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Observation of orthorhombic-tetragonal phase equilibria in $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$

M. Eibschütz and M. E. Lines
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

J. M. Tarascon and P. Barboux
Bell Communications Research, Inc., 331 Newman Spring Road, Red Bank, New Jersey 07701

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Recent orthorhombic-tetragonal (O-T) phase equilibria predicted by Khachaturyan and Morris have been observed experimentally in $YBa_2Cu_{3-x}Fe_xO_7$ ($0.01 \leq x \leq 0.2$) by Mössbauer techniques. The relative proportions of O and T phases are found to be functions of Fe concentration. The T phase grows from, the coexists with, the O phase as x increases. A nonzero fraction of T phase persists down to the smallest values of x. A model is presented to interpret the structural aspects of the O-T transition.

The high-T_c superconducting orthorhombic (O) phase of $YBa_2Cu_3O_7$ is only marginally stable with respect to a nonsuperconducting tetragonal (T) phase of equal composition. Experimentally, O-to-T phase transitions have been reported in $YBa_2Cu_3O_{7-\delta}$ as a function of temperature[1-3] (at $\approx 700\,°C$) and of stoichiometry[4-6] (at $\delta \approx 0.5$), and in $YBa_2Cu_{3-x}M_xO_{7-\delta}$ ($\delta \approx 0$) as a function of cation doping level x by $M = Fe$, Co, Al.[7-9] A recent Letter[10] suggests that any off-stoichiometric ($\delta \neq 0$ or $x \neq 0$) O phase may always be thermodynamically unstable at low enough temperatures against decomposition into a mixture of O and T phases, the instability with respect to congruent ordering always being replaced by one ($T \rightarrow T+O$) with respect to composition. If this is so, what is referred to as the O phase in the experiments of Refs. 1-9, may in fact be a mixed phase containing both O and T components in equilibrium.

The transformation concerns primarily the CuO [or Cu(1)] layers[11,12] of the crystal structure, which contain one Cu [Cu(1)] and two generally inequivalent oxygen [O(4) and O(5)] crystal sites. In the stoichiometric O phase with $x = \delta = 0$, these layers contain copper-oxygen [Cu(1)-O(4)] chains along a crystal axis (say Y) with the O(4) sites filled and the O(5) sites empty. The corresponding T phase then possesses a "random" XY distribution of oxygen anions on both O(4) and O(5) sites. Therefore, the O-to-T phase transition is, regardless of the driving mechanism, fundamentally one concerning a disordering of the Cu(1)-layer oxygen sublattice.

In this paper we report a Mössbauer study of $YBaCu_{3-x}Fe_xO_{7-\delta}$ ($\delta \approx 0$) which sheds light both on the nature of the transition and the oxygen disorder. First we establish that both O and T phases coexist in all our samples down to the smallest doping levels. We can also approximately estimate the relative volume fractions of the two phases as a function of x for small x. Second, we are able to establish that only two ($z' = 0,3$) of the five ($z' = 0,1,2,3,4$) possible Cu(1)-O XY-ligand coordination numbers z' are seen by Fe in the T phase, with the unique ($z' = 2$) Cu(1) site of the stoichiometric (superconducting) O phase being absent. In the O phase, Fe tends to induce a $z' = 3$ XY coordination, supporting the mechanism proposed by Tarascon *et al.*[8] in which a trivalent dopant (Fe appears to enter throughout as Fe^{3+}) breaks the Cu(1)-O(4) chains by preferring a larger oxygen coordination than is available by simple substitution of Cu(1) in the undoped material.

