Oxygen-vacancy-formation enthalpy in $YBa_2(Cu_{0.985}Fe_{0.015})_3O_{7-\delta}$ oxide superconductor

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^{57}Fe Mössbauer spectra of $YBa_2(Cu_{0.985}Fe_{0.015})_3O_{7-\delta}$ samples display multiple sites ($n = A$, B, C, and D) with the site intensity ratios I_n/I exhibiting profound thermal annealing effects in the temperature range $150\,°C < T_a < 550\,°C$ associated with oxygen desorption. Specifically, the ratio I_A/I is a function of T_a, and displays an activation enthalpy of site formation $\Delta H_A = 104(3)$ meV. We ascribe it to the filling of $O(1)$ oxygen vacancy sites in chains. The miniscule ΔH_A is probably the consequence of the undercoordinated nature of the orthorhombic structure which globally promotes a superelastic (soft) lattice.

Oxygen stoichiometry appears to play a crucial role in the transport of charge in the ceramic $YBa_2Cu_3O_{7-\delta}$ superconductor. Oxygen-deficient samples ($\delta > 0.4$) usually display[1] a semiconducting behavior prior to onset of superconductivity at T_c while oxygen-rich samples ($\delta \simeq 0$) display a metallic one. Furthermore, large variations in transition temperatures T_c associated with oxygen stoichiometry in $YBa_2Cu_3O_{7-\delta}$ have been observed and suggest that ordering of oxygen vacancies may be necessary to realize high T_c's. Indeed, when this ordering occurs the integrity of quasi-one-dimensional CuO_3 chains is held intact, although the basic reasons why the presence of such chains in the orthorhombic structure enhances T_c are not well understood.

Hyperfine interaction methods such as Mössbauer effect and perturbed angular correlations have proved to be powerful microscopic probes of point defects in condensed matter.[2] Such local methods can also be used to tag oxygen vacancies in these novel oxide superconductors, and to follow their formation kinetics microscopically as we shall demonstrate in the present Rapid Communication. We have used ^{57}Fe Mössbauer spectroscopy to probe in detail the nuclear hyperfine structure of well-characterized $YBa_2(Cu_{0.985}Fe_{0.015})_3O_{7-\delta}$ samples and find evidence[3] of four chemically inequivalent Fe sites (A, B, C, and D). Thermal annealing in the temperature range $150\,°C < T_a < 550\,°C$ leads to an activated growth of the Mössbauer site intensity ratio $IA/I(T_a) = C_A e + \Delta H_A/k_B T_a$ as oxygen progressively desorbs from the sample. These profound effects suggest that site A can be understood as an Fe dopant substitutional[3] at a $Cu(1)$ chain site and is formed when vacant oxygen $O(1)$ sites in the nearest-neighbor (NN) coordination of defect chain sites become occupied as oxygen migrates with increasing

annealing temperature T_a in the orthorhombic structure. Specifically, we identify the enthalpy change $\Delta H_A = 104(3)$ meV with migration of oxygen to $O(1)$ chain sites converting the defect chain sites C and D to substitutional A sites. The miniscule ΔH_A value deduced from the present work has broad consequences on both applications as well as origin of superconductivity in these novel oxides.

The samples used for the experiments were prepared by standard solid state reaction of Y_2O_3, $BaCO_3$, CuO, and ^{57}Fe enriched Fe_2O_3 in four steps. Each step consisted of thoroughly mixing the powders followed by sintering at $950\,°C$ for 12 h. In the final step, the sintered powder was annealed at $950\,°C$ in flowing oxygen for 12 h and slowly cooled to $75\,°C$ over a period of 6 h to yield a virgin sample. X-ray analysis of virgin samples indicate high-quality single-phase materials possessing an orthorhombic cell with $a = 3.822(5)$ Å, $b = 3.887(5)$ Å, and $c = 11.682(5)$ Å, and a transition temperature T_c midpoint of 88.6 K with a ΔT_c (90-10%) = 2.8 K, both in reasonable agreement with a previous report.[4] Thermal annealing of virgin samples in vacuum was performed by heating to a predetermined T_a for 3 h followed by a fast quench to room temperature in about 10 min. Lattice cell dimensions and transition temperatures T_c's of the vacuum annealed samples were systematically examined as a function of T_a and follow trends associated with oxygen desorption noted by previous workers.[5,6]

