PHYSICAL REVIEW B VOLUME 41, NUMBER 1 1 JANUARY 1990

Theory of electron distributions and ^{63}Cu and ^{17}O nuclear quadrupole interactions in the high-T_c system $YBa_2Cu_3O_7$

N. Sahoo, Sigrid Markert, and T. P. Das
Department of Physics, State University of New York at Albany, Albany, New York 12222

K. Nagamine
Meson Science Laboratory, Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

(Received 10 July 1989)

A first-principles unrestricted Hartree-Fock cluster investigation has been carried out on the electronic structure of the $YBa_2Cu_3O_7$ system. The results of this investigation provide satisfactory explanations of ^{63}Cu and ^{17}O nuclear-quadrupole-interaction data. The electron distributions obtained rule out the presence of Cu^{3+} ions and are supportive of the presence of Cu^{2+}. Cu^{+}, O^{2-}, and O^{-} ions with actual charges departing significantly from the formal charges, indicating the importance of covalency effects.

I. INTRODUCTION

A wealth of data has recently become available[1-6] on the hyperfine properties, especially nuclear quadrupole interactions (NQI's), of the copper oxide high-T_c systems by a variety of experimental techniques, including nuclear magnetic and nuclear quadrupole resonance,[1-3] Mössbauer effect,[4,5] and perturbed angular correlation.[6] These data provide an opportunity to obtain valuable information on the electron distributions that can be helpful in the understanding of the origin of the superconductivity in these systems. The first comprehensive attempts[7,8] at the theoretical understanding of the NQI data have utilized a point-ion model for evaluation of the electric field gradient (efg) at the nuclear sites. From these analyses, information can be derived[7] about the extent of covalency from comparison of the theoretical and experimental values of the efg. The next step in the understanding of the origin of the NQI data is to study the electronic structures of the high-T_c systems by *ab initio* procedures and use the calculated electronic structures to explain observed experimental data. In the present work, we have carried out first-principles unrestricted Hartree-Fock (UHF) cluster investigations[9] on the $YBa_2Cu_3O_7$ system and evaluated the ^{63}Cu and ^{17}O NQI parameters for all the sites where experimental data are available.[1-3] Our investigation provides both a satisfactory explanation of the available NQI data as well as information on the charge states of the different copper and oxygen ions. We are also able through our investigations to make a comparison between available x-ray photoemission spectroscopy (XPS) data[10] and theoretical predictions.

Section II presents the procedure used in the present work, including the clusters chosen for study of the NQI for ^{63}Cu and ^{17}O nuclei. Section III presents the results of our investigation and discussion. The conclusions from this work are presented in Sec. IV.

II. PROCEDURE

For our electronic-structure investigation, we have made use of the UHF cluster procedure,[9] which has been found to yield satisfactory agreement with experiment for the magnetic hyperfine properties of a number of systems involving impurity atoms in semiconductors[11] and NQI tensors in a number of ionic crystal systems[12-15] including ^{63}Cu in cuprous oxide[15] and ^{17}O in corundum.[13] Gaussian basis functions[16] were used for these investigations, the oxygen ion basis functions being obtained[12,13] by employing the Watson sphere model[17] to include the influence of the potential of the environment of this rather diffuse ion. For the copper ion we have used extensive basis functions[16] consisting of 10*s*, 7*p*, and 5*d* primitive Gaussian-type functions (GTF) contracted to 4*s* (6,2,1,1), 4*p* (4,1,1,1), and 2*d* (4,1) basis functions. For the oxygen negative ions, we have used a basis set consisting of 8*s* and 7*p* GTF contracted to 2*s* (4,4) and 1*p* (4) basis functions.

