Indication of high local fields in the $YBa_2Cu_{2.9375}Fe_{0.0625}O_\delta$ superconductor by Mössbauer spectroscopy

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Mössbauer spectra of a $YBa_2Cu_{2.9375}Fe_{0.0625}O_\delta$ superconducting sample were obtained at different temperatures ranging from 50 to 120 K. The results clearly show that Fe substitutes for Cu in this complex. All the spectra showed a pair of superimposed quadrupole doublets with essentially the same splittings but different isomer shifts, corresponding to two different environments of the substituted atoms. The values of the isomer shifts obtained correspond to low-spin Fe atoms, which implies strong local fields, or strong bonding between the atoms.

Since the discovery of high-T_c superconductors,[1] many studies have been made to elucidate their properties,[2-8] in order to obtain some insight into the fundamental mechanisms behind the superconducting behavior of these materials.

At present, the highest T_c is obtained in $YBa_2Cu_3O_{6.9}$, which has a perovskitelike structure and presents two inequivalent sites for the Cu ions. Cu(2) sites are surrounded by a pyramid of five oxygen atoms and their environment is quite well preserved over a wide range of temperatures and oxygen content; on the other hand, Cu(1) sites are situated in planar Cu—O squares (between Ba—O planes) which present oxygen vacancies. It is well known[9] that two crystallographic structures can coexist: a high-temperature phase (tetragonal) in which the Cu(1) ions are bonded to only two off-plane oxygens, and a low-temperature phase (orthorhombic) in which the Cu(1) ions form metallic linear chains with in-plane oxygens; that is, the Cu(1) is bonded to four oxygens. It is a general agreement[10] that superconductivity is highly sensitive to the oxidation state of Cu(1) and, therefore, it is important to study in detail the electronic and local structure around these sites. Mössbauer spectroscopy would be an adequate tool to study these properties if one could substitute a Mössbauer isotope in the Cu(1) sites, as was recently done for the La-Ba-Cu-O system.[11] In this framework, a new series of $YBa_2Cu_{3-x}Fe_xO_\delta$ samples $(6 \leq \delta \leq 7)$, with x ranging from 0.0125 to 0.125, were prepared and studied by Mössbauer spectroscopy to probe the Cu sites of the system. In this paper we report the results obtained with one sample in which $x = 0.0625$, at different temperatures in the interval from 55 to 120 K. The results from other compositions will be reported separately in the future.

The compounds investigated were prepared through the reaction of high-purity Y_2O_3, $BaCO_3$, CuO, and Fe_2O_3 powders. The mixtures were first ground, pressed, and heated at 900 °C for 18 h. After that, they were sintered at 1000 °C for 2 h and oven cooled in air.

The resistance measurements were made in disk-shaped samples of 1.2 cm diameter and about 0.18 cm thickness.

A bridge having a low-resistance sensitivity of $10^{-7}\,\Omega$ was used in the usual four-point-probe technique with silver-paint contacts. The measurements between 300 and 10 K were performed in a continuous-flow cryostat connected to a microcomputer to give an automatic system. Figure 1 shows the resistance versus temperature characteristics of the $x = 0.0625$ sample. This curve shows a temperature onset of superconductivity at 75 K and fully superconducting behavior at 55 K. It is interesting to note that the sample shows a relative resistance minimum at 120 K. The resistance versus temperature curves for the other samples have a similar behavior, but T_c decreases with increasing values of x.

X-ray powder diffraction patterns (Fig. 2), obtained with a diffractometer fitted to a secondary monochromator and Cu $K\alpha$ radiation, show noticeable differences from the typical pattern of the orthorhombic 1:2:3 phase[4] that might be interpreted by assuming a mixture of two phases, the orthorhombic 1:2:3 phase and a tetragonal one. This can be assured by examining slowly scanned patterns from selected regions corresponding to the doublets $[(103) + (110), (013)]$ and $[(116) + (123), (213)]$, which are the most characteristic ones, and which appear to be
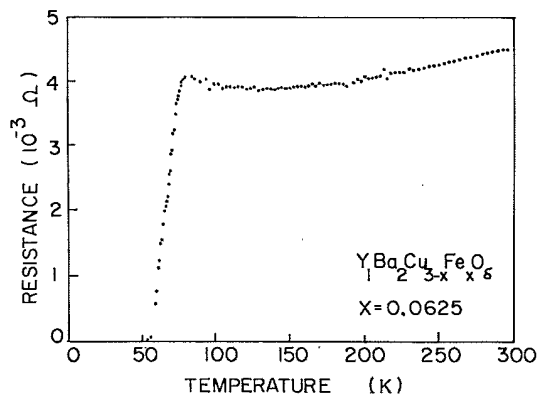

FIG. 1. Resistance as function of temperature for the $YBa_2Cu_{2.9375}Fe_{0.0625}O_\delta$ sample.

