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Electric Field Gradients at Copper Sites in the High T_c Superconductor $YBa_2Cu_3O_{7-x}$

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Quadrupole coupling constants of ^{63}Cu in the high T_c superconductor $YBa_2Cu_3O_{7-x}$, as determined by NQR or NMR studies, are compared with the values for representative Cu(II) complexes determined by analyzing the forbidden lines in their EPR spectra. It is shown that the two NQR lines at 22 and 31 MHz correpsond to the quadrupole coupling constants of a square planar Cu(II) complex and a square pyramidal Cu(II) complex, respectively. This result is in agreement with the assignment of these lines to Cu(1) and Cu(2) sites in YBCO based on the NMR spectra of oriented single crystals.

Introduction

Various experimental techniques have been used to study the high T_c superconductor $YBa_2Cu_3O_{7-x}$(YBCO) first prepared by Wu *et al.*[1] The nuclear quadrupole resonance(NQR) and nuclear magnetic resonance(NMR), which can give information on the electric field gradient(efg) at the nucleus, might be useful in clarifying the electronic structure at the copper sites of YBCO.

The NQR spectra of ^{63}Cu and ^{65}Cu in YBCO have been reported by several authors.[2-4] ^{63}Cu shows two distinct NQR lines at frequencies of approximately 22 and 31 MHz. These lines may be attributed to the two inequivalent copper sites, namely the Cu(1) site in one-dimensional CuO chains running along the *b* axis and the Cu(2) site in two-dimensional CuO sheets in the *a-b* plane; see Figure 1.[5] Earlier papers assigned the 22 and 31 MHz lines to the Cu(2) and Cu(1) sites, respectively.[3,4] However, recently Pennington *et al.* assigned the 22 MHz line to the Cu(1) site and the 31 MHz line to the Cu(2) site on the basis of their NMR studies on the oriented single crystals of YBCO.[6] An independent NMR study of Shimizu *et al.* on a highly oriented powder sample gave the same result.[7]

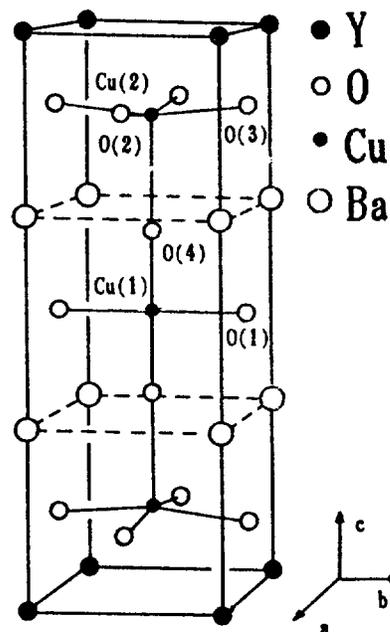Twenty years ago we determined the quadrupole coupl-

Figure 1. Unit cell of the $YBa_2Cu_3O_7$ crystal structure from Ref. 5.

Table 1. Nuclear Quadrupole Coupling Constants for Cu(II) Complexes

Configuration	Compound*	$Q'(10^{-4}cm^{-1})$
Square Planar	Cu(dbm)$_2$	3.2
	Cu(bzac)$_2$	3.3
	Cu(acac)$_2$	3.3
	Cu(dpm)$_2$	3.5
Square pyramidal	Cu(bzac)$_2$·C$_2$H$_5$OH	6.0
Octahedral	Cu(HCO$_2$)$_2$·2H$_2$O	10.4

*Cu(dbm)$_2$: bis(1,3-diphenyl-1,3-propanedionato)copper(II),
Cu(bzac)$_2$: bis(1-phenyl-1,3-butanedionato)copper(II), Cu(acac)$_2$:
bis(2,4-pentanedionato)copper(II), Cu(dpm)$_2$: bis(dipivaloylmethani-
do) copper(II).

ing constants of a series of Cu(II) complexes by analyzing the forbidden lines in their EPR spectra,[8] and interpreted efg as a sum of the valence electron term and the ligand charge term. In this paper, we use the same approach to interpret the recent NMR data for YBCO.

Interpretation of Nuclear Quadrupole Coupling Constants. Here we briefly review our earlier work relevant to the present problem. In our EPR work we used the following nuclear quadrupole coupling term in the spin Hamiltonian for an axial system:

$$H_Q = Q' \{I_z^2 - I(I+1)/3\} \qquad (1)$$

where Q' is the nuclear quadrupole coupling constant. The Q' values determined for a series of Cu(II) complexes with oxygen ligand atoms are listed in Table 1.

It is noted that the octahedral complex has the largest Q' value and that Q' decreases gradually as the axial ligand is removed one by one.

