Motional Broadening of ^{57}Fe Mössbauer-Effect Resonance in Cuprate Superconductors

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The temperature dependence of the ^{57}Fe resonance in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ samples shows evidence of a discontinuity in the observed linewidth $\Gamma(T)$, isomer shift, and quadrupole splitting at T_c. $\Gamma(T)$ is found to increase precipitously at $T < T_c$ with the excess width $\Delta\Gamma(T)$ thermally activated. This behavior is a signature of a fluctuating electric-field gradient in the planes with the fluctuations slowing down in the superconducting phase.

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There are growing indications from recent experiments that the onset of superconductivity in the cuprates leads to a local structural distortion in the CuO_2 planes. For example, ion channeling [1], extended x-ray-absorption fine-structure spectroscopy [2], and partial distribution functions deduced from pulsed neutrons [3] provide clear evidence of changes in the Cu-O interatomic correlations at T_c. These experiments also suggest that the underlying structural distortions are better understood as dynamic rather than static in character. Such local-scale information on the planes accessible from experiments is critical to understanding the elusive origin of the superconductivity in the cuprates.

In this Letter, we provide new evidence of a dynamic anomaly at T_c in Fe-doped $YBa_2Cu_4O_8$ obtained using the Mössbauer effect. The results show that the dopant localized in the CuO_2 planes experiences a fluctuating electric-field gradient (EFG; V_{zz}) due to the vibrational motion of the planar and apical oxygen atoms about an equilibrium value. In the normal phase, $V_{zz}(t)$ fluctuates rapidly ($\Delta\omega\,\tau_c \ll 1$) leading to motional averaging of the nuclear resonance with an observed linewidth given by the natural width (Γ_n) and absorber-thickness broadening. Here

$$\omega(t) = eQ[V_{zz} + \Delta V_{zz}(t)]/\hbar = \bar{\omega} + \Delta\omega(t) \qquad (1)$$

represents the quadrupole coupling frequency which is frequency modulated by the fluctuations $\Delta\omega$ about a mean value $\bar{\omega}$, and τ_c represents the memory time of the fluctuating EFG $[\Delta V_{zz}(t)]$. $\Delta\omega\,\tau_c \ll 1$ implies that the correlation time of the fluctuations τ_c is much smaller than the time $(1/\Delta\omega)$ for the nucleus to sense the fluctuating EFG. In the superconducting phase, τ_c increases, we suppose due to vibrational correlations of the planar oxygen atoms, as holes in the planes progressively exhibit Cooper pairing. In this temperature regime, broadening of the resonance linewidth is observed in proportion to τ_c. Furthermore, the isomer shift $\delta(T)$ and quadrupole splitting $\Delta(T)$ display discontinuities at T_c that are consistent with the slowing down of the envisaged stationary relaxation process in the superconducting phase.

The crystal structure of the 1:2:4 phase [4] closely parallels that of the 1:2:3 phase: Both phases contain the all-important pairs of CuO_2 planes. These pairs of planes are separated by floppy linear CuO_3 chains in the 1:2:3 phase but by double chains (Cu_2O_4) or ribbons in the 1:2:4 phase. The chemical stability and mechanical rigidity of the ribbons [5] over the linear chains is primarily responsible for the higher oxygen stability of the 1:2:4 phase. This aspect of structural chemistry, we believe, is also responsible for the qualitatively different Fe-doping behavior in these phases, largely because the ribbons possess an average coordination number (2.2) which is larger than that of the chains (1.7) but close to the rigidity percolation threshold (2.4) and this makes them mechanically stiffer and less amenable to distortion to locally satisfy the chemical bonding requirements of the dopant. Thus while the Fe dopant largely (~90%) replaces Cu(1) sites in the floppy linear chains of the 1:2:3 phase [6], it replaces Cu(2) (planar) sites exclusively in the 1:2:4 phase [7]. It is for this reason that at low Fe-doping concentrations ($0 < x < 0.03$), $T_c(x)$ changes little with x in the 1:2:3 phase but displays a rather steep decrease of ~8 K/at.% in the 1:2:4 phase [7]. The oxygen stability of the ribbons, the absence of twinning, the absence of magnetism, and the dopant site occupancy in the planes makes the 1:2:4 phase more convenient for studying the superconducting behavior of CuO_2 planes by means of the Fe probe.

