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Metallic doping sites in $Y_1Ba_2Cu_3O_{7-\delta}$

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Using aligned iron-doped 1:2:3 crystallites, the sign, direction, and asymmetry parameter of the electric-field-gradient tensor for the four quadrupole components of the Mössbauer spectrum have been established. Our results confirm that iron enters the 1:2:3 structure at multiple sites and specific assignments are suggested.

Metallic dopants directed at Cu sites in Cu oxide superconductors are known[1,2] to systematically alter crystallographic, magnetic, and superconducting properties. However, to understand these changes, it is crucial to establish the site occupancy and oxygen stoichiometry of the doped materials. Several workers[3-6] have reported the ^{57}Fe hyperfine structure in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. The Mössbauer spectra are unexpectedly rich, suggesting contributions from multiple sites, but disentangling the possibilities has proved to be difficult.[7] A useful step was the discovery[8] that the hyperfine structure is very sensitive to oxygen stoichiometry. Blue and co-workers[8] showed that these (reversible) effects can be traced to a systematic redistribution between four chemically distinct sites upon oxygen desorption (or absorption). These oxygen stoichiometry effects in the Y-based material appear to have close parallels in other rare-earth Cu oxide[9] superconductors.

The present work places severe restrictions on the possible site configurations by establishing for the first time the sign, spatial orientation, and asymmetry parameter $[\eta = |(V_{xx}-V_{yy})/V_{zz}|]$ of the electric-field-gradient (EFG) tensor. This was made possible by use of aligned crystallites with γ rays transmitted at various tilt angles (β) relative to the aligned axis (c axis).

Alignment of $YBa_2Cu_3O_{7-\delta}$ crystallites along the c axis using a magnetic field was demonstrated by Farrell *et al.*[10] With the same procedure, we have now aligned $YBa_2(Cu_{0.985}Fe_{0.015})_3O_{7-\delta}$ samples in epoxy and have confirmed their c-axis alignment by x-ray diffraction. In Mössbauer experiments, the use of single crystals[11] leads to a quadrupolar doublet intensity asymmetry (I_+/I_-), i.e., the ratio of the integrated area under the positive to the negative velocity resonance of a quadrupole doublet is no longer unity as it is in polycrystalline specimens. Room-temperature spectra of the aligned samples were taken as a function of tilt angle β in order to extract the site-specific β variation of $I_+/I_-(\beta)$. As noted previously,[8] spectra of virgin samples ($\delta = 0.05$, possessing A, B, C, and D sites) simplify considerably upon some oxygen desorption ($\delta = 0.17$) since the C and D sites are largely eliminated [compare Figs. 1(a) and 1(b)]. Taking advantage of this fact, we first obtained the behavior of sites A and B from spectra of oxygen-desorbed samples [Fig. 1(a)] and then proceeded to sites C and D from spectra [Fig. 1(b)] of the more complex virgin samples. Using this sequence to fit the spectra, we obtained $I_+/I_-(\beta)$ trends for various sites and these are summarized in Figs. 2(a) and 2(b). Perhaps most striking is the close similarity of the behavior of sites A and C. Both start out with an I_+/I_- near 0.60 at $\beta = 0$ increasing monotonically to about 1.2 at $\beta = \pi/2$. In sharp contrast, site D displays a smaller β dependence, while the weakly populated site B displays just the reverse of the behavior of sites A and C.

Theoretically, the intensity asymmetry of a quadrupole doublet in an aligned sample derives[11] from angular distributions (P_π and P_σ) of the π ($\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$) and σ ($\pm\frac{1}{2} \rightarrow \pm\frac{1}{2}$) quadrupole components, the nature of the crystalline alignment,[10] and the direction of propagation of γ rays relative to the crystal axis. Because of the small effective thickness of our aligned absorbers,[12] finite thickness effects can be ignored and the observed intensity

