K phases [Fig. 1(b)]. The relative amount of the 110-K phase was greater in samples with  $n = 4$  [Fig. 1(c)] and in samples with the nonstoichiometric nominal composition of 4:3:3:4. Also both the XRD and magnetic-susceptibility data show that longer sintering periods increased the relative amount of the phase with the highest  $T_c$ . The imaginary part of magnetic susceptibility  $\chi''$  measured from the sample with  $n = 4$  [Fig. 1(d)] shows a sharp peak at 75 K and a broader maximum at 100 K, close to the midpoints of the real parts.<sup>13,14</sup>

XRD studies on the influence of the Fe-doping level in the  $n = 3$  samples reveal that the peaks of the 10-K phase were shifted as a function of Fe content suggesting that iron can substitute for Cu in the 2:2:0:1 structure. In samples that did not have any noticeable amount of the 110-K phase, 1 at. % iron doping did not affect the magnetic ac susceptibility transition of the 2:2:1:2 phase. These results can be compared with those from the high-resolution XRD measurements of Ref. 12. On the other hand, in samples containing the 110-K phase, iron doping changed somewhat the shape of the superconductivity

transition. From this it may be deduced that Fe can substitute for Cu in the 2:2:2:3 compound.

The SIMS analyses indicated that the iron distribution was homogeneous throughout the sputtering of an individual crystallite. They also corroborated correctly the nominal composition with respect to iron.

The results of the 1 at. % iron doping on the magnetic ac susceptibility and XRD data of the  $n=3$  sample are shown in Figs. 2 and 3, respectively. Both the nondoped

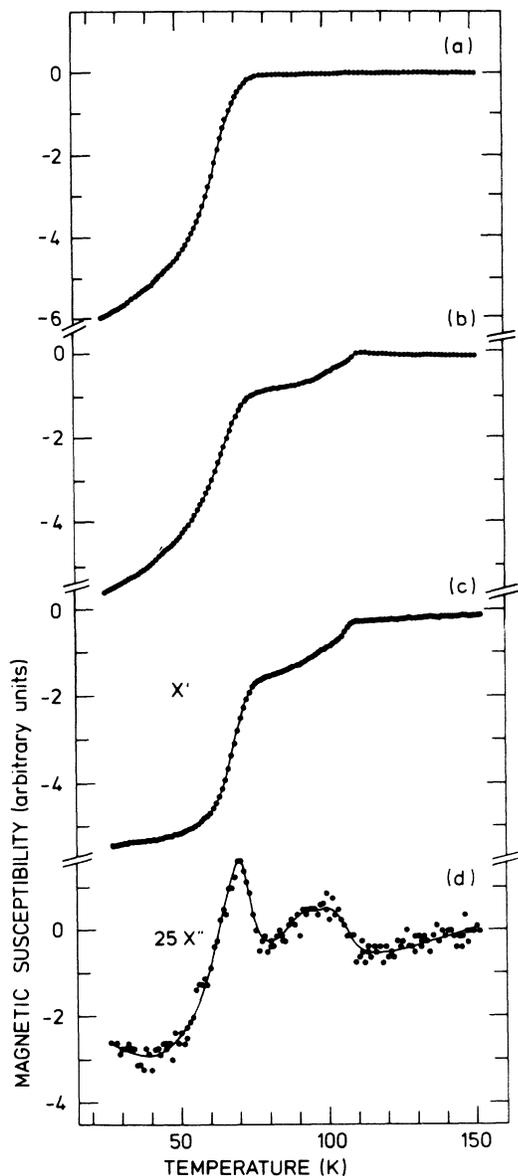


FIG. 1. Results of the magnetic ac susceptibility measurements of the influence of the nominal starting compositions on the superconducting properties of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$  compounds. a–c present the real part  $\chi'$  of susceptibility of samples corresponding to compositions (a) 2:2:1:2, (b) 2:2:2:3, and (c) 2:2:3:4. (d) shows the imaginary part  $\chi''$  of the sample with the composition of 2:2:3:4. The final sintering temperature has been 877 °C (10 h).

