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HYPERFINE INTERACTIONS IN IRON SUBSTITUTED
HIGH-T_c SUPERCONDUCTING OXIDES*

by

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ABSTRACT

The hyperfine interactions in Fe substituted copper oxide ternary and quaternary compounds with perovskite-related structures are studied, using the Local Density theory in an embedded cluster approach. The self-consistent electronic structure is examined for Cu and Fe sites in a number of plausible local geometries representative of La_2CuO_4 , $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$ and related materials. Mössbauer isomer shifts, electric field gradients, magnetic moments, and contact hyperfine fields are presented for comparison with experiment and discussed in light of lattice structure data.

Key-words: Superconductivity; H-T_c oxides; Fe substitution in Superconducting oxides; Hyperfine Interactions; Local density; Electronic structure; DV-X_α method; Mössbauer spectroscopy.

I. INTRODUCTION

The novel superconducting properties of copper oxide ternary and quaternary compounds with perovskite-related structure have provided motivation for intense study. Electric and magnetic fields at particular nuclear sites, as revealed by measured hyperfine interactions (HFI) provide particularly valuable information about electronic structure. NMR and NQR spectroscopy on Cu have provided a useful, but limited, set of data.¹ Many HFI experiments have been reported on materials doped with impurities, often in conjunction with studies of variation of T_c and changes of oxygen stoichiometry.²⁻⁵

⁵⁷Fe is particularly interesting for HFI measurements in these compounds, since it is expected to substitute for Cu, and through Mössbauer spectroscopy is capable of revealing local magnetic fields, charges densities, and electric field gradients. A considerable number of measurements have been reported, and a consensus is emerging on the general nature of spectra in carefully prepared single phase specimens.^{2,3,6} The resulting picture is not simple: for example even the most careful preparations of La_2CuO_4 may result in two different crystallographic phases, as discussed below. Indeed, the nuclear gamma resonance (NGR) spectra show two distinct Fe sites, with considerable intensity. The probability that local defect structure and distortions are induced by Fe doping is also high, both in $\text{Fe}:\text{La}_2\text{CuO}_{4+s}$ and the superconducting $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$ compounds.

In $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$ four or more distinct spectra are seen, with intensity

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which depends upon heat treatment, oxygen content and aging. Since there are two distinct Cu sites in these and related "1-2-3" compounds, one has also to look to defect structure or other chemical explanations of the multiline spectra. It is observed that oxygen content of the lattice tends to increase upon doping by iron, and that iron prefers four-fold and six-fold coordination to oxygen⁷. Both neutron diffraction and X-ray absorption fine structure (EXAFS and XANES) confirming earlier Mössbauer information seem to indicate that Fe substitutes primarily, if not exclusively, at the Cu(1) "chain" sites for doping up to c.a 5% Fe/Cu. At higher levels, the lattice structure changes from orthorhombic to tetragonal and substitution at Cu(2) "plane" sites is claimed to become significant.

In the present work we report theoretical calculations of charge and spin densities, and HFI for embedded clusters representative of Fe substituted La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$. The electric field gradient (EFG) for Cu, and EFG, isomer shift and magnetic hyperfine field are determined for Fe in plausible geometries, with various local concentrations of oxygen. A comparison is made with experiment in an effort to identify actual sites occupied by iron. In general, Fe is found to adopt high spin configurations, roughly described as Fe^{+2} and Fe^{+3} with significant covalent mixing of its 3d, 4s, 4p orbitals with the 2p orbitals of neighboring oxygen ligands.

II. MICROSTRUCTURE AND COPPER ENVIRONMENT

The crystal structure of the antiferromagnetic La_2CuO_4 phase was studied by Grande et al.;⁸ it has an orthorhombic structure and is related to the tetragonal superconducting phases of K_2NiF_4 structure when La_2CuO_4 is doped with excess oxygen, Sr, or Ba. Michel and Raveau⁹ studied, in detail, the Sr and Ba substitution in La_2CuO_4 compounds and showed that with increasing Ba- and Sr- substitution, the structure changes from the orthorhombic to the tetragonal form. Neutron diffraction results¹⁰ indicate that $\text{La}_2\text{CuO}_{4+\delta}$ with δ less than 0.08 will separate into an antiferromagnetic phase with $\delta = 0$ and a superconducting phase with $\delta = 0.08$ below room temperature. High resolution X-ray diffraction study¹¹ of $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4+\delta}$ reveals two macroscopically segregated tetragonal phases of nearly identical lattice parameters at room temperature. The authors classified the two phases as major phase (~88%) and minor phase (~12%). Cooling the sample to 10 K, the majority tetragonal phase distorts into another crystal structure with symmetry lower than orthorhombic. In view of the recent neutron and X-ray studies, it is clear the local environment of the Fe site in Fe doped $\text{La}_2\text{CuO}_{4+\delta}$ and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ can be quite complicated. If Fe occupies the Cu site without distorting the local symmetry, there will be two NGR spectra. However, with lattice distortion caused by the Fe substitution, and possible accumulation of local oxygen concentration, multiple line spectra could be expected. More detailed NGR and crystallographic studies, coupled to theoretical modelling are required to fully resolve this problem.

