# Structural implications of nuclear electric quadrupole splittings in high-$T_c$ superconductors

Frank J. Adrian

*Milton S. Eisenhower Research Center, The Applied Physics Laboratory,*
*The John Hopkins University, Laurel, Maryland 20707*
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The electric field gradients and nuclear quadrupole coupling constants are calculated for La in $La_2CuO_4$, Eu in $EuBa_2Cu_3O_7$, and Cu and Fe (as a replacement for Cu) in $YBa_2Cu_3O_7$. We use an ionic model which regards the high-$T_c$ superconductors as primarily ionic crystals modified by the introduction of a relatively small number of charge carriers via doping in $La_2CuO_4$ and non-stoichiometry in $YBa_2Cu_3O_{7-\delta}$ for $\delta < 0.5$. Good agreement between theory and experiment is obtained for the spherically symmetric free-ion species $La^{3+}$ and $Eu^{3+}$ with distortion of the partially filled $Eu^{3+}$ $^4F_0$ state by the ionic crystal field playing an important role. Comparison of theory and experiment for the Cu and Fe cases suggests Cu is present largely as $Cu^{2+}$ and supports the assignment of the low- and high-frequency nuclear quadrupole resonance lines to the chain and plane sites of $YBa_2Cu_3O_7$, respectively, while Fe is present as a mixture of $Fe^{2+}$ (ca. 25% to 50%) and $Fe^{3+}$.

## INTRODUCTION

Nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), and Mössbauer spectroscopies are especially useful methods for investigating the structure of solids because the observed shifts and splittings of the nuclear resonance lines often can be interpreted with the aid of relatively simple semiempirical theories to yield important information about the electronic structure of the material being investigated. Considerable progress has already been made in application of these techniques to high-$T_c$ superconductors, with some of the most useful information obtained so far being the nuclear electric quadrupole splittings of such nuclei as $^{139}La$ in $La_2CuO_4$ and $(La_{1-x}Sr_x)_2CuO_4$ (Refs. 1 and 2), $^{151}Eu$ in $EuBa_2Cu_3O_7$ (Ref. 3), $^{63}Cu$ in $YBa_2Cu_3O_7$ (Refs. 4–6) and perhaps $La_2CuO_4$ also,[1] and $^{57}Fe$ introduced as a substitute for Cu in $YBa_2Cu_3O_7$.[7-11]

Here we discuss these quadrupole splittings and their implications for the electronic environment around the various ions using a model that regards the high-$T_c$ superconductors as primarily ionic crystals modified by the introduction of a relatively small number of charge carriers by alkaline earth doping in $La_2CuO_4$ and non-stoichiometry in $YBa_2Cu_3O_{7-\delta}$ for $\delta < 0.5$ (Ref. 12). The electric quadrupole splittings can be calculated using this model together with certain assumptions about the electronic structures of the open-shell Cu and Fe ions. Comparison of the calculated values with experiment provides both a test of the ionic model and information about the electronic states and bonding interactions of the various ions. For the La and Eu nuclei the calculated values agree well with experiment. The results for Cu and Fe are more complicated because of the open-shell structure of these ions, and although they agree with experiment for reasonable assumptions about the charge states of the Cu and Fe ions, they also raise interesting questions for further experimental and theoretical investigation.

## THEORY AND DISCUSSION

In systems of this type, the nuclear electric quadrupole interaction, $e^2qQ$ where $Q$ is the nuclear quadrupole moment and $q$ is the electric field gradient at the nucleus and strictly speaking is a tensor quantity, will be composed of an intra-atomic or valence term [denoted $(e^2qQ)_{val}$] if the quadrupolar nucleus is located in an atom or ion having incomplete, and thus nonspherically, symmetric valence shells, and a term which is due to all contributions from ions and atoms other than the subject atom or ion [denoted $(e^2qQ)_{lat}$]. It is well known, however, that the lattice contributions usually are indirect rather than direct ones in that they result from distortion of the atomic or ionic orbitals of the subject atom or ion by the lattice interactions, the classic example being the Sternheimer antishielding which increases, often greatly, the contribution of an external ionic charge to $e^2qQ$.[13] Also, for a species with low-lying excited states, such as the manifold of $J$ states produced by spin-orbit coupling in $Eu^{3+}$ $(4f)^6$, distortion of the spherically symmetric ground state of the free ion by the crystal field of the surrounding ions may contribute significantly to $(e^2qQ)_{lat}$.

