Theory of copper hyperfine interactions in the La_2CuO_4 system

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The unrestricted Hartree-Fock cluster procedure is used to study the electronic structure of La_2CuO_4 and obtain the ^{63}Cu quadrupole coupling constant and asymmetry parameter of 88.4 MHz and 0.04, respectively, in satisfactory agreement with experiment. A magnetic hyperfine field of 105.2 kG is obtained at the ^{63}Cu nucleus, as compared to 78.78 kG from experiment. The effective charges on copper and oxygen ions and the mixing of copper and planar oxygen orbitals in the wave functions suggest significant covalent bonding between them. The magnetic moment on the copper ion is reduced by the influence of the covalency effect and will be compared with experiment.

I. INTRODUCTION

Following the discovery[1] of high-T_c superconductivity in the doped La_2CuO_4-based compound, a large number of investigations, both experimental and theoretical, have been carried out to understand the different aspects of these systems. It is generally believed that the occurrence of superconductivity in these copper oxide compounds has a direct relationship with the presence of CuO layers in these materials. As to the mechanism that is responsible for the pairing of the holes, that are considered to be responsible for the conduction in this system, a theory has yet to be established to explain all the basic experimental facts for these systems. Besides a qualitative explanation of these facts, a successful theory for the mechanism of high-T_c superconductivity must demonstrate its ability in a quantitative manner as well. A prerequisite for this is a complete knowledge of the electronic structures and their related properties in both the superconducting and normal phases of the materials.

A large amount of information regarding the electronic structures and hyperfine properties of these systems is available both for the superconducting and nonsuperconducting phases through experimental techniques like nuclear quadrupole and magnetic resonances (NQR and NMR), Mössbauer spectroscopy, and muon spin rotation (μSR). In the case of one-layer systems based on the La_2CuO_4 compound, many such studies have been performed, revealing the natures of nuclear quadrupole interactions (NQI) and magnetic hyperfine interactions (HFI) at ^{139}La and $^{63,65}Cu$ sites,[2,3] as well as at ^{119}Sn and ^{57}Fe at substitutional sites.[4] These allow one to test the accuracy of any calculated electronic structures by evaluating the nuclear quadrupole coupling constants (e^2qQ/h) and associated asymmetry parameters (η) and hyperfine fields ($H_{\rm hyp}$) at the sites of interest and comparing them with the observed values. In this paper we discuss our first-principles unrestricted Hartree-Fock (UHF) cluster investigation[5,6] to determine the electronic structure of the pure La_2CuO_4 system, using which we have analyzed the NQI and HFI properties for the ^{63}Cu site. In the case of NQI in La_2CuO_4 system, a point ion-model calculation was carried out in the past[7] to determine the value of e^2qQ/h at the ^{139}La site but no such investigation has been carried out for the ^{63}Cu site. Here we have determined both the e^2qQ/h and $H_{\rm hyp}$ using the UHF procedure for obtaining the charge and spin distributions in the system. Section II describes the procedure employed for the electronic structure calculation and evaluation of e^2qQ/h and $H_{\rm hyp}$ in the antiferromagnetic state. Section III presents our results and discussion. Section IV presents some concluding remarks.

II. PROCEDURE

The crystal structure[8] of La_2CuO_4 used in this investigation can be described as the orthorhombic distortion of K_2NiF_4 structure with lattice parameters a, b, and c of 5.363, 5.409, 13.170 Å, respectively. Many studies[9] have confirmed the antiferromagnetism in $La_2CuO_{4-\delta}$ with Néel temperature T_N varying from one sample to the other, depending on the concentration of oxygen vacancies in the sample. In the antiferromagnetic state, it is found that the copper moment lies on the CuO plane (c plane), leading to $H_{\rm hyp}$ at the ^{63}Cu nuclei on the same plane.

In the orthorhombic unit cell of the stoichiometric system, there are four formula units[8] ($4\times La_2CuO_4$) with all eight lanthanum occupying equivalent sites. Similarly all four copper sites are equivalent but in the case of oxygen there are two inequivalent sites, planar and apical. The planar oxygens O(p) are the first nearest neighbors of copper with Cu-O(p) distance being 1.9 Å whereas the apical oxygen O(a) is located at a distance of 2.4 Å away from the copper ion.