For ^{3}Cu($I = 3/2$), Q' is given by

$$Q' = e^2 qQ/4, \qquad (2)$$

where eq is the electric field gradient and eQ is the nuclear quadrupole moment. Since the Q value for ^{63}Cu is known to be -0.211 b,[9] the main problem here is to relate efg to molecular structure and bonding.

It is easy to estimate the Q' value of the free ion Cu^{2+}. The efg is given by

$$eq = -e<r^{-3}>_{3d}(1-R)\sum_i n_i<3\cos^2\theta_i-1>_{3d} \qquad (3)$$

where n_i is the orbital occupation number, $(1-R)$ is the Sternheimer core polarization correction,[8] and θ_i is the angle between the z axis and the vector from the metal nucleus to an electron in orbital i. $<3\cos^2\theta-1>$ values are $-4/7$ for $3d_{x^2-y^2}$ and $3d_{xy}$, $2/7$ for $3d_{yz}$ and $3d_{xz}$, and $4/7$ for $3d_{z^2}$. For most copper(II) complexes the unpaired electron is located in the $3d_{x^2-y^2}$ orbital. Using $<r^{-3}>_{3d} = 8.25$ a.u.[10] and $(1-R) = 0.822$,[9] we calculate $Q' = 15.8 \times 10^{-4}$ cm^{-1} when the unpaired electron is in the $3d_{x^2-y^2}$ orbital.

The Q' values in Table 1 are considerably smaller than the value calculated for the free ion Cu^{2+}. Two most important mechanisms responsible for this reduction in the efg are the rearrangement of electron charge density in the $3d$ orbitals brought about by the covalent bonding and the effect of the ligand charges. These two effects may be taken into account by writing

$$eq = (1-R)feq_{val} + (1-\gamma_\infty)eq_{lig} \qquad (4)$$

where f is the covalency correction, $(1-\gamma_\infty)$ is the Sternhemer antishielding correction,[8] and q_{val} and q_{lig} are efg's due to the valence electrons and the ligand charges, respectively. The quadrupole coupling constant can also be expressed as a sum of two terms.

$$Q' = Q'_{val} + Q'_{lig} \qquad (5)$$

$$Q'_{val} = \frac{1}{4}e^2Q(1-R)fq_{val} \qquad (6)$$

$$Q'_{lig} = \frac{1}{4}e^2Q(1-\gamma_\infty)q_{lig} \qquad (7)$$

For the octahedral complexes the net ligand contribution to Q' should be small. If Q'_{lig} is assumed to be zero for Cu(HCO$_2$)$_2$·2H$_2$O, then the reduction of Q' from 15.8×10^{-4} cm^{-1} for the free ion Cu^{2+} to 10.4×10^{-4} cm^{-1} can be explained by the covalency correction $f = 0.66$.

The covalency correction can be calculated, when the orbital populations are known. The Mulliken population analysis for the planar Cu(dpm)$_2$ shows a significant rearrangement of electron charge density in the 3d orbitals.[11] Comparing the efg obtained from this arrangement with the free ion value, we obtain $f = 0.54$.[8]

The ligand contribution cannot be neglected for square pyramidal and square planar complexes. Although calculated values of q_{lig} is small even for these complexes, it is known that the effect of q_{lig} can be amplified one to two orders of magnitude by the antishielding effect of the core electrons.[9] As one ligand is removed from the axial site of an octahedral complex, there is more negative charge in the xy plane compensating the positive electron hole in the $3d_{x^2-y^2}$ orbital. Thus the Q' value is reduced in the square pyramidal complex. If the f value is known, the Q' value for the square pyramidal Cu(bzac)$_2$·C$_2$H$_5$OH may be separated into Q'_{val} and Q'_{lig}. On assuming $f = 0.66$, we get $Q'_{val} = 10.4 \times 10^{-4}$ cm^{-1} and $Q'_{lig} = -4.4 \times 10^{-4}$ cm^{-1}. For $f = 0.54$, we get $Q'_{val} = 8.5 \times 10^{-4}$ cm^{-1} and $Q'_{lig} = -2.5 \times 10^{-4}$ cm^{-1}.

As one more ligand is removed from the axial site, the Q' valus is further reduced in the square planar complexes. Using $f = 0.54$ for Cu(dpm)$_2$, we calculate $Q'_{val} = 8.5 \times 10^{-4}$ cm^{-1} and $Q'_{lig} = -5.3 \times 10^{-4}$ cm^{-1}.

Thus the trend of the Q' values in Cu(II) complexes can be explained in terms of Q'_{val} and Q'_{lig}.