### La in $La_2CuO_4$

The computation of the ionic contribution to $e^2qQ$ is well illustrated by this case which is the simplest because La is undoubtedly present in $La_2CuO_4$ and $(La_{1-x}Sr_x)_2CuO_4$ as the closed-shell $La^{3+}$ ion. Thus, the quadrupole splitting should be determined solely by the electric field gradient of the surrounding ions at the $La^{3+}$ ion. The observed quadrupole splitting is nearly the same in the pure nonsuperconducting $La_2CuO_4$ and the doped superconductor and corresponds to a quadrupole coupling constant $|e^2qQ| = 89.4$ MHz with a negligible asymmetry parameter for the $I = \frac{7}{2}$ $^{139}La$ nucleus.[1]

The contribution of the ionic crystal field to $(e^2qQ)_{lat}$ for the case of an axially symmetric system (extension to nonaxial systems is straightforward) is

$$(e^2Qq)_{ionic} = e^2Q(1-\gamma)\sum_L Q_L(3\cos^2\theta_L - 1)/r_L^3, \quad (1)$$

where $\gamma$ is the Sternheimer antishielding factor of the subject atom or ion, and $Q_L$, $r_L$, and $\theta_L$ are, respectively, the charge of the $L$th ion, the distance of this ion from the subject nucleus, and the angle between the vector from this nucleus to ion $L$ and the symmetry axis for the field gradient tensor. In $La_2CuO_4$ the crystallographic $c$ axis is the symmetry axis.

Calculating the ionic field gradient at $La^{3+}$ in $La_2CuO_4$ as described previously[12] with ionic charges $La^{3+}$, $Cu^{2+}$, and $O^{2-}$, and introducing the experimental result $Q(^{139}La) = 0.21 \times 10^{-24}$ cm$^2$,[14] and the calculated value $\gamma_{La^{3+}} = -76$ (Ref. 15), gives $(e^2qQ)_{ionic} = -85.2$ MHz, in good agreement with the experimental value $\pm 89.4$ MHz.

### Eu in EuBa$_2$Cu$_3$O$_7$

Mössbauer investigations of $^{151}$Eu in EuBa$_2$Cu$_3$O$_7$ have shown that Eu is present as $Eu^{3+}$ with a $(4f)^6$ electron configuration,[16] and have indicated a quadrupole coupling constant $|e^2qQ| = 125$ MHz where $Q$ is the quadrupole moment of the $^{151}$Eu nucleus in its ground state.[3] The ionic field gradient will contribute to $e^2qQ$ here just as it did for La in $La_2CuO_4$; however, there is the likelihood of an additional contribution to $e^2qQ$ due to distortion of the open $(4f)^6$ shell of $Eu^{3+}$ by the crystal field. This can occur even though the free $Eu^{3+}$ ion has a spherically symmetric $(L = S = 3, {}^7F_{J=0})$ ground state because the separations of the lower $J$ levels in this multiplet are quite small. The energies of this $J = 0$ to 6 multiplet are $(\lambda/12)[J(J+1) - L(L+1) - S(S+1)]$, where $\lambda$ is the spin-orbit splitting constant of a La $4f$ electron.[17] Calculation of $\lambda$ from the formula (Ref. 18),

$$\lambda = 2\beta^2\langle\psi_{La4f}|r^{-1}dU/dr|\psi_{La4f}\rangle$$

where $\beta$ is the Bohr magneton, and $U$ is the average potential energy of an electron in La, using the results of Herman and Skillman[19] for $U$ and the La $4f$ orbital gave $\lambda = 0.22$ eV.

In addition, the calculated $e^2qQ$ depends on how the additional holes demanded by the YBa$_2$Cu$_3$O$_{7-\delta}$ nonstoichiometry for $\delta < 0.5$, which we denote as the nonstoichiometry holes to distinguish them from the holes intrinsically present on the $Cu^{2+}$ ion in the stoichiometric YBa$_2$Cu$_3$O$_{6.5}$, are distributed between the CuO$_2$ planes and the CuO chains.

