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Exchange-driven ferric low-spin high-spin transition in iron-doped $YBa_2Cu_3O_7$

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Mössbauer Zeeman measurements at 4.2 K on $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ ($\delta \approx 0$) with $x = 0.1$, 0.2, and 0.4 establish that the major feature at $x = 0.1$ corresponds to a low-spin (LS) $3d^5$ ($S = \frac{1}{2}$) configuration, but that for $x \gtrsim 0.2$ an increasing fraction of this LS spectrum transforms to a high-spin (HS) $3d^5$ ($S = \frac{5}{2}$) counterpart. An explanation is given in terms of a LS-HS transition driven by σ-bonded superexchange interactions between nearest-neighbor ferric ions in their HS states.

The superconducting orthorhombic O phase of $YBa_2Cu_3O_7$ is known to be only marginally stable with respect to an anionically disordered semiconducting tetragonal T phase of equal composition. One method of inducing the O-to-T phase transition is via cation doping in the fashion $YBa_2Cu_{3-x}M_xO_7$ with a small trivalent dopant such as $M = Fe$ or $M = Al$.[1] These ions substitute very dominantly in the chainar [or Cu(1)] sites of the O phase,[2,3] breaking up the Cu(1)-O chains via electrostatic forces which prefer a higher M-site oxygen coordination z than the $z = 4$ available without anion disordering.

Our earlier room-temperature Mössbauer study of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ ($\delta \approx 0$, $0.01 \leq x \leq 0.2$) (Ref. 2) deduced that, although the O and T phases coexist over a wide range of x, the structure is already quite dominantly T phase at $x = 0.1$. In this oxygen-disordered T phase the Cu(1)-substituted ferric ions reside in sites of only two different local ligand coordinations, $z = 5$ (capped tetragonal, labeled V_5) and $z = 2$ (axial, V_2), with the V_5 sites being increasingly preferred as x increases.[2] In this same phase magnetic susceptibility measurements[1] between 50 and 300 K exhibit an iron contribution of Curie-Weiss form $C/(T+\theta)$ with a Curie amplitude $C = Ng^2\mu_B^2 \times S(S+1)$ (in conventional magnetic notation) in which $S = 1.5 \pm 0.2$, indicative of a spin-$\frac{3}{2}$ or low-spin (LS) quantum state for $Fe^{3+}(3d^5)$.

In an effort to confirm the presence of the LS quantum state by direct observation, using Mössbauer Zeeman spectroscopy, we have uncovered a new and intriguing phenomenon. Thus, while a Zeeman-split Mössbauer spectrum is observed at 4.2 K for all iron concentrations $x \gtrsim 0.1$, and a characteristic LS spectrum does dominate the response for $x \lesssim 0.2$, an additional feature—in the form of a strong high-spin (HS) Zeeman component—rapidly develops for $x \gtrsim 0.2$ to dominate the spectrum at $x = 0.4$ (Fig. 1). The results suggest the development of a LS-HS transition at low T as a function of $x \gtrsim 0.2$. The only other possibility, that iron for $x > 0.2$ suddenly begins to populate a new site [Cu(2)?] with a permanent HS configuration can be excluded since, from Fig. 1(c), fully 75% of the iron sites are HS at $x = 0.4$, leaving significantly fewer LS sites at this concentration then at $x = 0.2$. Additional evidence that iron substitutes only for Cu(1) at least to $x = 0.23$ is available from recent neutron and electron diffraction studies by Bardet *et al.*[4]

The explanation can be found by deriving the d-electron eigenorbitals in capped tetragonal oxygen ligand coordination (on which V_5 sites the vast majority of ferric ions reside for $x \gtrsim 0.1$).[1,5] Not only are the LS ($S = \frac{1}{2}$) and HS ($S = \frac{5}{2}$) configurations for $3d^5$ found to be close in energy but, of these two, only the HS one possesses a magnetically active σ-bonded d orbital, giving rise to

