Magnetization and Mössbauer studies of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$

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ac-susceptibility, dc-magnetization, and ^{57}Fe Mössbauer spectra of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ ($x=0$, 0.1, and 0.2; $y=0.3$ and 0.4) are presented. Our data indicate bulk superconductivity in these compounds. In the case of $y=0.4$, the substitution of $x=0.1$ Ca increases both T_c and flux pinning. The Mössbauer parameters of the sample containing $y=0.4$ Fe and no Ca in comparison to those of $YBa_2Cu_{3-y}Fe_yO_{6+z}$ indicate that at least 85% of Fe substitutes the Cu(1) sites and about 15% goes to Cu(2) sites. The existence of superconductivity at such high concentrations of Fe and the revival of superconducting properties by Ca substitution are discussed.

I. INTRODUCTION

The effect of substitution of different elements on the structural and superconducting properties has been extensively studied[1] in the case of $YBa_2Cu_3O_{6+z}$. Among these, the substitution of Ba by Sr in $YBa_{2-k}Sr_kCu_3O_{6+z}$ deserves special attention. While some observed that, for $k>1$, the perovskite structure was not stable,[2] others have observed superconductivity at T_c (resistivity $\rho=0$) ranging between 72 and 90 K in Y-Sr-Cu-O depending on the preparation conditions.[3] Recently, Sunshine et al.[4] have studied in detail the effect of $3d$ metal doping at Cu sites on the structural and the superconducting properties of $YSr_2Cu_{3-y}M_yO_{6+z}$ ($M=Fe$, Co, Al). In particular, they concluded that the perovskite structure became unstable for $k=2$, $y=0$ but could be stabilized for $k=2$ only when $y>0.3$. Further, they reported superconductivity at $T_c=10$ K for $M=Fe$ ($y=0.30$) but not for $M=Al$. In view of the fact that the superconducting volume fraction was less than 2%, they could not attribute it uniquely to the perovskite phase. However, Suryanarayanan et al.[5] have reported on the electron diffraction and microscopy and energy dispersive x-ray analyses (EDX) of $Y_{1-x}Ca_xSr_2Cu_{2.6}Fe_{0.4}O_{6+z}$ ($x=0;0.1$). They observed zero resistivity at 10 K which increased to 25 K for $x=0.1$. On the other hand, Slater and Greaves[6] have also synthesized single-phase materials for $M=Al$, Co, Ga, Pb, and Fe, but did not report superconductivity for any of these M substitutions. However, they observed superconductivity with $T_c=30$ K in multiphase samples of nominal composition $Y_{1-x}Ca_xSr_2Cu_{2.4}Pb_{0.6}O_{6+z}$ for $x>0.4$. We report here on the ac-susceptibility, magnetization, and Mössbauer spectra of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ ($y=0.3$, 0.4, and $x=0$, 0.1, and 0.2) and discuss the influence of Ca and the occurrence of bulk superconductivity in these compounds.

II. EXPERIMENTAL TECHNIQUES

The polycrystalline samples have been prepared by solid-state sintering of the respective oxides or carbonates. The chemicals were of 99.999% purity. Y_2O_3, $SrCO_3$, $BaCO_3$, $CaCO_3$, CuO, and Fe_2O_3 were thoroughly mixed in required proportions and calcined at 950 °C in air for a period of 12–18 h. Iron oxide enriched with ^{57}Fe to 96% was used for the preparation of some of the samples. The resulting product was ground, mixed, pelletized, and heated in air at 980 °C for a period of 16–24 h. This was repeated once again. The samples were finally annealed in oxygen at 500 °C for a period of 60–72 h and furnace cooled. These are denoted as No. 1 ($x=0$, $y=0.3$), No. 2 ($x=0$, $y=0.4$), No. 3 ($x=0.1$, $y=0.4$), and No. 4 ($x=0.2$, $y=0.4$).

