Susceptibility, crystal-structure, and Mössbauer study of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ doped with iron

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Resistance and ac susceptibility measurements, [57]Fe Mössbauer spectroscopy, and powder x-ray crystal-structure refinements were used to study the high-temperature superconductor $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. The superconducting transition temperature decreased as the Fe content was increased. The crystal structure is markedly orthorhombic for $x=0$, but the cell parameters a and b are nearly equal for $0.015 < x < 0.100$. In addition, the difference between a and b decreases systematically with Fe content; they are equal at $x=0.100$. The Mössbauer spectra above about 10 K consist of three doublets; their site assignments are proposed. Measurements of the [57]Fe recoil-free fraction as a function of temperature yielded a Debye temperature of about 455 K. Below 10 K, magnetic ordering of iron was observed.

The high-temperature superconductor with nominal composition $YBa_2Cu_3O_{7-\delta}$ has recently attracted immense attention. Although electron pairs appear to form, the nature of the interaction remains in doubt. In order to explore the origins of the superconductivity in these oxides, we prepared samples doped with iron, both natural and [57]Fe enriched. We used [57]Fe Mössbauer spectroscopy to obtain information on the site occupancy of Fe, the lattice dynamics, and the possibility of magnetic ordering. In addition, we studied the effect of Fe doping on the ac susceptibility and the crystal structure.

Samples were made using 99.9% pure Y_2O_3, CuO, BaO, and Fe_2O_3 to form compounds with the nominal compositions $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$, $0.0 \leq x \leq 0.10$. Some samples were made with Fe 93% enriched in the isotope [57]Fe. After mixing in a ball mill, the samples were prefired at 750 °C for 3 h in air, slowly cooled, and reground. This powder was pelletized, fired at 970 °C for 6 h in oxygen at 1 atm pressure, and slowly cooled. Mössbauer absorbers were prepared by grinding a pellet and immobilizing the powder in benzophenone.

Critical temperatures were determined by both ac susceptibility and four-probe resistance measurements. The real part of the susceptibility χ' is shown in Fig. 1 for five values of x. The magnetic field used had an rms amplitude of 0.12 Oe and a frequency of 3.7 kHz. T_c decreased as the Fe content increased. Zero resistance (as measured with a high-impedance voltmeter) was observed at higher temperatures than those at which complete diamagnetic shielding $\chi' = -1/4\pi$ was evident in the susceptibility curves. The reason for this is clear: For zero resistance only one electrical short circuit (corresponding to one superconducting pathway) is required, whereas for complete diamagnetic shielding the entire surface of the sample must be superconducting.

Crystal structures were refined in space group $Pmmm$ with the Rietveld method using powder x-ray diffraction data. Refinement was initially done with all atomic sites fully occupied: Cu atoms at positions Cu(1) (0,0,0) and Cu(2) (0,0,z), Y atoms at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, Ba atoms at $(\frac{1}{2},\frac{1}{2},z)$, and O atoms at O(1) $(0,\frac{1}{2},0)$, O(2) $(\frac{1}{2},0,z)$, O(3) $(0,\frac{1}{2},z)$, and O(4) $(0,0,z)$. The starting z coordinates were estimated from previously published structures.[1,2] Because of the small amounts of Fe relative to Cu and their similar scattering powers, the contribution of Fe to scattering at the Cu sites was included with that of Cu. Isotropic temperature parameters were fixed at values reasonable for x-ray structure refinements. Peaks from minor contaminating phases were excluded from the refinement.