Figure 1 reproduces the room-temperature ^{57}Fe Mössbauer spectrum of a virgin sample [(a)] along with spectra of a virgin sample annealed at $T_a = 250$, 350, and $450\,°C$ in (b), (c), and (d), respectively. Most remarkable are the striking changes in the shape of spectra as a function of T_a which result in considerable simplification at elevated T_a's. For example, samples annealed at
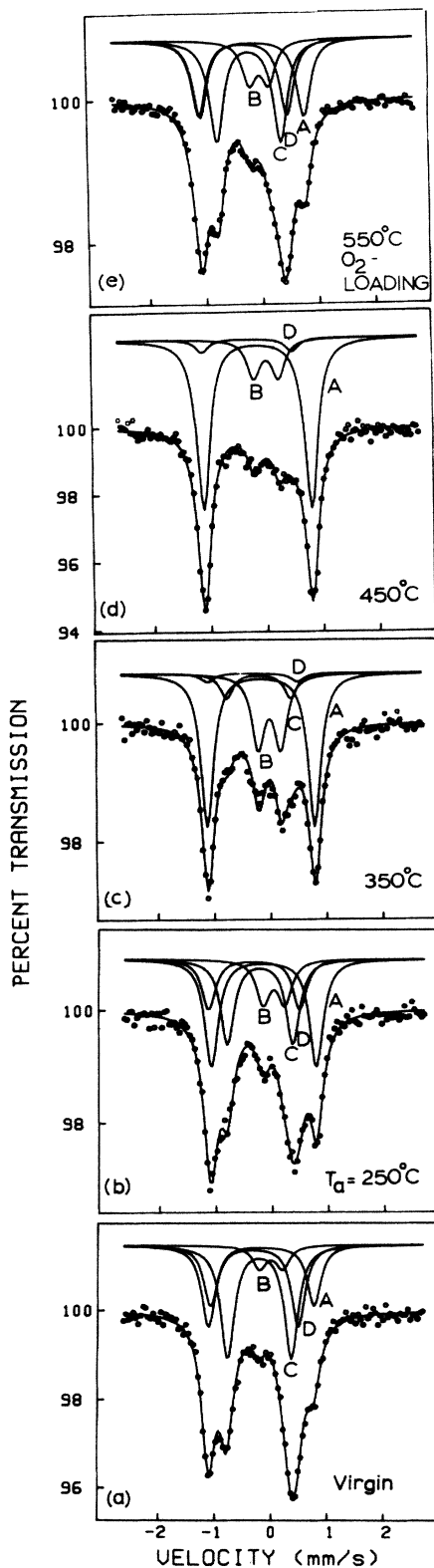
FIG. 1. Spectra of the high-T_c sample in the virgin state (a) and oxygen desorbed states [(b)–(d), obtained by vacuum annealing at indicated temperatures T_a] display profound growth of I_A/I with T_a. Soaking in flowing oxygen at 550 °C the desorbed sample (d) gave spectrum (e) which corresponds to the spectrum of the virgin sample (a). All spectra taken at 297 K, were fit to four quadrupole doublets (A, B, C, and D) whose parameters appear in Table I.

$T_a > 400$ °C show merely two well-resolved quadrupole doublets (A,B). To account for the observed line shape of the spectra at $T_a < 400$ °C we have found necessary to include besides A and B, two additional sites (C and D), the parameters of which are summarized in Table I. At the outset we can state here that none of these sites are characteristic of an Fe impurity present in the green phase Y_2BaCuO_5 or $BaCuO_2$ phase, both of which we have examined.[7] We note from Fig. 1 that the site intensity ratio I_A/I increases dramatically as a function of T_a as is illustrated in the plot of Fig. 2(a) which also gives $I_n/I(T_a)$ for the other sites. A plot of $\ln(I_A/I)$ as a function of $1/T_a$ drawn in Fig. 2(b) clearly displays an activated behavior for formation of site A.

The crystal structure[5] of orthorhombic $YBa_2Cu_3O_{7-\delta}$ provides for two types of Cu sites; a Cu(1) chain site and a Cu(2) layer site and chemical ordering of oxygen O(1) sites in the chains. Our Mössbauer results suggest specific microscopic structures of various Fe sites which are shown in Fig. 3. Sites B and A represent substitutional Fe (Fe^{3+} as revealed by isomer shifts) replacing respectively Cu(2) layer and Cu(1) chain sites of the orthorhombic structure. Sites C and D on the other hand represent defect sites and are formed when one of the two O(1) NN of site A either leaves the immediate vicinity of the Fe site creating a site C, or merely hops from the b edge [O(1) site] to the a edge [O(5) site] creating a site D. In our model, note that sites C and D can both readily convert to site A. The former occurring when the O(1) site is occupied and the latter occurring when oxygen hops from O(5) to O(1) site as shown in Fig. 3. We believe this process accounts for the I_n/I trends of Fig. 2(a) where site A is found to grow precipitously at the expense of sites C and D in the range 200 °C $< T_a < 500$ °C. We have recently also performed Mössbauer polarization experiments on oriented samples to establish the direction of the electric field gradient (V_{zz}) with respect to the c axis. These results discussed in Ref. 8 explicitly demonstrate that at site A, V_{zz} is perpendicular to the c axis and possesses axial symmetry ($\eta = 0$). These results unambiguously demonstrate the microscopic structure of site A to be a fourfold coordinated substitutional Fe chain site, in harmony with the physical picture advanced here. First-principles electric field gradient (EFG) calculations when available will undoubtedly provide better insights to the electronic structure of Fe sites in layers and chains.