The ionic crystal field contribution to $e^2qQ$, with the nonstoichiometry holes distributed equally among the chain Cu and O ions [this gives the ionic charges $Eu^{3+}$, $Cu(2)^{2+}$, $O(2)^{2-}$, $O(3)^{2-}$, $Ba^{2+}$, $O(1)^{-1.75}$, $O(4)^{-1.75}$, and $Cu(1)^{+2.25}$, in which the ion designations are the conventional crystallographic ones] is calculated from Eq. (1), using the YBa$_2$Cu$_3$O$_7$ crystal-structure data of David et al.[20] for that of the unknown but undoubtedly very similar EuBa$_2$Cu$_3$O$_7$ structure. With the value

$Q(^{151}$Eu$) = 1.16 \times 10^{-24}$ cm$^2$ (Ref. 14), and taking the Sternheimer antishielding factor to be $\gamma_{Eu^{3+}} = -80$ as suggested by Watson and Freeman[15] one obtains $e^2qQ_{ionic} = -264$ MHz.

The calculation of the contribution to $e^2qQ$ from distortion of the spherically symmetric $Eu^{3+}(4f)^6$, $L = S = 3$, $J = 0$ ground state by the crystal field, which admixes other $J$ states with this state, is most conveniently carried out by noting that for this $S = 3$ state the six $4f$ electrons of $Eu^{3+}$ must go into different $m_l$ states so that the ion is one electron short of having a spherically symmetric, half-filled $4f$ shell. This permits treatment of the problem in terms of a single missing electron or positive hole in the half-filled $4f$ shell with a fictitious spin of 3 provided that all matrix elements of spin operators are divided by the number of spins or 6. (This method readily yields the previously given formula for the spin-orbit energies of the different $J$ states.) The calculation is then straightforward, starting with the "one particle" ${}^7F_{J=0-6,M_J}$ states for which the spin-orbit Hamiltonian is diagonal. These states are then used to construct states that transform according to the various irreducible representations of the $C_{2h}$ symmetry group of the ionic crystal field, and with the aid of the Herman-Skillman Eu $4f$ orbital,[19] the crystal-field Hamiltonian is calculated including terms up to $l = 6$ in the ionic crystal-field potential.[12] This Eu $4f$ orbital was also used to calculate $\langle 1/r^3\rangle_{Eu,4f}$ and the quadrupole splitting constant of a Eu $4f$ hole, obtaining $(e^2qQ)_{Eu,4f_m=0} = 1200$ MHz. For the aforementioned assignment of the nonstoichiometry holes one finds that the distorted $Eu^{3+}$ ion has a ground state of $A_{1g}$ symmetry in the approximately tetragonal crystal field and a quadrupole splitting $(e^2qQ)_{4f,dist} = 370$ MHz due to distortion of the La $4f$ shell. Thus, the net calculated result is $e^2qQ = 106$ MHz whose agreement with the experimental value of $\pm 125$ MHz is quite good for this complicated case where the result is the difference between terms of opposite sign.

If the nonstoichiometry holes in YBa$_2$Cu$_3$O$_7$ are shared equally among the Cu and O ions in the CuO$_2$ plane [i.e., $Eu^{3+}$, $Cu(2)^{2.167+}$, $O(2)^{1.833-}$, $O(3)^{1.833-}$, $Ba^{2+}$, $O(1)^{2-}$, $Cu(1)^{2+}$, and $O(4)^{2-}$] the various contributions to the $Eu^{3+}$ quadrupole splitting are $(e^2qQ)_{ionic} = -366$ MHz, and $(e^2qQ)_{4f,dist} = 616$ MHz. This gives a net calculated quadrupole splitting constant of 250 MHz which is in considerably worse agreement with experiment than is the case where the holes are predominantly in the CuO chain. Although the complexity of the calculation limits the weight that can be placed on this indication of a preference of the holes for the CuO chain, it is consistent with the results of crystal-field calculations which suggest that Madelung energy considerations favor placing at least half the holes in the chain.[12]