The geometrical parameters for the clusters employed in our investigations were taken from the available crystal structure data[18] in $YBa_2Cu_3O_7$. A unit cell of this crystal is shown in Fig. 1. The Cu_3O_{12} cluster used in our investigation of the efg at the ^{63}Cu(1), ^{63}Cu(2), and ^{17}O(4) nuclei involves the atoms *A* to *O* in Fig. 1. These include the chain copper ion [Cu(1)] *A*, two planar copper ions [Cu(2)] *F* and *K*, two bridging O(4) ions *B* and *D* and other nearest oxygen neighbors *C*, *E*, *G*–*J*, and *L*–*O* of O(1), O(2), and O(3) categories of the three copper ions in the cluster. With this choice, the Cu(1), Cu(2), and O(4) ions each have all their nearest neighbors included in the cluster. For studying the efg at the ^{17}O nuclei at O(2) site [which is expected to have an electronic environment very similar to O(3)], for which experimental data are also available, it was necessary to use the O_7Cu_2 cluster consisting of atoms *F*–*J* and *P*–*S* in Fig. 1, with *J*

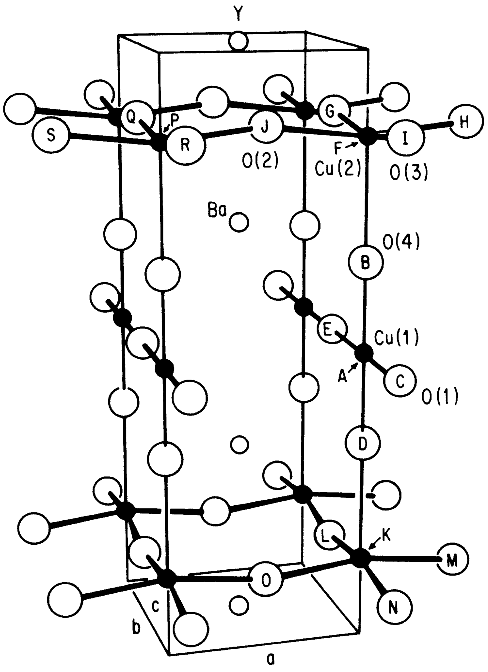

FIG. 1. Unit cell of $YBa_2Cu_3O_7$ (Ref. 18). The ions A–O are included in the Cu_3O_{12} cluster and F–J and P–S are included in the O_7Cu_2 cluster used in the present work.

representing an O(2) ion at the center. This cluster thus includes a central O(2) ion with its two nearest planar Cu(2) ions and all their oxygen nearest neighbors on the plane. Clusters larger than the ones described, including all the additional neighbors needed to keep the symmetry intact, would have been impracticable to use from a computational point of view. The influence of the other ions, outside the finite clusters we have chosen, on the electronic structure was incorporated by augmenting[9,12–15] the Hartree-Fock potential experienced by the electrons in the cluster with the potential due to the ions in the rest of the lattice, treating the latter as point charges. The charges on the yttrium and barium ions were taken as their formal charges of 3+ and 2+, respectively. For the copper and oxygen ions outside the cluster, the charges used were those obtained self-consistently for the ions within the cluster. A finite number of point ions were used to simulate the Madelung potential produced by the infinite number of ions of the crystal. The charges on the outermost shells of ions used were adjusted[12–15] to provide the proper Madelung potentials at all the sites of the ions in the cluster and net charge neutrality of the lattice.

The components of the efg tensor at the nucleus of interest can be obtained from the calculated electronic wave functions for the pertinent clusters using the expression[13]

$$V_{ij}=V_{ij}^{N}+V_{ij}^{e}+V_{ij}^{\text{ext}} , \tag{1}$$

where V_{ij}^{N} and V_{ij}^{e} represent the contributions to the ij $(i,j=x,y,z)$ component of the EFG tensor from the nuclear charges and electrons in the cluster while V_{ij}^{ext} represents the contribution from the ionic charges outside the cluster. These contributions are given by[19]

$$V_{ij}^{N}=\sum_{N}\zeta_N e\left[\frac{3x_{in}x_{jn}-\gamma_N^2\delta_{ij}}{\gamma_N^5}\right] , \tag{2}$$

$$V_{ij}^{e}=-\sum_{\mu}n_\mu\int e|\psi_\mu|^2\left[\frac{3x_ix_j-\gamma^2\delta_{ij}}{\gamma^5}\right]d\tau , \tag{3}$$

$$V_{ij}^{\text{ext}}=\sum_{I}\zeta_I e\left[\frac{3x_{iI}x_{jI}-\gamma_I^2\delta_{ij}}{\gamma_I^5}\right] . \tag{4}$$

