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Spin-Hamiltonian analysis for high-spin Fe^{2+} and Fe^{4+} ions at orthorhombic sites in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ and related oxides

Czeslaw Rudowicz*
Department of Applied Science, City Polytechnic of Hong Kong, Kowloon, Hong Kong

Wan-Lun Yu
Department of Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China

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Spectroscopic properties of the ground state of Fe^{2+} and Fe^{4+} ions located at the Cu(1) planar, pyramidal, and octahedral sites as well as at Cu(2) sites in the high-T_c superconductor $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ are studied. The ground state is, in most cases, an orbital singlet (spin $S=2$) well separated from the higher-lying states. Using the crystal-field results and the extended microscopic theory developed recently, the spin-Hamiltonian parameters b_k^q and g_i are determined for Fe^{2+} and Fe^{4+} ($S=2$) ions for a wide range of values of the microscopic parameters, namely, the spin-orbit (λ) and the spin-spin (ρ) coupling constants, and the energy-level splittings (Δ_i). Very large zero-field splitting (due to large b_2^0) is found for Fe^{2+} at Cu(1) planar sites, whereas rather large zero-field splittings are found for other cases. The variation of b_k^q and g_i with the Fe concentration (x) is also studied. The orthorhombic zero-field splitting parameters b_k^2 ($k=2$ and 4) for Fe^{2+} and Fe^{4+} ions at the Cu(1) octahedral sites become zero at $x>0.04$, where the crystal undergoes a transition from the orthorhombic to the tetragonal phase. Other spin-Hamiltonian parameters are found to be insensitive to x. It appears that, due to the large zero-field splittings, electron-paramagnetic-resonance (EPR) signals cannot be detected in the usual X or Q band. Some guidelines are provided for possible future high-frequency and high-field EPR studies of Fe^{2+} and Fe^{4+} ($S=2$) ions in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. The results of our *model calculations* are applicable also for Fe^{2+} and Fe^{4+} ($S=2$) ions at four-, five-, and sixfold-coordinated sites in other structurally similar oxides.

I. INTRODUCTION

Substitutions of Fe ions in $YBa_2(Cu_{1-x}Fe_x)O_{7-\delta}$ have been investigated extensively in order to find out how much the superconductivity depends on the lattice symmetry and the impurities. The dopant Fe ions lower the superconducting transition temperature T_c in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ (see, e.g., Refs. 1–8) and enter preferentially the Cu(1) sites, whereas the occupation of the Cu(2) sites takes place for higher Fe concentrations.[3,5,8,9–14] The valence state of Fe as determined from x-ray absorption[1,4,5,11,15,16,17] and Mössbauer studies[7–10,16,18–22] appears to be a mixture of +3, +2, and +4. In order to facilitate assignments of the Mössbauer spectra[8–10,13,18–20,22] with appropriate Fe sites, the quadrupole splitting and electric-field gradient (EFG)[9,21,23] have been calculated. Various alternatives for the ligand coordinations and valencies of the Fe sites in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ have been reviewed;[24,25] however, more recent Mössbauer studies[26–33] are partially inconsistent[28,29,31–33] with the analysis,[24,25] thus indicating existence of other Fe sites. Conclusive assignment of the coordination geometries of the various Fe species necessitates careful *model calculations* for not only EFG[26,30] but for other related physical quantities as well. In this paper, we deal with the energy levels and low-lying electronic states of Fe^{2+} and Fe^{4+} ions, which can be investigated experimentally by electron paramagnetic resonance (EPR).

The X- and Q-band EPR spectra have been detected[34–44] for bulk and powdered $YBa_2Cu_3O_{7-\delta}$. The lines at $g_z \sim 2.2$, and $g_y \sim 2.1$, and $g_x \sim 2.0$ were attributed to the Cu^{2+} ions[34–37,39,40] with possible superexchange interaction,[36,42,43], whereas the lines centered at $g=2.312$[38] and $g=2.080$[39] were attributed to Cu^{3+} ions.[38,39] EPR signals of Cr^{3+} in $YBa_2(Cu_{2.94}Cr_{0.06})_3O_{7-\delta}$[35], Gd^{3+} in $Y_{0.999}Gd_{0.001}Ba_2Cu_3O_{6+y}$ ($0 \leq y \leq 1$),[45] and Mn^{2+} in $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$[46–48] have also been observed. The question of magnetic order is crucial for the feasibility of detecting EPR signals. Antiferromagnetic order exists in the nonsuperconducting $YBa_2Cu_3O_{6+x}$ with the Néel temperature $T_N \sim 400 \pm 10$ K.[49,50] In the Fe-doped nonsuperconducting quenched samples, similar T_N's corresponding to the Cu(2) sites have been observed, indicating that T_N is not affected by the presence of Fe impurities.[22,51] Ordering of the Cu(1) sites has been observed at $T_{N2} \sim 200$ K.[52,53] For the superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ samples, the ordering of Fe moments occurs only at very low temperatures ($T \ll T_c$).[6,30,31,54–56] Thus, in principle, it should be feasible to observe EPR signals of Fe ions in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. Such studies could also help resolve other controversial questions concerning the source of EPR signals in $YBa_2Cu_3O_{7-\delta}$ single crystals[45] as well as the nature of magnetic order and its coexistence with superconductivity,[31,57,58] the effective magnetic moment at various Fe sites,[59,60] and the x dependence[6] of T_c in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$.