The present results also provide direct evidence for re-

TABLE I. Mössbauer isomer-shift (δ), quadrupole splitting (Δ), and site-intensity ratio (I_n/I) of various Fe sites from spectra of Fig. 1. The shifts are quoted relative to Pd metal at 297 K.

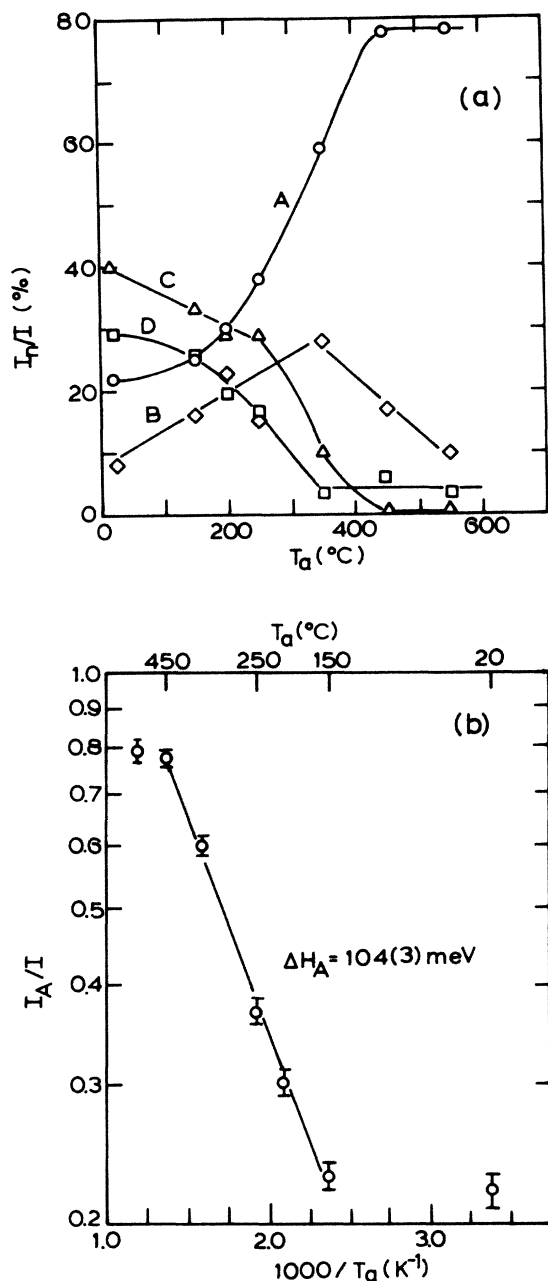| Site n	δ (mm/s)	Δ (mm/s)	I_n/I
A	−0.13(2)	1.84(2)	0.22(2)
B	0.02(2)	0.41(2)	0.09(2)
C	−0.19(1)	1.14(1)	0.40(2)
D	−0.29(1)	1.60(1)	0.29(2)

FIG. 2. (a) T_a dependence of the site intensity ratio I_n/I for $n = A$, B, C, and D deduced from spectra of Fig. 1; (b) plot of log I_A/I vs $1/T_a$ displays an activated growth of site A.

FIG. 3. Proposed microscopic structure and EFG (V_{zz}) axis of the two substitutional (B layer, A chain) and two defect (C,D) Fe sites observed in spectra of Fig. 1. C and D sites transform to A site, respectively, with filling in of an O(1) vacancy site, and an oxygen atom hopping from O(5) to O(1) location as illustrated.

