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Iron migration in the $(Y,Ca)Ba_2(Cu,Fe)O_{6+\delta}$ system

I. Felner*
Laboratoire Crismat, Institute des Sciences de la Matière et du Rayonnement, 14050 Caen, France

D. Hechel
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

A. Rykov and B. Raveau
Laboratoire Crismat, Institute des Sciences de la Matière et du Rayonnement, 14050 Caen, France

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Mössbauer spectroscopy of ^{57}Fe in $Y_{1-x}Ca_xBa_2Cu_{3-x}Fe_xO_{6+y}$ for $x=0.09$ was used to study the site distribution of Fe in oxygen-rich and oxygen-reduced samples. In the superconducting sample ($y=1$) ($T_c=85$ K) more than 90% of the Fe resides in the Cu(1) site. For $y=0$ the Cu(2) site orders magnetically at $T_N=425$ K. Based on the typical behavior of Fe in the magnetic Cu(2) site, we find that about 80% of the Fe occupies this site, thus we prove migration of Fe from Cu(1) to Cu(2) sites during depletion of oxygen at elevated temperatures. The spectrum above T_N is smeared because of a distribution in the quadrupole interactions.

Oxide superconductors have provided an unprecedented stimulus for solid-state scientists over the last six years. Among the basic studies of these materials, numerous investigations deal with the substitution of the elements composing the materials. Among them, the substitution for Cu in $YBa_2Cu_3O_7$ (YBCO) has been examined most extensively. A large number of investigations of general composition $YBa_2Cu_{3-x}Fe_xO_7$ have been undertaken, primarily because the ^{57}Fe Mössbauer spectroscopy (MS) is likely to play a significant role in understanding these materials. A survey of MS studies including other physical properties exhibited by Fe substitution is given in Ref. 1.

It is well accepted that partial substitution of Fe for Cu in YBCO induces an orthorhombic-tetragonal phase boundary near $x=0.09$ and progressively reduces T_c. For Fe concentration exceeding $x=0.4$, the materials are not superconducting. Some contradictory results are observed in the literature concerning the distribution of Fe over the two Cu sites existing in YBCO. From neutron-diffraction and extended x-ray-absorption fine structure (EXAFS) measurements, it is not possible to determine the amount of Fe residing in the Cu(2) sites. On the other hand, MS has been proven to be a powerful tool in the determination of Fe-site assignment in YBCO.[2-7] Although it is now apparent that the details of the MS spectra depend on the heat treatment and oxygen stoichiometry of the samples as well as on the amount of iron, a considerable amount of experimental evidence appears to be at least qualitatively well established. It is suggested that Fe atoms are found to occupy predominantly the Cu(1) site with an increased fraction occupying the Cu(2) sites as the total amount of Fe increases. Since Fe^{3+} has a larger valence than Cu^{2+}, it attracts oxygen to maintain charge neutrality. Estimations of oxygen occupancy are consistent with about $\frac{1}{2}$ additional oxygen atom being introduced into the chain oxygen sites for each Fe substituted into the compound. It was suggested that several different oxygen coordinations exist around Fe residing in the Cu(1) sites (Fig. 1). ^{57}Fe MS spectrum of oxygen-rich superconducting materials is composed of three or four doublets corresponding to these inequivalent Fe sites, which are immediately identified by their hyperfine parameters: isomer shift δ_{IS} and quadrupole splitting $\Delta = eqQ/2$.

The dominant doublets (denoted in this work as B and A) which account for 60–80% of the spectral area, have a very small δ_{IS} (relative to iron metal) and Δ of 1.9–2.0 and 1.0–1.2 mm/s are, respectively, corresponding to Fe ions in the Cu(1) sites with fourfold tetrahedral configuration assuming a small displacement of Fe from the original Cu site and to fivefold square-pyramidal coordination (probably in small clusters like Fe_2O_9). (An