The EPR silence of Fe in $EuBa_2(Cu_{1-y}Fe_y)_3O_{9-x}$ (Ref. 61) and $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ (Refs. 62–64) indicated by X-band studies has been attributed[63] to antiferromagnetic coupling of Fe cations to either another Fe ion or Cu ion. The question of the Fe^{3+} EPR signals aside, an alternative explanation is plausible for the Fe^{2+} and Fe^{4+} sites. Due to the large zero-field splitting (ZFS)[65] exhibited by Fe^{2+} and Fe^{4+} ($S=2$) ions in crystals,[6] their EPR signals may be well beyond the X band used so far.[61–64] Thus, detection of such EPR signals is feasible only using very high frequencies and/or high magnetic fields[67–69]. This makes direct EPR studies for the $S=2$ ions difficult. An independent insight into the spectroscopic properties of the $S=2$ ions can be gained via a microscopic spin-Hamiltonian (MSH) analysis,[65,70] which is developed here using our earlier results[71] on the crystal-field (CF) energies for Fe^{2+} and Fe^{4+} ions located at the Cu(1) planar, pyramidal, octahedral, and Cu(2) sites in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. The orthorhombic CF is found[71] to be very strong, resulting in a ground orbital singlet, well separated from the excited states for most of the Fe centers considered. This justifies using MSH analysis,[65,70] outlined in Sec. II, to carry out *model calculations* of the Zeeman parameters g_i and the ZFS[72] ones b_k^q. In Sec. III the numerical results are presented and discussed. The parameters g_i and b_k^q are calculated for a wide range of values of the microscopic parameters,[72] namely, the spin-orbit (λ) and the spin-spin (ρ) coupling constants, the energy-level splittings (Δ_i) within the ^5D multiplet of a $3d^4$ or $3d^6$ ion, and the mixing coefficients. The variation of g_i and b_k^q with the Fe concentration (x) is also studied. Values of b_k^q are provided in standardized form,[73,74] i.e., with the ratio b_2^2/b_2^0 in the range (0–1), thus enabling direct comparison with other EPR data. The predicted values of g_i and b_k^q are also applicable for Fe^{2+} and Fe^{4+} ions at four-, five-, and sixfold coordinated sites in other structurally similar oxides. In Sec. IV the conclusions on the assignment of sites and valence states as well as the conditions for detecting EPR signals due to Fe^{2+} and Fe^{4+} ($S=2$) ions are considered.

II. MICROSCOPIC SPIN-HAMILTONIAN ANALYSIS FOR $3d^4$ AND $3d^6$ IONS

In an orthorhombic CF the lowest ^5D multiplet of a $3d^4$ or $3d^6$ ion will be split into five orbital singlets.[75] Hence, provided that the excited states are well separated from the ground state, the spectroscopic properties of the $S=2$ ion are characterized by the spin-Hamiltonian[66]

$$\mathcal{H}=\mu_B(g_xS_xB_x+g_yS_yB_y+g_zS_zB_z)+f_2(b_2^0O_2^0+b_2^2O_2^2)+f_4(b_4^0O_4^0+b_4^2O_4^2+b_4^4O_4^4)\ , \tag{1}$$

using[66] $f_2=1/3, f_4=1/60$ and the Stevens operators $O_k^q(S_x,S_y,S_z)$.[66,72]

Based on tensor algebra and the recoupling of irreducible tensor operator products,[76] the explicit perturbation expressions for the SH parameters in (1) have been derived[77–80] earlier taking the spin-orbit (λ) and the spin-spin (ρ) coupling as perturbation. More recently, the MSH theory has been extended and using an ALTRAN program,[65] the expressions for g_i ($i=x,y,z$) and b_k^q ($k=2,4$) for orthorhombic symmetry (C_{2v},D_{2h},D_2) for the four possible energy-level schemes with a distinct ground state[75] arising from the ^5D multiplet of a $3d^4$ or $3d^6$ ion have been obtained by computer.[81] The SH parameters are thus related to λ,ρ, the CF energies within the ^5D multiplet Δ_i ($i=1$–4), and the mixing coefficient s. The spin-orbit contribution (λ^2) to b_2^q, the only one considered in early literature,[82,83] and additionally the λ^3 and λ^4 ones, are considered. The spin-spin contribution[78,80] ρ, ρ^2, and the mixed one $\lambda\rho$ affect b_2^q significantly. For b_4^q, which are significant for $3d^4$ and $3d^6$ ($S=2$) ions,[84,85] the contributions λ^4, ρ^2, and $\lambda^2\rho$ are considered. For g_i we consider the contributions λ and λ^2. The algebraic results have been incorporated directly into a FORTRAN program.[81]

As pointed out,[73,74] the ratio b_2^2/b_2^0, which describes the degree of rhombicity, can be confined to the "standard" range $0\le b_2^2/b_2^0\le 1$ (i.e., $0\le E/D\le 1/3$[66]) by a proper coordinate transformation. Then the transformed $[b_2^0]$ serves as a measure of the ZFS at zero external magnetic field.[72] The standardization procedure, which yields $0\le b_2^2/b_2^0\le 1$, has been built into the FORTRAN program to facilitate direct comparison with experimental EPR data.