Much has been published on the effect of Fe substitution for Cu in 1-2-3 compounds on structural, magnetic and superconducting properties. The macroscopic structural changes have been studied, in detail, by X-ray diffraction,¹²⁻¹⁴ neutron scattering,^{3,6,15} electron diffraction, and electron microscopy.^{16,17} X-ray and neutron diffraction results indicate that when $x < 0.03$ in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$, the room temperature structure is orthorhombic with the orthorhombicity decreasing with increasing Fe concentration. When $x \geq 0.03$, the structure is tetragonal. The microstructure changes with Fe concentration in a complicated way. The twin structure of the orthorhombic phase is gradually replaced by a tweed-like structure. Electron diffraction suggests the existence of mutually perpendicular microdomains of orthorhombic regions in the tweed structure. The microstructural origins of the tweed-like structure, however, are not yet completely resolved. Although it is generally agreed that the Fe substitutes primarily, at the Cu(1) "chain" sites, the near neighbor environment of the Fe in the crystal lattice is still not well defined. Site specific microscopic tools, such as X-ray absorption (XAS) and Mössbauer spectroscopies,^{18,23} have been applied to study the coordination of the Fe in the lattice. The XAS results seem to support the neutron, X-ray, and Mössbauer data that the Fe predominantly substitute for Cu in the Cu(1) site. The near-edge Fe-3d features and the EXAFS results suggest that the average coordination number of Fe nearest neighbors increases with increasing Fe content and an increase in the number of oxygen neighbors in the linear-chain plane, indicating an introduction of the extra oxygen atom on the

vacancies of the a-axis. To fit all the experimental Mössbauer spectra generally 5 or 6 subspectra were needed to represent various oxygen coordinations about the Fe site, see Table I. The exact coordination of the single Fe site, as well as the possible Fe clustering geometry, however, depends on the modelling of the subspectra by the investigator. The interpretation of the hyperfine spectra, the pre-edge structure of XANES and the near neighbor coordination of EXAFS are not unique; therefore the exact number of oxygen near neighbor ions and their geometrical arrangement are still open for debate.

III. INFERENCES ABOUT MICROSTRUCTURE OF FE-SUBSTITUTED COMPOUNDS FROM MÖSSBAUER SPECTROSCOPY

A. Lanthanum Cuprate

The first Mössbauer and magnetic measurements of $\text{La}_{1.85}\text{Sr}_{.15}\text{Cu}_{1-x}\text{Fe}_x\text{O}_4$ layered perovskite were reported by Matykiewicz et al.²⁴ for $x < 0.10$. At room temperature (RT) an asymmetric doublet was observed with an isomer shift (IS) of 0.3mm/s (relative to $\alpha\text{-Fe}$) typical of Fe^{3+} . Systematic study of metal doping effects on $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with 0.5% of ^{57}Fe have been made by Baggio Saitovitch et al.²⁵ for $0 < x < 0.35$. Perhaps related to the two Cu sites (two phases) found in this series of compounds, two doublets (A and B in Table I) were observed for $x < 0.15$ with similar IS values, but different quadrupole splittings (QS). Both QS decrease with the Ba content reflecting the

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modification in the lattice parameters, with $1.20 < QS_A < 1.71$ and $0.89 < QS_B < 1.40$. For $x > 0.15$ only the species associated with doublet A remains. The behavior of species B with doping would be consistent with the presence of holes localized near to the Cu site, arranged to compensate the charge difference between La^{3+} and Ba^{2+} ions; these holes would become delocalized with increasing metallic character for $x > 0.15$. However, this attractive explanation is ruled out by NGR measurement in the undoped $Fe:La_2CuO_4$ samples, where the two species are also observed. An alternative would be to associate the B spectra with the presence of oxygen vacancies near the Cu site. The 70:30 intensity ratio of the two doublets found in our measurements is, however, not consistent with the content of 3-5% vacancies usually found for La_2CuO_4 and $La_{2-x}Ba_xCuO_4$ and would require their location near to the Fe ions.

The behaviour of both species A and B as a function of temperature was followed by measuring *in situ* Mössbauer spectra of $Fe:La_2CuO_4$.²⁶ The results are not consistent with the neutron diffraction data of Jorgensen et al.²⁷ obtained for the two crystallographic phases of La_2CuO_4 with oxygen excess. The origin of the two species requires a consistent explanation which will be discussed on the basis of results for $La_{2-x}M_xCuO_4$ ($M = Sr, Ca, Ba$).

The NGR measurements for $T < 15$ K reported by Matykiewicz et al.²⁴ reveal a magnetic hyperfine field $B_{hf} \sim 44$ T consistent with the magnetic susceptibility data of an effective moment of $3-4 \mu_B$ per iron atom. The comparison of 4.2 K NGR data spectra for La_2CuO_4 and $La_{1.85}Ba_{0.15}CuO_4$ with 0.5% Fe/Cu was reported by Baggio Saitovitch et al.²⁸ The two well defined

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magnetic subspectra due to species A and B of $\text{Fe La}_2\text{CuO}_4$ transform to a broad magnetic hyperfine spectrum for $x = 0.15$. This result is consistent with the observation of Matykiewicz et al. for the corresponding Sr substituted oxide, which was fitted with a Lorentzian hyperfine field distribution around an average value of 45 T.²⁴

Imbert and Jehanno have shown a systematic change of orientation of the EFG axis relative to the B_{hf} direction with increasing doping in $\text{Fe:La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples.²⁹ Experiments on oriented powder samples reported by Dalmas et al.³⁰ indicate that while in the iron-free compound the EFG axis is the c direction, the substitution of Cu by iron induces an angle between the EFG at Fe atoms and c -axis directions.