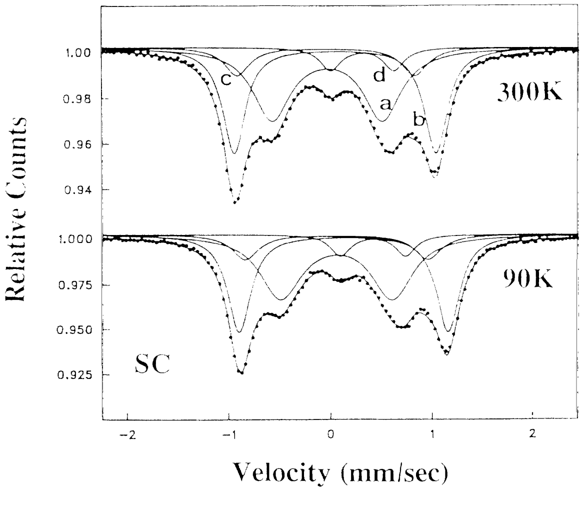

FIG. 1. Mössbauer spectra of the oxygen-rich ($T_c=85$ K) (Y,Ca)Ba(CuFe)O at 90 and 300 K.

alternative interpretation for doublet *B* is related to fourfold square-planar coordination which is the most popular configuration in YBCO.)[4,5] Both doublets are well observed in each oxygen-rich material and are, therefore, the fingerprint of Fe in the Cu(1) site. A better fit to MS spectra is obtained when one or two additional doublets are added. The third doublet *C* appears only for low Fe concentration with low intensities 0–15 % with low δ_{IS} and $\Delta = 1.5-1.8$ mm/s and is associated probably with fourfold configuration where the two oxygen atoms in the basal planes are perpendicular, or with another fivefold coordination, of $FeCuO_9$ clusters. However, this is of little interest in the present paper. What is of real importance is the small doublet *D* with δ_{IS} of 0.25–0.35 mm/s and Δ of 0.5–0.65 mm/s. This doublet may belong to Fe in the Cu(2) sites and its relative intensity represents the amount of Fe in this site. But doublet *D* may also be attributed to the sixfold octahedral coordination[4] for Fe in the Cu(1) site. Therefore, site distribution determined only on doublet *D* is not exclusive.

It is by now well known that YBCO loses its superconducting properties and the Cu(2) sites become magnetically ordered, when oxygen is depleted, and for $YBa_2Cu_3O_6$, the antiferromagnetic ordering occurs at T_N 420 K. Using MS technique on Fe-doped materials, it was shown that T_N is not affected by the presence of Fe and that Fe is thus a reliable probe of the magnetic behavior of the Cu(2) sites.[2-4] In this site, all Fe atoms are equivalent in terms of oxygen environment and have the fivefold pyramidal coordination. When Cu becomes magnetically ordered, it produces an exchange field at the Fe located in this site. The iron nuclei experience a magnetic hyperfine field leading to a well-defined sextet in the Mössbauer spectra. As the temperature is raised, the magnetic splitting decreases and disappears at T_N. A theoretical analysis,[8] to be discussed later, explains the exact procedure by which Fe probes the magnetic order in the Cu(2) site of YBCO and the typical temperature dependence of the magnetic splitting. It appears, therefore, that for oxygen-reduced YBCO samples, the fingerprint of Fe in the Cu(2) sites is based on a sextet, with a typical temperature dependence of the magnetic hyperfine field, which disappears around 420 K. In addition to the sextet, the central part of the Mössbauer spectra contains one or two doublets due to Fe in the Cu(1) site. Their hyperfine parameters are less important for the present issue.

Removal of oxygen at high temperatures (about 850 °C) in Ar or N_2 atmosphere (reductive conditions) followed by reintroduction of oxygen at about 400 °C (reoxygenation) in Fe-substituted YBCO was studied by several experimental techniques. MS, measured at room temperature, shows[9] that after the removal of oxygen, the magnetic sextet appears with higher intensity than doublet *D* in the starting material, and on reoxidation the doublet *D* is restored, also with higher intensity. Moreover, in contrast to the behavior of standard Fe-doped samples, in the reoxidized materials, orthorhombicity increases for *x* up to 0.24 but T_c is lower. The interpretation is that the Fe increases its occupancy in the Cu(2) sites because of the tendency to be highly coordinated.(6) With the thermal energy available at elevated temperatures, Fe migrates to the Cu(2) sites to achieve higher coordination. In the reoxidation, the Fe then does not have enough thermal energy to return to the original Cu(1) sites. However, these experiments on both oxygen-reduced and oxygen-rich materials, cannot give unambiguous evidence of site location. The site assignment based on the increase of doublet *D* at the expense of doublet *A* and *B* in the reoxidized materials is speculative, because the possible assignment of doublet *D* to the octahedral coordination may not be discarded. The increase in the sextet intensity, while measured only at room temperature, does not prove directly the migration, because the possibility of Fe precipitation or other iron oxide species in the reduction process has to be excluded. Moreover, transmission-electron microscopy and EXAFS studies[10] do not observe the migration process.