Single-phase $YBa_2(Cu_{1-x}Fe_x)_4O_8$ samples in the concentration range $0 < x < 0.03$ were prepared [7] by high-T (900 °C), high-P (2.4 GPa) sintering of Fe-doped 1:2:3 and CuO precursors. Mössbauer-effect measurements in the range 12 K $< T <$ 300 K were performed using a closed-cycle He cryostat (model DMX-20 from APD Cryogenics, Inc.), a T controller, and Si diodes to regulate the absorber temperature to ± 0.1 K. In these experiments, the γ-ray source (^{57}Co in Pd; 14.4 keV) was held at room temperature. Spectra were least-squares fitted with a superposition of four quadrupole doublets, labeled A, C, B', and B using software developed to run a 286-based processor. In the fits the centroid and doublet splitting of the majority sites (B,B') were kept unrestricted while only the doublet splitting for the minority sites (A,C) was kept fixed to values determined previously (see Table I) from 1:2:3 samples. Site parameters and assignments discussed earlier [7] are summarized in Table I. Briefly, the majority sites B and B' represent Fe localized in the planes possessing a quasioctahedral and a square-pyramidal oxygen coordination. The minority

TABLE I. Assignment, isomer shift (δ), and quadrupole splitting (Δ) of Fe sites observed in 1:2:4.

Site	Identification	δ [a] (mm/s)	Δ (mm/s)
B'	Plane; square pyramidal	0.31(1)	0.77(1)
B	Plane; quasioctahedral	0.15(1)	0.40(1)
C	Chain	0.09(1)	1.16(1)
A	Chain	0.04(2)	1.84(1)

[a]Relative to α-Fe at 300 K.

sites A and C, on the other hand, represent Fe localized in linear chains; such chains in the 1:2:4 phase are visualized as stacking faults.

Spectra of a 2%-Fe-doped 1:2:4 sample taken at 63 and 25 K appear in Fig. 1. These spectra show that the B' doublet dominates the line shape and accounts for nearly 70% of the total resonant intensity. At low T, the size of the resonant effect decreases and the width of the lines increases. Figure 2 shows the T dependence of the observed linewidth $\Gamma(T)$, the Debye-Waller factor $f(T)$, and the dc susceptibility $\chi(T)$ taken with a vibrating-sample magnetometer. From the $\chi(T)$ data, T_c of the 2%-Fe-doped sample is established to be 62.0(5) K, compared to $T_c = 80$ K for the pristine 1:2:4 material [Fig. 2(a)]. We note from Fig. 2(b) that $\Gamma(T)$ remains nearly constant in the normal phase, but increases precipitously in the superconducting phase. The Debye-Waller factor $f(T)$, proportional to the area under the line shape, on the other hand, remains continuous across T_c [Fig. 2(c)]

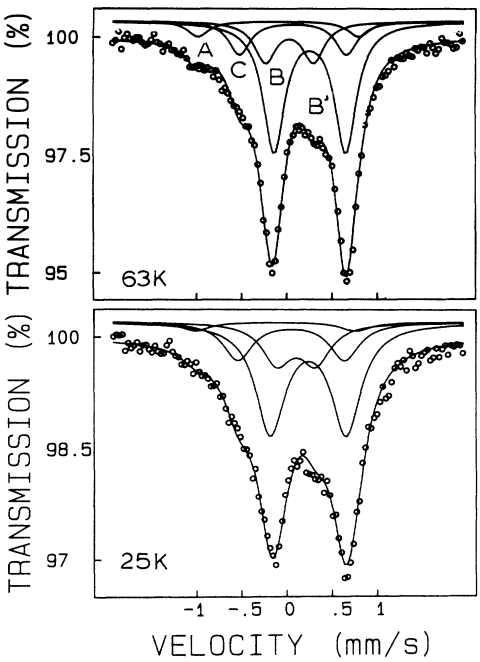

FIG. 1. Spectra of a 2%-Fe-doped 1:2:4 sample taken at indicated temperatures.