B. $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ Compounds

A number of ^{57}Fe NGR measurements on the $\delta = 0$ orthorhombic phase have been reported.^{2,18,31,34} By now a general consensus has emerged that Fe goes primarily to Cu(1) chain sites and that the several quadrupole doublets seen correspond to different oxygen configuration around the Cu(1) sites. Models have been proposed³⁵ which associated tetrahedral, pyramidal, and octahedral oxygen coordination with the principal subspectra seen at low Fe concentration, $x < 0.01$. We have found doublets A and B , characterized by $(IS, QS) = (-0.18, -1.56)$ and $(0.03, 1.35)$ mm/s, which represent the main features believed to be typical for Fe located at twin boundaries. These spectra have been tentatively assigned to iron in fourfold tetrahedral and

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fivefold pyramidal oxygen coordinated sites. A third doublet \mathcal{C} characterized by (0.19, 0.30) mm/s was assigned to six-fold octahedral oxygen coordination.

At higher Fe concentration and with reduced oxygen content, two new doublets (\mathcal{D}), (\mathcal{F}) appear, as shown in Table I. These spectra may be characterized by (IS, QS) = (0.04, -1.98) and (0.30, 0.55) mm/s. The first of these has been tentatively assigned to the square planar (FeO_4) configuration; i.e., the environment seen by Cu(1) in the unperturbed ideal $\delta = 0$ crystal³⁵. The interpretation of the last doublet remains controversial: we believe that it may be due to a spurious phase or iron clustering in Cu(1) plane, while some authors associate it with Fe occupation of Cu(2) site which can be enhanced by heat treatment under oxygen deficient atmosphere.³⁶

High temperature studies were carried out in both oxygen and air environments, under pressure of -1 atm.³⁷ The electronic configuration of iron is found to be very stable up to 320 C. Reversible transformations of intensity between the two principal doublets are observed, showing that well defined and stable chemical states are attained at these sites.

The thermally activated transformation of species \mathcal{A} into \mathcal{B} is consistent with the proposed fourfold tetrahedral and five fold pyramidal oxygen coordination, since a hopping of a neighboring oxygen from O(1) to O(5) position results in a transformation of tetrahedral to pyramidal coordination. The stability of the iron species is seen through a smooth variation of QS values which may be explained by temperature dependence of lattice parameters. Further, the decrease of the central shift with temperature can be accounted for by the second order Doppler shift; this indicates that the

"s" electron density at the Fe nucleus remains unchanged.

The observation of split magnetic hyperfine spectra in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_7$ at 4.2 K has been reported by several authors for samples with $x_c > 0.02$, as a consequence of the ordering of the Fe magnetic moments in these systems. Different critical Fe concentration x_c for the establishment of the saturated magnetic ordered state at 4.2 K has been reported; in our samples we find $x_c \approx 0.04$. The observed value can be associated with the size of Fe clusters which vary according to sample preparation conditions.

An analysis of the complex spectra has been reported by Baggio Saitovitch et al.³⁸ for samples with $x = 0.005$ in an applied external field ($B_{\text{ext}} = 5$ T) and with $x = 0.15$ ($B_{\text{ext}} = 0.5$ T). A consistent fit was obtained with a complete Hamiltonian, allowing arbitrary angles (θ) between EFG and B_{hf} and a small distribution of B_{hf} values. Although such a fit is not unique with respect to the sign of QS and θ values, the values of B_{hf} for the different Fe species are reliable: $B_{\text{hf}} = 16, 21.5, 44.7,$ and 25.3 for species A, B, C and D, respectively. The B_{hf} saturation value for A may be greater than 16 T, since this species is present only in the samples with Fe concentration below the critical value needed for spontaneous ordering at 4.2 K. The value reported was determined from NGR in an external magnetic field.³⁸

Neutron diffraction³⁹ and μSR ⁴⁰ measurements performed on $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_7$ may allow one to decide between antiferromagnetic or spin-glass-like ordering mechanisms and dynamic effects. However, from these experiments and the fits of Mössbauer data as a function of temperature,⁴¹ magnetic relaxation effects seem to be excluded in favor of a highly

anisotropic antiferromagnetic transition.

IV. THEORETICAL MODEL

An embedded cluster model is used to represent the electronic structure of a finite volume of the extended solid. Single particle orbitals are obtained in the framework of Local Density theory, using the Discrete Variational (DV-X α) method,⁴²⁻⁴⁵ Eigenfunctions of the effective Hamiltonian are expanded in a basis of numerical atomic orbitals, and the potential is iterated to self-consistency. Interaction of the cluster with the host crystal is treated by inclusion of the host density in generation of Coulomb and exchange-correlation potentials. Long range Coulomb interactions are treated by an Ewald summation procedure.

The LCAO expansion of eigenfunctions permits a Mulliken population analysis of the effective atomic configuration in physically meaningful terms. The atomic populations and related partial densities of states can be used to present a detailed description of the local atomic environment. The experimental quantities of immediate interest are calculated as follows:

(i) Charge and Spin Density

In the nonrelativistic spin polarized approach used here

$$\rho_{\sigma}(\vec{r}) = \sum_{\Gamma} f_{1\sigma} |\psi_{1\sigma}(\vec{r})|^2 \quad (1)$$

is the density of electrons of spin component $s_z = \sigma$. The occupation numbers $f_{1,\sigma}$ are chosen for the ground state according to Fermi-Dirac statistics, and the single particle orbitals $\psi_{1,\sigma}$ are generated self-consistently as described above. The charge and spin densities are $\rho_c = \rho_+ + \rho_-$ and $\rho_s = \rho_+ - \rho_-$, respectively, and can in principle be measured by X-ray and neutron diffraction on single crystal specimens. Crystals of sufficient size and quality have not yet been obtained to make these detailed measurements possible, to our knowledge.