For our theoretical investigations of the NQI at the ^{63}Cu site, two types of clusters were used, the choices being dictated by considerations of practicability and the symmetry around copper ion. One cluster has a central copper ion surrounded by four planar oxygens and two apical oxygens (CuO_6) at the corners of a rectangular octahedron. This cluster is shown in Fig. 1, the X and Y axes being taken along the crystal a and b axes, of the orthorhombic unit cell, while the Z axis is taken along the c axis. This choice has the advantage that the XZ and YZ planes involve reflection symmetry with respect to the planar oxygens, O(1) [O(3)] being transformed to O(2) [O(4)] on reflection about the XZ plane and O(1) [O(2)] being transformed to O(4) [O(3)] on reflection about the YZ plane. Consequently[10] the axes X, Y, and Z are principal axes for the field gradient tensor[10] for the central copper ion. One could alternately have chosen another set of axes, with X' along the Cu-O_1 direction and Y' along a direction perpendicular to Cu-O_1. For the tetragonal phase where a and b would have been equal, Y' would have coincided with Cu-O_4, but for the orthorhombic lattice, the Y' axis is somewhat off from Cu-O_4. Consequently X' and Y' would not be principal axes for the field-gradient tensor, making the calculation somewhat more complicated. This is the reason for our choice of X and Y axes in Fig. 1. The other cluster which was used to test the convergence of e^2qQ/h and η with respect to cluster size has four additional Cu ions (Cu_5O_6). Each of these Cu ions is located at the same distance from a planar oxygen as the central Cu ion in CuO_6 cluster. As will be seen when our results are discussed, this choice of clusters appears to be adequate to describe the anisotropy of the charge distribution around the ^{63}Cu nucleus responsible for the NQI, in a convergent manner with respect to cluster size. Our analysis in other solid ionic compounds[11] also indicated that good agreement with observed experimental NQI data is obtained using clusters of similar size. To include the effect of the rest of the lattice in the solid-state system, the cluster was considered, as is customary for ionic crystals, to be embedded[5,11,12] in an assembly of point charges at lattice points outside of the cluster ions. A sizable number of such charges, about 400, was employed, corresponding to lattice sites within a distance of about 12 Å from the central Cu ion. The charges on the outermost shells of these point ions were adjusted to reproduce the correct Madelung potential at all the nuclei in the cluster as well as to maintain charge neutrality of the system as a whole including the cluster and the chosen point charges. The charges assigned to these surrounding point ions except those on the outermost shells are the formal ones, 3+, 2+, and 2− for La, Cu, and O, respectively. Effective charges for Cu and O ions in the cluster obtained after the self-consistent procedure were also tried on the point ions for consistency purposes. We found that the final results for the hyperfine properties are not too sensitive to the choice of the charges on surrounding ions outside the cluster.

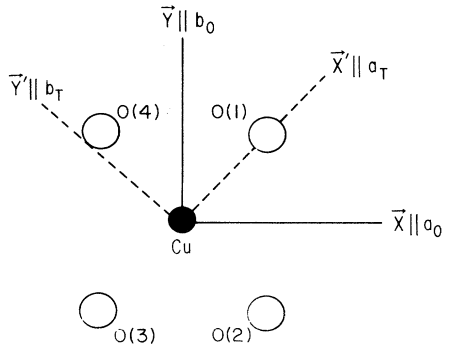

FIG. 1. Central copper and four planar oxygens of the CuO_6 cluster used in the UHF calculation in the orthorhombic phase. The choice of X and Y axes (solid lines) are made to be parallel to the orthorhombic crystal axes a_0 and b_0, respectively. X' and Y' are alternate choice of axes (dashed lines) which are, respectively, parallel to the tetragonal crystal axes a_T and b_T in the tetragonal phase. In the orthorhombic phase, the Y' axis does not pass through the oxygens O_4 and O_2.

As regards the magnetic hyperfine field H_{hyp}, a rigorous calculation of this quantity would require one to deal with the antiferromagnetic system with opposite spins at neighboring copper ions. Such a calculation would be very difficult for two reasons. First, one would have to deal with a large cluster involving a number of copper ions and all their nearest oxygen neighbors. Second, one would have to explicitly incorporate the many-body correlation effects associated with the charge transfer in the superexchange mechanism. We have therefore attempted a less ambitious analysis here. The CuO_6 cluster is considered to have a single unpaired electron representative of the spin distribution at, and near, a particular copper ion in a sublattice. The use of this cluster allows us to test the extent of delocalization of the unpaired spin distribution to examine one of the suggestions made,[13] namely, covalency effect, for explaining the reduction in the effective moment from μ_B for a single free Cu^{2+} ion to less than $0.5\mu_B$ observed in neutron diffraction measurements.[13,14] Second, it allows us to obtain the internal contribution within the cluster and complement it by a point lattice summation for the external contribution from the spins of other copper ions in the lattice.