In Eq. (2), ζ_N refers to the charge on the nucleus N within the cluster, x_{iN} the ith component of the position vector $\mathbf{r}_N$ of the nucleus N with respect to the site of the nucleus at which the EFG is being calculated. In Eq. (3) the summation over μ is carried out over all the molecular orbitals, $n_\mu=0$ or 1 being the occupancy of the orbital. Since we are using the UHF procedure, orbitals with different spin are treated separately, so the maximum occupancy of any orbital can only be 1. The x_i in Eq. (3) represents the ith component of the radius vector $\mathbf{r}$ of an electron with respect to the nuclear site at which the EFG is being studied. In Eq. (4), ζ_I represents the charge on the lattice ion I, $\mathbf{r}_I$ being the position vector of ion I with respect to the nucleus of interest, and x_{iI} is its ith component. The components of the EFG tensor in the principal axis system are obtained by the usual diagonalization procedure, the experimental parameters q and η being, respectively,[19] the largest principal component V_{zz} and the ratio $(V_{xx}-V_{yy})/V_{zz}$, the convention for choosing the axis being such that $|V_{xx}|<|V_{yy}|<|V_{zz}|$.

The core electrons are included in our UHF cluster calculation and are thus allowed to be polarized by the charges both inside and outside the cluster. Consequently, Sternheimer antishielding effects[20] associated with the efg from the electrons and nuclear charges within the cluster and outside ionic charges are explicitly incorporated. To obtain an assessment of the importance of covalent bonding on the EFG, we have evaluated for comparison, the EFG at the ^{63}Cu(1), ^{63}Cu(2), ^{17}O(2), and ^{17}O(4) arising from a point-ion model[21] with the charges on the lattice ions being the formal charges. The antishielding factors[20] were taken from recent literature.[26]

III. RESULTS AND DISCUSSION

We shall consider first the effective charges ζ on the various atoms in the Cu_3O_{12} cluster. There is no precise procedure available to relate the effective charges to the calculated electronic orbitals. A commonly used approximation for this purpose is the Mulliken population analysis[22] procedure employed here. This leads to the effective charges

$$\zeta_{\text{Cu}(1)}=1.49,\quad \zeta_{\text{Cu}(2)}=1.86,\quad \zeta_{\text{O}(1)}=-1.87 ,$$
$$\zeta_{\text{O}(2)}=-1.94,\quad \zeta_{\text{O}(3)}=-1.95,\quad \zeta_{\text{O}(4)}=-1.28 . \tag{5}$$

While the charges in Eq. (5) qualitatively support the assignment of formal charges of 1, 2, 2−, 2−, 2−, and 1−, respectively, on these ions, they also indicate that there is substantial delocalization of the charge distribution especially between the chain copper ion Cu(1) and its neighboring oxygen ions, primarily the two O(4). This is a result of very significant covalent bonding between Cu(1) and its neighbors, which was also clearly indicated by our electronic wave functions, the covalency associated with Cu(2) being significantly smaller. The relatively small observed bond distance[18] between Cu(1) and O(4) of 1.843 Å is also supportive of the strong covalent bonding between these ions and the consequent departure of the charges on these ions from the extreme ionic configurations of Cu^{2+} and O^{2-}.

Another important result of our investigations was that even when we started the iterations involved in the UHF cluster procedure with formal charges of 3+ and 2− on the Cu(1) and O(4) ions (instead of 2+ and 1−) outside the cluster, the results for the effective charges on the various ions within the cluster converged to those in Eq. (5). Our investigation therefore clearly supports the absence of Cu^{3+} and the presence of charge configurations for Cu(1) and O(4) reasonably close to 1+ and 1−, respectively, in keeping with current ideas in the literature.[23] The quantitative departures of Cu(1) and O(4) charges from the values of 1+ and 1− is a result of the covalent bonding between these ions indicating that the nonstoichiometric hole[23]in $YBa_2Cu_3O_7$, considering Cu^{2+} and O^2 as reference states, is distributed over Cu(1) and O(4). The magnitudes 967 and 551 eV of the one-electron eigenvalues for the Cu(1) 2*p*-like and O(4) 1*s*-like molecular orbitals obtained in this calculation are reasonably close to the two observed ionization energies 933 and 533 eV from XPS measurements.[10] This could be considered as providing qualitative support for the electron distributions and effective charges on the atoms obtained in the present work. A more quantitative comparison between experimental and theoretical ionization energies would require one to perform the more complex and time-consuming calculation involving the energy difference between the cluster used here and ones in which electrons have been ionized from Cu(1) 2*p*-like and O(4) 1*s*-like molecular orbitals.