(ii) Mössbauer Isomer Shift

The ^{57}Fe Isomer Shift (IS) reflects the monopole interaction of the nuclear charge volume and the overlapping electronic charge density. It can be written as

$$\text{IS} = A_{\text{IS}} \Delta\rho_c(0) \quad (2)$$

where A_{IS} depends upon nuclear ground and excited state radial distributions, and $\Delta\rho_c$ is the difference in electron density at the nucleus for the host

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crystal and a reference system such as metallic iron.⁴⁶ Presently accepted values of A_{15} lie in the range $-0.25 \pm 0.05 \text{ mm-a}_0^3/\text{sec}$.

(iii) Electric Field Gradient

Transitions between the $I = 3/2$ excited state and $I = 1/2$ nuclear ground state of ^{57}Fe lead to an observed quadrupolar splitting QS which is directly proportional to the electric field gradient. A convenient form is given as

$$QS = BQV_{zz} \left(1 + \frac{\eta^2}{3} \right)^{1/2} \quad (3)$$

where $B = 11.77 \text{ (mm-a}_0^3)/(\text{barn-sec}) = 200.1 \text{ (MHz-a}_0^3)/\text{barn}$ and Q is the nuclear quadrupole moment. Suggested values of Q range between 0.08 and 0.21 barn.⁴⁵ The electronic contribution to QS is defined by the eigenvalues of the field gradient tensor, labelled in order of increasing absolute value as V_{xx} , V_{yy} , V_{zz} . The experimentally determined quantities are the principal value V_{zz} and the asymmetry parameter.

$$\eta = \left| (V_{yy} - V_{xx})/V_{zz} \right|.$$

(iv) Magnetic Hyperfine Field

Interaction of the nuclear magnetic moment with spin magnetism of electrons at the nucleus leads to an energy

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$$E_s = -g_N \mu_N H_s(0) \quad (4)$$

with the Fermi contact field $H_s(0) = A_s \rho_s(0)$ where $A_s = 52.42$ Tesla - a_0^3 .

Experimental values of IS, QS, and $H_s(0)$ are extracted as part of a nonlinear fitting procedure using the complete electron-nuclear interaction Hamiltonian and including line width and amplitude parameters. The sign of V_{zz} can be determined in the paramagnetic state by the analysis of NGR spectra in the presence of B_{ext} . Systematic studies of oriented samples (single crystals or powder) at different angles with respect to the γ -ray direction give information about the size of V_{zz} and its direction relative to the crystal axes. The NGR spectrum in the magnetic ordered state contains information about the sign of V_{zz} and its orientation relative to B_{hf} .

V. RESULTS

A. La_2CuO_4

Self-consistent-field DV-X α calculations for La_2CuO_4 have been previously reported⁴⁸. The effective charge state of Cu was found to be $Cu^{+1.78} 3d^{9.09} 4s^{0.08} 4p^{0.04}$, or somewhat less ionic than the nominal $Cu^{2+} d^9 s^0$ state. The validity of this model was checked by comparison of calculated Cu K-edge X-ray absorption near edge structure (XANES) and experiment.^{49,60} The good quantitative agreement of XANES theory and experiment, and comparison

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with reference compounds Cu_2O , CuO , and KCuO_2 lends some confidence to the theoretical model, particularly with respect to the charge distribution.

Fe-impurity calculations were carried out on 31 atom clusters $\text{M-O}_6\text{-La}_8\text{-Cu}_4\text{-O}_{12}$ embedded in the previously obtained La_2CuO_4 self-consistent lattice. Here "M" is either Cu or Fe, to facilitate comparison and permit computation of HFI for either nucleus. The resulting valence electron charge and spin populations are given in Table II. We can see from table that the $\text{Cu}^{2+}d^9s^0$ configuration is augmented by covalent charge sharing with oxygen ligands, attaining an effective charge of $\sim 1.8 e$. The La ions are found to be quite close to the "ideal" trivalent state. Spin on the copper ion at the center is small, $\sim 0.04\mu_B$, and increases at the periphery to $+0.10\mu_B$. Spin moments at the "surface" of a cluster are systematically overestimated with the presently used boundary conditions. This is due to the forced localization of surface-atom orbitals which do not have access to basis functions of all atoms of their first coordination sphere. Thus, the present theoretical results predict small or zero moment at Cu sites in the perfect La_2CuO_4 crystal. However, magnetic susceptibility and neutron diffraction measurements^{33,51} show that a Cu moment of $\sim 0.25\mu_B$ is present in the pure La_2CuO_4 , with antiferromagnetic order observed at 240 K.

Turning now to the iron-centered cluster, we find a configuration of essentially $\text{Fe}^{2+}d^6$ with the maximal spin of $4\mu_B$ in agreement with experimental values of $3-5\mu_B$. Covalent interactions with oxygen add $\approx 0.1e$ to both 4s and 4p atomic orbitals, giving a net charge $1.81 e$ very close to that of the host Cu. When one electron is removed from the cluster to test the stability of

this configuration, the net charge only increases to 1.85 e. Thus it appears that, with the exception of possible dramatic lattice relaxation effects, divalent iron substitutes for divalent copper in this lattice (but see below for comparisons with NGR). Perturbations on surrounding neighbors are small, but perceptible. For example the two axial oxygens lose 0.05 e charge, and all six oxygen neighbors gain a spin polarization moment of $0.03-0.04\mu_B$. An antiferromagnetic coupling of the next nearest neighbor Cu sites, with a moment $0.10\mu_B$ equal to that found in the pure Cu case can be noted.