versibility of site occupancy in a desorption-absorption cycle. This is illustrated in Fig. 1(e) where we reproduce a spectrum of a virgin sample thermally annealed at 550°C in a flowing oxygen atmosphere following vacuum annealing at $T_a = 450$°C [Fig. 1(d)]. The change in the line shape from Figs. 1(d) to 1(e) illustrates somewhat dramatically the effect of oxygen uptake. We note that the site intensity ratios I_n/I deduced from spectra of Figs. 1(e) and 1(a) are indeed quite similar to each other, and this illustrates rather directly the reversibility of oxygen
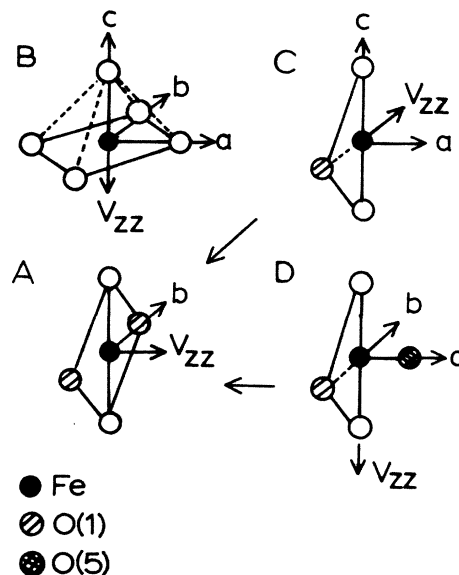
site occupancy in a desorption-absorption cycle. It is for this reason we believe that T_c's of vapor-deposited oxide superconducting films (usually oxygen deficient and semiconducting) can be restored by a mere thermal anneal in oxygen or even plasma oxidation at low or moderate temperatures.[9]

The small formation enthalpy of O(1) vacancies is unusual and it probably reflects[10] the globally soft or superelastic nature of the host oxide. Phillips[10] has recently proposed that the mechanical stiffness threshold in perovskites in determined largely by NN central forces and corresponds to (average coordination number) $N_c = 6$. This means that a defect-free solid such as BaPbO$_3$ ($N_c = 7.2$), or La$_2$CuO$_4$ ($N_c = 6.86$), can be regarded to be intrinsically rigid or subelastic being overcoordinated ($N_c > 6$), while the oxygen-deficient YBa$_2$Cu$_3$O$_7$ ($N_c = 5$) is globally superelastic because it is undercoordinated ($N_c < 6$). The high-T_c superconductor YBa$_2$Cu$_3$O$_7$ is mechanically stabilized by the presence of much weaker second-neighbor forces which promotes a large electron-phonon interaction.[10] These global constraint arguments permit one to also understand why a small-sized and weakly polarizable O^{2-} ion can easily diffuse in a microscopically soft lattice. The present results have an important bearing on materials applications as well. The results of Fig. 2 demonstrate that oxygen vacancies are already mobile at $T_a = 150$°C (as inferred from changes in Mössbauer I_n/I) even though oxygen does not appear to leave the samples in measurable quantities until a temperature $T_a = 250$°C (as revealed by thermogravimetric analysis measurements[9]) is reached. These low temperatures put restrictions on processing of these materials for

device applications in which undoubtedly capping of thin films by noble metal films would be required.

In conclusion, we provide the first measurement of oxygen vacancy formation enthalpy in the prototypical high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ using Fe dopant as a microscopic probe. In principle such measurements can be extended to other rare-earth bearing cuprates and the effect of rare-earth cation size on vacancy formation enthalpies analyzed.

Note added in proof. Microscopic configurations of the substitutional sites A and B proposed in this work are confirmed by experiments on aligned crystallites. Structure of defect sites C and D on the other hand appears to be less certain largely because other possible configurations of these sites have not been ruled out at this time.

[1] Resistivity results on oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ samples are so numerous that our citations are bound to be incomplete. Starting from the pioneering work of J. Bednorz and K. Müller, Z. Phys. B **64**, 189 (1986), and the discovery of $T_c \simeq 95$ K material by M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987), more detailed work has appeared on $YBa_2Cu_3O_{7-\delta}$ and includes B. Batlogg, R. J. Cava, C. H. Chen, G. Kourouklis, W. Weber, A. Jayaraman, A. E. White, K. T. Short, E. A. Rietman, L. W. Rupp, D. Werder, and S. M. Zahurak, in *Novel Superconductivity*, edited by Stuart Wolf and Vladimir Z. Kresin, (Plenum, New York, 1987), p. 653; also see Aravinda M. Kini, Urs Geiser, Huey-Chuen, I. Kao, K. Douglas Carlson, Han H. Wang, Marilyn R. Monaghan, and Jack M. Williams, Ingorg. Chem. **26**, 1834 (1987).

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[3] Previous workers have analyzed similar spectra in terms of 2 quadrupole doublets (with large intensity asymmetries) and a third impurity site. Site A has been previously observed in $RBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ samples for $R = Y$ by Z. Q. Qiu *et al.* (unpublished); $R = Gd$ by H. Tang *et al.*, Phys. Rev. B **36**, 4018 (1987); and $R = Eu$ by J. M. D. Coey and K. Donnelly, Z. Phys. B **67**, 513 (1987), and assigned in each instance to substitutional Fe, replacing $Cu(1)$ sites in chains.

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