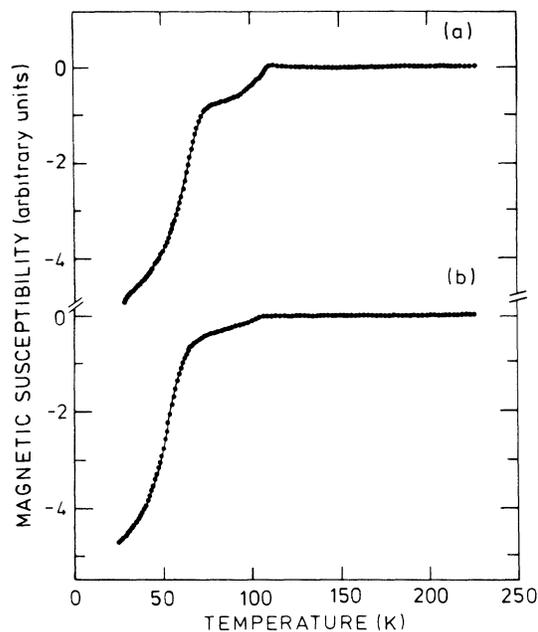


FIG. 2. Influence of iron doping on the compound corresponding to nominal composition  $n=3$ . The samples were sintered at 877 °C for 10 h. Compared to the nondoped sample (a) the amount of the 110-K phase in the 1 at. % doped sample (b) is significantly reduced.

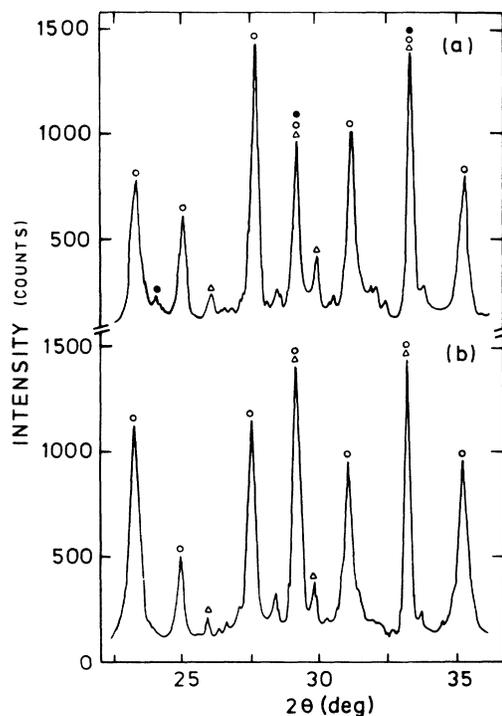


FIG. 3.  $\text{Cu-K}\alpha$  x-ray-diffraction data of (a) nondoped and (b) iron-doped ( $x=0.01$ ) samples with the composition 2:2:2:3 (final sintering at 877 °C for 10 h). The symbols  $\Delta$ ,  $\circ$ , and  $\bullet$  denote the peaks corresponding to phases with  $T_c$ 's of 10, 80, and 110 K, respectively.

and  $^{57}\text{Fe}$ -doped samples were sintered at  $877^\circ\text{C}$ . The XRD peaks corresponding to 10-, 80-, and 110-K phases are clearly visible in the spectrum of the nondoped sample [Fig. 3(a)]. When 1 at. % of Cu is replaced by  $^{57}\text{Fe}$ , the peaks of the 110-K phase are barely visible [Fig. 3(b)]. Judging from the magnetic-susceptibility measurements 1 at. % Fe doping reduced the relative amount of the 110-K phase and the superconductivity transition temperature ( $T_{\text{onset}}$ ) was dropped from 110 to 107 K (Fig. 2). In the sample doped with 3 at. % of iron the highest  $T_c$  phase was no longer found. For the 80-K phase,  $T_{\text{onset}} = 77$  K of the nondoped sample was reduced to 75 and 70 K by introducing 3 and 7 at. % iron, respectively.