III. SPIN-HAMILTONIAN PARAMETERS FOR Fe^{2+} AND Fe^{4+} IONS IN $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$

The x-ray crystallographic data[3,86] and the superposition model[87] have enabled calculations[71] of the CF energies Δ_i and the mixing coefficient s for the Fe^{2+} and Fe^{4+} ($S=2$) ions at the three Cu(1) sites and the one Cu(2) site in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ for various Fe concentrations. In the superconducting phase, the local symmetry at each site can be considered as the *first kind* orthorhombic[75] symmetry and the energy-level scheme is of the type αOII3 and αOII1 (in the notation of Ref. 75) for Fe^{2+} and Fe^{4+}, respectively. This corresponds to case No. 4 for Fe^{2+} and case No. 1 for Fe^{4+} in the computer program,[81] with appropriate arrangement of the CF energies Δ_i. The CF results[71] are used here as an input for the MSH analysis[81] (Sec. II). The parameters g_i and b_k^q in (1) are evaluated using the range of values of λ and ρ suitable for Fe^{2+} and Fe^{4+} ($S=2$) ions at the four sites in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ as well as in other structurally similar oxides (see below). The validity of the superposition model is well established for the S-state ions in various insulators.[86] The application of this model to the ^5D ($3d^4$ and $3d^6$) ions has not yet been fully tested due to the lack of sufficient experimental data. The present predictions will enable a more detailed fitting of the CF and SH parameters when the pertinent EPR data become available in the future. Then the validity of the model could be verified. On the other hand, not all the site/species combinations may be observed in Fe-doped $YBa_2Cu_3O_{7-\delta}$ samples. However, since the MSH results are also useful for other oxides with similar structure, it is worthwhile to present all eight cases here. If it turns out that the exchange interactions prevent direct EPR studies of Fe-doped $YBa_2Cu_3O_{7-\delta}$, the MSH results

TABLE I. The spin-Hamiltonian parameters for Fe^{2+} ions at various sites in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ with $x=0.01$ calculated using the crystal-field energies Δ_i listed in Table II of Ref. 71 and (a) $\lambda=-100, \rho=0.18$, (b) $\lambda=-80, \rho=0.18$, (c) $\lambda=-100, \rho=0.95$, (d) $\lambda=-80, \rho=0.95$ (all in cm^{-1}). All b_k^q values are in units of cm^{-1}, whereas g_i are dimensionless. The range of magnitudes induced by the uncertainties ($\pm\delta$) in Δ_i is indicated explicitly for two illustrative cases. Standardized values of b_k^q and g_i (see text) are provided in brackets.

A. At the Cu(1) planar sites with the axis system $x\|b, y\|a, z\|c$.

	$a(\Delta)$	$b(\Delta-\delta)$	$b(\Delta)$	$b(\Delta+\delta)$	$c(\Delta-\delta)$	$c(\Delta)$	$c(\Delta+\delta)$	$d(\Delta)$
g_x	1.90	1.85	1.94	1.97	1.77	1.90	1.95	1.94
g_y	1.94	1.90	1.98	2.01	1.81	1.94	1.99	1.98
g_z	2.46	2.46	2.43	2.37	2.42	2.46	2.42	2.43
b_2^0	−27.9	−22.9	−20.5	−17.1	−26.7	−30.0	−26.8	−22.6
b_2^2	0.6	−0.3	1.1	1.4	−4.2	−0.3	−0.9	0.4
b_4^0	4.0	4.9	1.7	0.7	12.2	4.2	1.9	1.8
b_4^2	−4.7	−5.6	−2.0	−0.9	−14.9	−5.4	−2.5	−2.4
b_4^4	0.8	1.0	0.4	0.2	2.8	1.1	0.6	0.5

B. At the Cu(1) pyramidal sites with the axis system $x\|a, y\|c, z\|b$.

	$a(\Delta-\delta)$	$a(\Delta)$	$a(\Delta+\delta)$	$b(\Delta)$	$c(\Delta-\delta)$	$c(\Delta)$ S1(S2)	$c(\Delta+\delta)$ S1(S2)	$d(\Delta)$ S1(S2)
g_x	2.12	2.09	2.07	2.08	2.12	2.09 (2.09)	2.07 (2.07)	2.08 (2.08)
g_y	2.12	2.11	2.10	2.09	2.12	2.11 (2.02)	2.10 (2.02)	2.09 (2.02)
g_z	2.02	2.02	2.02	2.02	2.02	2.02 (2.11)	2.02 (2.10)	2.02 (2.09)
b_2^0	4.9	4.0	3.5	2.8	5.8	5.0 (−5.1)	4.5 (−5.2)	3.7 (−4.3)
b_2^2	0.3	2.0	2.7	1.6	3.5	5.3 (−4.9)	6.0 (−3.7)	4.9 (−3.2)
b_4^0	0.09	0.05	0.03	0.02	0.15	0.08 (0.04)	0.05 (0.03)	0.04 (0.02)
b_4^2	−0.09	−0.01	0.01	−0.002	−0.06	0.02 (0.15)	0.03 (0.10)	0.02 (0.09)
b_4^4	0.13	0.05	0.03	0.02	0.17	0.09 (0.33)	0.06 (0.19)	0.05 (0.17)