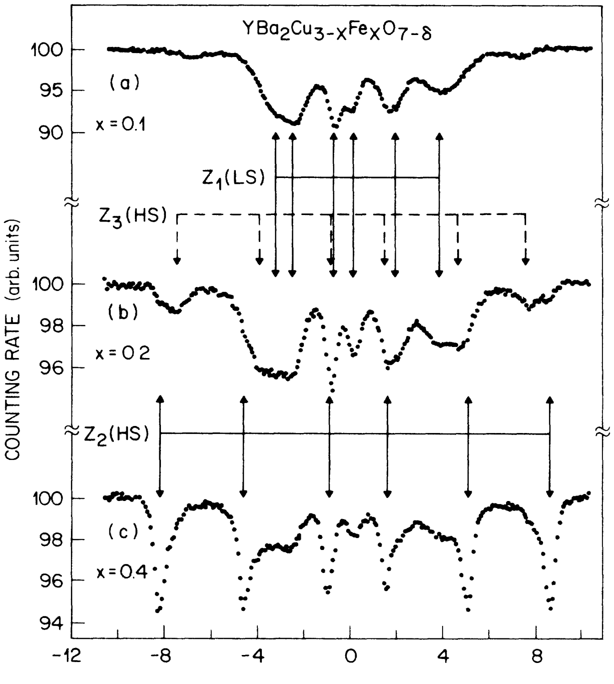

FIG. 1. 4.2-K Mössbauer Zeeman spectra for $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ for iron concentrations (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.4$. We show the positions of the six Zeeman lines L_i of Eq. (1) for each of the three spectra Z_i ($i = 1$–3) defined in Table I.

large (antiferromagnetic) exchange interactions $2J\mathbf{S}_i \cdot \mathbf{S}_j$ between Cu(1)-plane nearest-neighbor (NN) iron spins (details follow). Therefore, some HS energy levels, E(HS), but not their LS counterparts E(LS), are dramatically lowered by (antiparallel) paramagnetic NN spin correlations $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ which can reach values approaching saturation, viz., $-S(S+1)$, in disordered two-dimensional lattices[6] at low temperatures T. If $E(\text{LS}) < E(\text{HS})$ in the absence of the exchange terms, then a LS-HS can occur as T is lowered, driven by two-dimensional paramagnetic spin correlations, provided that the iron concentration x is large enough.

The ^{57}Fe Mössbauer absorption spectra were obtained in a standard transmission geometry with a ^{57}Co-in-Rh source. Details about the absorber preparation using enriched ^{57}Fe were given in Ref. 1. The 4.2-K Mössbauer Zeeman spectra for $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7-\delta}$ for $x = 0.1$, 0.2, and 0.4 are given in Fig. 1.

A single-site Zeeman spectrum for ^{57}Fe contains, in general, six component lines L_i $(i = 1-6)$ which, in order of increasing velocity, are positioned to lowest order in field gradient at[7]

$$\begin{aligned}
L_1 &= \Delta_{\text{IS}} - g_1\mu_N H + u \,, \\
L_2 &= \Delta_{\text{IS}} - g_2\mu_N H - u \,, \\
L_3 &= \Delta_{\text{IS}} - g_3\mu_N H - u \,, \\
L_4 &= \Delta_{\text{IS}} + g_3\mu_N H - u \,, \\
L_5 &= \Delta_{\text{IS}} + g_2\mu_N H - u \,, \\
L_6 &= \Delta_{\text{IS}} + g_1\mu_N H + u \,,
\end{aligned} \tag{1}$$

in which $g_1 = 0.2448$, $g_2 = 0.1418$, $g_3 = 0.0388$; Δ_{IS} is the isomer shift, H is the hyperfine field, and u is the first-order quadrupole shift.

In the spectra of Fig. 1, parts or all of three separate Zeeman spectra Z_i $(i = 1-3)$ can be discerned, with the respective Δ_{IS}, H, and u values as given in Table I. The components $Z_i(L_i)$ are shown in the figure. Spectrum Z_1, which completely dominates at small $x \approx 0.1$, has a hyperfine field essentially equal to that expected for $S = \frac{1}{2}$ in the absence of any significant supertransferred[8] component H_{ST} (viz. $H \approx 150S + H_{\text{ST}}$ for $\Delta_{\text{IS}} \approx +0.1$,[9] H in kOe). Spectrum Z_2, which develops rapidly for $x \gtrsim 0.2$, has a hyperfine field corresponding to HS $3d^5$ configuration $S = \frac{5}{2}$ together with a significant additional supertransferred component ≈ 75 kOe ($H \approx 180S + H_{\text{ST}}$ for $\Delta_{\text{IS}} \approx 0.4$).[9] Spectrum Z_3, which is a minor but recognizable feature at all x, is evidently also $S = \frac{5}{2}$ but with essentially zero H_{ST}.

