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CONVERSION-ELECTRON AND TRANSMISSION MÖSSBAUER STUDY OF $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$

X. Z. Zhou ⁽¹⁾, A. H. Morrish ⁽¹⁾, Q. A. Pankhurst ⁽¹⁾ and M. Raudsepp ⁽²⁾

⁽¹⁾ Dept. of Physics, University of Manitoba, Winnipeg, Canada R3T 2N2

⁽²⁾ Dept. of Geological Sciences, University of Manitoba, Winnipeg, Canada R3T 2N2

Abstract. – The surface and bulk properties of the high-temperature superconductor $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ were compared by means of conversion-electron and transmission ^{57}Fe Mössbauer spectroscopy at room temperature. A model, based on the crystal structure and an enhanced oxygen content at the grain surfaces, is proposed.

In the high- T_c superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, copper and oxygen are usually considered to be the principal players. The substitution of Fe for the Cu and the use of ^{57}Fe Mössbauer spectroscopy is a powerful approach to the study of these materials. A room temperature Mössbauer spectrum consists of three doublets [1, 2]. Based on the Mössbauer parameters, these doublets, designated 1, 2, and 3, were assigned to pyramidal, planar, and octahedral sites, respectively [3]. At low temperatures, the iron orders magnetically [2, 3]. A good fit to these hyperfine field split spectra was obtained by retaining the quadrupole splittings and relative spectral areas observed for the doublets at $T = 77\text{ K}$ [4, 5]. This success supports the correctness of the original site identifications.

To date, only transmission Mössbauer spectroscopy (TMS) data have been reported. Now, conversion-electron Mössbauer (CEMS) results will be presented. With CEMS only about the upper 100 nm layer (primarily the upper 50 nm) is sampled. Therefore, CEMS when coupled with TMS provides a way to compare the surface and bulk characteristics.

Ceramic samples of $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ ($x = 0.015$ and 0.05) were prepared with ^{57}Fe -enriched $\alpha\text{-Fe}_2\text{O}_3$. Cost and availability considerations required that the amount of $^{57}\text{Fe}_2\text{O}_3$ used was relatively small. The other oxides, Y_2O_3 , CuO and BaO , all 99.9 % pure, were first mixed in a ballmill. Then the $^{57}\text{Fe}_2\text{O}_3$ was added and mixed by hand in a mortar. The mix was heated to 750°C for 3 hrs under 1 atm oxygen, slowly cooled, and reground. The particles were made into pellets, fired at 970°C for six hrs under 1 atm oxygen, and again slowly cooled.

Two pellets with a fixed x were made at the same time; this ensured that they were essentially identical. The TMS disk-shaped absorber was made by grinding up one pellet and suspending the particles in benzophenone in random orientation. The CEMS absorber was the other pellet; it was placed inside the gas detector with its surface perpendicular to the direction of the incoming γ rays. The source was ^{57}Co in a Rh host. All spectra were collected at room temperature.

The CEMS and TMS spectra for $x = 0.015$ are shown in figures 1a and b, respectively; those for

Fig. 1. – Mössbauer spectra (dots) at room temperature of $\text{YBa}_2(\text{Cu}_{0.985}\text{Fe}_{0.015})_3\text{O}_{7-\delta}$ (a) for CEMS and (b) for TMS. The solid lines are the least squares fits for three doublets and their sum.

Fig. 2. – Mössbauer spectra (dots) at room temperature of $\text{YBa}_2(\text{Cu}_{0.95}\text{Fe}_{0.05})_3\text{O}_{7-\delta}$ (a) by CEMS and (b) by TMS. The solid lines indicate the least squares fits.

$x = 0.05$ are shown in figures 2a and b, respectively. Except for the emission and absorption character of the CEMS and TMS techniques, respectively, all spectra are qualitatively similar. Each was fitted with three doublets, Mössbauer parameters and relative areas are listed in table I. Since doublet 1 has about 2/3 the

Table I. - Quadrupole splittings (ϵ), isomer shifts relative to α -Fe(δ), linewidths (Γ), all in mm s^{-1} , and relative areas (%) for the three doublets fitted to the conversion electron (CEMS) and transmission (TMS) Mössbauer spectra of $\text{YBa}_2(\text{Cu}_{1-x}\text{}^{57}\text{Fe}_x)_3\text{O}_{7-\delta}$. Doublets 1, 2 and 3 correspond to iron in the pyramidal, planar and octahedral sites, respectively.

Composition	Mode	Doublet	ϵ	δ	Γ	Area
$x = 0.015$	CEMS	1	1.01	-0.04	0.46	63
		2	1.91	0.05	0.29	23
		3	0.59	0.38	0.28	14
	TMS	1	1.01	-0.03	0.45	66
		2	1.93	0.04	0.29	25
		3	0.58	0.36	0.29	9
$x = 0.05$	CEMS	1	0.96	-0.04	0.47	66
		2	1.98	0.08	0.29	22
		3	0.68	0.37	0.28	12
	TMS	1	0.97	-0.01	0.43	68
		2	1.90	0.07	0.29	23
		3	0.57	0.36	0.28	9

total area for all spectra, it is associated, as before [3], with Fe in the pyramidal sites (two of the three Cu positions in the unit cell). Doublet 2, which has a large quadrupole splitting, is assigned to the planar Cu(1) sites, since an earlier calculation has shown that the electric-field gradient at a planar site is about 1.9 times larger than at a pyramidal site [4]. The isomer shift and quadrupole splitting for doublet 3 are typically those for octahedrally coordinated ferric ions [3]. The sum of the areas of doublets 2 and 3 is about 1/3 of the total and corresponds to the relative numbers of Cu atoms in square-planar sites.

As is well known, the iron-free compound is markedly orthorhombic with space group Pmmm. However, once iron is added, the a and b cell parameters are nearly equal [3]. In a Rietveld refinement of X-ray diffraction data, the oxygen occupancy at (1/2, 0, 0), which is zero for $x = 0.0$, becomes non-zero. As the iron concentration increases oxygen occupancy in this site progressively increases and the total oxygen

content increases [3]. At $x = 0.10$, $a = b$ and the tetragonal space group P4/mmm yields agreement factors similar to a Pmmm refinement [3]. The Pmmm and P4/mmm structures are illustrated in figures 3a and b, respectively. Here the open small circles represent oxygen ions and the filled small circles the copper (or iron) ions. The larger open circles are Ba or Y, as indicated. Figure 3b shows the octahedrally coordinated copper (or iron) sites.

From table I, the area of doublet 3 is appreciably larger in the CEMS mode than in the TMS mode for both $x = 0.015$ and $x = 0.05$. The data also suggest, although it is less clear, that this increase in area is at the expense of doublet 2. Since the number of octahedral sites is related to the oxygen content, it follows that the oxygen concentration at the surface of a grain exceeds that at the interior. This conclusion has implications concerning the critical temperature T_c , and on the region of a grain that becomes superconducting.

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Fig. 3. - Structure of $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ for (a) Pmmm and (b) P4/mmm space groups.

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