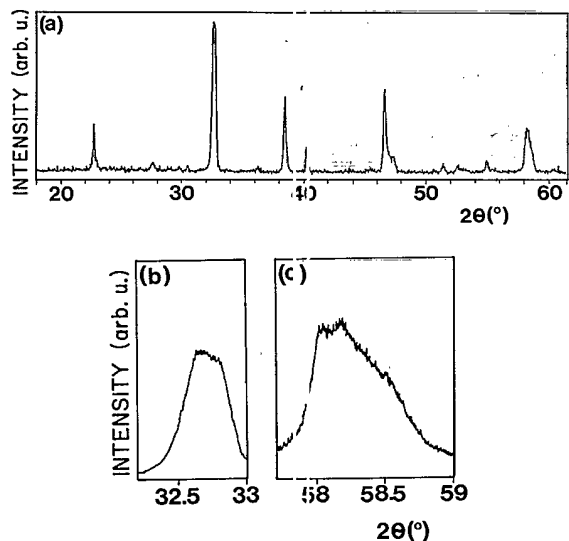FIG. 2. (a) X-ray powder diffractogram for the YBa$_2$-Cu$_{2.9375}$Fe$_{0.0625}$O$_\delta$ sample. (b) and (c) Low scan diffraction patterns of selected features.

like the ones from the two-phase mixture reported by Schuller *et al.*[12]

In order to obtain the Mössbauer spectra, the pellet was crushed into very fine grains and the resulting powder was encapsulated to fit into the sample holder of a closed-cycle helium refrigerator. All the spectra were obtained in the transmission geometry, using a ^{57}Co-in-Pd Mössbauer source kept at room temperature.

Taking into account the ionic radius of Cu (0.60, 0.57, and 0.54 Å in fourfold coordination for valence states of +1, +2, and +3, respectively, or 0.46 Å for Cu^{1+} in twofold coordination),[13] and the similar values of the ionic radii of Fe^{2+}(0.64 Å) and Fe^{3+}(0.49 Å), one is tempted to think that the Fe atoms go into the Cu sites of the structure, rather than into the Y or Ba sites, which have larger ionic radii (0.9 and 1.35 Å, respectively). On the other hand, the fact that the variable amount of Fe affects the value of T_c (Ref. 14) is also an indication that these atoms go to the Cu sites, and more precisely to the Cu(1) sites.
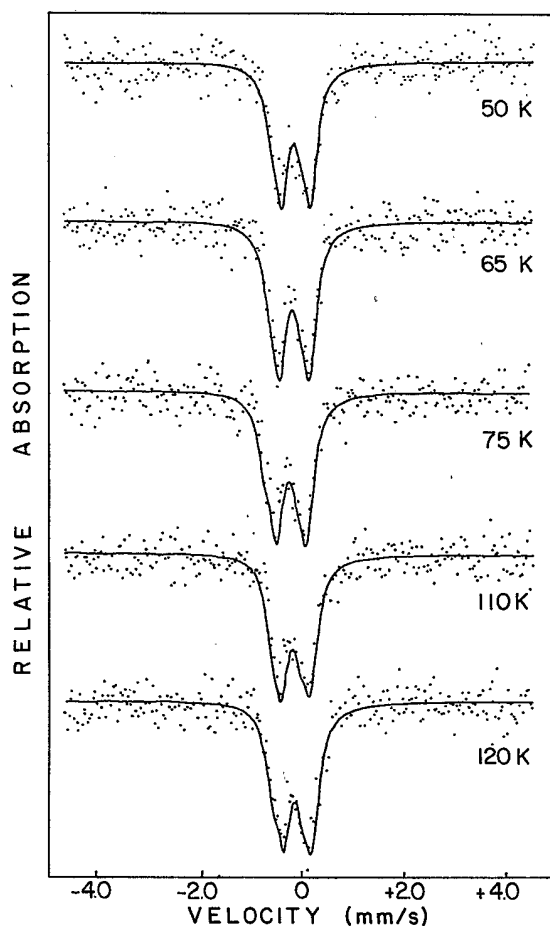
Each of the Mössbauer spectra obtained showed a de-

FIG. 3. Mössbauer spectra of the YBa$_2$Cu$_{2.9375}$Fe$_{0.0625}$O$_\delta$ sample for different temperatures.

formed doublet line profile, without hyperfine structure, indicating that it is not a pure quadrupole splitting, but rather a pair of superimposed quadrupole doublets. The experimental data were computationally fitted to two pairs of symmetrical Lorentzians and the results, together with the experimental points, are shown in Fig. 3 from $T=50$ K to $T=120$ K. Table I shows the calculated Mössbauer parameters for five different temperatures. [All the isomer shifts are given with respect to sodium ni-