As regards the choice of basis sets for the calculation of the Hartree-Fock wave functions for the cluster, extensive sets[15] of Gaussian basis functions were employed. For the copper ion, in the terminology that is commonly used in Hartree-Fock cluster calculations, 4s, 4p, and 2d (6211/4111/41) Gaussian functions were utilized, while for the oxygen ion basis set, 3s and 2p (721/41) functions were used. As in our earlier investigations in other ionic

crystals[11] and the 123 copper oxide system,[6] the oxygen basis set used was optimized for the O^{2-} ion in a Watson sphere with radius $R_W = 1.5$ Å in order to simulate the stabilization of O^{2-} in the crystal. The UHF quantum-mechanical procedure was then applied to minimize the total energy of the cluster, obtaining the coefficients of the molecular orbitals of the converged wave function. This was performed utilizing the Gaussian 88 system of programs.[16] The electric field gradient (EFG) and the contact and dipolar contributions to the magnetic hyperfine field H_{hyp} at the ^{63}Cu nucleus were then calculated using these wave functions, the details of the procedure for which have been described elsewhere.[6,11] It should be noted that in calculating e^2qQ/h, no Sternheimer antishielding factor for the distortion of the core electron distribution, is needed because the core electrons were included in our all-electron calculations thereby implicitly incorporating antishielding effects. This eliminates the uncertainty of having to use appropriate approximate Sternheimer factors[17] in the solid-state system.

III. RESULTS AND DISCUSSION

The nuclear quadrupole coupling constant e^2qQ/h and asymmetry parameter η for ^{63}Cu have been measured[18,19] by NQR and NMR techniques in the superconducting [$La_2CuO_{4+\delta}$, $(La_{1-x}Sr_x)_2CuO_4$] and antiferromagnetic [$La_2CuO_{4-\delta}$] materials. The hyperfine field H_{hyp} has been measured[19] only in the latter. The values of the nuclear quadrupole resonance frequencies $\nu_Q = \frac{1}{2}e^2qQ(1+\eta^2/3)^{1/2}$ have been found to be 31.9 MHz and $\eta = 0.03$ in the antiferromagnetic system while in the two types of superconducting systems mentioned above, the values of ν_Q are found to be slightly higher, namely, 36.0 and 35.3 MHz, respectively. These results suggest that it is appropriate to consider the value of ν_Q to lie within the range 31.9 and 36.0 MHz for La_2CuO_4 corresponding to values of e^2qQ/h of 63.8 and 72.0 MHz, respectively, since η is close to zero. For the antiferromagnetic sample [$La_2CuO_{4-\delta}$] with δ very small, the hyperfine field H_{hyp} is obtained from NMR measurement[19] as 78.78 kG. It has been found experimentally that T_N is very sensitive[20] to δ, being ≈ 0 K for $\delta = 0$ and ≈ 290 K for $\delta \approx 0.03$. While the role of the oxygen deficiency in inducing antiferromagnetic alignment is not well understood, it is perhaps safe to assume that once such an alignment has taken place, one would expect the hyperfine field, certainly the internal part of it arising from the unpaired electrons in the ion containing the nucleus itself (which we will see later to be the major contributor to H_{hyp}) will not be sensitively influenced by the oxygen content. We shall therefore assume H_{hyp} to be insensitive to δ and thus use the results of our investigations on the La_2CuO_4 system to compare with the value of 78.78 kG in the system with finite[21] but small δ. Evidence[22] for supporting this assertion is available in the literature.