The motivation of the present paper is to prove directly the migration process from the Cu(1) to the Cu(2) site (and vice versa), using the Mössbauer measurements in the whole temperature range. We are aware of the fact that MS, especially when several sites are simultaneously present, cannot give unambiguous evidence of site location, but our site assignments are based on consistent measurements performed at several temperatures using the fingerprints for each site described above. Here detailed MS of $Y_{1-x}Ca_xBa_2Cu_{3-x}Fe_xO_{6+\delta}$ with $x = 0.09$ are present. We use the same materials assigned as $O_{SC}O_{LT}$ and Ar_{FC} in Ref. 11 (SC = slow cooled, LT= low temperature, FC= fast cooled) and our first objective in this investigation was to check the reproducibility of the MS at room temperature. It is shown that the depletion of oxygen at 850 °C in Ar atmosphere (where the oxygen pressure is very low) sharply increases the Fe occupancy in the Cu(2) sites by an order of magnitude (at least) and that our site assignments are straightforward.

The ^{57}Fe-doped (Y,Ca)BaCuO sample was prepared by a solid-state reaction of stoichiometric mixtures of the constituent oxides and carbonates, following the procedure described recently in Refs. 9 and 11. The oxygen-saturated sample $O_{SC}O_{LT}$ was annealed under oxygen atmosphere at 960 °C for 24 h and then slow cooled to 400 °C (1 °C/min) and annealed at that temperature for 9 h. The oxygen-reduced sample (Ar_{FC}) was annealed at 850 °C in flowing Ar for 12 h and then fast cooled to ambient temperature in Ar at the rate of 15 °C/min. X-ray-diffraction studies confirm the purity of the samples and yield a tetragonal structure with $a = 3.858(1)$ and $c = 11.688(1)$ and $a = 3.860(1)$ and $c = 11.820(1)$ Å for the as-synthesized oxygen-rich and oxygen-reduced samples, respectively.[11] The oxygen-rich sample is superconducting with $T_c = 85$ K. MS studies were performed using a conventional constant-acceleration spectrometer and a 50 mCi ^{57}Co:Rh source. The spectra at various temperatures were least-squares fitted with several subspectra corresponding to inequivalent iron sites.

MS studies of the SC sample performed at 90 and 300 K are shown in Fig. 1. Both spectra are composed of four quadrupole doublets as described above and their hyperfine parameters obtained at 300 K are given in Table I. These values are in perfect agreement with data

TABLE I. Isomer shifts, quadrupole splittings, linewidth, and relative intensity of the doublets for the SC (at 300 K) and magnetic (450 K) (Y,Ca)Ba(Cu,Fe)O materials.

	Sample	δ_{IS} mm/s +(0.001)	Width mm/s +(0.01)	$\frac{1}{2}$ eq$Q$ mm/s +(0.01)	Intensity % +2
SC	*A*	−0.024	0.45	1.07	44
300 K	*B*	0.049	0.27	1.97	39
	C	−0.042	0.30	1.73	11
	D	0.315	0.24	0.62	6
Magnetic	*E*	−0.002	0.33	1.79	7
450 K	*F*	0.198	0.28	0.65	5
	G	0.200	0.31	0.20	61
	H	0.210	0.35	0.95	27

reported by Rykov *et al.*[11] The two intense doublets (*A* and *B*) account for 83% of the spectral area and serve as our fingerprint for Fe in the Cu(1) site. Doublet *D* with relative intensity of 6% corresponds, probably to Fe in the Cu(2) sites, but might also represent the octahedral configuration in Cu(1).