X-ray-diffraction analyses (XRD) were carried out using Cu K_α radiation. Superconducting transitions were also checked by measuring both the real (χ') and the imaginary (χ'') parts of the ac susceptibility in a field of 0.2 Oe and at a frequency of 1500 Hz. Magnetization measurements were performed as a function of temperature and field, using a home-built 6 T vibrating-sample magnetometer having a sensitivity of 10^{-6} emu. Zero-field-cooled measurements were carried out after cooling the sample in a field smaller than 0.1 Oe. Remanent magnetization was measured at 5 K after magnetizing the sample up to 20 kOe and then switching off the field. Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer in the usual transmission geometry. The ^{57}Co (Rh) source and the absorber were at room temperature. A least-squares program was used to fit the spectra with Lorentzian line shapes.

III. RESULTS AND DISCUSSION

XRD analyses of sample Nos. 1, 2, 3, and 4 indicated that these crystallized in the perovskite phase. The lattice parameters are collected in Table I and are found to agree with the data reported earlier.[4,5] We recall[5] that the average surface composition of No. 2 (as revealed by EDX) was $Y_{1.1}Sr_{2.1}Cu_{2.6}Fe_{0.45}O_t$ $(6.9 < t < 7.1)$. About 70% of No. 2 had this composition in volume. About 15% had varying contents of Y, Sr, Cu, and Fe. Similar comments apply to No. 3, which contained 78% of $Y_{1.05}Ca_{0.1}Sr_{2.05}Cu_{2.65}Fe_{0.45}O_t$. A uniform distribution of Ca was observed.

The real (χ') and the imaginary (χ'') parts of the ac susceptibility of sample No. 1 at two different ac fields $(h_{ac} = 0.1$ and 0.22 Oe) as a function of temperature are shown in Fig. 1. The drop in χ' which occurred at $T_c = 30$ K in 0.1 Oe shifted to 29.5 K in 0.22 Oe. The shift in the χ'' peak was much more pronounced. It shifted from 17.5 to 13.5 K when the ac field was increased from 0.1 to 0.22 Oe. Further, the transitions broadened when the ac field increased. In both cases, starting from 5 K, the field penetrated the sample indicating superconductivity between weakly connected grains.

The superconducting transition temperatures were also obtained by dc methods (Fig. 2). The samples were cooled in a remanent field smaller than 0.1 Oe and the magnetization was measured as the samples warmed up in a field of 5 Oe. As the Fe concentration increased from 0.3 to 0.4 K, T_c decreased from 28 to 8 K. For a constant $y = 0.4$, T_c increased to 28 K with $x = 0.1$ (No. 3) and decreased to 15 K with $x = 0.2$ (No. 4). In the case of all these samples, as T increased, magnetization decreased rapidly. The data indicate that the grains are weakly coupled through Josephson junctions. In the case of the sample with $x = 0.1$ and $y = 0.4$ [Fig. 2(b)], it is possible that the change in slope observed at around 20 and 25 K may reflect the presence of other superconducting phases or inhomogeneous oxygen distribution among the grains.

The remanent magnetization (M_r) values of sample Nos. 2, 3, and 4 at 5 K were obtained after reaching a maximum applied field of 20 kOe and then switching it off. The recorded values of M_r were 0.124, 0.154, and 0.178 emu/cm³ for $x = 0$, 0.1, and 0.2, respectively. Thus, M_r increased as a function of x though T_c decreased for $x = 0.2$ after going through a maximum at $x = 0.1$. This shows that more and more vortices were pinned as the Ca content increased, suggesting that addition of Ca increased the pinning centers. The χ'' peak became sharper on Ca substitution and the room-temperature resistivity smaller.[5] This implies that the

FIG. 1. Real $(\chi'$: lower half) and imaginary $(\chi''$: upper half) parts of ac susceptibility (in arbitrary units) of $YSr_2Cu_{2.7}Fe_{0.3}O_{6+z}$ as a function of temperature. $(+, \blacktriangle)$ $h_{ac} = 0.11$ Oe; $(\Diamond, \blacklozenge)$ $h_{ac} = 0.22)$ Oe.