After the first two sintering and grinding cycles of the iron-doped samples, the Mössbauer spectra measured at RT showed two very distinct magnetic components, most likely due to impurity phases. After an additional sintering and a consecutive grinding, these impurities disappeared and the crystallinity was improved as judged by

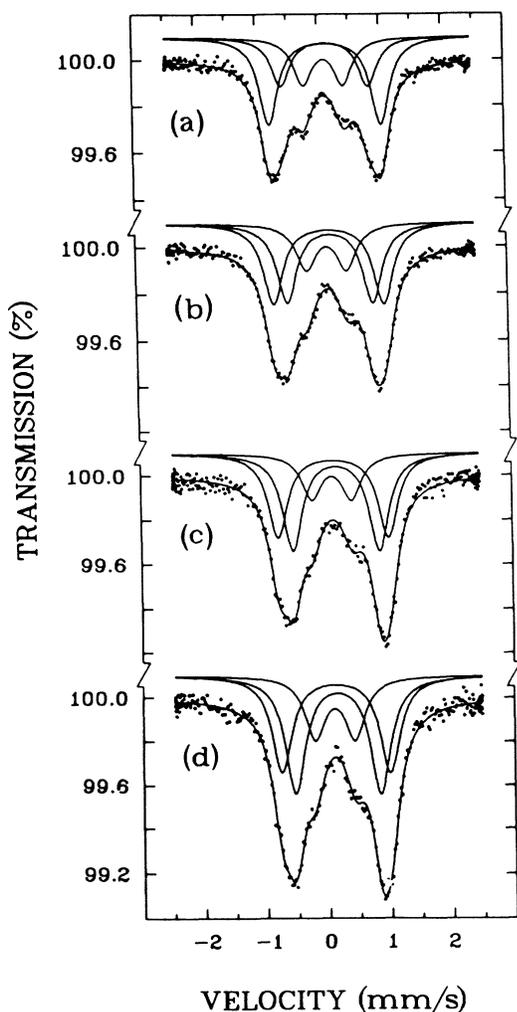


FIG. 4. Room-temperature Mössbauer spectra measured of samples with the nominal stoichiometric composition of  $n=2$  after heat treatments of (a)  $825^\circ\text{C}$ , (b)  $877^\circ\text{C}$ , (c)  $884^\circ\text{C}$ , and (d)  $884^\circ\text{C}$  (100 h). The  $^{57}\text{Fe}$  doping level was 1 at. %.

the peak-to-background ratio of the XRD spectrum.

Figure 4 shows Mössbauer spectra measured for samples with the nominal stoichiometry of  $n=2$  and  $x=0.01$  prepared using final sintering temperatures of (a)  $825^\circ\text{C}$  (for 15 h), (b)  $877^\circ\text{C}$  (10 h), (c)  $884^\circ\text{C}$  (10 h), and (d)  $884^\circ\text{C}$  (long heating, 100 h). Satisfactory fitting of the data was obtained using three symmetrical quadrupole doublets with splittings of approximately 1.8, 1.4, and 0.6 mm/s. The consecutive sinterings cause significant changes in the relative intensities of the first two components while the relative intensity of the smallest doublet does not change at all.

The spectra measured for samples with the nominal composition of  $n=3$  and  $x=1\%$  are shown in Fig. 5. The final sintering temperatures have been (a)  $877^\circ\text{C}$ , (b)  $884^\circ\text{C}$ , and (c)  $884^\circ\text{C}$  (long heating). Only two doublets are observed. Their relative intensities are determined by the number of consecutive sinterings.

In Fig. 6, the spectra of samples with various iron concentrations  $x$  of 1, 5, 10, and 20 % are shown. The nominal composition of the samples was  $n=3$ . At high iron concentrations the component with the smallest QS becomes most prominent.

The Mössbauer spectra of  $^{57}\text{Fe}$ -doped ( $x=1\%$ ) non-stoichiometric 4:3:3:4 compositions are shown in Fig. 7. The heat treatments were performed at (a)  $877^\circ\text{C}$  and (b)  $884^\circ\text{C}$  (long heating). The spectra were fitted using three doublets. The large values of the linewidths ( $\sim 0.5$  mm/s) suggest that a higher number of different oxygen coordinations of iron may be encountered in these materials.