The hyperfine parameters calculated for the two cases are presented in Table III. It is well known that core polarization/relaxation effects have to be taken into account to give an accurate description of $\rho_c(0)$ and $\rho_s(0)$. In the present work, core contributions were determined by separate numerical atomic calculations using the self-consistent atomic configurations. In this way basis set truncation limitations were entirely avoided. We will use the charge density $\rho_c(0)$ obtained here to define a reference state for interpreting IS of the 1-2-3 compounds. As noted previously, the experimental IS lies at +0.29 mm/sec with respect to α -iron; typically associated with the trivalent $Fe^{3+}d^5s^0$ configuration. The apparent conflict between theory and experiment is an indication of the essentially covalent Fe-O interaction and shows the limitations of simplified population analysis. As shown below, the calculated IS trends are in the correct direction in comparing La- and Y-based compounds, but somewhat exaggerated in magnitude.

It is interesting to note that the EFG matrix elements of Cu and Fe are of similar magnitude, but differ in sign. This points out the importance of

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the particular open d-shell configuration of the ion, and makes clear the inapplicability of simple point charge sums. External ion point charges do play an important role in determining the observed EFG, as discussed below.

Using Eqn. (3) with $Q(^{63}\text{Cu}) = -0.18b^{52}$ and $Q(^{57}\text{Fe}) = 0.08b$ and the data of Table III, we find $QS(^{63}\text{Cu}) = 59.1 \text{ MHz}$ and $QS(^{57}\text{Fe}) = 1.67 \text{ mm/sec}$. We should note that the older value of $Q(^{57}\text{Fe}) = 0.21b$ is preferred by some workers, and its use would approximately double the predicted iron QS. The NQR data for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ extrapolated to $x = 0$ give a value of $\nu_Q = 36 \text{ MHz}$ and a magnetic hyperfine field of $\sim 2 \text{ kOe}$. Analysis of antiferromagnetic resonance (AFMR) data leads to a value of $\nu_Q = 32 \text{ MHz}$. The calculated ^{57}Fe QS is fortuitously in almost perfect agreement with experiment. Contributions of ions exterior to the 31 atom variational cluster were summed explicitly, and found to amount to $< 10\%$ of the total.

The calculated Fe magnetic hyperfine field $H_{\text{h}}(0) = -45.8 \text{ T}$ is slightly smaller in comparison to the B_{hf} of species \mathcal{A} and \mathcal{B} found in the 4.2 K NGR spectra of La_2CuO_4 with 0.5% ^{57}Fe , see Table I. However, $H_{\text{h}}(0)$ is only the electronic spin contact contribution and no attempt has been made to include orbital and dipolar contributions from other crystal sites.

The magnetic hyperfine tensor M_{ab} is accessible through NMR anisotropy measurements on suitable nuclei; unfortunately no convenient Fe isotope is available, and angle resolved ^{63}Cu , ^{65}Cu NMR spectra on good single crystals do not seem to be available at present.

B. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

In view of the strong experimental evidence for substitution of Fe primarily at Cu(1) chain sites, most of the model cluster calculations focussed on this environment. In view of the propensity of Fe for oxygen, and electron diffraction measurements suggesting clustering of iron along twin boundaries, a number of different geometries and compositions need to be considered. The number of plausible clusters is considerable; the ones treated here are indicated schematically in Table IV. In order to study a number of cases within limits of computational resources, the cluster size was kept as small as seemed possible, generally retaining first and second neighbors of Fe in the variational space. The remainder of the host crystal was included through the embedding potential. For most of the calculations an idealized lattice consisting of Y^{3+} , Ba^{2+} , $\text{Cu}^{2.333+}$ and O^{2-} ions was used. Accurate self-consistent-field calculations for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $\delta = 0, 0.5, 1.0$ have been reported, using both band structure⁵³ and cluster⁵⁴ approaches. The self-consistent DV-X α potentials were used for a few iron impurity clusters, with only minor changes noted in the local electronic structure. The external ion contribution to the EFG likewise changed by ~15%, giving net differences (1-2% of total) negligible in comparison with errors inherent in the present small cluster size.

The effective atomic configurations, spin moments and hyperfine parameters found for Fe at each of the cluster geometries are given in Table V. Results are reported for unrelaxed atomic positions; i.e., all atoms are

placed at sites of the ideal host crystal with $\delta = 0$, using data determined by X-ray and neutron diffraction.

As is evident from Table V, the magnetic hyperfine field is generally dominated by the negative core polarization contribution. For a fixed 4s,p population the core field will be proportional to the driving 3d electron moment; the proportionality of moment and $H_{\text{c}}(0)$ is often assumed in analyses of experimental data. However, with variation of the diffuse 4s,p occupancy due to interactions with ligands, this proportionality is lost. The sizable positive 4s contributions to $H_{\text{c}}(0)$ have been previously invoked to explain properties of iron alloys and metallic impurity systems.