C. At the Cu(1) octahedral sites with the axis system $x\|b, y\|a, z\|c$.

	$a(\Delta-\delta)$	$a(\Delta)$	$a(\Delta+\delta)$	$b(\Delta)$	$c(\Delta-\delta)$	$c(\Delta)$ S1(S6)	$c(\Delta+\delta)$ S1(S2)	$d(\Delta)$ S1(S2)
g_x	2.13	2.10	2.09	2.09	2.13	2.10 (2.06)	2.09 (2.09)	2.09 (2.09)
g_y	2.07	2.07	2.07	2.06	2.07	2.07 (2.07)	2.06 (2.06)	2.06 (2.06)
g_z	2.05	2.06	2.06	2.05	2.05	2.06 (2.10)	2.06 (2.06)	2.05 (2.06)
b_2^0	4.9	2.31	1.1	1.20	3.2	0.42 (−1.1)	−0.89 (1.1)	−0.8 (0.9)
b_2^2	−2.6	−1.76	−1.33	−1.16	−2.55	−1.71 (−0.2)	−1.29 (−0.69)	−1.1 (−0.6)
b_4^0	0.21	0.08	0.04	0.03	0.26	0.11 (0.12)	0.06 (0.07)	0.06 (0.06)
b_4^2	−0.15	−0.04	−0.11	−0.01	−0.10	−0.01 (0.03)	0.004 (0.03)	0.004 (0.03)
b_4^4	0.68	0.30	0.16	0.14	1.27	0.60 (0.5)	0.35 (0.30)	0.34 (0.28)

TABLE I. (*Continued*).

D. At the Cu(2) sites with the axis system $x\|c, y\|a, z\|b$.

	$a(\Delta)$	$b(\Delta)$	$c(\Delta-\delta)$ S1(S2)	$c(\Delta)$ S1(S2)	$c(\Delta+\delta)$	$d(\Delta-\delta)$	$d(\Delta)$	$d(\Delta+\delta)$
g_x	2.16	2.18	2.11 (2.11)	2.16 (2.16)	2.19	2.17	2.18	2.19
g_y	2.16	2.18	2.07 (1.81)	2.16 (1.89)	2.17	2.14	2.18	2.17
g_z	1.89	1.94	1.81 (2.07)	1.89 (2.16)	1.93	1.89	1.94	1.96
b_2^0	7.0	6.9	2.0 (−6.7)	7.1 (−7.7)	8.8	5.7	7.3	7.6
b_2^2	5.4	2.5	11.4 (2.8)	8.2 (−6.5)	7.4	5.6	5.4	5.5
b_4^0	3.5	1.5	7.3 (1.9)	4.0 (1.2)	2.5	3.2	1.8	1.1
b_4^2	−3.6	−1.5	−9.0 (12.7)	−3.3 (8.1)	−1.4	−3.5	−1.2	−0.5
b_4^4	0.7	0.3	2.4 (40.3)	0.6 (20.4)	0.2	0.9	0.2	0.1

would still be useful as a first step in the analysis of the properties of Fe^{2+}, Fe^{4+}, and Cu ion clusters.

A. Low Fe concentrations

This subsection deals with the SH parameters for Fe^{2+} and Fe^{4+} ions in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ with $x=0.01$. The values (in cm^{-1}) $\lambda=-100, -80, \rho=0.18, 0.95$ for Fe^{2+}, and $\lambda=125$, 100, $\rho=0.25$, 0.9 for Fe^{4+}, are adopted (see below), yielding four sets of $\{g_i, b_k^q\}$ for each site. The uncertainties $(\pm\delta_i)$ in the CF energies Δ_i, which are due to the ones in the superposition model parameters[71] $\bar{A}_2$, $\bar{A}_4$, and t_4, induce uncertainties in g_i and b_k^q as indicated by lower and upper values or additional columns in the Tables IA–ID and IIA–IID for each case.

No values of λ and ρ are available for Fe^{2+} and Fe^{4+} in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. Justification for the upper (u) and the lower (l) limits of λ and ρ used is as follows. For the free Fe^{2+} and Fe^{4+} ion, the calculations[88] yield $\lambda=-114$ and 125 cm^{-1}, respectively. In crystals, λ is smaller due to the covalency reduction,[72] e.g., $\lambda=-100$ cm^{-1} for Fe^{2+}:MgO,[89] -80 cm^{-1} for $GeFe_2O_4$, Fe^{2+}:$FeCo_2O_4$; and Fe^{2+}:$FeNi_2O_4$.[90] No data for $\lambda(Fe^{4+})$ in crystals are found and $\lambda_l=100$ cm^{-1} is taken. The calculated values[91] 0.18 cm^{-1} and 0.25 cm^{-1} are taken as ρ_l (Fe^{2+}) and ρ_l (Fe^{4+}), respectively. Pryce's[92] value ρ $(Fe^{2+})=0.95$ cm^{-1}, which includes the second-order effect of the spin-orbit interaction in the triplets,[83,93] can be adopted as ρ_u for SH calculations within ^5D. For Fe^{4+}, we estimate ρ_u as 0.9 cm^{-1} by interpolating the values[92] for Mn^{3+} and Cr^{2+} $(3d^4)$ ions.