EFG's at Copper Sites of YBCO. Before the NMR data of Pennington *et al.* is analyzed, the oxidation states of the copper atoms in YBCO will be considered briefly. YBCO is metallic above T_c, and its electronic structure may be described by a band model. Still we can assign average oxidation states to the copper atoms in YBa$_2$Cu$_3$O$_{7-x}$. x varies according to sample preparations,[22] the value for best samples being 0.1-0.2. If the oxidation states of Y, Ba and O in the YBCO are assumed to be $+3$, $+2$, and -2, respectively, the average oxidation state of Cu is 2.3-2.2, indicating that Cu^{3+} might exist along with Cu^{2+} in YBCO.

X-ray photoelectron and X-ray absorption spectra of YBCO have been measured by a number of workers in order to determine the oxidation states of the copper atoms. It is generally agreed that the Cu(2) site is occupied by Cu^{2+}, but there is some disagreement on the valence of the copper atom occupying the Cu(1) site. Most X-ray photoelectron

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spectra have been interpreted in terms of Cu^{2+} in the Cu(1) site with an electron hole at a nearby oxygen atom.[12-15] But some workers believe that Cu^{3+} contribute to their photoelectron spectra.[16] In addition, some calculations on the band structure of YBCO support the existence of Cu^{3+} in the Cu(1) site.[17,18]

Now we turn to the NMR data of Pennington *et al.*[6] They defined the following frequencies:

$$\nu_{\alpha\alpha} = \frac{eQV_{\alpha\alpha}}{2h} \tag{8}$$

where $V_{\alpha\alpha}$ ($\alpha = x$, y or z) is the principal component for the electric field gradient tensor. It is convenient to define $Q'_{\alpha\alpha}$ for ^{63}Cu:

$$Q'_{\alpha\alpha} = \frac{\nu_{\alpha\alpha}}{2c} \tag{9}$$

where c is the speed of light. Then the nuclear quadrupole coupling constant Q' is the same as Q'_{zz}.

Pennington *et al.* determined the following $\nu_{\alpha\alpha}$ ($\alpha = a$, b or c) values along the crystal a, b and c axes.

	a	b	c
31.5 MHz line:	$\pm$(-15.8,	-15.8,	31.46) MHz
22.0 MHz line:	$\pm$(19.0,	-19.2,	0.15) MHz

The 31.5 MHz line, being axially symmetric and having the z principal axis along the crystal c axis, was assigned to the Cu(2) site. The Q' value corresponding to $\nu_{zz} = 31.46$ MHz is 5.25×10^{-4} cm^{-1}. This value is close to that of a square pyramidal Cu(II) complex; see Table 1.

The 22.0 MHz line then should be assigned to the Cu(1) site. Cu(1) has a square planar configuration, and its z principal axis is expected to lie along the crystal a axis. Thus we assume ν_{aa} to be positive. The ν_{aa} value corresponds to $Q' = 3.17 \times 10^{-4}$ cm^{-1}, which is close to those of square planar Cu(II) complexes in Table 1.

In order to explain the large in-plane anisotropy of the 22 MHz line, we will estimate the contributions of valence electrons and the ligand charges to each of the principal components of the electric field gradient tensor. The contributions of the valence electrons are related by

$$Q'_{xx}(val) = Q'_{yy}(val) = -0.5Q'_{zz}(val). \tag{10}$$

The ligand contribution will be estimated using a point charge model. We assume the ideal structure YBa$_2$Cu$_3$O$_7$ with $1 \times Y^{3+}$, $2 \times Ba^{2+}$, $3 \times Cu^{2+}$, $4 \times O^{2-}$[O(2) and O(3)], and the electron hole delocalized over one O(1) and two O(4)'s. The charges of O(4) and O(1) may be designated n and $(-5-2n)$, respectively, since their total charge should be -5. Using the internuclear distances 1.85Å for Cu-O(4) and 1.94Å for Cu-O(1),[5] we have calculated the ligand contribution to $V_{\alpha\alpha}$ for various n values. The result for $n = -1.8$ is shown below.

$$V_{xx}(lig) = -0.99 \times 10^{14} \ e.s.u. \ (//b \ axis)$$
$$V_{yy}(lig) = -3.53 \times 10^{14} \ e.s.u. \ (//c \ axis)$$
$$V_{zz}(lig) = -4.52 \times 10^{14} \ e.s.u. \ (//a \ axis)$$

Since $(1-\gamma_\infty)$ is isotropic in the first approximation, $Q'_{\alpha\alpha}$ (*lig*) values should be proportional to $V_{\alpha\alpha}$. Now we can solve the following equations.

$$Q'_{xx}(val) + Q'_{xx}(lig) = -3.20 \times 10^{-4}$$
$$Q'_{yy}(val) + Q'_{yy}(lig) = 0.03 \times 10^{-4}$$
$$Q'_{zz}(val) + Q'_{zz}(lig) = 3.17 \times 10^{-4}$$

For $n = -1.8$, we get the following $Q'_{\alpha\alpha}$ values in units of 10^{-4} cm^{-1}.