The uncertainty in the magnitude of the core term is considerable, due to approximations inherent in the local density exchange-correlation potential. The simple Kohn-Sham-Slater model with exchange parameter $\alpha = 0.7$ used in the cluster calculations give many molecular and solid state valence-electron properties to sufficient accuracy. However, it has been noted that such (exchange only) potentials tend to overestimate magnetic moments and hyperfine field.⁵⁵ Lindgren and others have noted that the von Barth-Hedin (vBH) potential, which includes a correlation term produces more satisfactory core-electron fields. We find that for the Fe atomic configurations arising in $\text{YBa}_2\text{Cu}_3\text{O}_7$ impurity clusters, the $H_{\text{c}}(0)$ core-electron values given by the vBH potential are 77% of those given by the exchange-only calculations. These revised and probably more accurate values are noted in the tables. In any case, the principal trends, and the important consequence of positive, environment-sensitive 4s,p contributions to $H_{\text{c}}(0)$ are unaltered.

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We may compare the Fe effective atomic configurations for clusters A-G of the 1-2-3 compound with each other, and with the "reference" results for La_2CuO_4 . The net charge ranges from $\sim 1.8 e$, comparable to the " Fe^{2+} " state seen in the La compound, to $\sim 2.5 e$ which could be characterized as " Fe^{3+} " in six-fold coordination and Fe-clustering environments. We see that charge estimates based on orbital populations are lower than those expected from IS measurements in both cases. The magnetic moment is predicted to be large in all cases, $3.6\text{-}4.3\mu_B$. The Fe 4sp conduction electron spin densities are found to be positive, an indication of covalent mixing with neighboring oxygen anion orbitals. Such positive diffuse spin densities have been previously encountered in Fe-impurity alloy systems.⁵⁶

Valence electron contributions to IS range over 0.44 mm/sec and (Fe 1s,2s,3s) core contributions vary by 0.25 mm/sec . This result shows that core relaxation in the self-consistent potential plays an important part in determining the IS, and valence-only models are of limited utility. The range of IS found for clusters A-G is 0.56 mm/sec , close to that seen experimentally, 0.48 mm/sec . The most negative value, for cluster A, is associated with the ideal four-fold Cu(1) site, and not with the twin boundary "tetrahedral" site (cluster B) proposed previously. The calculated IS values are all negative with respect to the La_2CuO_4 result; this is in general accord with experiment. However, the difference appears to be about a factor of two too large. There are two principal features which could account for the exaggerated IS shift calculated in the 1-2-3 compound:

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1. Relatively small size of the variational cluster, containing two coordination shells around the probe nucleus,
2. Local lattice relaxation.

Based upon previous experience, it is doubtful that increasing the variational cluster size would modify $\rho_c(0)$ sufficiently to cause factor of two changes. To test this possibility, we constructed a bipyramidal $\text{Fe}_2\text{O}_9\text{Cu}_6$ cluster (G: see below) which consists essentially of cluster (F) and its mirror image. The results given in Tables V and VI show no changes in IS with respect to the single pyramidal cluster.

On the other hand, the open structure around the Cu(1) site associated with either a- or b- direction oxygen vacancies can lead to facile local relaxation and distortion. In fact, displacement of Fe off of the Cu(1) site is considered to be likely in the cluster B "tetrahedral" case. Investigation of local lattice relaxations requires self-consistent determination of cohesive energies and a search for local stable points. This is beyond the scope of the present work.

The largest theoretical QS values occur for grain boundary clusters B and D, 1.57 and 1.40 mm/sec respectively. Thus the calculations support the previous assignment of the principal NGR subspectrum to the tetrahedral four-fold site. However, we find that the ideal Cu(1) site has a relatively low QS of ~0.6 mm/sec, in contradiction to the previous assignment. It is interesting to note that a modest reduction of the Fe-O bondlength of cluster A would increase the (y-z) plane covalent charge transfer and the related V_{bb} , V_{cc} EFG components. This distortion would then be

consistent with the continued assignment of subspectrum D with cluster A.

A similar remark applies to pyramidal cluster F, whose intermediate value of IS and $H_{\text{h}}(0)$ are consistent with assignment to subspectrum B. Aside from noting a general agreement in the span of experimental and theoretical QS values, it is unwarranted to draw further detailed conclusions. As noted by other workers^{57,58} the predicted QS is very sensitive to d-electron occupancy, and small changes in computational approximations (here, cluster size in particular) and interatomic distances can change the results considerably.

The calculated magnetic hyperfine field H_{h} ranges from -34 to -7 T, using the simple Kohn-Sham exchange potential. The largest value occurs for cluster E corresponding to the ideal Cu(2) plane. It is known that magnetic ordering among Cu(2) ions takes place at low temperature, so enhanced magnetism calculated for this site is reasonable. The second highest value (cluster C) represents six-fold oxygen coordination; thus increased oxygen coordination yields generally larger H_{h} . The H_{h} values are all less than the calculated and experimental result for La_2CuO_4 which is consistent with experiment. The sequence H_{h} : tetrahedral(B) < pyramidal(F) < octahedral(C) is in accord with the experimental assignments of subspectra A, B, C respectively. The absolute magnitudes for tetrahedral and pyramidal cases are in good agreement, while the theoretical octahedral value is a bit low. As with the EFG, the ideal Cu(1) site is anomalous, with calculated field being much too low with respect to subspectrum D. This is yet another indication of probable lattice relaxation at this "simple substitutional" cluster.