In the CF analysis,[71] the coordinate system has been chosen, with $x\|c$, $y\|b$, and $z\|a$ for the three Fe(1) sites and $x\|a$, $y\|b$, and $z\|c$ for the Fe(2) site. The ground orbital singlet is then $|yz\rangle$ and $|x^2-y^2\rangle^*$ for Fe^{2+} and Fe^{4+}, respectively, at each of the four sites considered. For some sites, the ratio of b_2^2/b_2^0 greater than 1 is obtained. To obtain a direct measure of the degree of rhombicity, the axis system must be transformed[73,74] so that this ratio is in the "standard" range (0–1). In Tables IA–ID and IIA–IID we adopt the axis system which yields the standardized ZFS parameters for most of the data sets in a given table. However, in some cases a few data sets require additional transformations as indicated in brackets. The standardization transformations also change the ground-state "labels". For example, for the Fe^{2+} (1) octahedral site in the original axis system, the ground state is $|yz\rangle$ and thus $b_2^0=-0.275$ cm^{-1} and $b_2^2=4.35$ cm^{-1} $(b_2^2/b_2^0=-15.8)$ are obtained with $\lambda=-100$ and $\rho=0.18$ cm^{-1}. Hence, using the standardization transformation[73] S_4 $(z\to y, x\to z$, and $y\to x)$, the values of b_2^0 and b_2^2 (in cm^{-1}) become 2.312 and 1.762, respectively, whereas the ground state becomes $|xy\rangle$ in the transformed axis system $(x\|b, y\|a$, and $z\|c)$ as indicated in Table IC.

It is seen from Tables IIA–IID that b_4^0, b_4^2, and b_4^4 are small in comparison with b_2^0 and b_2^2 for Fe^{4+} ions, since the major contributions are $b_4^q \propto \lambda^4/\Delta_i^3$ and $b_2^q \propto \lambda^2/\Delta_i$. Consequently $b_4^q/b_2^q \sim (\lambda/\Delta_i)^2 \sim (10^{-3}-10^{-4})$ because of the large CF energies Δ_i.[71] On the other hand, Fe^{2+} ions (Tables IA–ID) exhibit b_4^q comparable in magnitude to b_2^q, due to smaller Δ_i. The calculated ZFS parameters are compared with $b_2^0(\equiv D)=9.9$ and $b_4^0(\equiv 5a/2)=-1.5$ cm^{-1} observed in Fe^{2+}:$CdSiP_2$[83], $b_2^0=9$ to 10 cm^{-1} calculated for Fe^{2+}:GeX_2O_4 (X=Fe, Co, or Ni),[90] $b_2^0=0.375$ cm^{-1} observed in Fe^{4+}:$SrTiO_3$,[94] $b_2^0=12$ and $b_4^0=0.22$ cm^{-1} calculated for Fe^{2+}:$BaFeSi_{10}O_4$,[95], $b_2^0=1.822$ and $b_4^0=-0.075$ cm^{-1} observed in Fe^{4+}:$CdSiP_2$.[83] The largest reported value of $b_2^0=-24$ cm^{-1} is for Fe^{2+}:$CdPS_3$.[68] For Fe^{2+} at Cu(1) planar, b_2^0 is even larger (see Table IA) indicating the divergence of the perturbation theory (see below).

B. Dependence of the spin-Hamiltonian parameters on the Fe concentration

The microscopic SH relations[81] and the superposition model relations[71] enable us to investigate the variation of the SH parameters with the Fe concentration (x) in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. The structural changes induced by Fe ions, especially the orthorhombic to tetragonal transition (see, e.g., Refs. 1–4, 7, 96–100), may thus be elucidated. Figures 1 and 2 show b_2^2 for Fe^{2+} and Fe^{4+}, respectively, at the Cu(1) octahedral sites as a function of x, predicted using the data[3] on the unit-cell parameters (a,b,c) and the atom coordination[87] (note also a recent study[101]). The nonstandard values of b_2^2, i.e., referred to in the original axis system, are used in Figs. 1 and 2 since this does not affect the decrease of b_2^2 to zero, which as is seen, occurs at $x \geq 0.04$. This finding agrees with the experimental data indicating the orthorhombic to tetrago-

TABLE II. The spin-Hamiltonian parameters for Fe^{4+} ions at various sites in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ with $x=0.01$ calculated using the crystal-field energies Δ_i listed in Table IV of Ref. 71 and (a) $\lambda=125, \rho=0.25$, (b) $\lambda=100, \rho=0.25$, (c) $\lambda=125, \rho=0.90$, (d) $\lambda=100, \rho=0.90$ (all in cm^{-1}). The values of b_2^q are in units of cm^{-1} while b_4^q is in units of 10^{-3} cm^{-1}, whereas g_i are dimensionless. The range of magnitudes induced by the uncertainties in Δ_i is indicated for two illustrative cases by the relative differences corresponding to the upper $(\Delta+\delta)$ and lower $(\Delta-\delta)$ limits.