Each position in turn was checked for the presence of vacancies by refining the site occupancy. Occupancies of the Cu(2), Y, Ba, O(2), O(3), and O(4) sites refined to
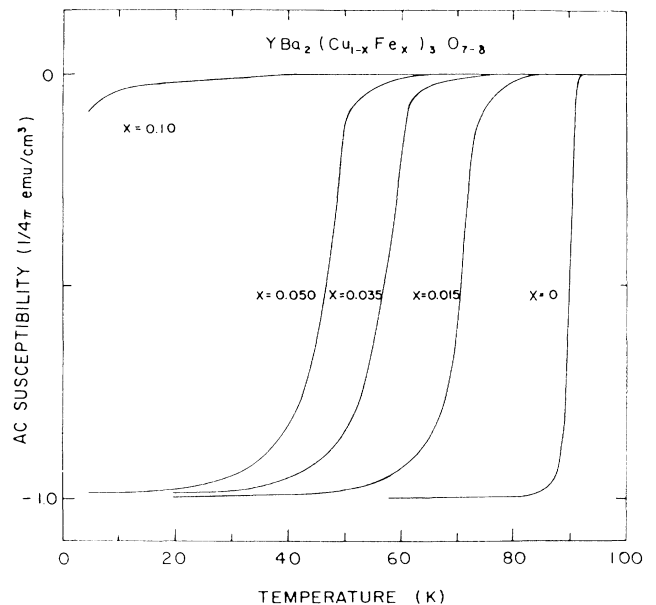

FIG. 1. The real part of the ac susceptibility at 3.7 kHz and 0.12 Oe rms as a function of temperature.

TABLE I. Selected structure refinement results for $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$.

x	z Cu(1)	z Ba	z O(2)	z O(3)	z O(4)	n O(1)	O
			Space group $Pmmm$				
0.015	0.3562(4)	0.1854(2)	0.384(3)	0.369(4)	0.151(2)	0.71(7)	6.71
0.035	0.3566(4)	0.1852(2)	0.378(7)	0.376(7)	0.152(2)	0.62(8)	6.62
0.050	0.3578(4)	0.1860(2)	0.396(7)	0.365(7)	0.157(2)	0.91(8)	6.91
0.100	0.3562(4)	0.1836(2)	0.360(6)	0.398(6)	0.159(2)	0.96(6)	6.96
			Space group $P4/mmm$				
0.100	0.3589(4)	0.1837(2)	0.380(1)		0.157(2)	0.55(4)	7.10

		Cell dimensions			
x		a (Å)	b (Å)	c (Å)	V (Å^3)
0.015	$Pmmm$	3.8564(2)	3.8682(2)	11.6540(6)	173.85
0.035	$Pmmm$	3.8608(3)	3.8669(3)	11.6521(7)	173.96
0.050	$Pmmm$	3.8688(3)	3.8716(3)	11.6336(6)	173.25
0.100	$Pmmm$	3.8704(6)	3.8692(6)	11.6294(6)	174.15
0.100	$P4/mmm$	3.8698(1)	3.8698(1)	11.6295(6)	174.16

values not significantly different from 1.0. These sites were fixed at full occupancy for the final refinement. The O(1) sites showed significant vacancies for all x values (Table I). The Cu(1) site occupancy was 0.90(1) for all refinements. We also checked for occupancy of a potential fifth oxygen position O(5) at ($\frac{1}{2}$,0,0). In our previous refinements[3] of Fe-free $YBa_2Cu_3O_{7-\delta}$, the occupancy of O(5) refined to values not significantly different from zero. Recent neutron-diffraction refinements[1,2] confirm the ordering of oxygen vacancies at O(1). Cell dimensions of the Fe-free compound are markedly orthorhombic [$a = 3.8258(2)$, $b = 3.8859(3)$, $c = 11.671(1)$]; the a and b cell parameters of the Fe-doped materials, however, are nearly equal in size, and become more tetragonal in character with increasing Fe content (Table I). As a and b are nearly equal, the O(1) and O(5) sites are highly correlated during refinement in space group $Pmmm$. Thus, the distribution of oxygen between the two sites is imprecisely determined. For $x = 0.015$, the occupancies of the O(1) and O(5) sites are about 0.60(10) and 0.15(8), respectively. Attempts to refine these occupancies at higher concentrations of Fe gave unacceptably high uncertainties but showed that the oxygen in the $z = 0$ plane becomes progressively disordered at O(5) with increasing Fe content. The oxygen ordering is probably responsible for the higher degree of orthorhombic distortion observed in the Fe-free material. Refinement results are reported for refinements with all oxygen ordered at O(1) (Table I). This strategy does not give information about oxygen ordering in the $z = 0$ plane, but avoids the high correlations which would adversely affect other parameters. However, as O(2) and O(3) are symmetrically equivalent in the tetragonal structure, they are highly correlated in orthorhombic structure refinements with a and b parameters approximately equal. Thus, the z parameters of these positions were also imprecisely determined. In summary, we refined all four structures in space group $Pmmm$ in order to document the tendency of the a and b cell parameters to approach equality with increasing Fe content. Indeed, refinement of the most Fe-rich structure ($x = 0.100$) in tetragonal space

group $P4/mmm$ yielded agreement factors similar to the $Pmmm$ refinement.