A detailed analysis of Mössbauer quadrupole and Zeeman spectra establishes that Fe substitutes for Cu almost exclusively in sites which are actively involved in the O-to-T phase structural transition [i.e., in the Cu(1) sites]. One other site, not significantly perturbed by the O-to-T phase transition, is also weakly populated throughout, and has been tentatively identified with Fe entering a Cu(2) site.[11]

Among the vast quantity of recent publications on the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ there is already a substantial subset involving Mössbauer spectroscopy on iron-doped samples.[9-18] These include both quadrupole and Zeeman spectra and they clearly show the presence of at least three inequivalent iron sites and at least two different magnetic moments. However, there is as yet no consenus as to their interpretation and confusion abounds. Although there seems to be little doubt[19] that Fe does substitute for Cu in $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$, confusion has arisen because, as we shall demonstrate below, the existing spectra are all of a mixed phase ($O+T$) character and are extremely sensitive to oxygen stoichiometry.

Using enriched ^{57}Fe dopant, and iron concentrations ranging from 0.2 down to 0.01, our statistics are sufficient for us to be able to see for the first time the change in quadrupole spectrum which takes place on passage from the dominantly tetragonal T phase [at $x \gtrsim 0.05$ (Refs. 7-9)] to the dominantly orthorhombic superconducting phase (at $x \ll 0.05$) (see Fig. 1). There are, in general, five visible peaks which we label L_1 to L_5 in order of increasing Mössbauer velocity. They include two major quadrupole doublets (L_1,L_5) and (L_2,L_4) and a small additional peak L_3 which is one half of a minor amplitude doublet, the other line of which is obscured beneath L_4.

The first obvious observation from Fig. 1 is that on passage to the O-phase limit as $x \rightarrow 0$ ($\delta \approx 0$) the line L_5 disappears. Line L_4 in Fig. 1(a) must therefore involve the overlap of two major lines (i.e., even ignoring the L_3'

complement to L_3) and the O phase spectrum therefore contains at least one quadrupole doublet L_1,L_4 in addition to the L_2,L_4 already recognized. Discounting for the moment the minor L_3 feature, it is clear that two Mössbauer doublets (L_1,L_4 and L_2,L_4) are to be associated with the O phase, and two more (L_1,L_5 and L_2,L_4) with the T phase. Whether the two L_2,L_4 doublets corresponding to the O and T phases are identical, or slightly different, will be deduced from the quantitative fitting procedure. Allowing for their possible difference, the quadrupole spectra in Fig. 1 could involve as many as four major and one minor quadrupole doublet since, with the (T phase) line L_5 developing gradually in intensity from essentially zero at $x \approx 0$, at least some of the spectra in Fig. 1 (viz. those with smaller values of x) must be mixed phase $O+T$.

We least-squares fit each of the Mössbauer spectra of Fig. 1 to the sum of five[20] Lorentzians and record their positions L_i (Fig. 2) and areas A_i [Fig. 3(a)] (Ref. 21) as functions of x. A consistent interpretation can be given in terms of the mixed $O+T$ phase picture, with two primary (symmetric) quadrupole doublets being present in each phase, but with an x-dependent population. In the limit $x \rightarrow 0$ ($\delta \approx 0$) the system approaches the 100% O phase ($A_5 \rightarrow 0$), which implies an essentially complete overlapping of the two O phase L_4 lines. This enables us to define the principal O phase doublets L_1,L_4 and L_2,L_4, which we label, respectively, $a(O)$, and $b(O)$ in Fig. 2. As x increases, the T phase develops at the expense of the O phase until, at $x = 0.2$, the system is dominantly T phase. This enables us to define the principal T phase doublets $a(T)$ and $b(T)$ (see Fig. 2) as the limiting T phase line combinations L_1,L_5 and L_2,L_4, respectively. The weak L_3 line persists throughout and is clearly present in both phases. Its complementary line L_3' has been independently located from an oxygen deficient sample $\delta \approx 1$. The

