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SUBSTITUTED SUPERCONDUCTING OXIDES*

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Theoretical and experimental Mössbauer spectroscopy studies have been made concerning charge and spin densities and magnetic hyperfine fields (H_{hf}) in iron-substituted superconducting oxides. Calculations were carried out in the self-consistent-field embedded cluster model using local density theory (SCF-X α) with a variational atomic orbital basis. Spectral densities and changes in charge and spin density were monitored around neighboring Cu sites, as well as Fe impurity site, in $La_2Cu_{1-x}Fe_xO_4$ and $YBa_2Cu_{3-x}Fe_xO_{7-y}$ compounds. Mössbauer isomer shifts (IS), quadrupole splittings (QS) and H_{hf} are obtained by fitting multiline models to the observed spectra and are compared with SCF-X α results for specific lattice sites. The influence of oxygen vacancies and partial oxygen disorder is modelled and compared with the experimental data on variable oxygen content and disorder.

I. INTRODUCTION

Hyperfine interactions provide a local probe of electric and magnetic fields which in turn provide information on the probe nucleus location and surrounding electronic structure. Nuclear magnetic resonance (NMR),

Mössbauer spectroscopy (MS), and the gamma-ray perturbed angular correlation (PAC) techniques have thus been used in extensive efforts to elucidate the electronic and site properties of the superconducting oxides. In order to gain more information than that obtainable from copper isotopes in the La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ compounds a variety of substituents have been considered, on virtually every crystal lattice site.

Here we will concentrate on the iron substituted superconducting oxides, of special interest for Mössbauer spectroscopy. Complex multiline spectra have been reported by many groups, including ourselves /1,2/, and a general consensus has begun to emerge about the shape of the spectra. However, a general understanding of the meaning of the three or more sites invoked to fit the data has been more difficult to obtain. Theoretical calculations of the hyperfine parameters at plausible sites are required to help develop adequate interpretation of the MS data.

We have carried out self-consistent-field local density calculations on clusters embedded in the crystalline solid, using the Discrete Variational (DV- $X\alpha$) method. Numerical atomic orbital basis functions are used to generate an expansion of the cluster eigenfunctions, and Mulliken population analysis is employed in the Self-Consistent-Charge approximation to the potential /3,4/. Long range Coulomb terms were included by a modified Ewald summation, and the exchange-correlation interaction was treated by the Kohn-Sham-Slater spin polarized approach. Cluster ranging in size from nine to thirty five atoms were used to represent different sites in the La- and YBa- based compounds. Charge and spin densities were evaluated by direct summation of eigenfunction densities, multiplied by Fermi-Dirac occupation numbers. Electric Field Gradient (EFG) matrix elements were evaluated numerically, using techniques previously developed /5/.

II. SELF-CONSISTENT CHARGE AND SPIN DISTRIBUTIONS

In Table I are presented the calculated self-consistent Mulliken atomic orbital charge and spin populations for Cu, Fe, and Ni at copper sites in La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$. One can see here the great stability of the $\text{Cu}^{\text{II}}\text{d}^9$ configuration in the electronic ground state at various sites in these hosts. In these and computations on other related crystal structures we find little or no evidence for the $\text{Cu}^{\text{III}}\text{d}^8$ configuration often invoked in constructing superconducting pairing models. Although Cu^{III} may be available as a low energy excitation, it apparently does not enter into the static lattice as envisioned in the classical valence counting schemes starting from a formal O^{2-} ionic picture. On the other hand, the population of the diffuse Cu 4s, 4p states is variable, responding to the local oxygen bonding environment. As oxygen is removed from the variational clusters, we do see evidence (not presented here) of formation of the $\text{Cu}^{\text{I}}\text{d}^{10}$ reduced oxidation state. These results are in general agreement with recent X-ray photoelectron and XANES measurements and experimental interpretation /6/.

In all the sites studied, iron shows a strong tendency to form the " Fe^{3+}d^5 " configuration, modified by admixture of 0.5-0.8 d electrons due to covalent mixing with oxygen ligand orbitals. This identification is based upon analysis of the density of states, which shows in addition to crystal-field-split levels dominated by Fe 3d character, a broad band of oxygen-dominated levels with some bonding Fe-d character. The resulting d-electron populations (5.5-5.8) and net charge (2.3-1.7) are very consistent with those calculated for trivalent sites in materials like wustite Fe_{1-x}O and magnetite Fe_3O_4 . The diffuse 4s, 4p character is seen to be similar to that of Cu on the same site. A high spin configuration of $3.0-4.4\mu_B$

is found, and a significant polarization is also induced on neighboring oxygen and copper sites. Both Cu and Fe are seen to be noticeably more ionic in the La-compound, in comparison to the YBa-compound.

The nickel substituent is also given in Table I for comparison with Fe; as expected its magnetism is considerably reduced. In fact, the moment of $1.5\mu_B$ in the La-system is consistent with its ionicity, while the order of magnitude smaller values in the Y-compound indicate the more extensive mixing with neighbor sites with resulting damping of moment.