We consider first the results of our investigation on the NQI at the ^{63}Cu site in La_2CuO_4. Using the electronic wave functions for the CuO_6 cluster embedded in the potential due to the formal charges at the lattice sites outside the cluster, the components of the EFG tensor at the ^{63}Cu site were calculated and diagonalized by the usual procedure to obtain the principal components. The maximum principal component V_{zz} was found to have a total value of $-2.2316\ ea_0^{-3}$, e being the electronic charge and a_0 the Bohr radius. The direction Z of the corresponding principal axis was found to be along the c axis of the crystal. Of the total value of V_{zz}, $-2.2320\ ea_0^{-3}$ came from the electronic and nuclear charge contributions from within the cluster itself. The remaining small positive contribution of $0.0004\ ea_0^{-3}$ arises from the rest of the lattice points outside the cluster. Using the value of the quadrupole moment Q of the nucleus ^{63}Cu of -0.18 barns in the literature[23] and our calculated value of $q = V_{zz}$, the nuclear quadrupole coupling constant e^2qQ/h comes out as 94.4 MHz. This value is in reasonable agreement with, although somewhat higher than the experimental value which as discussed earlier can be considered to lie between 63.6 and 72 MHz. The other two principal axes X and Y coincide with the crystal b and a axes, respectively. These axes are expected to be the principal axes from symmetry considerations as explained in Sec. II. However the specific assignment of X and Y depends on the magnitude of V_{xx} and V_{yy} since the usual convention in the literature[24] is that $|V_{zz}| > |V_{yy}| > |V_{xx}|$ and $\eta = (|V_{yy}| - |V_{xx}|)/|V_{zz}|$. For the asymmetry parameter η, the value obtained from this calculation turned out to be small, namely, 0.02, consistent with the small experimental value[19] of 0.03.

To study the sensitiveness of the results with respect to the surrounding charges and the cluster size, two additional calculations were performed. Thus, using the same cluster CuO_6 and basis functions, another calculation was carried out using the effective charges on the surrounding point ions that resulted from the self-consistent procedure. As remarked in Sec. II, the result did not change very significantly after applying this self-consistency, the new values of e^2qQ/h and η being 88.4 MHz and 0.04, respectively. The convergence with respect to cluster size was examined by making use of the larger cluster Cu_5O_6 described in Sec. II. For simplicity of computation, this calculation was done in the paramagnetic state where the total spin of the cluster, S was 5/2. Since we are concerned with the NQI which is electrostatic in nature and not magnetic, this should not pose any problem in interpreting our result. No dramatic change was noticed in the NQI on going to the larger cluster where we found e^2qQ/h to be 92.0 MHz and asymmetry parameter η of 0.03, an indication of the very good convergence with regard to cluster size. In terms of basis sets we have also examined different sets of basis functions for our calculations and again we noticed that there was no substantial change in our results for the NQI and the reasonably satisfactory agreement with experiment.

As a test of the extent of covalent bonding between copper and oxygen ions, using NQI as a probe, we have studied the coupling constant e^2qQ/h at ^{63}Cu using the point model. Considering all La, Cu, and O to carry charges of $+3$, $+2$, and -2 respectively, based on their

formal charges, we get an EFG of 0.086 ea_0^{-3}. This has to be multiplied by $(1-\gamma_\infty)$ where γ_∞ is the Sternheimer antishielding factor for Cu^{2+} ion and the nuclear quadrupole moment $Q(^{63}Cu)$. A calculation of γ_∞ for Cu^{2+} is available in the literature[25] including the self-consistency effect, yielding a value of -7.59. This value of γ_∞ leads, from the EFG due to the point ions in the lattice, to e^2qQ/h of -31.2 MHz, which has to be combined with the EFG due to the d_{xy} hole[26] on Cu^{2+} of about[27] 164 MHz, leading to a net e^2qQ/h of 132.8 MHz which is much too large compared to experiment. This result testifies to the importance of covalent bonding between copper and oxygen atoms. In addition to the fact that our result for e^2qQ/h including covalency effects in a first-principle manner is in good agreement with experiment, our electronic wave functions as well as the calculated charges indicate the presence of significant covalent bonding between copper and planar oxygens. Thus, considerable admixture was found between the copper d_{xy} orbital and the p_x and p_y orbitals of the planar oxygens. Additionally, the effective charges on copper, planar oxygen, and apical oxygen were, respectively, 1.55, -1.89, and -1.95, using the averages from our small and large cluster calculations. This also indicates substantial covalent bonding between copper and oxygen, especially the planar ones.

It is instructive to analyze the total contribution to the EFG obtained from our cluster calculation in terms of individual effects arising from the atomic components of the various occupied molecular orbitals. In Table I we have presented a breakdown of the contributions from various sources to the net EFG and the corresponding e^2qQ/h from our CuO_6 cluster calculation. The contribution from specific atomic orbitals listed have been obtained by collecting these contributions from each of the occupied molecular orbitals and summing up over the latter. An examination of these contributions indicates that a major part of the net EFG does arise from the Cu d orbitals. These contributions represent the combined effects of two sources. First there is the polarization leading to the Sternheimer antishielding effects associated with the potential due to the nuclear charges and the external ions outside the cluster. Second there is the contribution arising from the Cu d hole, including the influence on the hole distribution of the covalent bonding between the copper and oxygen ligand orbitals. The Cu p contribution also represents the combined effects of Sternheimer antishielding and covalency contributions.