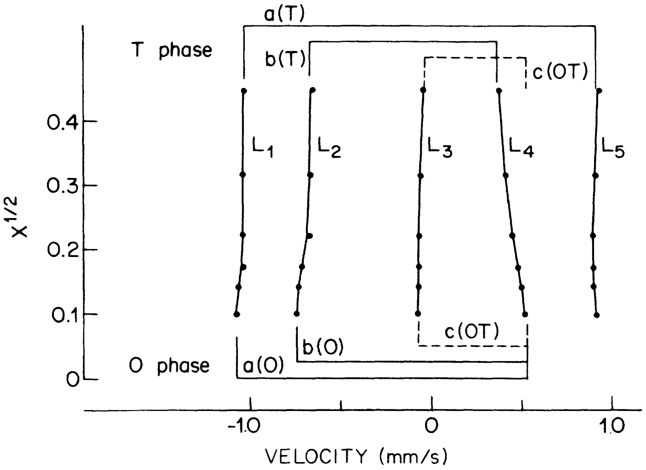


FIG. 2. The converged Lorentzian peak positions $L_i (i=1-5)$ as a function of iron concentration identifying (see text) the two Cu(1)-site doublets $a(O)=L_1L_4$, $b(O)=L_2L_4$ associated with the O phase ($x \rightarrow 0$) and also those $a(T)=L_1L_5$ and $b(T)=L_2L_4$ associated with the T phase ($x \gtrsim 0.2$). Also shown (dashed line) is the L_3 doublet $c(OT)$ which is not involved in the O-T transition and which we tentatively identify with Fe entering a Cu(2) site.

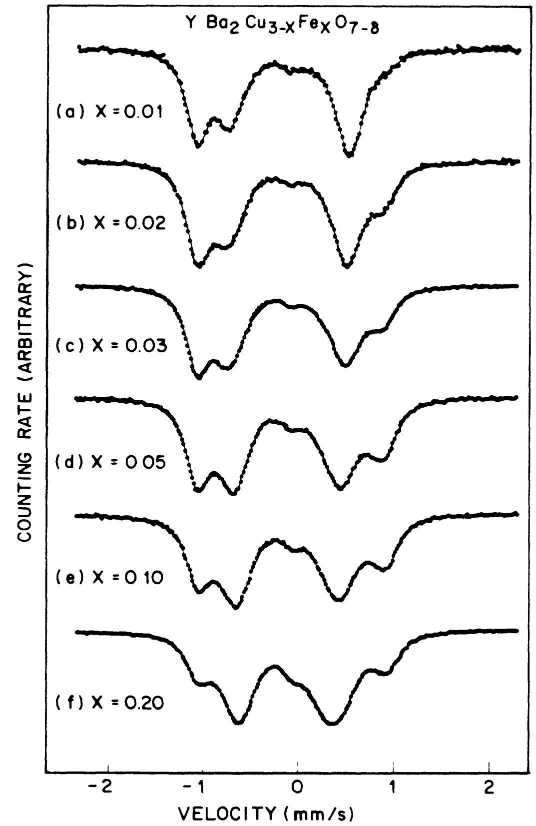


FIG. 1. The room-temperature Mössbauer spectra of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ ($\delta \approx 0$) for six iron concentrations between $x=0.01$ and $x=0.2$. The solid lines show a fit to the sum of five floating-width Lorentzians corresponding only to the five clearly visible features of each spectrum.

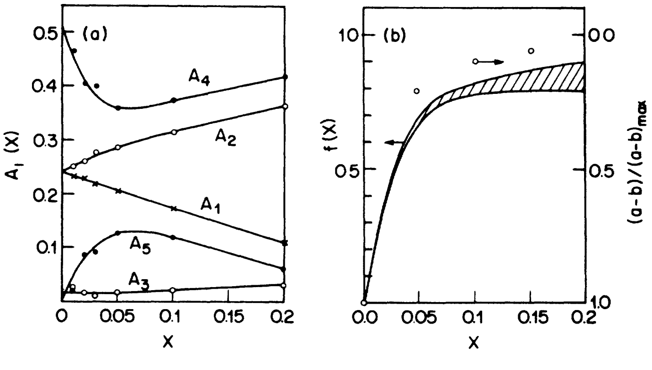


FIG. 3. (a) Lorentzian line areas $A_i (i=1-5)$, normalized to $\sum_i A_i = 1$, as a function of iron concentration x. The curves interpolate smoothly between the six A_i values which are determined directly from the six spectra of Fig. 1. (b) The fraction $f(x)$ of the material which is T phase, as deduced from an interpretation of the line areas $A_i(x)$. The shading indicates uncertainties which derive from the fact (see text) that the A_i equations do not possess a single unique solution. Also shown for comparison (open circles) are x-ray measurements of the degree of orthorhombic distortion $a-b$ as given in Ref. 9.

quadrupole splittings (QS), and isomer shifts (IS) are set out in Table I where we label the L_3,L_3' doublet as $c(OT)$.