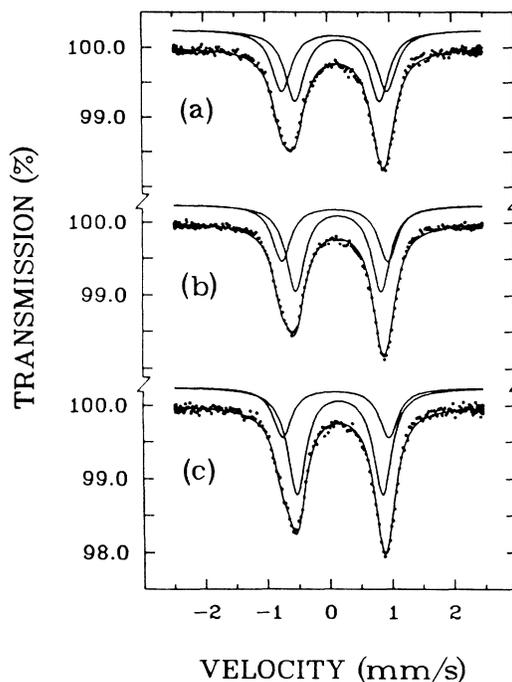


FIG. 5. Spectra measured of samples with nominal stoichiometric composition of  $n=3$  after heat treatments of (a)  $877^\circ\text{C}$ , (b)  $884^\circ\text{C}$ , and (c)  $884^\circ\text{C}$  (100 h).

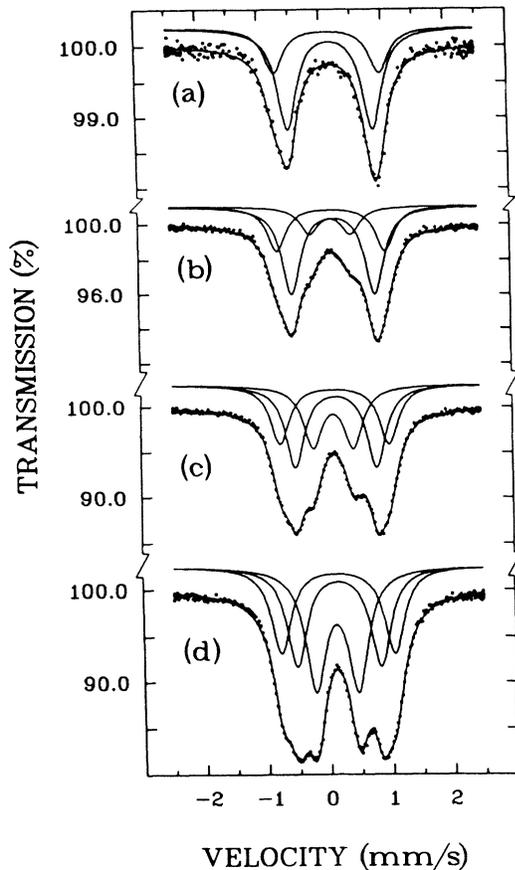


FIG. 6. Influence of iron doping on the Mössbauer spectra of samples with composition  $n=3$  after the heat treatment of  $884^\circ\text{C}$ . Spectra were measured at room temperature using various iron concentrations of (a) 1, (b) 5, (c) 10, and (d) 20 at. %.