The calculated Fe^{3+} high spin configuration is consistent with observed magnetic splittings in the MS and heat capacity measurements. However a range of magnetic hyperfine fields (H_{hf}) appears to be present at low temperatures, and the isomer shifts (IS) deduced by fitting three of four line spectra do not correspond very well with values commonly seen in trivalent compounds. Since it is probable that several sites are simultaneously occupied by substituent Fe, one is faced with difficulties in assigning a particular spectrum to a particular site and valence state. Thus calculations were undertaken to characterize the IS, EFG, and H_{hf} at several plausible sites. The following section gives a preliminary report of our findings.

III. HYPERFINE INTERACTIONS FOR Fe AT Cu SITES

In Table II are presented valence electron contributions to the electric and magnetic hyperfine interaction parameters at Cu sites in La_2CuO_4 and $YBa_2Cu_3O_7$. We have considered not only the substitution site in the La-compound and the chain (Cu(1)) and plane (Cu(2)) substitution sites in the YBa-compound, but also two additional geometries:

- (i) The Cu(1) site with octahedral coordination

due to two additional oxyanions in the nominally vacant O(5) site. Since the lattice is observed to take up oxygen upon doping by iron, and Fe^{3+} is often found in octahedral coordination, this is an interesting possibility.

(ii) A (110) displacement from the Cu(1) site giving approximately tetrahedral coordination. Not only is the tetrahedral coordination of Fe^{3+} very common in oxides, but neutron diffraction data can be fitted better with a two-site model with significant population of displaced Fe ions.

Here $V_{zz} = \langle \rho_c (3z^2 - r^2) / r^5 \rangle$, $V_{xx-yy} = \langle \rho_c (x^2 - y^2) / r^5 \rangle$, $V_{xy} = \langle \rho_c xy / r^5 \rangle$ and $\rho_c(0)$ and $\rho_s(0)$ are the charge and spin density at the nuclear site, respectively. Note that x, y, z here refer to crystalline a, b, c axes and not necessarily to field gradient principal axes.

The isomer shift difference for ^{57}Fe between two sites is $\Delta\delta \approx A_c \rho_c(0)$ and the contact magnetic hyperfine field is given by $H_{hf} \approx A_s \rho_s(0)$ with $A_c = -0.25 \text{ mm}/(a_0^3 \cdot \text{s})$ and $A_s = 524 \text{ kG}/a_0^3$. The IS constant, which depends upon the nuclear excited and ground state mean-square radius, is fairly well determined so that A_c is uncertain to perhaps $\pm 15\%$. The range of calculated IS differences covers the range of observed values.

The observed quadrupolar splittings range from 0.3 to 2.0 mm/s, and are related to the EFG parameters by $\Delta E = B V_{zz} (1 + \eta^2/3)^{1/2}$ where V_{zz} now refers to the local principal field gradient axis and the asymmetry parameter $\eta = |V_{xx-yy}/V_{zz}|$ is the ratio of the principal and secondary axis values. Using the currently favored value of the ^{57}Fe quadrupole moment of $Q = 8.2 \text{ fm}^2$ the value of $B \sim 0.83 \text{ mm} \cdot a_0^3/\text{s}$; the older value of 21 fm^2 would more than double this coupling constant /7/.

Lattice sums with point ions /8/ having the formal valence charges give very similar values for the EFG at the Cu site in La- and at Cu(1) and Cu(2) in the YBa-based mate-

rials. These off-site terms, given in Table III, contribute of the order of 5-7% of the observed ^{57}Fe EFG, using the value $Q = 8.2 \text{ fm}^2$. The formal lattice sums for Cu(1) and Cu(2) sites are somewhat problematical; we placed trivalent ions at Cu(1) and divalent ions at Cu(2), but evidence for the former is weak. Recently SCF-X α calculations have been made which variationally determine the crystalline charges without making any assumptions about site ionicity /9/. The self-consistent ionic charges and the resulting lattice sums are given in Table III; the SCF lattice sums are 80-90% of the formal lattice sums by virtue of the reduced theoretical ionic charges. Thus $\sim 95\%$ of the experimental EFG can be attributed to local electronic response, which requires detailed SCF modelling. In other words, Sternheimer Shielding (antishielding) factors of the order of 20 are indicated.