The development of the T phase as x increases from zero can be deduced from an analysis of the areas A_i ($i=1,2,4,5$) of Fig. 3(a) in terms of the major symmetric doublet components $a(O)$, $b(O)$, $a(T)$, $b(T)$, recognizing from Fig. 2 that A_1 is a sum of $a(O)$ and $a(T)$, A_2 of $b(O)$ and $b(T)$, A_4 of $a(O)$, $b(O)$, and $b(T)$, and A_5 of $a(T)$ alone. At concentration x, let a fraction $f(x)$ of the material be T phase, with Fe populating $a(T)$ and $b(T)$ sites in the ratio $p_a^T(x){:}1-p_a^T(x)$; and a fraction $1-f(x)$ be in O phase, with Fe populating $a(O)$ and $b(O)$ in the ratio $p_a^O(x){:}1-p_a^O(x)$. Since, by powder symmetry,[21] we must have $A_1+A_2=A_4+A_5=\frac{1}{2}$, the normalized line areas are defined completely by the two equations

$$2A_1=(1-f)p_a^O+fp_a^T,\quad 2A_5=fp_a^T. \tag{1}$$

Crystallographically it is known that the $x\approx 0$, $\delta\approx 0$ phase is essentially orthorhombic. It follows that the physical relevant solution of Eqs. (1) in the limit $x\rightarrow 0$, for which from Fig. 3(a) $2A_1\approx 0.5$ and $2A_5\approx 0$, is $f(0)\approx 0$, $p_a^O(0)\approx p_b^O(0)\approx 0.5$. The two O-phase sites are therefore about equally populated for small x. Also, since at $x=f=0$ we know from Fig. 3(a) that the value of $2\partial A_5/\partial x=p_a^T\,\partial f/\partial x$ is $\gtrsim 10$, and p_a^T must be less than 1 by definition, it follows that $\partial f/\partial x>10$, as $x\rightarrow 0$ so that the T phase develops extremely rapidly from the O phase in the small x limit.

For general x the Eqs. (1) possess no unique solution although, if we insist on monotonic behavior, $f(x)$ is rather closely defined [Fig. 3(b)]. In particular by subtraction, we derive the single equation $2(A_1-A_5)=(1-f)p_a^O$, from which we see that the $O+T$ phase does not become 100% T phase ($f=1$) until $A_1=A_5$. Clearly, from Fig. 3(a), this does not occur within the range $0<x<0.2$. Thus, although the O-to-T phase-equilibrium transition is already $\approx 70\%$ complete by $x=0.05$, further T phase development is very slow [see Fig. 3(b)]. This finding is in qualitative accord with x-ray measurements[9] of the c plane unit-cell dimensional difference a-b as a function of x [Fig. 3(b)] which finds complete tetragonality at $x=0.3$.[22]

We may now locate the iron sites and ligand coordinates with which the major Mössbauer doublets are to be associated. The crystal structure of O phase $YBa_2Cu_3O_7$ is now well known.[11] It contains two inequivalent Cu sites, commonly referred to as Cu(2), in the CuO_2 planes, and Cu(1), in the CuO planes. The T phase develops[3] from the O phase by a disordering of the oxygen lattice within the Cu(1) layers in a manner which transforms the ordered (chainar) configuration to a statistically disordered planar one. Since both the a and b quadrupole doublet intensities are markedly affected by the $O+T$ phase-equilibrium development, all four must be associated with Fe substituting for Cu(1) in some manner.