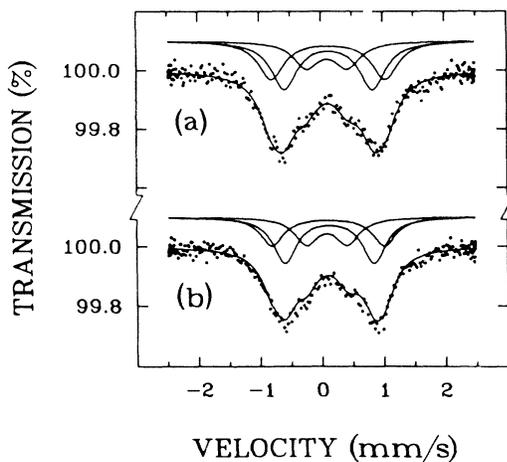


FIG. 7. Room-temperature Mössbauer spectra measured of samples with the nominal nonstoichiometric composition of 4:3:3:4 after the heat treatments of (a)  $877^\circ\text{C}$  (10 h) and (b)  $884^\circ\text{C}$  (100 h).

In Table I, we present our Mössbauer data for all the spectra shown in Figs. 4–7. The fitting parameters given in the table are the quadrupole splitting (QS), the isomer shift (IS) relative to iron metal, the relative intensity ( $I$ ) of the doublets and the linewidth ( $\Gamma$ , same value used in each component).

#### IV. DISCUSSION

Extra sinterings cause changes in Mössbauer spectra after iron is soluted to these materials; the changes in QS and  $\Gamma$  suggest only more random distribution of  $^{57}\text{Fe}$  between Cu sites. The values for the linewidths are somewhat smaller than presented in Ref. 11 for a  $\text{Bi}_2\text{Sr}_2\text{Cu}_{0.5}\text{Fe}_{0.5}\text{O}_y$  sample. All values for isomer shifts indicate the  $\text{Fe}^{3+}$  oxidation state in these samples.

In all of our spectra there is a doublet corresponding to the energy splitting of QS of 1.69–1.85 mm/s. Its relative intensity is rather high and is significantly reduced by extra sinterings; for samples with  $n=2$  it is between 35 and 48 % and for samples with  $n=3$  between 32 and 46 %. An increase in iron concentration makes the QS larger, whereas extra sinterings decrease it slightly. Bremert *et al.*<sup>9</sup> also found this component in their spectra.

The second component corresponds to the QS values between 1.31 and 1.44 mm/s. For samples with  $n=3$  and iron doping  $x=0.01$ , this component covers 54–68 % of the measured intensity. An increase in iron content makes this proportion smaller. Extra sinterings increase the relative intensity of this component in all cases.

The third doublet with the smallest QS values varying between 0.64 and 0.68 mm/s is clearly present for samples with  $n=2$ , but its relative intensity is slightly reduced with additional sinterings. It is not noticeable in spectra of samples with  $n=3$  and  $x=0.01$ . The increase of iron doping enhances its relative intensity strongly, suggesting that this component originates from an impurity phase.

#### V. CONCLUSIONS

The high- $T_c$  materials containing Bi usually consist of a mixture of several superconducting phases and of minor amounts of impurity compounds. In addition, the crystal structures of these phases are relatively complex, hampering the studies of microscopic physical properties. Thus, it is necessary to compare results from several different types of measurements in order to determine the phase content in a given sample. In this work, we used the Mössbauer spectroscopy as a primary method in the phase identification. The magnetic-ac-susceptibility measurements and x-ray diffraction were used to give additional information about the different phases in the samples.

The effects of different sintering temperatures and starting nominal compositions were studied on iron-doped and on nondoped samples. It was found out that in order to prepare the 110-K material, the most important factor is the starting nominal composition, but the

TABLE I. The fitting parameters of RT spectra of Figs. 4–7. The symbols given in the table are the quadrupole splitting (QS), the isomer shift (IS) relative to iron metal, the relative intensity ( $I$ ) of the doublets, and the linewidth ( $\Gamma$ ). The statistical errors are given in parentheses.