### Fe substituted for Cu in YBa$_2$Cu$_3$O$_7$

Of the various transition-metal ions which can be substituted for Cu up to roughly 10% with only gradual lowering of the superconducting transition temperature iron is of special interest because $^{57}$Fe is a Mössbauer nu-

cleus. There have been a number of Mössbauer spectroscopic investigations of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ which generally agree in finding that the $^{57}Fe$ Mössbauer line is split into three nuclear quadrupole doublets denoted $A$, $B$, and $C$ with splittings of approximately 2.0, 1.1, and 0.6 mm/s or 23.2, 12.8, and 6.7 MHz, respectively.[7–11] The isomer shifts of the $A$ and $B$ doublets have the same value of 0.14 mm/s relative to Fe metal whereas the $C$ doublet has a larger shift of 0.29 mm/s.

These investigations differ considerably, however, regarding the relative intensities of the $A$, $B$, and $C$ lines (although the intensity of the $C$ doublet is generally considerably less than that of the other lines, especially at low Fe concentrations), and the dependence of these intensities on Fe concentration, sample preparation, etc., with corresponding differences in the assignment of the doublets to Fe at the two different Cu sites in $YBa_2Cu_3O_7$. The majority opinion of the experimental investigations is that the $A$ and $B$ doublets be assigned to the Fe at the Cu(1) (chain) and Cu(2) (plane) sites, respectively. The reasons for this assignment are the greater intensity of the $B$ doublet consistent with the Cu(2) sites being twice as abundant as Cu(1) sites, and the fact that the calculated ionic field gradient at Cu(1) is almost twice that of the field gradient at Cu(2) in agreement with the ratio of the $A$ and $B$ quadrupole splittings. Tamaki et al.[9] propose the reverse assignment, however, finding, in contrast to other work, that the intensity of the $A$ doublet is generally considerably greater than that of the $B$ doublet, and that the latter's intensity is quite sensitive to Fe and O concentrations and the thermal history of the sample, as might be expected for the Cu(1) site whose nearest-neighbor oxygen ions are probably more easily added or removed than are the oxygens of the $CuO_2$ plane. Our results will indicate that an assignment based on the ratio of the calculated ionic field gradients, which assumes that the substituted iron is present solely as the spherically symmetric $Fe^{3+}$ with no valence contribution to $e^2qQ$, is questionable. Nonetheless, the present investigation will also suggest that it is reasonable, though not completely definite, to assign the $A$ and $B$ doublets to Fe at the Cu(1) and Cu(2) sites, respectively.

Assuming for the moment the substituted iron is present as $Fe^{3+}$, which has a spherically symmetric $^6S$ ground state whose separations from the other states of the $Fe^{3+}$ $(3d)^5$ configuration are too great for appreciable distortion of the $^6S$ state by the crystal field,[21] then $(e^2qQ)_{val}$ should be zero, and the field gradient and quadrupole splitting will be determined solely by the ionic crystal field. This calculation of $(e^2qQ_m)_{ionic}$ is straightforward using Eq. (1), the calculated value of $\gamma_{Fe^{3+}}$ $=-9.1$,[22] and a determination of the quadrupole moment of $^{57}Fe$ in its metastable state which gave the result $Q_m=0.213$ (10) $^{-24}$ cm.[23] This result was obtained from the quadrupole splitting of the relatively simple Fe dimer in inert gas matrices which should avoid many of the difficulties involved in determining this quantity from Fe Mössbauer data, and which, furthermore, is consistent with a number of other relatively recent determinations of $Q_m$.[24] If the nonstoichiometry holes are distributed uniformly among the chain Cu and O ions, as done previously

in the Eu calculation, one obtains the results $(e^2qQ_m)_{ionic}=73.4$ MHz and $|\eta|_{ionic}=0.31$ for the Cu(1) site, and $(e^2qQ_m)_{ionic}=51.4$ and $|\eta|_{ionic}=0.11$ for the Cu(2) site, where the major principal axis of the quadrupole splitting tensors is along the $a$ and $c$ crystallographic axes for the Cu(1) and Cu(2) sites, respectively. The corresponding quadrupole splittings are 37.9 and 25.8 MHz. The first of these is considerably greater than any observed splitting and while the second calculated splitting might be attributed to the $A$ line it cannot explain either the absence of a larger 37.9 MHz splittings or the origin of the $B$ doublet.