In order to make a comparison with experiment, the valence electron contributions of Table II have to be combined with core electron and nuclear contributions from the cluster, and with a lattice summation for ions exterior to the cluster. Thus

$$V_{zz}(\text{total}) = \sum_{\nu}^{\text{cluster}} Q_{\nu}^{\text{C}} (3z_{\nu}^2 - r_{\nu}^2) / r_{\nu}^5 - \langle \rho_{\text{C}} (3z^2 - r^2) / r^5 \rangle + \sum_{\nu}^{\text{exterior}} q_{\nu} (3z_{\nu}^2 - r_{\nu}^2) / r_{\nu}^5$$

where $Q_{\nu}^{\text{C}} = Z_{\nu} - N_{\nu}^{\text{C}}$ is the charge of the ionic core for the ion at site ν , q_{ν} are net ionic charges. For example, we find $V_{zz}(\text{total}) = + 0.20 a_0^{-3}$ for Cu in La_2CuO_4 and $+0.83 a_0^{-3}$ for Fe at the same site. Using smaller value of Q for ^{57}Fe we obtain a predicted ΔE of 0.69 mm/s, with the older value $Q = 21 \text{ fm}^2$, we obtain a predicted ΔE of 1.77 mm/s. In the Mössbauer spectra of $\text{Fe}:\text{La}_2\text{CuO}_4$ two doublets with $\Delta E = 1.48 \text{ mm/s}$ and 1.73 mm/s are found

and the understanding of the behavior of these two species with Ba doping needs still to be clarified /10/.

Detailed comparison with experiment for various sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ will be given elsewhere. At present we can say that lattice contributions exterior to the local cluster (31 atoms were used for La_2CuO_4 and 9-39 atoms for $\text{YBa}_2\text{Cu}_3\text{O}_7$) amount to less than 5% of the total EFG, and are thus of the same order or less than uncertainty in the variational calculations. The calculated electronic contributions span about half of the range of the splittings deduced for a three or four line spectrum in $\text{YBa}_2\text{Cu}_3\text{O}_7$. While it is clear that a more accurate determination of the origins of the EFG at different sites will not of itself completely resolve the questions about site occupancy and valency, we believe that taken with other data this result can be very useful.

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Table I - Self-consistent-field local density Mulliken populations for charge and spin (μ_B) at the copper sites in La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ for Cu, and Fe and Ni substituents.

site \rightarrow	La_2CuO_4		$\text{YBa}_2\text{Cu}_3\text{O}_7$		chain	plane
	charge	spin	charge	spin	charge	spin
Cu 3d	9.17	0.19	9.01	0 ^a	8.88	0 ^a
4s	0.07	-0.00	0.22	.	0.48	
4p	0.08	-0.00	0.86		0.10	
Net:	1.68	0.19	0.92		1.55	
Fe 3d	5.47	4.44	5.77	2.97	5.73	3.98
4s	0.09	-0.01	0.32	0.05	0.20	0.08
4p	0.13	-0.01	0.17	0.03	0.37	0.17
Net:	2.30	4.42	1.74	3.05	1.70	4.23
Ni 3d	8.24	1.45	8.05	0.04	8.24	0.11
4s	0.08	-0.00	0.31	0.00	0.19	0.00
4p	0.11	-0.00	0.16	0.00	0.29	0.00
Net:	1.56	1.45	1.47	0.05	1.30	0.11

a) Spin-restricted calculation.

Table II - Valence Electron Contributions (e/a_0^3) to hyperfine interactions at the copper sites in La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ for Cu and Fe substituent.

site ->	La_2CuO_4	$\text{YBa}_2\text{Cu}_3\text{O}_7$:	chain	: plane	
Cu V_{zz}	-0.72	-0.68		-0.32	
V_{xx-yy}	0.0	-0.02		0.10	
Fe V_{zz}	-1.35	-0.24 ^a	0.18 ^b	-0.71 ^c	0.12
V_{xx-yy}	0.0	0.58	0.01	0.26	0.0
V_{xy}	0.0	0.0	0.0	0.36	0.0
$\rho_C(0)$	2.86	7.21	5.76	--	5.51
$\rho_S(0)$	0.24	1.66	0.76	--	0.72

a) Normal site: O(5) vacant.

b) Octahedral coordination: O(5) occupied.

c) Tetrahedral coordination: offset in (110) direction.

Table III - Effective ionic charges and lattice sums in La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$. (x,y,z) correspond to crystalline (a,b,c) axes.

La_2CuO_4		charges		
<u>Ion</u>	<u>formal</u>		<u>SCF</u>	
La	+3		2.8004	
Cu	+2		1.7198	
O(1)	-2		-1.7935	
O(2)	-2		-1.8672	
$\text{YBa}_2\text{Cu}_3\text{O}_7$		charges		
<u>Ion</u>	<u>formal</u>		<u>SCF</u>	
Y	+3		2.7300	
Ba	+2		1.9936	
Cu(1)	+3 ?		1.7192	
Cu(2)	+2 ?		1.7584	
O(1)	-2		-1.6193	
O(2)	-2		-1.7336	
O(3)	-2		-1.7637	
O(4)	-2		-1.6665	
EFG at Cu sites (a_0^{-3})				
		V_{xx}	V_{yy}	V_{zz}
La_2CuO_4	formal charges	-0.0462	-0.0462	+0.0924
	SCF	-0.0403	-0.0403	+0.0807
$\text{YBa}_2\text{Cu}_3\text{O}_7$	formal charges Cu(1)	+0.1684	-0.0555	-0.1130
	SCF	+0.1321	-0.0483	-0.0824
	formal charges Cu(2)	-0.0559	-0.0425	+0.0984
	SCF	-0.0454	-0.0370	+0.0824