	QS (mm/s)			IS (mm/s)			$I$ (%)			$\Gamma$ (mm/s)
	1	2	3	1	2	3	1	2	3	
4(a)	1.81(1)	1.41(2)	0.64(1)	0.254(3)	0.253(5)	0.233(6)	48(3)	27(3)	25(1)	0.37(1)
4(b)	1.78(1)	1.38(2)	0.64(1)	0.256(3)	0.276(3)	0.227(6)	39(2)	39(2)	22(1)	0.39(1)
4(c)	1.78(2)	1.40(2)	0.64(2)	0.249(5)	0.294(4)	0.231(9)	37(3)	43(3)	20(1)	0.39(1)
4(d)	1.75(2)	1.38(2)	0.64(2)	0.254(4)	0.285(4)	0.240(7)	35(3)	43(2)	22(1)	0.39(1)
5(a)	1.69(2)	1.36(1)		0.252(4)	0.298(4)		46(3)	54(3)		0.38(1)
5(b)	1.71(1)	1.38(1)		0.246(4)	0.301(3)		40(2)	60(2)		0.37(1)
5(c)	1.71(2)	1.38(1)		0.244(6)	0.305(3)		32(3)	68(2)		0.36(1)
6(a)	1.70(3)	1.37(1)		0.246(8)	0.293(3)		31(4)	69(4)		0.38(1)
6(b)	1.75(1)	1.34(1)	0.66(1)	0.260(3)	0.291(1)	0.250(5)	28(1)	55(1)	17(1)	0.36(1)
6(c)	1.76(1)	1.31(1)	0.65(0)	0.269(2)	0.292(1)	0.250(2)	30(1)	40(1)	30(1)	0.38(1)
6(d)	1.82(1)	1.34(1)	0.68(0)	0.276(2)	0.291(2)	0.256(1)	28(1)	33(1)	39(1)	0.39(1)
7(a)	1.85(8)	1.43(7)	0.67(5)	0.255(11)	0.258(9)	0.237(19)	34(10)	43(10)	23(3)	0.50(4)
7(b)	1.82(8)	1.44(6)	0.66(4)	0.244(14)	0.264(9)	0.226(16)	29(10)	45(10)	26(3)	0.47(3)

relative amount of the 110-K phase can be increased by using long sintering times at temperatures close to the melting point.

A very interesting question is related to the presence of “excess” oxygen in the Bi-based high- $T_c$  oxides. The Mössbauer spectra of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$  samples measured using the  $^{57}\text{Fe}$  resonance are very sensitive to the different oxygen contents and thus to oxygen environments around  $^{57}\text{Fe}$  nuclei at the Cu site.<sup>3</sup> If this is also the case with the Bi samples, many different quadrupole components are to be expected. Like in the Mössbauer spectra of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$  compounds, 2 or 3 quadrupolar components can also be seen in the  $^{57}\text{Fe}$  spectra of Bi-containing superconductor materials. Though consecutive sinterings at higher temperatures should increase the 110-K phase content, the amounts of starting constituents seem in principle to determine the spectral structure.

There is a sixfold copper coordination in the 2:2:0:1 phase, 4+1 coordination in the 2:2:1:2, and finally 4+1 and 4 coordinations in the 2:2:2:3 phase. Thus a direct structural comparison is difficult. The first component (QS, 1.8 mm/s), present in all samples with a decreasing relative intensity with respect to the number of sinterings, is assigned to the 10-K phase. The second doublet (QS, 1.4 mm/s) is believed to originate from the only copper site in the 80-K phase and also from the similar kind of nearest-neighbor oxygen coordinations of iron in the 110-K phase. This doublet covers less than 50% of the

intensity when no 110-K phase is present and over 65% when there is a significant fraction of the material with  $T_c = 110$  K. Our results suggest that the third doublet (QS, 0.6 mm/s) is due to an iron-containing impurity compound. All values of the isomer shifts suggest a 3+ oxidation state of Fe in these samples.

In the nonsuperconducting phases of both the La-Sr-Cu-O and the 1:2:3 systems antiferromagnetic ordering is observed. After a certain number of subsequent annealing and grinding procedures, iron is soluted into the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  compounds and the room-temperature Mössbauer spectra show no magnetic splittings. Mössbauer studies on antiferromagnetic, nonsuperconducting Bi-containing cuprates (“parent phases”) with crystal structures close to that of the superconducting ones may help to clarify the analogy between the Bi-based high- $T_c$  materials and the La-Sr-Cu-O and 1:2:3 systems.

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