TABLE I. Mössbauer parameters as a function of temperature for the YBa$_2$Cu$_{2.9375}$Fe$_{0.0625}$O$_\delta$ sample. A_1, A_2: absorptions. Γ_1, Γ_2: linewidths. Δ_{Q_1}, Δ_{Q_2}: quadrupole splittings. Δ_{IS_1}, Δ_{IS_2} (Pd), (SNP) isomer shifts with respect to paladium and sodium nitroprusside.

| Mössbauer parameters	50	65	75	110	120
A_1	0.0013	0.0013	0.0014	0.0015	0.0016
Γ_1	0.31	0.31	0.30	0.30	0.30
Δ_{IS_1}(Pd)	-0.18 ± 0.01	-0.18 ± 0.02	-0.20 ± 0.01	-0.17 ± 0.01	-0.16 ± 0.01
Δ_{IS_1}(SNP)	0.26 ± 0.01	0.26 ± 0.02	0.24 ± 0.01	0.27 ± 0.01	0.28 ± 0.01
Δ_{Q_1}	0.61 ± 0.03	0.59 ± 0.03	0.63 ± 0.03	0.54 ± 0.02	0.58 ± 0.02
A_2	0.0035	0.0035	0.0034	0.0030	0.0029
Γ_2	0.31	0.31	0.32	0.32	0.32
Δ_{IS_2}(Pd)	0.03 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.04 ± 0.01
Δ_{IS_2}(SNP)	0.47 ± 0.01	0.46 ± 0.01	0.45 ± 0.01	0.45 ± 0.01	0.48 ± 0.01
Δ_{Q_2}	0.57 ± 0.01	0.58 ± 0.01	0.58 ± 0.01	0.55 ± 0.01	0.54 ± 0.01
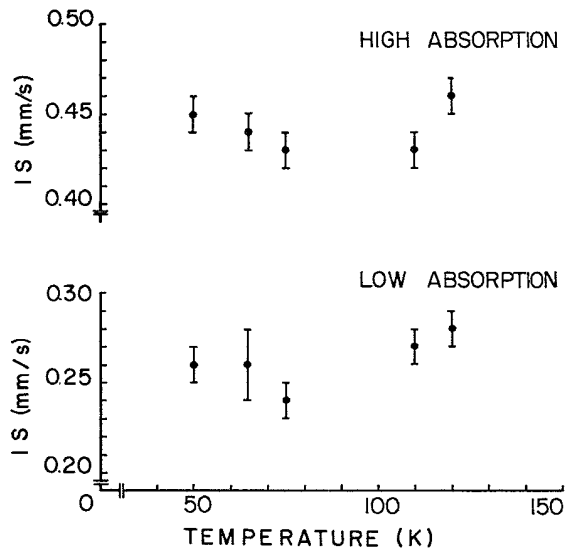
FIG. 4. Isomer shifts for each doublet (high and low absorption), as a function of temperature, of the sample.

torprusside (SNP).]

Figures 4 and 5 show the temperature dependence of the isomer shifts (Δ_{IS}) and quadrupole splittings (Δ_Q) of each doublet. The values of the Δ_{IS} correspond to Fe(II) and/or Fe(III) low-spin atoms and, therefore, there is a high degree of covalent overlap between the iron atoms and the oxygen ligands. The high field responsible for the spin inversion could also be the reason for the metallic-to-semiconductor character change in the resistivity of this sample.

The Fe atoms have three possibilities: (a) they only go to the Cu(2) sites; (b) they only go the Cu(1) sites; or (c) they go to both sites. In case (a) the spectra should be a pure quadrupole doublet because, as was pointed out earlier, the surroundings of these sites do not change with the oxygen content. In case (b) there is the possibility of a pair of quadrupole doublets, due to the oxygen deficiencies in the perovskite structure, which gives rise to the phase mixture observed in the x-ray pattern. In case (c) the spectra should consist of, at least, a pair of quadrupole doublets with a large difference of their quadrupole splittings; however, the close values of the quadrupole splittings obtained in this experiment suggest that the Fe atoms go into Cu(1) sites and the small difference between the Δ_Q's may be due to a back bonding[15,16] of 0.2 electron during the oxidation, leaving the overall electron charge density essentially unaltered. This would produce different Δ_{IS}, due to the different screening of the $3s$ electrons, but almost the same Δ_Q values for both doublets.