A. At the Cu(1) planar sites with the axis system $x \| c, y \| b, z \| a$.

	a	*b*	*c*	*d*
g_x	2.00	$2.00^{+0.00}_{-0.00}$	$2.00^{+0.00}_{-0.00}$	2.00
g_y	1.99	$2.00^{+0.00}_{-0.00}$	$1.99^{+0.00}_{-0.00}$	2.00
g_z	1.95	$1.96^{+0.01}_{-0.00}$	$1.95^{+0.01}_{-0.00}$	1.96
b_2^0	−3.23	$-2.33^{+0.07}_{-0.07}$	$-5.15^{+0.11}_{-0.11}$	−4.25
b_2^2	0.74	$0.57^{-0.00}_{+0.01}$	$1.48^{-0.01}_{+0.02}$	1.32
b_4^0	0.8	$0.4^{-0.01}_{+0.00}$	$1.2^{-0.1}_{+0.1}$	0.6
b_4^2	−0.4	$-0.2^{+0.0}_{-0.0}$	$-0.9^{+0.0}_{-0.1}$	−0.6
b_4^4	−0.3	$-0.2^{+0.0}_{-0.0}$	$-1.7^{+0.0}_{-0.0}$	−1.6

B. At the Cu(1) pyramidal sites with axis system $x \| c, y \| b, z \| a$.

	a	*b*	*c*	*d*
g_x	2.00	$2.00^{+0.00}_{-0.00}$	$2.00^{+0.00}_{-0.00}$	2.00
g_y	1.99	$1.99^{+0.00}_{-0.00}$	$1.99^{+0.00}_{-0.00}$	1.99
g_z	1.96	$1.97^{+0.00}_{-0.01}$	$1.96^{+0.00}_{-0.01}$	1.97
b_2^0	−2.92	$-2.12^{-0.07}_{+0.07}$	$-4.75^{+0.11}_{-0.12}$	−3.94
b_2^2	1.51	$1.14^{-0.02}_{+0.03}$	$2.81^{-0.03}_{+0.05}$	2.45
b_4^0	0.7	$0.3^{+0.0}_{-0.0}$	$1.1^{-0.0}_{+0.1}$	0.6
b_4^2	−1.1	$-0.6^{+0.1}_{-0.0}$	$-2.5^{+0.1}_{-0.3}$	−1.7
b_4^4	−0.7	$-0.4^{+0.0}_{-0.0}$	$-2.7^{+0.0}_{-0.1}$	−2.5

C. At the Cu(1) octahedral sites with the axis system $x \| b, y \| a, z \| c$.

	a	*b*	*c*	*d*
g_x	1.97	$1.97^{+0.01}_{-0.00}$	$1.97^{+0.00}_{-0.00}$	1.97
g_y	1.97	$1.98^{+0.00}_{-0.00}$	$1.97^{+0.00}_{-0.00}$	1.98
g_z	2.00	$2.00^{+0.00}_{-0.00}$	$2.00^{+0.00}_{-0.00}$	2.00
b_2^0	2.68	$1.98^{-0.04}_{+0.05}$	$4.64^{-0.08}_{+0.07}$	3.93
b_2^2	−0.89	$-0.65^{-0.02}_{+0.01}$	$-1.48^{-0.02}_{+0.02}$	−1.2
b_4^0	0.2	$0.1^{+0.0}_{-0.0}$	$0.1^{+0.0}_{-0.0}$	0.1
b_4^2	−1.5	$-0.7^{-0.00}_{+0.01}$	$-2.6^{-0.02}_{+0.03}$	−1.3
b_4^4	−3.7	$-1.9^{+0.2}_{-0.3}$	$-8.7^{+1.0}_{-1.3}$	−5.4

D. At the Cu(2) sites with the axis system $x \| a, y \| b, z \| c$.

	a	*b*	*c*	*d*
g_x	1.99	$2.00^{+0.00}_{-0.00}$	$1.99^{+0.00}_{-0.00}$	2.00
g_y	1.99	$1.99^{+0.00}_{-0.00}$	$1.99^{+0.00}_{-0.00}$	1.99
g_z	1.93	$1.95^{+0.00}_{-0.00}$	$1.93^{+0.00}_{-0.00}$	1.95
b_2^0	−4.17	$-2.93^{-0.01}_{+0.01}$	$-6.13^{+0.02}_{-0.01}$	−4.90
b_2^2	0.37	$0.28^{-0.02}_{+0.01}$	$0.66^{-0.03}_{+0.02}$	0.56
b_4^0	2.0	$0.9^{+0.0}_{-0.0}$	$2.9^{-0.1}_{+0.0}$	1.5
b_4^2	−0.5	$-0.2^{+0.0}_{-0.1}$	$-0.9^{+0.1}_{-0.0}$	−0.5
b_4^4	−1.1	$-0.6^{+0.0}_{-0.0}$	$-3.6^{+0.1}_{-0.0}$	−3.0