In view of evidence of twin boundary iron clustering, a bipyramidal

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cluster(G) was studied. The 21 atoms cluster has composition $OFe_2O_8Cu_{10}$ and consists essentially of two "F" clusters, with a shared vertex oxygen. In addition to throwing some light on a proposed assignment of subspectrum \mathcal{F} , cluster G permits some evaluation of cluster size effects. Charge and spin density and derived HFI parameters are given in Tables V and VI. We see that the charge populations and spin moments at the Fe are only slightly perturbed, in comparison to the F cluster. On the other hand, the EFG components are grossly altered by the strong Fe-O-Fe bonding along the b-axis. This leads to a calculated $QS=+1.08$ mm/s similar to subspectrum \mathcal{B} .

CONCLUSIONS

We have reported theoretical calculations of hyperfine interactions in iron substituted copper high- T_c superconductors, using an embedded cluster model. The local density results have been discussed in light of Mössbauer measurements, structural data, and proposed local defect and oxygen vacancy arrangements. Uncertainties about details of the local cluster geometry and bond lengths, and limitations of cluster size chosen make it impractical to identify each observed NGR line with certainty. However, the theoretical and experimental results form a consistent body of data. These data support the tentative assignment of spectral features $\mathcal{A}, \mathcal{B}, \mathcal{C}, \mathcal{D}$ to tetrahedral, pyramidal, octahedral, and square coordination of oxygen to the probe iron site, with some reservations. These reservations arise from quantitative

discrepancies between calculated IS, QS, and $H_{\mu}(0)$ seen in perspective of overall qualitative agreement in shifts and trends. Most, if not all of the discrepancies can be attributed to local lattice relaxation; in particular shortening of Fe-O bond lengths with respect to the Cu(1) - O distances characteristic of the ideal lattice. Bond length relaxation and dislocation of Fe off the Cu(1) site in low symmetry complexes should be studied in the future, in context of total energy calculations. The bipyramidal $Fe_2O_9Cu_6$ complex, seems to be a good candidate for the spectral feature of β which grows with iron concentration. The present calculations should be considered as a starting point for more extensive first principles modelling. The highly accurate results obtained recently by LD band structure methods on defect-free 1-2-3 compounds show that the LD approach is adequate to the task.

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**Table I. Mössbauer parameters for 0.5% Fe/Cu substitution.
The IS and QS were measured at 300 K, B_{hf} at 4.2 K.**

Compound	IS (mm/s)	QS (mm/s)	B_{hf} Tesla
La_2CuO_4	A	0.80	49
	B	0.81	47
$La_{1.85}B_{8.15}CuO_4$	0.25	1.40	45
YBa₂Cu₃O₇ Subspectrum			
A	-0.18	-1.58	16.0*
B	0.03	-1.20	21.5
C	0.15	-0.80	44.7
D	0.04	-1.98	25.8
E	0.80	0.55	44.0

*The B_{hf} at saturation is probably larger.

Table II. Charge and spin atomic orbital populations for $M-O_6-La_3-Cu_4-O_{12}$ clusters embedded in La_2CuO_4

		M = Copper		M = Iron	
		Charge	Spin	Charge	Spin
M	3d	9.09	-0.041	5.96	3.966
	4s	0.08	0.001	0.09	-0.007
	4p	0.04	0.000	0.11	-0.010
	total	1.78	-0.040	1.81	3.945
O ^a	2s	1.98	0.000	1.98	0.001
	2p	5.82	0.001	5.78	0.029
	total	-1.81	0.001	-1.76	0.030
O ^b	2s	2.00	0.000	2.00	0.003
	2p	5.94	-0.000	5.92	0.037
	total	-1.94	-0.000	-1.91	0.040
La	5p	5.99	0.000	5.96	0.001
	5d	0.09	-0.001	0.07	-0.000
	6s	0.02	-0.000	0.02	0.000
	total	2.90	-0.001	2.94	0.001
Cu	3d	9.04	0.098	9.19	-0.096
	4s	0.12	-0.002	0.06	0.000
	4p	0.02	-0.000	0.05	-0.000
	total	1.81	0.096	1.70	-0.096
O ^c	2s	2.00	0.000	2.00	-0.000
	2p	5.93	0.004	5.94	-0.005
	total	-1.93	0.004	-1.94	-0.006

a) Two axial sites

b) Four sites in (a,b) Cu-O plane

c) Average of two inequivalent sites in O_{12} shell

Table III. Hyperfine interaction parameters calculated for central atom of $M-O_6-La_3-Cu_4-O_{12}$ cluster embedded in La_2CuO_4

	M = Copper	M = Iron
Charge density $\rho_c(o)$ (e/a_0^3)		
Valence ^a	3.515	2.051
Core ^b		11868.202
Spin density $\rho_s(o)$ (e/a_0^3)		
Valence	0.018	0.182
		$H_s(0) = -45.8$ Tesla
Core		-1.056
Electric Field Gradient ^c		
V_{aa} (e/a_0^3)	-0.820	0.888
V_{bb}	-0.820	0.888
V_{cc}	1.640	-1.775 QS = 1.67 mm/sec
Magnetic hyperfine tensor ^d		
M_{aa}	-0.067	-0.297
M_{bb}	-0.067	-0.297
M_{cc}	+0.133	0.593

a) Variational result from cluster calculation

b) Core levels recalculated for effective atomic configuration

c) a, b, c refer to crystallographic axes; $V_{aa} = \langle \rho_c (3x_a^2 - r^2)/r^5 \rangle$ etc.

d) $M_{aa} = \langle \rho_s (3x_a^2 - r^2)/r^5 \rangle$ etc.