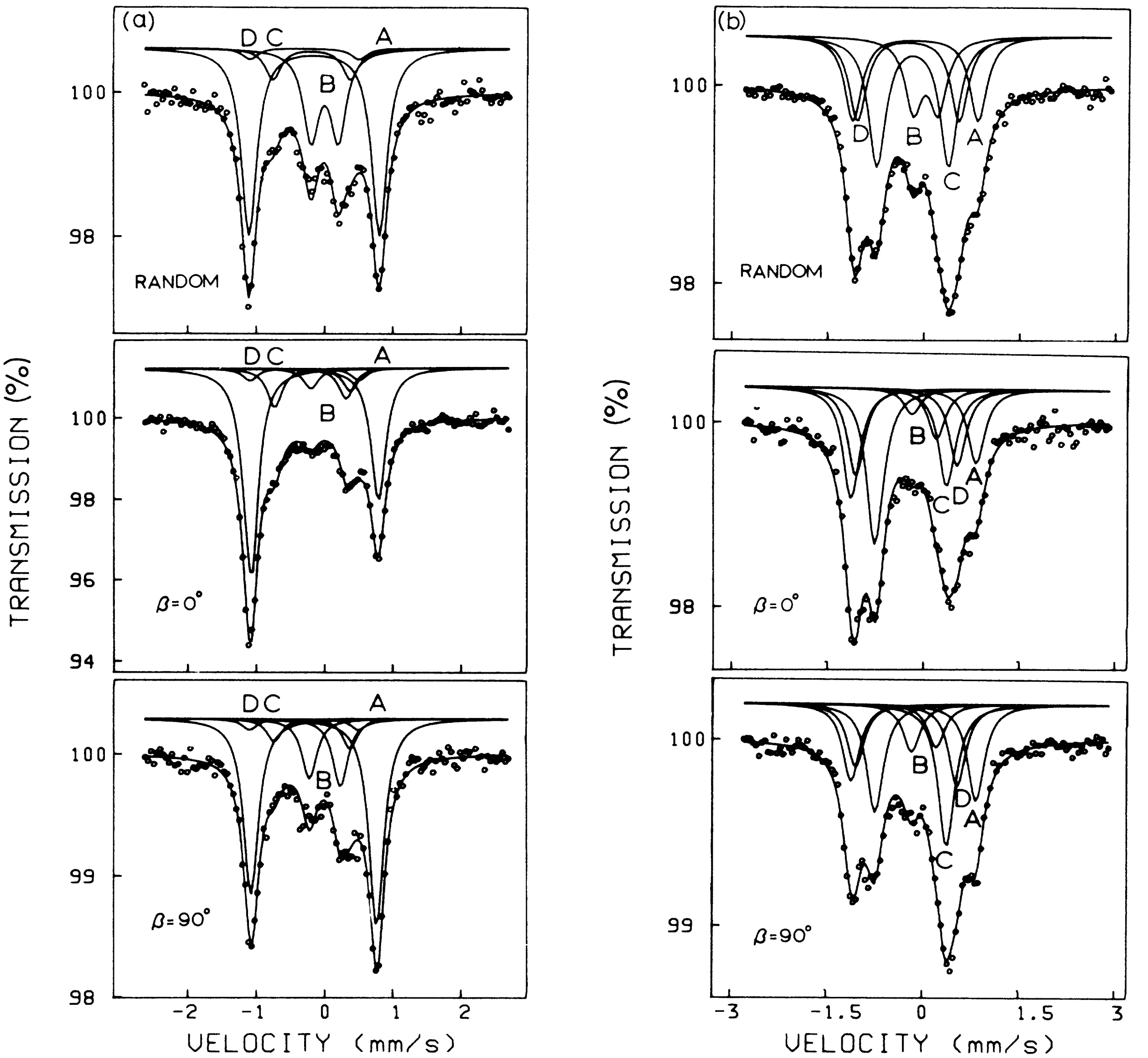

FIG. 1. Spectra of sintered $YBa_2(Cu_{0.985}Fe_{0.015})_3O_{7-\delta}$ samples (random) in (a) an oxygen desorbed state ($\delta = 0.17$) and (b) virgin state ($\delta \simeq 0.05$). Each vertical panel displays spectra of the same sample in an aligned state and examined at indicated tilt angles β in Mössbauer experiments at 300 K using ^{57}Co in Pd as an emitter.

asymmetries I_+/I_- are a direct manifestation of the $P_{\pi \atop \sigma}(\theta,\phi)$ angular distributions, which are given[11] by

$$P_{\pi \atop \sigma}(\theta\phi) = \frac{1}{2} \pm \frac{1}{8(1+\eta^2/3)^{1/2}}[3\cos^2\theta - 1 + \eta\sin^2\theta\cos2\phi] , \qquad (1)$$

where θ,ϕ define the γ-ray direction in the principal axis system of the EFG tensor.