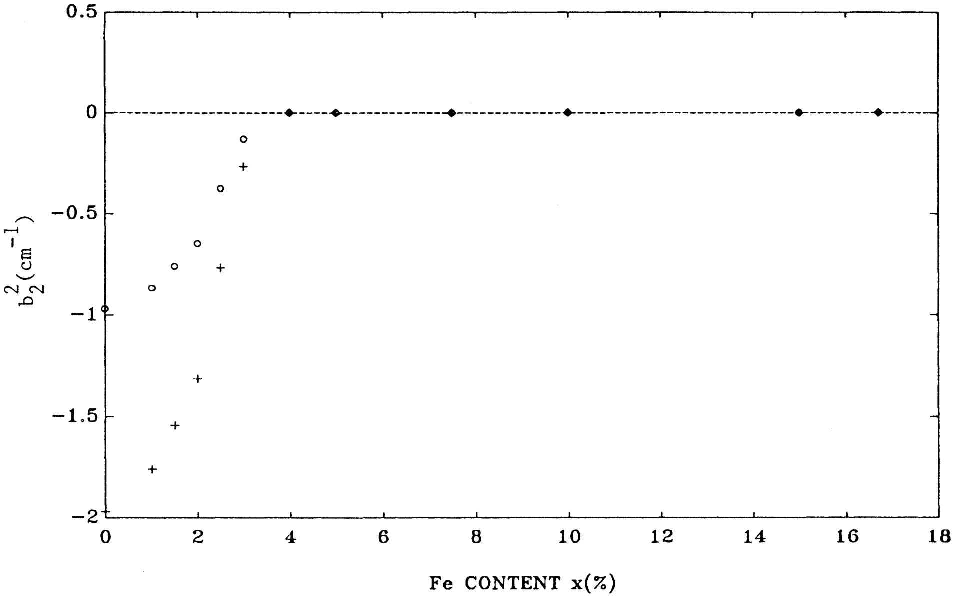

FIG. 1. The spin-Hamiltonian parameter b_2^2 for Fe^{2+} ions at the Cu(1) octahedral site in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ vs the Fe concentration (x) calculated with $\rho=0.95$, $\lambda=-100$ (circles) and $\rho=0.18$, $\lambda=-70$ (crosses) (in cm^{-1}).

nal ($a=b$) phase transition at $x_c \approx 0.03-0.04$.[1–4,7,96–100] The superconductivity is preserved in this transition and disappears only when the concentration x reaches the value of about 0.13–0.15. The critical concentration x_c depends on the heat treatment and the oxygen deficiency δ. A value of x_c in the vicinity of 0.02 has also been reported.[52,53,96] The point symmetry of Fe(1) planar (D_{2h}), Fe(1) pyramidal (C_{2v}), and Fe(2) pyramidal (C_{2v}) sites is unchanged during the phase transition, whereas for Fe(1) octahedral sites, the symmetry increases from D_{2h} to D_{4h}.

The effect of an increase in the Fe content, which causes the changes in crystallographic parameters (a,b,c),[1–4,96–100] on the CF parameters and energy levels is rather negligible, except for two cases.[71] First, the orthorhombic CF parameters B_2^2 and B_4^2 for Fe^{2+}(1) octahedral and Fe^{4+}(1) octahedral sites vanish in the tetragonal phase and thus the states $|xy\rangle$ and $|xz\rangle$ degenerate.

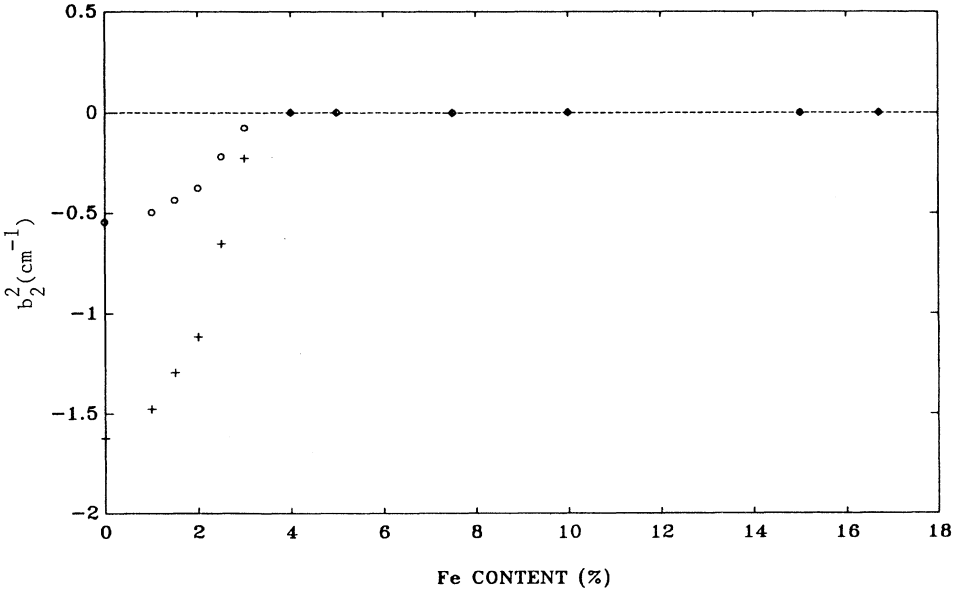

FIG. 2. The spin-Hamiltonian parameter b_2^2 for Fe^{4+} ions at the Cu(1) octahedral site in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ vs the Fe concentration (x) calculated with $\rho=0.9$, $\lambda=125$ (crosses) and $\rho=0.25$, $\lambda=80$ (circles) (in cm^{-1}).