sample became more homogeneous and the superconducting grains were well connected. The change in T_c could be related to the concomittant changes in hole density as a function of Ca concentration as was also shown[7] in the case of $Y_{1-x}Ca_xSrBaCu_{3-y}Al_yO_{6+z}$ where Al goes to the chain sites. One should note that the inhomogeneities often decrease the remanent magnetization. Such a decrease was found,[8] for example, in the case of Zn-substituted $YBa_2Cu_3O_7$. Since $M_r \approx J_c R$, where R is an effective current carrying length, a decrease of M_r can be attributed either to a decrease of this effective length R or to a decrease of the critical current J_c. On the other hand, Masuda *et al.*[9] have studied the effect of Ca doping on the flux pinning of $LaBa_2Cu_3O_{6+z}$. These authors found (from magnetization measurements at 30 K) that the critical current of $LaBa_2Cu_3O_{6+z}$ decreased faster than that in the case of $LaBa_{1.8}Ca_{0.2}Cu_3O_{6+z}$. They observed a small amount of Ca-related precipitates such as Ca_2CuO_3 and $CaCu_2O_3$ which could account for the flux-pinning centers in the Ca-doped samples. In the absence of detailed microstructural studies of our samples, we do not rule out such possibilities. Other reasons could be related to a decrease in oxygen disorder and to an increase in electron mean free path as Ca content increased

TABLE I. Lattice parameters (in Å) of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$.

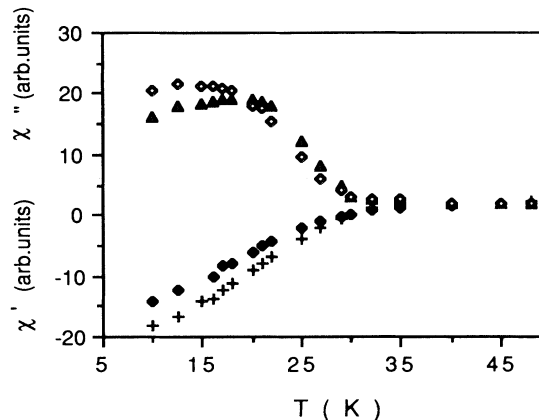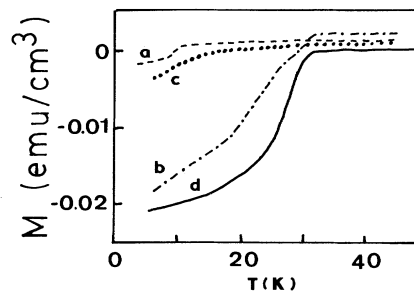| Sample No.	x	y	a	b
1	0	0.3	3.806	11.415
2	0	0.4	3.808	11.397
3	0.1	0.4	3.802	11.410
4	0.2	0.4	3.800	11.420

FIG. 2. Magnetization (zero-field cooled) of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ as a function of temperature. The data were taken in a field of 5 Oe. (a) $x = 0, y = 0.4$; (b) $x = 0.1$, $y = 0.4$; (c) $x = 0.2, y = 0.4$; (d) $x = 0, y = 0.3$.

from 0 to 0.2.

A typical Mössbauer spectrum of $Y_{1-x}Sr_2Cu_{2.6}Fe_{0.4}O_{6+z}$ is given in Fig. 3. We used a fitting model restrained by a single value of the linewidths for the four symmetrical doublets.[10] The values of the hyperfine parameters are given in Table II for typical samples together with analogous data for $YBa_2Cu_{2.7}Fe_{0.3}O_{7.07}$ oxygen-saturated samples which are superconducting and show similar hyperfine spectra.[11] For the samples with x different from zero, the results are the same within the limits of experimental error, except for the populations which are directly related to the thermal treatment. We note that the fitting results are not unique. For example, the introduction of a $D4$ site with a lower isomer shift (IS) value, lower quadrupole splitting (QS), and slightly smaller intensity gives an equally good fit (the same is true for the Ba system). A detailed comparison of the values of the hyperfine parameters of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ and $YBa_2Cu_{3-y}Fe_yO_{6+z}$ oxygen-saturated samples shows that they are almost the same (within the limits of the experimental error), except for a slight increase of IS values for the $D1$ doublet and a small decrease of the QS values for the doublets $D1,D2$, and $D3$ in the Sr system. The variation of QS with y in these doublets is the same in both systems. In addition, the relative intensities of the components are also the same, showing analogous variation with y. However, this result must be considered only as a common trend, as the relative intensities depend strongly on the thermal treatment. The small change in the hyperfine parameters probably results form the slightly larger unit cell volume of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ as compared to the initial Y-Ba-Cu-O:Fe system.