but reveals a remarkable drop at $T \lesssim T_s = 30$ K, identified as a softening temperature for lattice vibrations. It is important to stress that these $\Gamma(T)$ and $f(T)$ results are independent of the way one deconvolutes the spectral line shapes largely because $\Gamma(T)$ is determined by the width of the majority (B') site doublet while $f(T)$ is determined by the total integrated area under the resonance. Figure 3 shows a plot of the T dependence of $\delta(T)$ and $\Delta(T)$ for

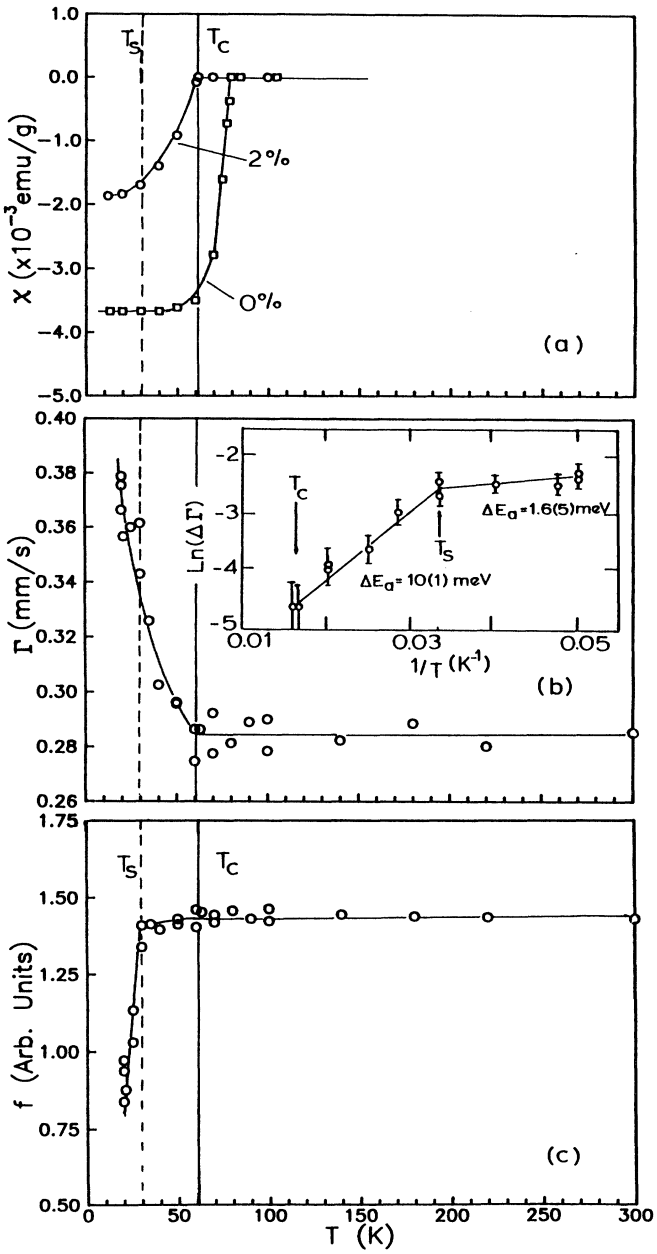

FIG. 2. T dependence of (a) dc susceptibility $\chi(T)$, (b) observed FWHM $\Gamma(T)$, and (c) Debye-Waller factor $f(T)$ for a 2%-Fe-doped sample. Inset of panel (b) shows a plot of $\ln(\Delta\Gamma)$ against $1/T$ displaying activated behavior of the excess linewidth ($\Delta\Gamma$) in the superconducting phase.