It is worth emphasizing that perovskites are the sort of crystals that exhibit the highest tendency to a Jahn-Teller distortion, due to the high-intensity local electric fields that cause ferroelectricity. The fact that in the present experiment a low-spin state for iron is obtained, indicates that the local electric fields are high enough to preserve this state. One may be tempted to think that in these perovskitelike structures, the anomalies detected in the Mössbauer parameters around the superconducting tran-
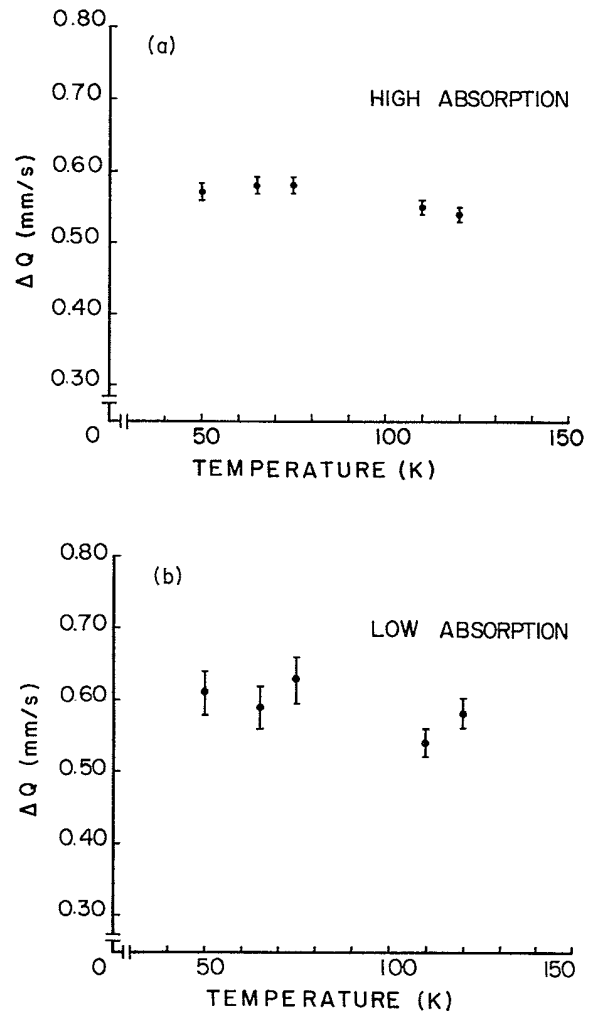

FIG. 5. Quadrupole splitting as function of temperature. (a) High absorption doublet. (b) Low absorption doublet.

sition temperature, namely, a reversal of the Δ_{IS} and Δ_Q dependence with temperature (these can be observed in Figs. 4 and 5), might be caused by this frustrated Jahn-Teller distortion. This is extremely important because this phenomenon may provide a clue to disentangle the mechanisms responsible for superconductivity in these high-T_c materials.

In conclusion, the evidence obtained in these experiments is that the Fe atoms go to the Cu(1) sites and behave as low-spin Fe(II) and/or Fe(III). This implies a strong bonding of the Fe (and Cu) atoms in the lattice. On the other hand, the change in the Δ_{IS} and Δ_Q dependence with temperature suggests the possibility of a Jahn-Teller structural change in the superconductive perovskite.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Q. Warg, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. F. Remeike, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[4]H. Steinfink, J. S. Swinnea, Z. T. Sui, H. M. Hsu, and J. B. Goodenough, J. Am. Chem. Soc. **109**, 3348 (1987).

[5]A. Ourmazd, J. A. Rentschler, J. C. H. Spence, M. O'Keeffe, R. J. Graham, D. W. Johnsor, Jr., and W. W. Rhodes, Nature (London) **327**, 308 (1987).

[6]R. Beyers, G. Lim, E. M. Engler, R. J. Savoy, T. M. Shaw, T. R. Dinger, W. J. Gallagher, and R. L. Sandstrom, Appl. Phys. Lett. (to be published).

[7]H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987).

[8]R. Escudero, L. Rendón, T. Akachi, R. A. Barrio, and J. Tagüeña-Martinez, Phys. Rev. B **36**, 3910 (1987).

[9]P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. (to be published).

[10]B. Raveau, in *Proceedings of the Workshop on Novel Mechanisms of Superconductivity, Berkeley, CA, 1987,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

[11]J. Giapintzakis, J. M. Matykiewicz, C. W. Kimball, A. E. Dwight, B. D. Dunlap, M. Slaski, and F. Y. Fradin, Phys. Lett. A **121**, 307 (1987).

[12]I. K. Schuller, D. G. Hinks, M. A. Beno, D. W. Capone II, L. Soderholm, J. P. Locquet, Y. Bruynseraede, C. U. Segre, and K. Zhang, Solid State Commun. (to be published).

[13]R. D. Shannon, Acta Crystallogr. Sect. A **32**, 751 (1976).

[14]Y. Maeno and T. Fujita, in *Proceedings of the Workshop on Novel Mechanisms of Superconductivity, Berkeley, CA, 1987,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

[15]N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy* (Chapman and Hall, London, 1971).

[16]A. Vértes, L. Korecz, and K. Burger, *Mössbauer Spectroscopy* (Elsevier, New York, 1979).