This situation is not changed by another assignment of the nonstoichiometry holes such as a uniform distribution among the Cu and O ions of the $CuO_2$ plane. This gives the only slightly changed results $(e^2qQ_m)_{ionic}=79.8$ MHz and $|\eta|_{ionic}=0.16$ for the Cu(1) site, and $(e^2qQ_m)_{ionic}=46.2$ and $|\lambda|_{ionic}=0.11$ for the Cu(2) site. Now the calculated splittings are 40.1 and 23.1 MHz in similar disagreement with experiment.

Such disagreement is not wholly unexpected since it is likely that iron does not enter the $YBa_2Cu_3O_7$ lattice exclusively as $Fe^{3+}$ but may have an appreciable $Fe^{2+}$ character. $Fe^{4+}$ is believed to be very unlikely, however, because the ionization potential of $Fe^{3+}$ is so large compared to that of $Cu^{2+}$ (54.8 vs 36.8 eV, Ref. 25) that $Cu^{2+}$ would be oxidized to $Cu^{3+}$ and/or $O^{2-}$ to $O^-$ in preference to forming $Fe^{4+}$. If $Fe^{2+}$ is present it will be as the $^5D$ state because the ionic crystal field is too small relative to the intra-atomic interactions[21] to change appreciably the energy ordering of the free-ion term states. The ionic crystal field is large enough, however, compared to the spin-orbit splittings in this ion,[21] to play an important role in determining the orientation of the unsymmetrical charge distribution of this $^5D$ state. The situation is similar to that dealt with in $Eu^{3+}$ in that the nonsymmetric part of the $Fe^{2+}$ charge distribution can be described in terms of a single $3d$ electron in excess of a half-filled $3d$ shell. Unfortunately, although this case is simpler than the $Eu^{3+}$ case because spin-orbit effects are small, the crystal-field energies of the Fe $3d_{xz}$, $3d_{yz}$, and $3d_{3z^2-1}$ orbitals, calculated as described previously,[12] do not differ sufficiently to specify which orbital or orbitals will be occupied by the extra electron in $Fe^{2+}$. Here, the $z$ axis is the major principal axis of the electric field gradient tensor and is along the $a$ and $c$ crystallgraphic axis, respectively, for the Cu(1) and Cu(2) sites. Fortunately, consideration of the two extreme possibilities will show that our principal result changes only quantitatively, not qualitatively, with the occupancy of these orbitals.

The assumption that the $3d_{xz}$ and $3d_{yz}$ orbitals are equally occupied yields an axially symmetric valence quadrupole interaction of a magnitude of one half the Fe $3d_m=0$ quadrupole coupling along the $z$ axis, i.e., $(e^2qQ_m)_{val}=\frac{1}{2}(e^2qQ_m)_{Fe^{2+},3d}$. Using the formula $(e^2qQ_m)_{Fe^{2+},3d}=\frac{4}{7}Q_m(1-R_{Fe^{2+},3d})\langle 1/r^3\rangle_{Fe^{2+},3d}$, where the Sternheimer shielding parameter $R_{Fe^{2+},3d}$ has been calculated to be 0.22 by Ingalls,[26] and Hartree-Fock atomic orbitals of $Fe^{2+}$ (Ref. 27), yields the result $\langle 1/r^3\rangle_{Fe^{2+},3d}=5.08a_0^{-3}$, $(e^2qQ_m)_{val}=-57$ MHz. Now the Fe quadrupole splitting at the $i$th site may be written

as

$$(e^2qQ_m)_{\text{Fe},i} = (e^2qQ_m)_{\text{val}}\chi_i + (e^2qQ_m)_{\text{ionic}}, \qquad (2)$$