Room-temperature Mössbauer spectra for the $x = 0.015$ and $x = 0.100$ compounds are shown in Fig. 2. In both cases, the spectra comprise three overlapping Lorentzian doublets; the corresponding fitted parameters are given in Table II. The major difference between the two spectra is in the relative absorption areas of the doublets denoted 2 and 3 in Table II. Assuming that Fe is nonpreferentially substituting for the copper in the structure, we may relate these spectral areas to the relative site occupancies. Doublet 1 accounts for about two-thirds of the spectral area in both compounds; therefore, we associate it with the
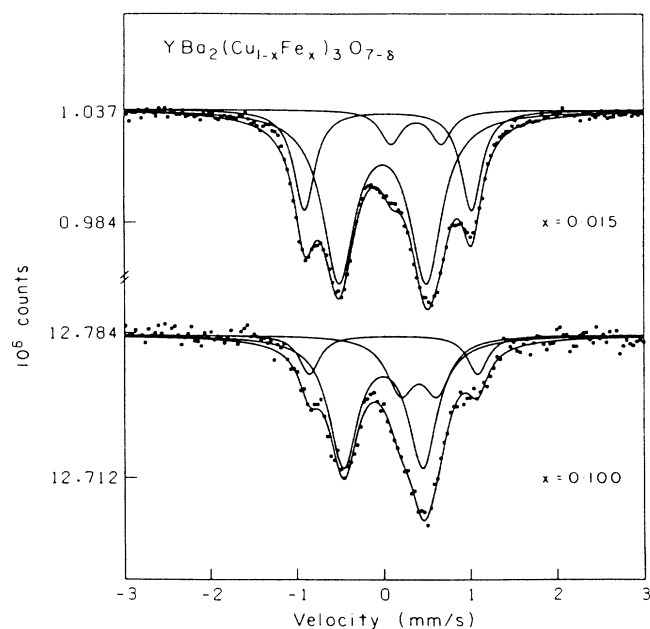

FIG. 2. Room-temperature ^{57}Fe Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ samples for $x = 0.015$ and $x = 0.100$.

TABLE II. Isomer shift relative to α-Fe (δ), quadrupole splitting (Δ), and linewidth (Γ), all in mm s^{-1}, and relative areas, for doublets 1, 2, and 3 of the room-temperature Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$.

	$x=0.015$				$x=0.100$			
	δ	Δ	Γ	Area	δ	Δ	Γ	Area
1	−0.03	1.00	0.45	66	−0.03	0.91	0.40	62
2	0.04	1.93	0.29	25	0.09	1.94	0.28	13
3	0.36	0.58	0.29	9	0.38	0.42	0.39	25

square-pyramidal coordination of the Cu(2) sites which account for two of the three Cu sites in the unit cell. Thus, doublets 2 and 3 would relate to Fe at the square-planar Cu(1) sites. The isomer shift and quadrupole splitting parameters of doublet 3 are typical of octahedrally coordinated Fe^{3+}; this implies that it corresponds to Cu(1) sites for which all the nearest-neighbor oxygen sites O(1) and O(5) are occupied. Doublet 2 has a quadrupole splitting $\Delta = 1.9$ mm/s which is unusually large for high-spin Fe^{3+} and may be attributed to Fe situated in the highly atypical (for Fe^{3+}) coordination of the square-planar Cu(1) site. Although the large Δ of doublet 2 might be regarded as evidence of a 2+ oxidation state for Fe, the extremely oxidizing synthesis conditions of these compounds makes the presence of Fe^{2+} very unlikely. Theoretical estimates of the magnitude of the quadrupole splitting that would be experienced by a high-spin Fe^{3+} ion at the Cu(1) and Cu(2) sites, made on the basis of a simple point charge model, confirmed that a large Δ would appear at the square-planar site, with a magnitude approximately twice that appearing at the square-pyramidal site. The increase in the relative area of doublet 3 at the expense of doublet 2 as x was increased is probably indicative of the preference of the ferric ions for octahedral coordination. This increase in area is consistent with the structure refinements which showed that the disordering of oxygen from the O(1) to the O(5) site seemed to increase systematically as the Fe content increased.