The XRD data of $YSr_2Cu_{2.8}Fe_{0.2}O_{6+z}$ indicated the multiphase nature of the sample as reported earlier.[4] Since the hyperfine parameter values and the relative intensities observed in the Sr and Ba systems are almost the same, no component in the Mössbauer spectra of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ can be attributed to an iron containing impurity phase even in the case of $y = 0.2$ samples. Thus, it seems likely that in $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$, for $0.2 < y < 0.4$, all the iron is in the perovskite phase which requires a certain concentration ($y > 0.3$) of Fe for structural stability, as was pointed out earlier.[4,6] The similarity of the Mössbauer parameters of the $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ and $YBa_2Cu_{3-y}Fe_yO_{6+z}$ samples enables us to use some of
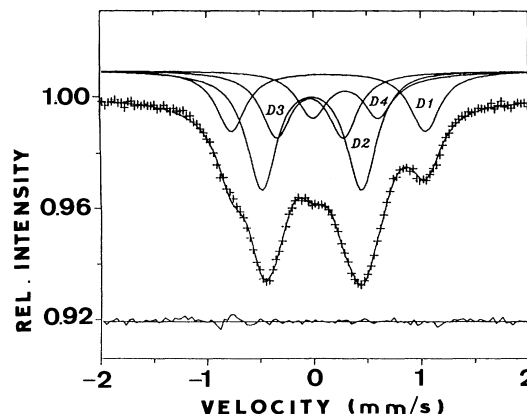

FIG. 3. The ^{57}Fe Mössbauer spectrum of $YSr_2Cu_{2.6}Fe_{0.4}O_{6+z}$ at room temperature. The fitting model is shown. The misfit line is given in the lower part of the figure.

the results obtained in the numerous Mössbauer investigations of the Y-Ba-Cu-O:Fe system.[12] Thus, we can definitely conclude that at least 85% of the iron substitutes for copper at Cu(1) sites, while about 15% (corresponding to doublet $D4$) could be situated at Cu(2) sites.

We would like to make the following comments concerning the occurrence of superconductivity in our samples. Let us note that Sunshine et al.[4] have observed a very large resistive transition with $T_c = 10$ K in $YSr_2Cu_{2.7}Fe_{0.3}O_{6+z}$ and a small diamagnetic dc susceptibility, using a superconducting quantum interference device (SQUID) magnetometer, from which they estimate only a 2% superconducting fraction. The field under which it was measured was not explicitly mentioned nor the method—whether the sample was field cooled or zero-field cooled. We have measured the superconducting screening effect by the ac-susceptibility technique, where an alternating field (1500 Hz) of 0.22 Oe was used. The maximum signal observed in the case of sample No. 1 corresponds to about 20 to 30 % of that observed in the case of a well characterized $YBa_2Cu_3O_{6.95}$ of similar shape and size. Further, the impurities observed in the EDX analyses[5] in the case of sample Nos. 2, 3, and 4 correspond to well-established insulators. Hence, we find it difficult to attribute the observed diamagnetic transitions in ac-susceptibility and dc-magnetization measurements to these insulating impurity phases.

TABLE II. The Mössbauer parameters (IS—isomer shift relative to iron metal; QS—quadrupole splitting; S—relative population; HW—linewidth) of the four doublets (see Fig. 4) in the spectra of $YSr_2Cu_{3-y}Fe_yO_{6+z}$ with $y = 0.2$ and 0.4. The IS, QS, and HW of the other samples (including Ca-substituted) are within ± 0.02 mm/s of the values given in the table. The S values are in the limits set by the samples ($x = 0, y = 0.2$) and ($x = 0, y = 0.4$). The data for a $YBa_2Cu_{2.7}Fe_{0.3}O_{7.07}$ sample (Ba) is given for comparison (11).