Table IV. Schematic of Fe impurity clusters calculated for $\text{YBa}_2\text{Cu}_3\text{O}_7$

Cluster	Composition	Geometry
A: Ideal Cu(1) chain Site	FeO_4Cu_4	
B: Cu(1) site, twin boundary	FeO_4Cu_4	
C: Cu(1) site, six-fold coordination	FeO_6Cu_4	
D: Cu(1) site, twin boundary, Fe clustering	$\text{FeO}_4\text{FeCu}_3$	
E: Ideal Cu(2) plane site	FeO_5Cu_4	
F: Cu(1) site, twin boundary excess oxygen	FeO_5Cu_4	

Table V. Atomic configuration, spin moment and hyperfine parameters for Fe in impurity clusters for YBa₂Cu₃O₇. See Table IV for cluster geometry.

Cluster	A	B	C	D	E	F	G
Charge							
3d	5.55	5.83	5.34	5.38	5.62	5.51	5.51
4s	0.27	0.16	0.05	0.07	0.25	0.17	0.17
4p	0.21	0.20	0.10	0.10	0.34	0.24	0.26
total	1.96	1.81	2.51	2.45	1.79	2.08	1.96
Spin							
3d	3.581	3.417	3.711	4.184	4.123	3.775	3.707
4s	0.082	0.080	0.021	0.030	0.060	0.062	0.072
4p	0.044	0.067	0.020	0.022	0.087	0.073	0.071
total (μ_B)	3.706	3.562	3.750	4.234	4.270	3.910	3.250
ρ_c (e/a_0^3)	5.869	4.098	4.645	4.515	4.611	4.555	4.7540
valence	11868.913	11868.442	11869.456	11869.320	11868.715	11869.011	11868.828
core							
ρ_s (e/a_0^3)	0.829	0.551	0.406	0.673	0.465	0.531	0.558
valence							
core	-0.967 ^a	-0.912	-1.029	-1.158	-1.119	-1.031	-1.013
	(-0.745)		(-0.590)		(-0.862)	(-0.797)	(-0.784)
EFG tensor ^b							
V_{aa} (e/a_0^3)	-0.105	-0.798	+0.140	-0.595	+0.408	-0.108	+0.265
V_{bb}	-0.561	-0.795	-0.191	-1.100	-0.196	-0.306	-0.375
V_{cc}	+0.665	1.594	+0.051	+1.695	-0.213	+0.414	+0.110
V_{ab}	-0.001	-0.682	0.000	-0.015	0.000	+0.002	+0.001

Table V. Contd.

Cluster	A	B	C	D	E	F	G
Magnetic anisotropy tensor (a_0^3)							
M_{aa}	+0.394	+0.253	-0.208	+0.333	-0.056	+0.490	+0.933
M_{bb}	-0.341	+0.253	+0.640	+0.435	+0.087	-0.135	-0.351
M_{cc}	-0.053	-0.506	-0.432	-0.768	-0.031	-0.355	-0.582
M_{ab}	0.000	-0.013	0.000	-0.034	0.000	0.000	0.000

a) Core polarization calculated using effective atomic configuration in solid, with exchange-correlation parameter $\alpha = 0.7$. Values in parentheses are calculated with von Barth-Hedin exchange-correlation potential.

b) Values are given for valence electron matrix elements $V_{aa}^{\text{valen}} = \langle \rho_c (3x_a^2 - r^2) / r^5 \rangle$ etc. The total EFG required to determine the quadrupole splitting is found by combining contributions of the exterior crystal ions and core electrons and nuclei of the local cluster with the appropriate sign:

$$V_{aa}^{\text{total}} = \sum_i q_i (3x_{ai}^2 - r_i^2) / r_i^5 - V_{aa}^{\text{valen}} .$$

Table VI. Calculated isomer shift (mm/sec), quadrupole splitting (mm/sec), and magnetic hyperfine field (Tesla) for Fe impurity clusters for $\text{YBa}_2\text{Cu}_3\text{O}_7$. See Table IV for cluster geometry.

Cluster	A	B	C	D	E	F	G
IS	+0.00 ^a (-1.13)	+0.56 (-0.57)	+0.17 (-0.96)	+0.23 (-0.90)	+0.36 (-0.77)	+0.30 (-0.83)	+0.30 (-0.83)
QS ^b	+0.65	+1.57 ^c	+0.13	-1.40	+0.31	+0.40	+1.08
H _s ^d	-7.23 (+4.40)	-18.92	-32.67 (-9.65)	-25.42	-34.28 (-20.81)	-26.21 (-13.94)	-23.85 (-12.53)

a) Set to 0 here; values in parentheses are w.r.t. reference state Fe: La_2CuO_4 using IS = $A_c\Delta\rho_c(0)$,

$A = -0.25 \text{ mm} \cdot a_0^3/\text{sec}$.

b) Principal component = V_{zz} ; using Eq. (3) with $BQ = 0.83 \text{ mm} \cdot a_0^3/\text{sec}$ and

$\eta = |(V_{xx} - V_{yy})/V_{zz}|$. This value of B corresponds to the estimate $Q(^{57}\text{Fe}) = 0.08 \text{ b}$; older values would approximately double the coupling constant.

c) After diagonalization of V_{ij} ; eigenvalues are 1.529, -1.413, -0.117.

d) Using $H_s = A_c\rho_s(0)$, $A_s = 52.42 \text{ Tesla } a_0^3$. Values in parentheses obtained with von Barth-Hedin correlation potential.

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