In the oxygen-reduced sample, a well-defined sextet which accounts for 78% of the spectral area is readily observed (Fig. 2) and is attributed to magnetic Fe in the Cu(2) sites. The main effect to be seen in Fig. 2 is that as the temperature is raised, the magnetic splitting decreases and disappears around 425 K. The variation of the normalized magnetic hyperfine field $(H_{\text{eff}})(T)/H_{\text{eff}}(0)$, where $H_{\text{eff}}(0)$ is 505 kOe,[8] as a function of the reduced temperature $\tau = T/T_N$ is shown in Fig. 3 and will be discussed later. At 90 K, an additional broad sextet is added, probably due to the magnetic order of Fe in the Cu(1) site,[4,12] which disappears at higher temperature. The broad hyperfine features may reflect the large degree of disorder in the Cu(1) site. The hyperfine parameters for the intense sextet at 300 K are $H_{\text{eff}} = 309(5)$ kOe, $\delta_{IS} = 0.31(1)$ and, an effective quadrupole splitting $\Delta_{\text{eff}} = -0.44(1)$ mm/s with a linewidth of 0.38(1) mm/s. The central part is fitted by two doublets (labeled *E* and *F*) which were developed after the collapsing of the minor sextet. Their parameters are $\delta_{IS} = 0.10(1)$ and 0.28(1) and $\Delta = 1.96(1)$ and 0.72(1) mm/s with relative intensities of 15 and 7 %, respectively.

The typical variation of H_{eff} in all Fe-doped YBCO-based materials, has the same shape when plotted in a normalized form versus the reduced temperature.[8] All the normalized H_{eff} values fall on a universal curve regardless of Fe and/or oxygen concentrations and whether *Y* is replaced by Pr. The theoretical model assumes that the temperature dependence of magnetizations of Cu(2) and of Fe^{3+} as a probe, behave like spin $\frac{1}{2}$ or spin $\frac{5}{2}$ systems and that the Fe-Cu exchange is only 0.26% of the Cu-Cu exchange strength. The theoretical curve for the Fe-Cu exchange in the Cu(2) site is given by $\sigma_{\text{Fe}}(\tau) = H_{\text{eff}}(T)/H_{\text{eff}}(0) = B_{5/2}(0.26 \times 5\sigma_{\text{Cu}}(\tau)/\tau)$, where $B_{5/2}$ is the Brillouin function of Fe^{3+} and $\sigma_{\text{Cu}} = \sigma_{1/2}(\tau)$ is the universal function calculated in an easy way. This function (solid line) together with the theoretical function

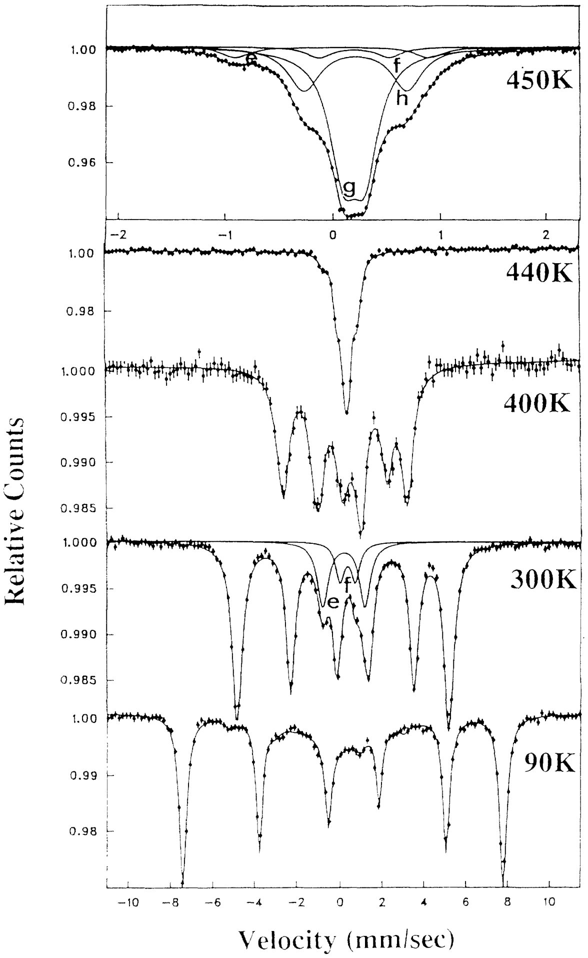

FIG. 2. Mössbauer spectra of the magnetic (Y,Ca)Ba(Cu,Fe)O ($T_N = 425$ K) at various temperatures. (Note the expanded scale for the spectrum at 450 K.)