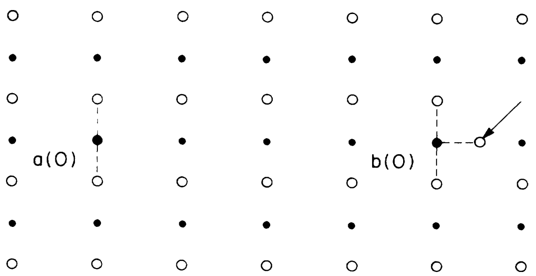
TABLE I. QS and IS for the O phase and T phase doublets of Fig. 2. Isomer shifts are given with respect to iron metal at room temperature.

	$a(O)$	$b(O)$	$a(T)$	$b(T)$	$c(OT)$
QS (mm/s)	1.59	1.27	1.94	1.04	0.56
IS (mm/s)	−0.18	−0.02	−0.02	−0.06	+0.33

To locate the Cu(1) sites associated with the a- and b-type doublets, we look first at the T phase. Since $\delta\approx 0$ for the samples of Fig. 1, the mean ligand coordination in the XY plane must be closely equal to that of the O phase, viz., $\langle z'\rangle=2$. Yet of the five possible XY-ligand coordination numbers $z'=0-4$, only two are seen, even to values $x\approx 0.8$.[8] It follows that one must correspond to $z'=3$ or 4; and the other to $z'=0$ or 1. Since the $a(T)$ doublet persists in oxygen deficient samples right down to $\delta\approx 1$, while $b(T)$ disappears in this limit, $a(T)$ must be associated with $z'=0$. This site, with full ligand coordination $z=2$ (including the 2 Z-axis ligands which are always present) we label as a $V_z=V_2$ site, where V_2 (axial) is the local ligand field potential. Since it is not possible to assemble a lattice, ordered or disordered, involving sites with only completely empty ($z'=0$) and fully filled ($z'=4$) XY ligands, it follows further that $b(T)$ must be associated with a $z'=3$ ($z=5$) V_5 capped-tetragonal site. A "two-site" model for a disordered T phase of V_2 and V_5 sites is easy to prepare, see Fig. 4(b), and is likely to be valid for large Fe concentrations $x\rightarrow 1$.

The O phase, in the absence of Fe, possesses a single

(a) O phase



(b) T phase

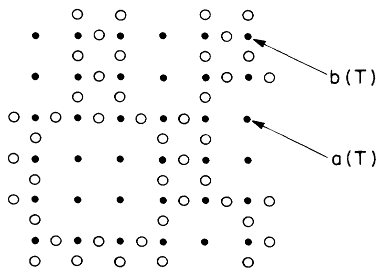


FIG. 4. (a) Schematic of an iron-doped CuO plane in the O phase of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ ($\delta\approx 0$) identifying the iron sites to be associated with the Mössbauer doublets $a(O)$ and $b(O)$; open circle = oxygen, small and large filled circles = Cu and Fe, respectively. (b) Model for the same layer in the T phase with high Fe concentration $x\rightarrow 1$.

$z'=2$, V_4 symmetry (quadratic planar), Cu(1) site. Since we observe two O phase Mössbauer doublets, Fe must have perturbed the lattice to produce the second site. Noting the closely similar form (i.e., QS and IS from Table I) of the $b(O)$ and $b(T)$ doublets, we tentatively associate the same nearest-neighbor ligand symmetry ($z'=3$, V_5) to $b(O)$ that we found for $b(T)$. By elimination, this leaves $a(O)$ to be associated with the $z'=2$, V_4 site, and suggests the chain breaking role of Fe depicted in Fig. 4(a).

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[20] We fit only the five visible features, since a unique statistically reliable fit using more Lorentzians cannot be obtained.

[21] The spectra of Fig. 1 actually exhibit a small orientationally induced asymmetry of lines areas. The areas plotted as A_i in Fig. 3(a) have been slightly rescaled to make $A_1+A_2=A_4+A_5$.

[22] Note that x in the present paper is equivalent to $3x$ of Ref. 9.