Mössbauer spectra of the ^{57}Fe-enriched sample $x=0.015$ were recorded at a number of temperatures down to 1.8 K. Between room temperature and about 10 K there was no qualitative change in the spectra, other than the normal temperature dependence of the total absorption area. The absence of any anomaly or discontinuity in the temperature range implies that no major structural phase change occurred at T_c. By relating the absorption area to a single Mössbauer recoil-free fraction for the Fe in the compound, we obtained a good fit for a Debye model with $\Theta_D = 455 \pm 15$ K, a figure which is close to that reported by Coey and Donnelly.[4] This is not an exceptionally high Θ_D, implying that if the high-T_c superconductivity were to be described by conventional BCS theory, an unusually strong electron-phonon coupling would be required.

Below 10 K, the spectra show clear indications of magnetic ordering (Fig. 3). At 5.1 K appreciable broadening is apparent and "wings" are discernible in the outer reaches of the spectrum. Also, the spectrum is markedly asymmetric. Such behavior is typical of relaxation effects. At 3.7 K the broadening and asymmetry were even more marked. At 1.8 K, hyperfine field splitting of the order of 25 T is apparent, although relaxation is still occurring.

It is interesting to speculate on this observed ordering in light of a recent suggestion that the superconducting mechanism may involve antiferromagnetism rather than phonons.[5] The susceptibilities of our Fe-doped $YBa_3Cu_3O_{7-\delta}$ compounds above T_c are small, implying either antiferromagnetic coupling or Pauli paramagnetism. The parent compound of a related cuprate perovskite group La_2CuO_{4-y} is known to be antiferromagnetic for $0 < y \leq 0.03$;[6] there is also some evidence that for small y the material may be superconducting below about 40 K.[7] Thus, it is possible that the magnetic order seen in the Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ below 10 K may be indicative of a long-range ordering of the copper sublattices, which might in some way be an attribute of high-T_c superconductivity.
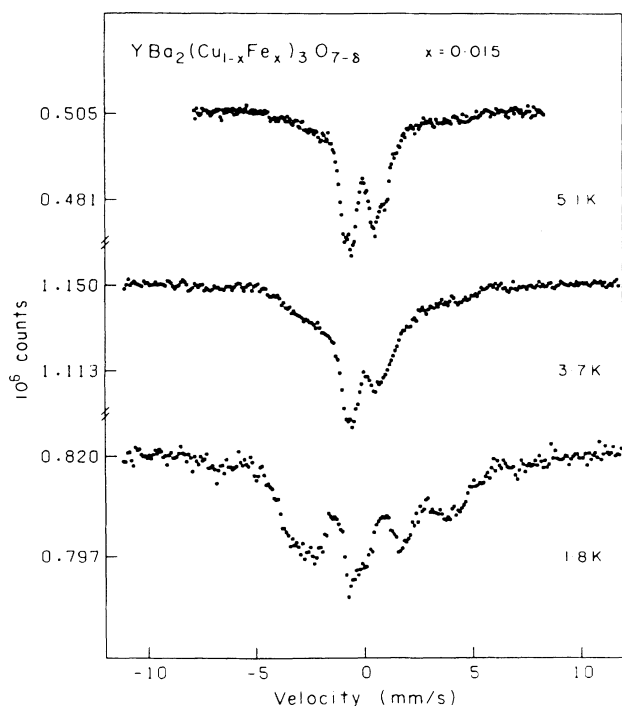
FIG. 3. Mössbauer spectra of the ^{57}Fe enriched sample $(x=0.015)$ at low temperatures.

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