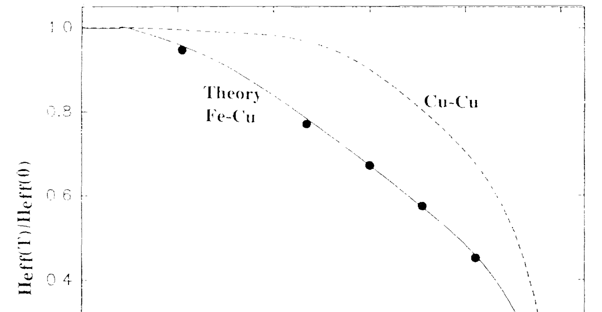

FIG. 3. Temperature dependence of the normalized hyperfine field acting on ^{57}Fe in the Cu(2) site. The theoretical curves for Cu-Cu and the Fe-Cu exchange strength are shown as dashed and solid curves, respectively. (Note that the experimental points fit the theoretical curve.)

$\sigma_{1/2}(\tau)$ for the Cu-Cu exchange (dashed line) are shown in Fig. 3. The fact that our experimental data fit the theoretical curve is our conclusive proof that the major sextet in Fig. 2 is due to Fe in the Cu(2) sites.

Summarizing Figs. 2 and 3, we may say with high confidence that in the oxygen-reduced sample, about 80% (at least) of Fe ions reside in the Cu(2) sites. Since the MS for the SC sample shows only about 7% Fe in this site, the present results prove clearly that during the annealing at 850 °C in Ar, Fe, with its tendency to be in a high-coordination state, migrates from Cu(1) to Cu(2) sites. This migration is reversible. For the reduced sample, which was heated at 950 °C under oxygen and then slow cooled to ambient temperature, SC as well as the orthorhombic structure were restored and the MS obtained were similar to Fig. 1.[11] In that case, during the annealing, Fe ions moved back to their original preferable Cu(1) site.

As a final point of interest, the feature of the MS for the oxygen-reduced sample measured above T_N (450 K) is noteworthy. One would expect that the sextet of the Cu(2) site will collapse to one doublet, since all Fe ions are equivalent in terms of oxygen environment. Unexpectedly, Fig. 2 shows a complicated spectrum (note the expanded scale) and the major problem confronting any quantitative analysis is that a distribution of quadrupole splittings has to be assumed. The answer as to why this distribution occurs probably lies in the fact that the high population of Fe in the Cu(2) site (about 2.5%) creates a condition where direct Fe-Fe possible interactions may exist. Moreover, in this material 9% of Y^{3+} is replaced by Ca^{2+}. The different charges and ionic radii, although these ions are in second-nearest-neighbor position to Fe, all lead to a distribution in the quadrupole interactions. Artificially, we fitted the spectrum at 450 K, with consistency to the two doublets observed below T_N which belong to Fe in the Cu(1) site, and with four doublets whose parameters are listed in Table I. Note the similarity between doublets *C* and *E*. The most qualitative informative result is the unexpected low $\Delta = 0.20$ mm/s obtained for the major doublet *G*, which is inconsistent with Δ_{eff} obtained below T_N. Such a phenomenon was observed also in $LaSr_2Fe_3O_x$.[13] However, this result is in fair agreement with the small Δ (zero) obtained for Fe in the Cu(2) sites in $YBa_2Cu_4O_8$.[14]

Based on the studies reported here we may summarize the behavior of Fe in the (Y,Ca)Ba(Cu,Fe)O system studied.

(i) For the as-synthesized SC sample, more than 90% of Fe ions reside in the Cu(1) site.

(ii) In the oxygen-reduced sample where the Cu(2) sites are magnetic ($T_N \sim 425$ K) about 80% of Fe ions occupy the Cu(2) sites, thus during removal of oxygen at high temperatures, most of Fe ions migrate from Cu(1) to Cu(2) sites. This migration is reversible, by heating in oxygen at high temperatures.

(iii) Above T_N we see distribution in the quadrupole splittings probably caused by the high Fe and Ca concentrations. The quadrupole splitting for the majority of Fe ions in the Cu(2) sites is small ($\Delta = 0.2$ mm/s).

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*Permanent address: Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel.

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