where $\chi_i$ is the fractional $Fe^{2+}$ character of iron substituted at this site. Using the calculated values of the valence and ionic quadrupole tensors we may estimate the $\chi_i$ for the different sites from the experimental data. The results depend, of course, on the assignment of the splittings. If the 23.2 and 12.8 MHz splittings are assigned to $Cu(1)$ and $Cu(2)$, respectively, we obtain $\chi_1 = 0.54$ and $\chi_2 = 0.47$ for the case where the nonstoichiometry holes of $YBa_2Cu_3O_7$ are in the Cu-O chain. The other case where the nonstoichiometry holes are in the $CuO_2$ plane yields essentially the same results. These values are identical within the accuracy of the comparison and seem reasonable, particularly insofar as the nearly identical isomer shifts of the iron species giving the $A$ and $B$ lines indicate they are in similar valence states. If the high-frequency transition is assigned to the $Cu(1)$ site then we fit the experimental results with $\chi_1 = 0.9$ and $\chi_2 = 0.1$. The large dissimilarity of these results seems unreasonable and constitutes grounds for rejecting this assignment.

If, on the other hand, the extra $3d$ electron occupies the $3d_{3z^2-1}$ orbital then $(e^2qQ_m)_{\text{val}}$ is doubled to $-114$ MHz. In this case, one obtains $\chi_1 = 0.27$ and $\chi_2 = 0.24$ if the high-frequency transition is assigned to the $Cu(1)$ site and $\chi_1 = 0.45$ and $\chi_2 = 0.05$ if it is assigned to $Cu(2)$. Again, only the assignment resulting from assigning the high-frequency splitting to $Cu(1)$ seems reasonable.

Thus, Fe substituted for Cu in $YBa_2Cu_3O_7$ appears to be a mixture of $Fe^{3+}$ and $Fe^{2+}$ with the fractional $Fe^{2+}$ character ranging from 0.25 to 0.5 depending on the $3d$ orbital occupied by the extra electron in $Fe^{2+}$. It is noteworthy that, in order to account for the Fe quadrupole splittings, the extra electron in $Fe^{2+}$ must be in the $d_{xz}$, $d_{yz}$, and/or $d_{3z^2-1}$ orbitals; if this extra electron were in the $d_{x^2-y^2}$ or $d_{xy}$ orbitals, which is unlikely because of their large crystal-field energies, then $(e^2qQ)_{\text{val}}$ would have the same sign as $(e^2qQ)_{\text{ionic}}$ and it would be impossible to account for the observed quadrupole splittings without invoking the unlikely existence of $Fe^{4+}$. It has recently been proposed that more than one type of Cu $3d$ and O $2p$ valence orbitals are involved in the valence and/or conduction bands of the superconducting oxides.[12] The $d_{xz}$, $d_{yz}$ pair combined with the $d_{x^2-y^2}$ is one possibility, although consideration of the crystal-field energies of the oxygen orbitals that form bonds with the various Cu $3d$ orbitals favors somewhat the $d_{x^2-y^2}$ and $d_{xy}$ pair. In any event, there may be an important hint at the mechanism of superconductivity contained in this indication that Fe, and quite likely other transition metals, substituted for Cu in $YBa_2Cu_3O_7$ can host a mobile electron or hole in an orbital other than $3d_{x^2-y^2}$, whereas zinc, whose substitution for Cu is more damaging to superconductivity than is transition-metal substitution,[28] can only host a $3d_{x^2-y^2}$ hole to the extent it is present as $Zn^{3+}$.

This model is also consistent with the idea that the $C$ doublet is due to Fe ions in $Cu(1)$ sites that have an additional nearest-neighbor oxygen[7-11] as this would reduce $(e^2qQ)_{\text{ionic}}$ and thereby reduce the total quadrupole split-

ting for reasonable $Fe^{2+}/Fe^{3+}$ ratios.

Clearly, this is an interesting problem that could provide important clues to superconductivity in these materials, and as such merits further investigation. The signs of the quadrupole coupling tensors are of obvious importance but unfortunately, difficult to determine. Determination of the asymmetry parameters of this tensor could also be quite helpful.