α	$Q'_{\alpha\alpha}$(val)	$Q'_{\alpha\alpha}$(lig)	$Q'_{\alpha\alpha}$(total)
x	-4.47	1.27	-3.20
y	-4.47	4.50	0.03
z	8.94	-5.77	3.17

The covalency correction calculated from Q'_{zz} (*val*) is $f = 0.57$. The value of f is dependent upon the choice of n. For the range of reasonable values $f = 0.5$-0.7, n is (-1.75)-(-1.85) and the corresponding charge of O(1) is (-1.5)-(-1.4). The fact that O(4) has a greater negative charge than O(1) is in agreement with the shorter Cu-O(4) distance compared to Cu-O(1).

The Sternheimer antishielding correction calculated from Q'_{zz}(*lig*) for $n = -1.8$ is $(1-\gamma_\infty) = 10$, which is comparable to the calculated value 16.5[9] or 18.6[19] for Cu$^+$(3d^{10}). The fact that the antishielding correction is as large as 10 indicates that the electron charge density of the Cu^{2+} ion is distorted significantly by the ligand charges. Therefore separating the *efg* into a valence electron term and a ligand charge term is rather arbitrary. However, the strong dependence of Q' on the configuration of the Cu(II) complex and the large in-plane anisotropy of the *efg* for the Cu(1) site in YBCO can be explained only if the contribution of the ligand charges to the *efg* is assumed to be comparable to that of the valence electron term.

We have shown that the NQR and NMR data on the electric field gradients of ^{63}Cu in YBCO can be adequately explained in terms of the Cu^{2+} ions in the square planar and square pyramidal configurations. A Cu^{3+} ion in a square planar configuration would have a quite different quadrupole coupling constant. Unfortunately, no NQR data is available for authentic Cu(III) complexes. All known Cu(III) complexes with the exception of K$_3$CuF$_6$ are diamagnetic. For a square planar, diamagnetic Cu(III) complex with the vacant $3d_{x^2-y^2}$ orbital, its eq_{val} should be at least twice that of a square planar Cu(II) complex. We estimate $Q' > 10 \times 10^{-4}$ cm^{-1} for such a Cu(III) complex. The fact that the experimental Q' value for Cu(1) in YBCO is much smaller than this estimation indicates that the copper ion occupying the Cu(1) site is not Cu^{3+}. NQR measurements on authentic Cu(III) complexes[20,21] are needed to confirm this argument.

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# The Structural Features and Rotational Barriers in Indenyl Allyl Metal Complexes

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The electronic structure, conformational preferences, and rotational barriers have been studied for transition metal indenyl allyl complexes by means of extended Hückel calculations. After geometrical optimization the exo conformation of allyl moiety is favored over the endo. The rotational barrier of indenyl ring in (Indenyl)Mo(CO)₂(Allyl) is computed to be 3.8 kcal/mol. Population analysis is applied to account for the conformational preferences and rotational barriers. A series of substituted allyl complexes has been also optimized. It shows steric hindrance plays a crucial role in setting the allyl orientation.

Introduction

There is interest in the conformational preferences and rotational barriers in polyene transition metal complexes. It is a common field which has been investigated by theoreticians and experimentalist. There are many experimental data on rotational barriers of organometallic compounds, as well as on conformational preferences studied mainly by NMR technique and diffraction methods.[1] Recently several studies have been reported on the polyene allyl complexes which show a variety of reactivity and interesting stereospecificity on the allyl group. The crystal structures of ML_n(allyl)(polyene), polyene = cyclopentadienyl(Cp) or indenyl(In), show exo orientation (1) of allyl group.[2] However, these complexes exhibit exo–endo (2) interconversion. This paper describes the electronic structure of transition metal indenyl dicarbonyl allyl complexes with an emphasis on conformational preferences and rotational barriers. We have also examined a series of substituted allyl complexes to
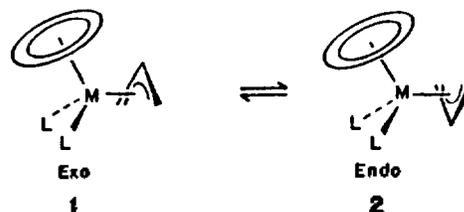
determine the orientation of the allyl moiety. There are two kinds of rotational barrier in indenyl allyl complexes. Those are concerned with indenyl and allyl units. We shall first concentrate our attention on the electronic and geometrical requirements for the allyl moiety. But before we do so, it is necessary to investigate the metal fragment orbitals. Our computations are of the extended Hückel method with details given in the Appendix.

The (Indenyl)M(CO)₂ Fragment. The orbitals of (In)M(CO)₂ fragment is very similar to that of CpM (CO)₂ fragment which can be obtained in a number of ways.[3,4] We shall briefly describe the salient features of the analysis. The