TABLE I. The Zeeman hyperfine parameters associated with the three discernable component spectra Z_i $(i = 1-3)$ in the 4.2-K Mössbauer spectra of Figs. 1(a), 1(b), and 1(c). Isomer shifts (IS) given with respect to iron metal at room temperature.

i	LS or HS	H (kOe)	u (mm/s)	Δ_{IS} (mm/s)
1	LS	225 ± 5	$+0.3 \pm 0.1$	$+0.1 \pm 0.05$
2	HS	525 ± 5	0.05 ± 0.05	$+0.4 \pm 0.05$
3	HS	460 ± 10	0.1 ± 0.1	$+0.4 \pm 0.1$

The minor spectrum Z_3 seems not to be involved in the LS-HS transition and we tentatively associate it with a small concentration of Fe replacing Cu(2) in CuO_2 planes, the condition $H_{\text{ST}} \approx 0$ then reflecting the fact that NN iron pairs in these sites are rare if Fe enters in a quasirandom fashion.

The LS-HS transition therefore involves spectra Z_1 and Z_2, which are to be associated with Cu(1)-substituted iron at the overwhelmingly dominant V_5 oxygen coordination (Fig. 2). The electronic states of iron d electrons in arbitrary ligand coordinations can be derived[10] by standard crystal-field methods.[11,12] In Fig. 2 we show these levels E_i not only for V_5, but for the minority V_2 site and (for reference) an octahedral V_6 site as well. The five d-electron energies E_d are expressed, for each V_n, with respect to an absolute zero $\sum_d E_d = 0$ and in the commonly used[13] Dq units, defined such that the octahedral splitting is $10Dq$. The actual levels in twofold and fivefold oxygen coordination in the T phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ will not correspond precisely to the model adopted, which presupposes an exactly equal chemistry for each ligand and uses free-ion values for the d orbital radial dimensions, but should have at least semiquantitative validity.

Populating these V_n levels with the five d electrons of the ferric ion ($3d^5$), each enters with spin parallel to the resultant of those already present so long as the "Hunds rule" energy E_H is larger than the difference in energy between the competing "parallel-spin" and "paired-spin" crystal-field levels. Experimentally, Dq for Fe^{3+} in V_6 oxygen coordination is known to be ≈ 14000 cm^{-1} ($\pm 10\%$) (Refs. 13 and 14) while E_H is of order 30000

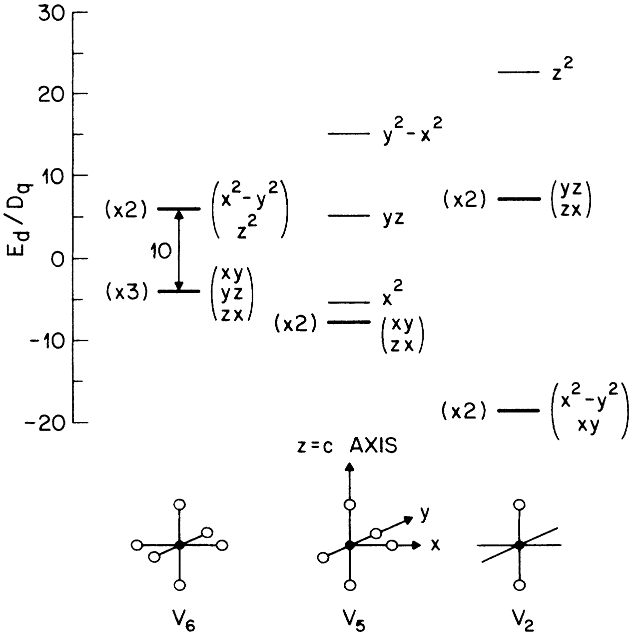

FIG. 2. The d electron eigenstates and energy levels E_d of iron in sixfold, fivefold, and twofold oxygen coordination, with axes x,y,z as sketched on the schematic ligand configuration for V_5. Energy units Dq are chosen such that the triplet-doublet splitting in V_6 octahedral coordination is $10Dq$ by definition.

cm^{-1}. Thus, $R=E_H/Dq\approx 22$ for V_6. In other ligand coordinations R is less precisely known but is probably within the range $15<R<30$. From Fig. 2, we estimate the possible ground-state configurations for V_5 and V_2

$$V_5\text{: } S=\tfrac{3}{2} \text{ if } R<23;\quad S=\tfrac{5}{2} \text{ if } R>23\,; \tag{2}$$

$$V_2\text{: } S=\tfrac{1}{2} \text{ if } R<26;\quad S=\tfrac{3}{2} \text{ if } R>26\,. \tag{3}$$