### Cu in $YBa_2Cu_3O_7$

NMR and NQR investigations of Cu in $YBa_2Cu_3O_7$ have shown two different Cu sites with $^{63}Cu$ NQR frequencies of 22 and 31.5 MHz.[4-6] These two transitions exhibit marked differences in the temperature dependence of their relaxation rates especially in the superconducting region[4,6] that may be an important clue to the superconducting mechanism, toward which end the assignment of the transitions becomes especially important. Unfortunately, this assignment has proved difficult and controversial. Two groups have assigned the low-frequency transition to the $Cu(2)$ site on the basis of the relative intensities of the two transitions,[4,5] and the similarity of the temperature dependence of the relaxation rate of the thus assigned $Cu(2)$ transition to that of the nearby Y nucleus.[4] Another investigation has proposed the reverse assignment, however, also on the basis of the relative intensities of the transitions.[6] Moreover, this work[6] found that the low-frequency transition has a very large asymmetry parameter, which has been elegantly confirmed and extended by a Cu NMR investigation of aligned single crystals of $YBa_2Cu_3O_7$ which completely determined the field gradient tensors of the two Cu ions with respect to the crystallographic axes.[29] The nonaxially symmetric character of the low-frequency field gradient tensor, and even more so the fact that it is nearly zero along the $c$ crystallographic axis,[29] is highly inconsistent with its assignment to the axially symmetric $Cu(2)$ site. The following analysis will support this latter assignment of the NQR transitions and show that the two Cu ions are largely in the $Cu^{2+}$ state.

The ionic crystal-field contributions to the copper quadrupole splittings follow directly from those just calculated for iron upon substitution of the copper antishielding factor $\lambda_{Cu} = -17$,[30] and the $^{63}Cu$ quadruple moment $Q(^{63}Cu) = -0.211 \times 10^{24}$ $cm^2$,[31] for $\lambda_{Fe}$ and $Q(^{57}Fe_m)$. Here, however, we compute the actual field gradient tensor, defined with respect to the crystallographic $a$, $b$, and $c$ axes as $(e^2qQ) = [(e^2qQ)_{aa}, (e^2qQ)_{bb}, (e^2qQ)_{cc}]$ for comparison with the single-crystal results. The results, taking an average over the very similar values resulting from assignment of the nonstoichiometry holes to the Cu-O chains and the $CuO_2$ planes, are $Cu(1)$ site: $(e^2qQ)_{\text{ionic}} = (-136.5, 53.3, 83.2)$ MHz; $Cu(2)$ site: $(e^2qQ)_{\text{ionic}} = (42.9, 33.8, -76.7)$ MHz.

As in the Fe case these ionic crystal-field gradients give NQR transition frequencies [68.8 and 38.4 MHz for the $Cu(1)$ and $Cu(2)$ sites, respectively] that disagree strongly with experiment suggesting contributions to the quadrupole interaction from the Cu valence electrons. More-

over, such a contribution is almost certainly present because there are many indications that Cu is present largely as $Cu^{2+}$,[32,33] which has a large $(e^2qQ)_{val}$ due to the single missing electron or hole in its $3d$ shell. The ionic crystal field[12] requires that this hole be in the $3d_{x^2-y^2}$ orbital where $z$ is parallel to the $a$ and $c$ crystallographic axes for the $Cu(1)$ and $Cu(2)$ sites, respectively, so that $(e^2qQ)_{val}$ will be axially symmetric and, since $Q(^{63}Cu)$ is negative, positive along the $z$ axis. Calculation of the quadrupole interaction due to this hole orbital using $Cu^{2+}$ Hartree-Fock orbitals[27] is similar to that just described for iron, and including the calculated Sternheimer shielding[31] $(1 - R_{Cu^{2+}}) = 0.82$, gives the result $(e^2qQ)_{val,zz} = 191$ MHz.

Applying the same analysis used in the Fe case, cf. Eq. (2), where $\chi$ is now the fractional $Cu^{2+}$ character, and assuming that the 22 and 31.5 MHz transitions are due to $Cu(1)$ and $Cu(2)$, respectively, yields $\chi_1 = 0.93$ and $(e^2qQ)_{Cu(1)} = (40.3, -35.1, -5.2)$ MHz, and $\chi_2 = 0.73$ and $(e^2qQ)_{Cu(2)} = (-26.9, -36.0, 62.9)$ MHz. These values are in good agreement with the experimental values[29] $(e^2qQ)_{Cu(1)} = \pm (38.0, -38.4, 0.4)$ MHz and $(e^2qQ)_{Cu(2)} = \pm (-30.6, -30.6, 62.9)$ MHz even though the calculated value of the $Cu(1)$ field gradient along the $c$ axis, although small, is not zero as observed, because this quantity is the difference between larger quantities and less than a 5% change in the ionic field gradients would make it zero. The calculated asymmetry parameter of the $Cu(2)$ site is 0.14 in agreement with the observed value.[6] On the other hand, it is impossible to obtain any semblance of agreement between theory and the single-crystal experiment[29] if the low-frequency transition is assigned to $Cu(2)$.