Hence, at high Fe concentrations, the ZFS parameters b_2^2 and b_4^2 vanish for the two sites. Second, the first excited energy Δ_{xz} for Fe^{2+} at Cu(2) sites decreases considerably to about 30 cm^{-1}. This would lead to a divergence of the SH theory for $Fe^{2+}(2)$ at high Fe concentrations since the spin-orbit coupling can no longer be considered as a perturbation. Thus, the ZFS parameters for $Fe^{2+}(2)$ (Table ID) as well as b_2^2 and b_4^2 for Fe^{2+} and Fe^{4+} at Cu(1) octahedral sites (Tables IC and IIC) apply for low ($x<0.04$) Fe content only.

IV. SUMMARY AND CONCLUSIONS

Using our recent crystal-field and superposition model predictions,[71] the spin-Hamiltonian parameters g_i and b_k^q for Fe^{2+} and Fe^{4+} ions located at the Cu(1) planar, Cu(1) pyramidal, Cu(1) octahedral, and Cu(2) sites in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ are calculated. Since our *model calculations* provide the range of magnitudes rather than the "exact" values of g_i and b_k^q, they are applicable also for Fe^{2+} and Fe^{4+} ($S=2$) ions at four-, five-, and sixfold coordinated sites in other structurally similar oxides, e.g., La_2CuO_4, (Ref. 4), spinels[90] (where two or more transition metals occupy different sites), minerals,[95] and ABO_3-type oxides.[94] Moreover, our theoretical results are comparable with the few experimental ones available for other compounds, thus indicating the reliability of the microscopic theory. The values of b_2^0, which account for the magnitude of the zero-field splitting (ZFS), are found to be rather large and thus the resonance frequencies[65] would lie well beyond the X or Q band employed in EPR studies. This makes plausible the alternative explanation of the EPR silence of Fe ions in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ observed using the X band,[61–64] as being due to the inaccessibility of the EPR transitions in the X or Q band.

Keeping in mind the large ZFS and considering the phase diagram for $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ in the x-T_c plane,[3,6,52,53] it can be expected that the detection of EPR signals of the high-spin ($S=2$) Fe^{2+} and Fe^{4+} ions in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ may be feasible using high frequency and/or high magnetic field at temperatures above and possibly below the superconducting critical temperature T_c, i.e., ranging between 90 and 10 K and with the concentration x between 0.01 to 0.13, respectively. It would be of great interest to perform such studies on single high quality $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ crystals, which have recently become available,[102,103] for it would enable detection of any changes in the EPR signals which may be induced by the onset of superconductivity. This paper provides guidelines for the planned high-frequency and/or high-field EPR studies[67–69] of Fe^{2+} and Fe^{4+} ions in the three samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ with $x\cong 0.007$, 0.017, and 0.073 available to us. However, the analysis of EPR spectra may be very complex due to the microdomain structure[103–105] and possible Fe cluster formation.[52,106]

The most probable assignment[25] (see Ref. 24 also) of iron sites in $YBa_2Cu_3O_{7-\delta}$ based on Mössbauer spectroscopy data is as follows: (a) Cu(2):Fe^{3+} ($S=5/2$), (b) Cu(1) pyramidal:Fe^{3+} ($S=3/2$), (c) Cu(1) planar:Fe^{4+} ($S=2$) or Fe^{3+} ($S=3/2$), (d) Cu(1) threefold:Fe^{2+} ($S=1$) or Fe^{3+} ($S=3/2$). Although not conclusive, the assignments[24,25] strongly support the existence of Fe^{4+} ($S=2$) at the Cu(1) planar sites and are confirmed by our model calculations. The other Fe^{4+} ($S=2$) and Fe^{2+} ($S=2$) sites considered here may also be present in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$.[1,5,10,18,21,27,28,54,56,59,63] Moreover, recent studies[6,7,28,29,31–33] indicate the presence of other Fe sites, not classified in Refs. 24 and 25, some of which might be attributable to the Fe^{4+} ($S=2$) and Fe^{2+} ($S=2$) ions. The spectroscopic properties of Fe^{3+} ($S=5/2$) ions require separate consideration. The microscopic spin-Hamiltonian theory for the ^6S-state ions is much more complex than that for the ^5D-state ions. Recently, a comprehensive approach to the zero-field splitting of the ^6S-state ions at tetragonal symmetry sites has been developed.[107] An extension to orthorhombic symmetry and application to Fe^{3+} ($S=5/2$) in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ is now in progress.

The very large values of b_2^0 for $Fe^{2+}(1)$ planar sites should be treated with caution since the perturbation theory may overestimate the spin-Hamiltonian parameters for this case. For the near degeneracy of the ground and the first excited state revealed for $Fe^{2+}(2)$ sites at high concentrations, a two-dimensional spin-Hamiltonian model[78] may be an alternative. A recently developed crystal-field computer package[108] enables CF analysis within the whole $3d^4$ and $3d^6$ configuration. The near degeneracy for the $Fe^{2+}(2)$ sites can thus be more accurately determined. Preliminary calculations reveal also that the spin triplets ($^3\Gamma_i$), arising from the higher ^{2S+1}L multiplets, contribute significantly to ZFS, especially for Fe^{2+} ions in $YBa_2Cu_3O_{7-\delta}$.[109]

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*Author to whom correspondence should be addressed.

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