TABLE I. Contributions from various sources to the electric field gradient at ^{63}Cu site in La_2CuO_4.

Orbital	$V_{zz}(ea_0^{-3})$	e^2qQ/h (MHz)
Cu d_{xy}	4.847	-205.0
Other Cu d orbitals	-8.652	365.9
Cu p orbitals	1.732	-73.3
$O(p)^a$ p orbitals	0.503	-21.3
$O(a)^a$ p orbitals	-0.258	10.9
Other orbitals	0.077	-3.2

[a] $O(p)$ and $O(a)$ denote planar and apical oxygens, respectively.

The latter is expected to arise mainly from the $3p$ orbital and the former from the $4p$ orbital. The contributions from oxygen p orbitals represent primarily the screening of the nuclear charges on the oxygen ions. The net d-orbital contribution of about 161 MHz is quite close to that for a single d_{xy} hole, the equality representing a fortuitous cancellation between the change in the d-hole contribution due to covalency effect and the Sternheimer antishielding effect arising from the polarization of the d orbitals. This feature of the results can be better understood by analyzing the populations in the various d orbitals, which are of interest themselves in understanding the nature of the overall electronic charge distribution. These orbital populations are found from our calculation using the Mulliken approximation to be[26]

$$\begin{aligned} &n(d_{3z^2-r^2})=2.000 \quad n(d_{x^2-y^2})=2.036 , \\ &n(d_{xz})=2.056 \quad n(d_{yz})=2.035 , \\ &n(d_{xy})=1.178 . \end{aligned} \tag{1}$$

The net d populations in the $d_{x^2-y^2}$, d_{xz}, and d_{yz} states come out to be larger than 2. This is because the d populations in these orbitals have both $3d$ and $4d$ characters. The d_{xy} orbital has a population of 1.178, substantially less than 2 indicating a hole character of about 0.822. This hole population is less than 1 as one would expect from covalent bonding between copper and its oxygen neighbors. The contribution to the EFG from such a hole would be about 135 MHz using the value of 164 MHz for a single d_{xy} hole as discussed earlier. From Table I on the other hand the net d-orbitals contributions from our all-electron UHF calculation comes out as 165 MHz. The difference can be physically understood as arising from the Sternheimer polarization effect of the EFG produced by the nuclear charges and electronic distributions on the oxygen ions. The fact that these contributions are of the same sign whereas that due to the point ion model with $2-$ charges on oxygens led to a negative EFG, opposing the hole contribution as discussed earlier, can be understood as follows. Thus, earlier first-principle calculations[28] of Sternheimer antishielding effects on Fe_2O_3 taking account of the overlapping electron distributions on iron and oxygen ions had shown that the EFG due to the nuclear charges on the oxygen ions were subject to a much larger Sternheimer antishielding effect than the electrons, which had substantial penetration into the electron distribution on the Fe^{3+} ion. This leads to a significantly different EFG at the nucleus of Fe^{3+} ion as compared to that from the approximation using $2-$ point charges for these near neighbor oxygens as is customary in simple point ion model calculations. These effects also apply to the present situation where we have copper surrounded by oxygen ions.

Turning next to the magnetic hyperfine interaction, we now discuss the results of our investigation of the hyperfine field at the ^{63}Cu site. The pertinent experimental data were available through the analysis of the NMR spectra for the antiferromagnetic $La_2CuO_{4-\delta}$ system. The observed Larmor frequency[19] of 92.39 MHz for ^{63}Cu in this material has been associated with a hyperfine field