Consider an Fe site which has a square-planar coordination that would result if Fe replaced a Cu(1) chain site in the orthorhombic structure. Symmetry requires the principle EFG axis V_{zz} at such a site to be the local fourfold axis (i.e., the a axis) with V_{xx} and V_{yy} lying along the c and b axes. The EFG should be axially symmetric, i.e., $\eta = 0$. For γ rays propagating along the c axis ($\beta = 0$) at such a site, θ is always $\pi/2$ and the ratio P_π/P_σ is 0.6 from Eq. (1). At a nonzero tilt angle β, the crystallite random orientation in the basal plane leads to $\langle\cos^2\theta\rangle = \sin^2\beta/2$ and $\langle\sin^2\theta\cos2\phi\rangle = (3\cos^2\beta - 1)/2$, so that

$$P_{\pi \atop \sigma}(\beta) = \tfrac{1}{2} \mp \frac{1}{16(1+\eta^2/3)^{1/2}}\{(1-\eta)[3\cos^2\beta - 1]\} . \qquad (2)$$

The continuous lines drawn in Fig. 2(a) show the ratio $P_\pi/P_\sigma(\beta)$ from Eq. (2) for several η values. A characteristic feature of the plots is their increase with β and asymmetry when $\eta = 0$, but complete symmetry when $\eta = 1$.

Consider next an EFG having its V_{zz} component directed along the c axis, as it would be for Fe replacing Cu(2) layer sites that possess a square pyramidal coordination. When γ rays propagate at a tilt angle β, then, $\theta = \beta$ and

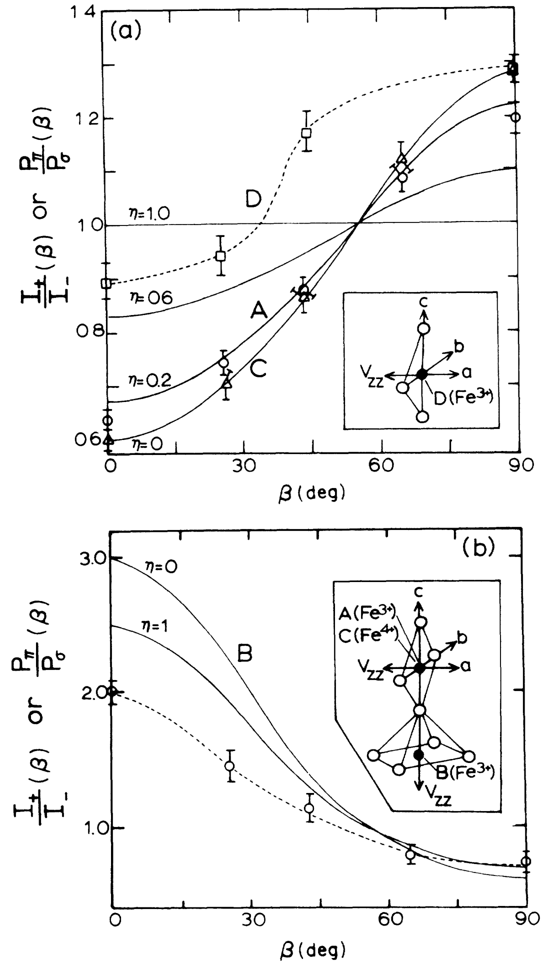

FIG. 2. Tilt-angle (β) variation of observed quadrupolar doublet intensity asymmetry I_+/I_-. (a) for sites A (○), C (△), and D (□); (b) for site B; The smooth curves show plots of $P_\pi/P_\sigma(\beta)$ calculated from Eq. (2) in (a) and Eq. (3) in (b) for indicated η values. The broken line curves for site D and site B are merely a guide to the eye. The insets show suggested configurations of sites A, B, C, and D.

$\langle\cos 2\phi\rangle = 0$ so that Eq. (1) gives

$$P_{\substack{\pi\\ \sigma}}(\beta) = \tfrac{1}{2} \pm \frac{1}{8(1+\eta^2/3)^{1/2}}(3\cos^2\beta - 1)\,. \qquad (3)$$

Figure 2(b) shows the decreasing behavior of $P_\pi/P_\sigma(\beta)$ according to Eq. (3) for the two extreme values, $\eta = 0$ and 1; note that $P_\pi/P_\sigma(0) = 3$ and $P_\pi/P_\sigma(\pi/2) = 0.6$. With these results in hand, we now consider site assignments suggested by our data.