Given the foregoing conclusion, an interesting new puzzle appears to be raised by a very recent experiment which found that reducing the oxygen content of $YBa_2Cu_3O_{7-\delta}$ from $\delta = 0.0$ to 0.3 reduces the relaxation rate of the 31.5 MHz transition much more than the other.[34] Given the ease of removal of oxygens from the chain sites, this result appears to be reasonable if the 31.5-MHz transition is assigned to the chain, as the authors appear to be doing,[4] but it presents a significant challenge for further investigation if the 31.5-MHz transition is due to the plane Cu ions.

The amounts of $Cu^{2+}$ character required to account for the Cu NQR data in $YBa_2Cu_3O_7$ seem reasonable and consistent with a picture of this species as being largely an ionic crystal despite its remarkable superconductive behavior. Given the reasonable assumption that the unpaired electron density on a Cu ion is related to its $Cu^{2+}$ character, then the finding that the chain Cu ions have somewhat greater $Cu^{2+}$ character than do the plane Cu

ions is consistent with the somewhat greater Knight shift of the chain Cu ions.[6]

The assignment of a 73% $Cu^{2+}$ character to the $Cu(2)$ site suggests the following interesting although speculative analysis. A simple tight-binding band calculation for the $CuO_2$ plane of the type described by Jorgensen $et al.$,[35] with a Cu-O transfer integral $t_{Cu,3d\sigma;O,2p\sigma} = 1.6$ eV,[36] and a difference between the Cu and O on-site energies of $E_{Cu,d} - E_{O,p} = 4.6$ eV will reproduce the indicated average $Cu(2)$ charge. Now this on-site energy difference may be regarded as the energy required to transfer an electron from $O^{2-}$ to $Cu^{2+}$ in the $CuO_2$ plane because if this energy becomes very large then the ions of this plane are all $Cu^{2+}$ and $O^{2-}$ ions. The present value of 4.6 eV is considerably smaller than the 12 eV estimated from considerations of the crystal Madelung energy and the energies required to form the various ions,[12] although it is likely that consideration of finite ion size effects when calculating the Madelung energies will considerably reduce the estimate obtained from the crystal-field model. It is larger than the values typically used for this parameter in Hubbard models of the $CuO_2$ plane.[37] With these values and an estimate of the energy required to transfer a hole from one $Cu^{2+}$ to another, i.e., $2 Cu^{2+} \rightarrow Cu^+ + Cu^{3+}$, which can be estimated as $U_{Cu,d} = 12.7$ eV from the $Cu^+$ and $Cu^{2+}$ ionization energies of 20.3 and 36.8 eV,[25] respectively, and the attractive energy of $-3.7$ eV between the resulting electron-hole pair in the $CuO_2$ plane, one can calculate the antiferromagnetic coupling between the spins on two adjacent $Cu^{2+}$ ions in the $CuO_2$ plane from the formula,[37,38] $J = 4t^4_{Cu,3d\sigma;O,2p\sigma}/(E_{Cu,d} - E_{O,p})^2 U_{Cu,d}$. This yields $J = 0.098$ eV in reasonable agreement with experimental values of 0.1–0.14 eV in the superconducting oxides.[39,40] Thus, there do appear to be some interesting, albeit tentative, consistencies between the results of rather different experiments in these superconductors.

In summary, a relatively simple model based on the idea that the high-$T_c$ superconducting oxides are largely ionic crystals appears to be useful for interpreting the results of Mössbauer and NQR experiments and obtaining therefrom information about the electronic states of the quadrupolar ions including the all important Cu ions.

## ACKNOWLEDGMENTS

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