Since the room temperature Δ_{IS} for both these T-phase sites is essentially the same,[2] the correct spin state at this temperature must be LS ($S=\frac{3}{2}$) for both, implying that R is larger for axial than capped tetragonal chemistry.[15]

The LS-HS transition can now be rationalized provided only that the two closely spaced d levels (viz. the singlet x^2 and doublet xy, zx) are reversed at the Cu(1)-plane V_5 site from that depicted in Fig. 2. Consider a NN pair of V_5-site ferric ions in the Cu(1) plane. With the singlet x^2 orbital lowest, the LS state has its Cu(1)-plane σ orbitals either empty (y^2-z^2) or doubly occupied (x^2); and both consequently nonmagnetic. LS exchange interactions are consequently weak, in agreement with the small H_{ST} of Z_1. However, in the HS state, all five d orbitals are singly occupied and magnetic. As a result, strong antiferromagnetic exchange can now take place via σ-bonded orbitals in both the x and y directions, to as many as three NN irons, if they are present. It also follows that the LS state local d electrons contribute extensively to electric field gradients for both V_5 and V_2, probably dominating lattice contributions.[16] We note only that for the dominant V_5 site, for which the local d-electron contribution is expected to be negative and parallel to x (see Fig. 2), the u shift of $+0.3\pm0.1$ (Table I) is consistent with these conditions and with the known pure quadrupole splitting magnitude of 1.04 mm/s (Ref. 2) if the magnetic moment tends to order perpendicular to x (almost certainly parallel to z, i.e., the c axis) as $T\rightarrow 0$.

Since V_2 sites have no Cu(1)-plane oxygen ligands, no exchange can ever arise involving these sites and they remain LS throughout.[17] The LS-HS transition therefore involves only Cu(1)-plane V_5 sites [each threefold oxygen coordinated in the Cu(1) plane] and, in particular, clusters of NN irons on these sites, ranging from dimers, trimers, n-mers, etc., right up to the infinite cluster if x is large enough.

The most basic model can be developed by first considering a dimer. Let the LS state $S=S_0=\frac{3}{2}$ be lower in energy than the HS state $S=S_1=\frac{5}{2}$ by an energy Δ for the isolated monomer. Assuming a full quenching of orbital moments and ignoring dimer exchange except between HS configurations, we write a dimer spin-Hamiltonian involving spins at sites a and b in the form

$$\begin{aligned}\mathbf{H}=(\hat{\eta}_a+\hat{\eta}_b)\Delta+2J\hat{\eta}_a\hat{\eta}_b(\mathbf{S}_\eta)_a\cdot(\mathbf{S}_\eta)_b\\ -g\mu_B[(S_\eta^z)_a+(S_\eta^z)_b]H^z\,,\end{aligned} \tag{4}$$

in which $\hat{\eta}_a$ and $\hat{\eta}_b$ are operators with eigenvalues $\eta=0$, 1; and H^z is an applied field parallel to z. It can be solved exactly for the magnetic response. However, here we need focus only upon the zero-field eigenstates $E(\eta_a,\eta_b)$, viz:

$$\begin{aligned}&E(0,0)=0,\quad E(0,1)=E(1,0)=\Delta\,,\\ &E(1,1)=2\Delta+J[S'(S'+1)-2S_1(S_1+1)]\,,\end{aligned} \tag{5}$$

where $S'=0,1,\ldots,2S_1$. The ground state is the LS-LS state $E(0,0)$ if $\Delta>JS_1(S_1+1)$, or the singlet $S'=0$ HS-HS state $E(1,1)$ if $\Delta<JS_1(S_1+1)$.

For larger n-mer clusters the mathematics increases in complexity, but the basic nature of the possible ground states remains clear, being fully LS or fully HS depending upon whether Δ is $>$ or $<mJ\mathcal{S}^2$, respectively, where m is the mean number of exchange paths per spin (monotonically increasing from 1 to 3 as n goes from 2 to ∞) and $\mathcal{S}^2$ is a number between S_1^2 and $S_1(S_1+1)$. We note, in particular, that whereas the LS state is highly (viz. $4n$-fold) degenerate within the model, the HS state is a singlet (even n) or doublet (odd n) representing basically a fully aligned spin-$\frac{5}{2}$ antiferromagnetically correlated cluster. Thus, if $\Delta/J=m\mathcal{S}^2$ with m having some value between 1 and 3, then the exchange is large enough to produce a HS ground state for larger clusters but not for smaller ones.