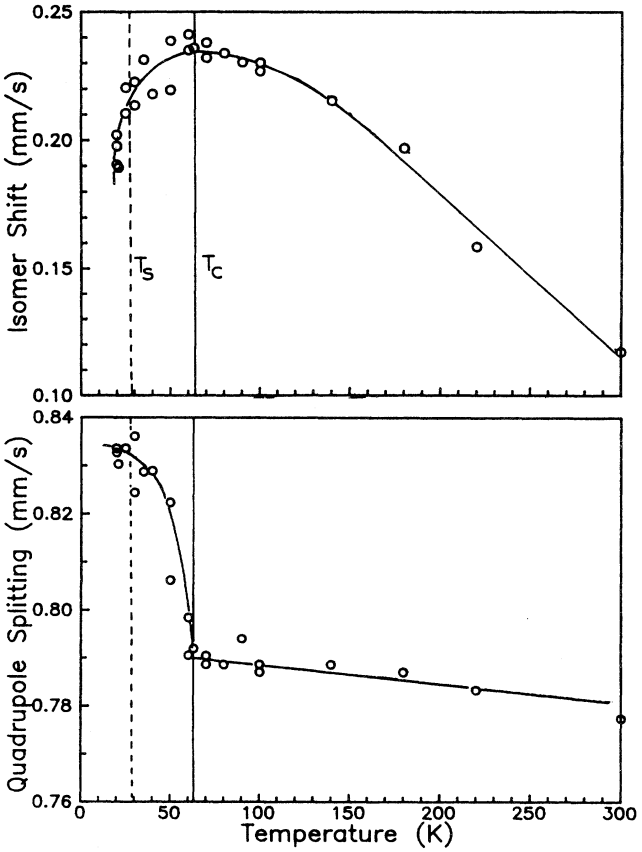

FIG. 3. T dependence of the B' site quadrupole double splitting (Δ) and isomer shift (δ) displaying discontinuities at T_c.

the majority site B' and these display clear evidence of discontinuities at T_c. Note that $\delta(T)$ increases with decreasing temperature as expected, and this behavior is suddenly interrupted at T_c and reversed at $T \lesssim T_c$. Concomitantly, $\Delta(T)$, which remains more or less T independent in the normal phase, exhibits a sharp increase at $T < T_c$. These anomalies are also found at other Fe-doping concentrations ($0 < x < 0.03$) and are quite reproducible.

These T-dependent Mössbauer-effect results are characteristic of a stationary relaxation process, i.e., an extranuclear field (in our case the EFG) fluctuating about an equilibrium value [8,9]. The theory of Mössbauer line shapes in the presence of stationary relaxation has been extensively developed [8–10]. In the normal phase, motional narrowing results because $\tau_c \sim 10^{-12}$ s, determined by the oxygen vibrational frequency, is much less than $1/\Delta\omega \gtrsim \hbar/2\Delta \sim 10^{-8}$ s, determined by the nuclear quadrupole coupling energy ($\sim 2\Delta$). For stochastic fluctuations in the intermediate relaxation regime ($\Delta\omega\tau_c \sim 1$) the resonance line shape continues [9,11] to be Lorentzian,

$$I(\omega) \sim \frac{\Gamma/2+\gamma}{(\omega-\bar{\omega}-\xi)^2+(\Gamma/2+\gamma)^2}, \tag{2}$$

but with an excess width $\Delta\Gamma = \gamma$ and a centroid that is shifted to lower energies by an amount $\bar{\omega}+\xi$. γ and ξ, given by

$$\gamma = \overline{(\Delta\omega)^2}\tau_c = \int_0^\infty dt\, \overline{\Delta\omega(t)\Delta\omega(0)}, \tag{3}$$

$$\xi = \overline{(\Delta\omega)^3}\tau_c' = \int_0^\infty dt \int_0^t \overline{\Delta\omega(\tau)\Delta\omega(t')\Delta\omega(0)}\, dt', \tag{4}$$

represent second-order and third-order correlation functions of the fluctuations. A semilogarithmic plot [inset of Fig. 2(b)] of the excess linewidth $\Delta\Gamma(T) = \Gamma(T \lesssim T_c) - 0.28$ mm/s as a function of $1/T$ displays an activated behavior of $\tau_c = \tau_c^0 \exp(\Delta E_a/kT)$ with two slopes: $\Delta E_a = 10(1)$ meV in the range $T_s < T < T_c$ and $\Delta E_a = 1.6(5)$ meV at $T \lesssim T_s$.