Sites A and C. The $I_+/I_-(\beta)$ trends for sites A and C *uniquely*[13] correspond to $P_\pi/P_\sigma(\beta)$ plots for $\eta \lesssim 0.20$ in Fig. 2(a), identifying the positive velocity resonance of the quadrupole doublet pairs with the π component, and implying a positive sign for both e^2QV_{zz} coupling and eV_{zz} (Ref. 14) at sites A and C. We conclude that, at both these sites, V_{zz} is positive, perpendicular to the c axis and the EFG tensor is nearly axially symmetric ($V_{xx} \simeq V_{yy}$). As discussed above, these restrictions on the EFG are compatible with Fe entering a Cu(1) chain site. The positive sign of V_{zz} is readily traced to the negative oblate charge distribution of the four O^{2-} anions (in xy plane). The sharp and reversible transfer of population strength from C to A site upon oxygen desorption,[8] is strongly suggestive that these sites represent two distinct charge states at the same location; site A: Fe^{3+} and site C: Fe^{4+} [see inset of Fig. 2(b)]. The isomer shift[8] of site A is characteristic of Fe^{3+} while that of site C is similar to that of Fe^{4+} in $SrFeO_3$ (Ref. 15) and, furthermore, the sharp O stoichiometry dependence[8] of the ratio of I_C/I_A resembles the ξ dependence of $[Fe^{4+}]/[Fe^{3+}]$ ratio[15] in $SrFeO_{3-\xi}$. Since the ionic radii of Fe^{3+} and Cu^{2+} are nearly identical, the finite η value reported here for this site may reflect the inequality of Cu–O(1) and Cu–O(4) bond lengths. On the other hand, for Fe^{4+} which has a smaller ionic radius than Fe^{3+}, some rearrangement of the square-planar coordination around Fe^{4+} takes place towards more symmetry as suggested by $\eta = 0$.

Site B. The $I_+/I_-(\beta)$ trend of this site [Fig. 2(b)] coupled with the rather small value of e^2QV_{zz}, suggests either a Cu(2) layer or possibly even a distorted octahedral site. The fact that $I_+/I_- > 1$ at $\beta = 0$ argues that the positive velocity resonance be identified with the π component, so that V_{zz} is directed along the c axis and is positive [inset of Fig. 2(b)]. A square pyramidal or octahedral Fe configuration can also be realized at a Cu(1) chain site if the normally vacant O(5) oxygen sites (along a axis) are populated. We label such a site as a B' site. Because the B' sites have their V_{zz} directed perpendicular to the c axis, their presence will lower the net I_+/I_- asymmetry as observed.

Site D. Two striking features of the $I_+/I_-(\beta)$ trend for this site are the smaller overall change in I_+/I_- with β and the displacement of the crossover point (where $I_+/I_- = 1$) to a smaller tilt angle in relation to site A or C trend. The former feature is the signature of a large $\eta \simeq 0.6$ and the latter of a spatially anisotropic Debye-Waller factor, a point discussed elsewhere. The large η is a significant result, for it rules out symmetric cation configurations with 1, 2, 4, 5, or 6 oxygen neighbors, all of which have $\eta \simeq 0$, namely, a linear (1 or 2), square planar (2 or 4), square pyramidal (5), or octahedral (6) arrangement. A threefold-coordinated Fe chain site having two O(4) and one O(1) oxygen neighbors will give rise to an EFG having $\eta \simeq 1$. However, this particular site cannot be understood as freely forming in a chain by having an O(1) or an O(4) oxygen site vacant in the vicinity of site A because experiments show[8] that site D is absent in oxygen-deficient ($\delta > 0.5$) tetragonal samples but reversibly appears in oxygen-rich ($\delta < 0.5$) orthorhombic samples. A natural explanation is that this site is associated with chains at (110) twin boundaries. In sintered samples twinning planes proliferate[16] in the orthorhombic phase and disappear in the tetragonal phase, behavior that is also displayed[8] by the site D integrated strength (I_D/I). Normally, a Cu(1) chain site at a (110) twinning plane is fourfold coordinated. A threefold-coordinated Fe chain site (with $\eta \simeq 1$) in such a plane will result if one of the two possible O(1) oxygen neighbors of the dopant is vacant, as shown in inset of Fig. 2(b). The role of twinning planes for high-T_c superconductors is of intense current interest[16] and site D might serve as a twinning plane probe in bulk samples.

As with recent neutron diffraction work,[17] our results emphasize the extra information available from aligned samples and confirm that at least four distinct sites are involved for iron in the 1:2:3 structure. Since all the metallic dopants studied[1,2] so far have a similar effect on the superconducting properties, it is likely that multiple sites will prove to be a ubiquitous feature of doping in the 1:2:3 system.

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[13] The positive sign of e^2QV_{zz} derives from the fact that for $\eta = 0$ and $\beta = 0$, $I_+/I_- = P_\pi/P_\sigma = 0.6$. The negative sign of e^2QV_{zz} would require $I_+/I_- = P_\sigma/P_\pi$ which is clearly ruled out at $\beta = \pi/2$, since $I_+/I_- = 1.28$ but $P_\sigma/P_\pi = 0.78$.

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