of 78.78 kG. There are many studies in the literature regarding the directions of sublattice copper moments and the long-range spin structure in the antiferromagnetic state. One of these suggested[29] that there are two possibilities for the magnetic structure in La_2CuO_4. Thus this study[29] proposed that the sublattice spins could be either parallel to the a axis or the b axis. However there has been more evidence from[30] neutron diffraction and magnetic moment measurements favoring the local moment to be along the b axis. Since the difference in the lattice parameters a and b is very small and the cluster employed for the magnetic hyperfine field investigation involves only one Cu ion, our results cannot reveal any significant difference in the hyperfine field when one takes the Cu moment along the a or b axis. This is because, with the very small difference between the lengths of the a and b axes, our calculations lead to a nearly axially symmetric spin distribution with respect to the c axis. This was also the case for the charge distribution as evidenced by the small asymmetry parameter for the NQI. From our investigation, the spin density at ^{63}Cu was found to be -0.06 atomic units corresponding to a contact isotropic hyperfine field of -31.3 kG while the dipolar contribution with Cu spin quantized along the a axis was calculated to be 136.3 kG. On combining the contact and dipolar hyperfine fields, one gets a net hyperfine field of 105.0 kG. In principle, the field due to neighboring sublattices should also be included. To make an estimate of this contribution, we have calculated the dipolar field at the ^{63}Cu nucleus due to the magnetic moments at the four nearest neighbor Cu ions, assuming the localized moments to be one Bohr magneton each. The calculated hyperfine field from this source turned out to be 2 kG, less than 2% of the local hyperfine field. The effect of the more distant copper spins is not expected to influence this result by more than a factor of 2. Thus, the hyperfine field appears primarily to originate internally from the spin distribution within the CuO_6 cluster. When the sublattice magnetic moments were assumed to lie along the b axis, the hyperfine field at ^{63}Cu was calculated to be 105.2 kG which is almost equal to the value obtained with Cu moment along the a axis, as remarked earlier. On comparing the experimental data,[19] our result thus appears to give good agreement, being only 1.32 higher than the observed value.

Our electronic results lead to a net magnetization on the Cu ions of $0.88\mu_B$, indicating a significant delocalization by about 12% of the Cu magnetic moment. However, the delocalization is not sufficient to explain the observed magnetic moment of about $0.5\mu_B$ from neutron diffraction data. Thus, while covalency effects proposed[14] as one possible source for the reduced moment on Cu do appear to lead to a significant reduction, one needs to consider other effects to explain the experimentally observed magnetic moment. One possible source could be the influence of correlation effects associated with the superexchange mechanism. A quantitative analysis of this source would require a much larger cluster than used here and a comprehensive treatment of many-body effects, which is beyond the scope of this work. Another possibility is the presence of correlation and charge and spin fluctuation effects associated with the origin of the superconductivity in this material.

IV. CONCLUSIONS

The good agreement between our results and the experimental quadrupole coupling constant and asymmetry parameter for the ^{63}Cu in La_2CuO_4 system indicates that the electronic charge distribution—especially its departure from spherical symmetry— is well described by the UHF procedure. To obtain further confirmation of this fact it will be very helpful to have ^{17}O nuclear quadrupole interaction data in the future as in the case of the $YBa_2Cu_3O_{7-x}$ high-T_c system.[31] Our analysis of the electronic wave functions and the comparison of our results and experiment shows that there is very substantial covalent bonding between copper and its planar oxygen neighbors which strongly influences the ^{63}Cu NQI. Our cluster calculation also provides a value for the magnetic hyperfine field at ^{63}Cu in reasonable agreement with the experimental value. Covalency effects were also found to reduce the magnetic moment on the Cu ion significantly from that due to a single localized d hole, but their influence was not substantial enough to explain the experimental value of less than $0.5\mu_B$. To improve agreement with experiment in this respect, other sources including many-body effects associated with the superexchange mechanism responsible for the antiferromagnetism and with the mechanism responsible for the superconductivity would have to be explored. The main conclusion of this work is the occurrence of very substantial covalent bonding between copper and the planar oxygens which has to be taken into account in any quantitative theories for the origin of superconductivity in this system.

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[21]The value of δ in Ref. 18 is assumed to be less than 0.03 based on the premise that in Ref. 18, where the hyperfine field was measured, T_N is $\approx$230 K, while for $\delta=0.03$, $T_N\approx$290 K.

[22]See note at end of Y. J. Uemura, W. J. Kossler, X. H. Yu, J. R. Kempton, H. E. Schone, D. Opie, C. E. Stronach, D. C. Johnston, M. S. Alvarez, and D. P. Goshorn, Phys. Rev. Lett. **59**, 1045 (1987).

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[26]The d_{xy} orbital with our choice of X and Y axes (Fig. 1) corresponds to $d_{x^2-y^2}$ with the choice of axes X' and Y'. The latter choice, as explained in Sec. II, is the one that is often made in the literature for the tetragonal phase as opposed to the orthorhombic phase considered here. The local EFG due to both $d_{x^2-y^2}$ and d_{xy} are the same for any choice of axes.

[27]This value is obtained by adjusting the value of 191 MHz by F. J, Adrian (Ref. 7) by the ratio of the ^{63}Cu quadrupole moment of -0.18 barn (Ref. 22) that we have used to -0.21 barn used in Ref. 7.

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