In superconductors, one expects the vibrational and electronic degrees of freedom associated with the planes to be coupled. This coupling provides for a correlated motion of the oxygen atoms as holes progressively pair at $T < T_c$. The presence of these correlations leads to a qualitative increase in τ_c, and to a reduced mean-squared displacement of the oxygen atoms recently observed in channeling experiments [1]. In our experiments, we understand the increased $\Gamma(T)$ and centroid shift of the resonance to lower energies as the result of an increased τ_c ($\gtrsim 10^{-8}$ s) in qualitative accord with the predictions of Eqs. (3) and (4). Through the fluctuating EFG the Fe dopant in the planes monitors these coherent effects in the superconducting phase. The quadrupole-splitting increase at $T \lesssim T_c$ merely reflects a progressive loss in motional averaging as τ_c increases.

The charge and spin assignment of the dopant (site B') is formally Fe^{3+} high spin ($S_z = \frac{5}{2}$) as inferred from the magnitude of the shift δ (Table I) and recently confirmed by a measurement of the internal magnetic field (44.6 T) at 4.2 K by us. Thus the highest occupied states of Fe^{3+}, as those of Cu^{2+} cation in the planes, are the half-filled antibonding $d_{x^2-y^2}$ states [12] at E_F which are strongly hybridized with the O $p\sigma$ states. A possible interpretation of the present results is that the EFG fluctuations derive from an in-plane breathing mode [13] that modulates the Fe $3d_{x^2-y^2}$ level population at E_F. The activation energy of 10(1) meV associated with $V_{zz}(t)$ may then represent the superconducting gap opening at E_F in the planes. For $\Delta E_a = 10(1)$ meV and $T_c = 62$ K, we note that the ratio $2\Delta E_a/kT_c = 3.6(3)$, a value close to the BCS prediction [14], but this may be coincidental, as other experiments typically show a larger ratio [15] in the range 6–8. These results taken together provide striking evidence of a dynamic slowing down of the EFG in the planes at $T \lesssim T_c$ that may be associated with the opening of the superconducting gap at E_F. The absence of these physical effects in the Fe-doped 1:2:3 phase [16] is the consequence of the dopant largely localizing in the chains in solid-state-reacted bulk samples as we eluded to earlier.

A surprising feature of the present results [Fig. 2(c)] is

the continuous $f(T)$ variation across T_c and the remarkable drop at T_s. The anomaly at T_s may represent a displacive transition in the CuO_2 planes resulting from vibrational mode softening. It is instructive to recall here that in the $10\ K < T < T_c$ temperature range, the "b" cell-length variation in the 1:2:4 phase is rather anomalous [4]; one observes a negative thermal expansion along the b axis ($db/dT < 0$) but a positive one along the a and c axes. This may represent a soft-mode-induced strain frozen in along the b axis. Finally, the flat $f(T)$ profile in the $30\ K < T < 300\ K$ range [Fig. 2(c)] observed presently is parallel to the one noted earlier [17] for Fe dopant in ThO_2. These flat $f(T)$ profiles constitute evidence of Fe locally moving in an anharmonic potential such as a flat-bottomed or double-well potential, probably in response to the nearest-neighbor oxygen sites vibrating anharmonically. These results are in sharp contrast to the harmonic $f(T)$ variation noted earlier for the rare-earth [18] and Fe-dopant sites segregated in chains [16] of the 1:2:3 phase.

In summary, we report for the first time evidence of two distinct anomalies in the 1:2:4 phase; one electronic and the other vibrational in character. Line broadening of the ^{57}Fe Mössbauer-effect resonance is observed in the superconducting phase and ascribed qualitatively to a slowing down of the fluctuating EFG in the planes. Second, a precipitous drop in the Debye-Waller factor is observed at $T \lesssim 30$ K and is associated with a vibrational mode softening in the planes. There are preliminary indications that these Mössbauer-effect anomalies are present in the thallates as well, thereby suggesting a more generic physical origin of these T_c-related anomalies tied to the planes of the cuprate superconductors. A successful theory of these materials must account for these phenomena.

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