| System | y | IS (mn/s) | | | | QS (ms/s) | | | | s (%) | | | | HW (mn/s) |
		$D1$	$D2$	$D3$	$D4$	$D1$	$D2$	$D3$	$D4$	$D1$	$D2$	$D3$	$D4$	
$YSr_2Cu_{3-y}Fe_yO_{6+z}$	0.2	0.14	-0.02	-0.02	0.30	1.80	0.99	0.72	0.59	39	29	18	14	0.33
$YSr_2Cu_{3-y}Fe_yO_{6+z}$	0.4	0.14	-0.02	-0.03	0.30	1.81	0.93	0.53	0.62	21	41	22	16	0.34
$YBa_2Cu_{3-y}Fe_yO_{6+z}$	0.3	0.05	-0.01	-0.04	0.37	1.96	1.10	0.79	0.67	34	33	21	12	0.33
	Error	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.03	1	2	2	3	0.02

It is well accepted[13,14] that the Ca^{2+} ion has a stronger preference for eightfold coordination and for concentrations smaller than 20 to 30%, as in the present case, could replace Y^{3+}. Further, the neutron-diffraction experiments of a related compound $Y_{1-x}Ca_xSr_2CoCu_2O_7$ have shown that Ca substitutes[15] for Y. It is quite conceivable that in the case of the $y =0.4$ sample, 85% of Fe going to the Cu chain sites and 15% of Fe going to the Cu plane sites could reduce the hole density by the charge-transfer mechanism[16] and further introduce disorder in the Cu-O conducting planes, resulting in a low superconducting transition temperature. This seems to be compensated to some extent by Ca doping. It is interesting to note that in the case of the insulating $YBa_2Cu_3O_6$ it was pointed out that the superconductivity could be restored by reducing the electron density by a proper replacement of Y, though Ca was not explicitly suggested.[17] Such a substitution would result in the lowering of the Fermi level and the system would tend to move away from a spin-density wave instability.[17] Modification of the oxidation state of the Cu-O layer by Ca was also pointed out earlier.[13,14,18] Indeed, Hall data indicated[5] that the hole density increased from 4.5 to $4.9 \times 10^{21}/cm^3$ as 0.1 Ca was added to the $y =0.4$ sample. It is important to point out here that in a related compound, $Y_{1-x}Ca_xSrBaCu_{2.6}Fe_{0.4}O_{6+z}$, as x was increased from zero to 0.15, T_c increased from zero to 30 K, moving the system away from an antiferromagnetic state to a superconducting state which was accompanied by an increase in the hole density.[7] As a final comment, it should be noted that the behavior of Fe in the $YBa_2Cu_3O_{6+z}$ system is not well understood probably becuase of the complex chemistry involved. In this respect, it is interesting to note that the superconducting transition temperature of $YBa_2Cu_{3-y}Fe_yO_{6+z}$ films depended[19] more on the substrate temperature during deposition and the cooling rate of the films rather than on the Fe concentration for $y <0.4$. For example, the film containing 15% Fe, which was slow cooled, was an insulator, whereas by fast cooling, superconductivity could be observed at 55 K.

IV. CONCLUSIONS

We have reported on the ac-susceptibility, dc-magnetization, and the Fe Mössbauer spectra of $Y_{1-x}Ca_xSr_2Cu_{3-y}Fe_yO_{6+z}$ ($x =0$, 0.1, and 0.2; $y =0.3$ and 0.4). Our data indicate bulk superconductivity in these compounds. In the case of $y =0.4$, the substitution of 0.1 Ca increases both T_c and flux pinning. The Mössbauer parameters of our samples in comparison to those of $YBa_2Cu_{3-y}Fe_yO_{6+z}$ indicate that (for $y =0.4$) at least 85% of Fe substitutes the Cu(1) sites and about 15% goes to Cu(2) sites. The existence of superconductivity at such high concentrations of Fe and the revival of superconducting properties by Ca substitution are not well understood. Further studies should elucidate the role played by structural stability, hole density, and Fe on the superconducting properties of this system.

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