The case for iron-doped $YBa_2Cu_3O_{7-\delta}$ ($\delta\approx 0$) can be semiquantitatively assessed from Fig. 1 where we see that about 8% of iron has undergone a $Z_1\rightarrow Z_2$ (LS-HS) transformation at 4.2 K at a concentration $x=0.2$. At this concentration, we see from the room-temperature quadrupole spectra[2] that $x\approx 0.17$ enters V_5 sites and, hence, fills some 25% of the available sites in a complete V_5 sublattice [which contains $\frac{2}{3}$ of the cation sites in the Cu(1) layers when $\delta=0$].[5] Elementary statistics now tells us that if Fe enters randomly into the V_5 sites, then 42% will be monomers, 24% dimers, 13% trimers, 8% tetramamers, etc., and that the last $\approx 8\%$ are filled by n-mers with $n\gtrsim 5$. We conclude that it takes at least a five cluster of V_5 irons to acquire sufficient exchange per iron to produce a HS ground state in this system. If iron clustering occurs at $x=0.2$, as suggested by Ref. 4, then this "critical number" could be significantly larger than five.

If we consider just the lowest two states of an n-mer with a singlet HS ground state and a $4n$-fold degenerate LS state at an energy E_0 above it, then the percentage HS

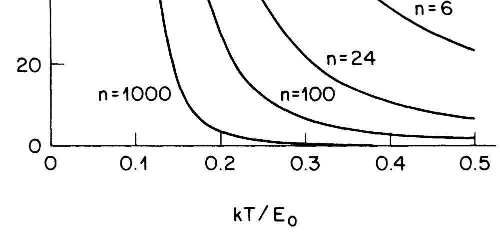

FIG. 3. The percentage of high-spin character p_{HS} as a function of temperature as calculated from Eq. (6) for V_5 ferric clusters containing 6, 24, 100, and 1000 ions.

character $p_{\rm HS}$ at temperature $T \lesssim E_0/k$ for this cluster is

$$p_{\rm HS}(n) = 1/(1+4ne^{-E_0/kT}) , \qquad (6)$$

which is plotted in Fig. 3 for $n = 6$, 24, 100, and 1000. The "sharpness" of the HS → LS transition as a function of T is seen to increase with increasing cluster size. In the limit of the infinite cluster the transition appears to be of first order[18] although, of course, one cannot extrapolate to it via the two-level model of Eq. (6). Although we are not yet able to determine a value for J, it is expected to be very large, in line with that known to exist in other quasi-σ-bonded ferric systems.[19]

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[5] For $\delta \approx 0$, there can be, at most, $2N'/3$ V_5 sites in a Cu(1) plane with N' total cations. With V_5 preferentially occupied to an increasing degree as x increases from zero, we expect the V_5 sites to be filled when x is a little larger than $\frac{2}{3}$. Beyond this concentration, the V_2 site should be filled by default, but it proves difficult to maintain $\delta \approx 0$ (or even to obtain reproducible samples) when $x \gtrsim 0.5$.

[6] Even a fully iron-filled V_5 lattice is, with a two-dimensional coordination number of only 3, unlikely to sustain a long-range order via Heisenberg interactions at any nonzero temperatures.

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[15] Note that the Cu(2) site is also of V_5 coordination. Since Fe^{3+} in this site is HS throughout (Z_3 spectrum of Table I) we infer that $R \approx 23$ for V_5, being slightly larger at the Cu(2) than the Cu(1) (V_5) site, possibly on account of the larger mean ligand bondlengths (i.e., smaller Dq) at the former location.

[16] As suggested by the finding $|u(\mathrm{LS})| \gg |u(\mathrm{HS})|$ in the Z_1,Z_2 spectra of Table I.

[17] The fact that we cannot separately identify them in the Z_1 spectra of Fig. 1 implies either that their population is not sufficiently large to see them or that their u shift is fortuitously close to that of Z_1.

[18] For example, this is true for an "interacting-dimer" model of the infinite V_5 lattice in which the dimer spin correlations within and between dimers are calculated self-consistently.

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