Turning next to the NQI in $YBa_2Cu_3O_7$, experimental data on the coupling constant e^2qQ and η are now available[1−3] for both the chain and planar ^{63}Cu nuclei and the ^{17}O nuclei of the oxygen neighbors O(4) and O(2) of the chain and planar copper atoms, respectively. These are presented in Table I, along with our theoretical results from the UHF cluster model and those from the point-ion model.[21] The important features of the ^{63}Cu experimental data are the larger e^2qQ for the planar ^{63}Cu(2) nuclei compared to the chain ^{63}Cu(1) nuclei, the near-axial symmetry of the ^{63}Cu(2) efg tensor, and the strong departure of the ^{63}Cu(1) tensor from axial symmetry. For the ^{17}O nuclei, the e^2qQ for the nuclei of O(4) are larger than that for O(2), the symmetry of the efg tensor being nearly axial for the former, while for the latter there seems to be some evidence of departure of η from zero. Our results for the principal components of the efg tensors were obtained from the electron distributions determined through UHF cluster calculations by the usual procedure employed in the literature[12,13] as described in Sec. II. In relating the principal components q for the efg tensors for the various nuclei to the corresponding e^2qQ, we have used for the quadrupole moments, $Q(^{17}O) = -0.02578$ b[24] and $Q(^{63}Cu) = -0.18$ b.[15] The latter value is chosen[15] to be 15% smaller than the value of −0.211 b available in the literature[25] to account for relativistic and many-body effects on the efg in Cu atoms. These effects were not incorporated in the earlier calculation[25] of the efg in Cu atom used to extract $Q(^{63}Cu)$ from the measured e^2qQ in this atom.

Our results for the e^2qQ and η for ^{63}Cu(1), ^{63}Cu(2), ^{17}O(2), and ^{17}O(4) nuclei from UHF cluster investigations are listed in the fourth and fifth columns in Table I. The contributions to the efg tensors at these nuclei from the ions outside the clusters were calculated using the charges in Eq. (5). Because of the relatively small sizes of these contributions (about 1%) as compared to the intracluster contributions, the use of formal charges discussed earlier would not have affected the net efg tensor significantly. Also listed for comparison, in the second and third columns of Table I are the values of e^2qQ and η for the point-ion model, the appropriate charges on the ions one has to use in this case being the formal charges 1, 2, 2−2, 2−, 2−, and 1− for the Cu(1), Cu(2), O(1), O(2), O(3), and O(4), which are supported by the results of our UHF cluster calculations. The formal charges on yttrium and barium ions were taken as 3+ and 2+ as in the UHF cluster work. For the point-ion calculation, one needs to use the antishielding factors γ_∞ for the ions in-

TABLE I. ^{63}Cu and ^{17}O nuclear-quadrupole-interaction parameters from present work compared with experimental data and results from point-ion model.

	Point-ion model[a]		Present work		Experiment	
Nucleus	e^2qQ (MHz)	η	e^2qQ (MHz)	η	$\lvert e^2qQ \rvert$ (MHz)	η
^{63}Cu(1)	−123.0	0.99	57.3	0.30	38.4[b]	1.00[b]
^{63}Cu(2)	−84.5	0.12	96.7	0.04	62.9[b]	0.02[b]
^{17}O(2)	−6.2	0.03	−8.0	0.27	5–6[c]	0.0–0.2[c]
^{17}O(4)	1.6	0.28	−10.4	0.20	7.7[c]	0.0[c]

[a] Based on ionic configurations Y^{3+}, Ba^{2+}, $Cu(1)^+$, $Cu(2)^{2+}$, $O(1)^{2-}$, $O(2)^{2-}$, $O(3)^{2-}$, and $O(4)^-$ in the lattice.

[b] From Ref. 2.

[c] From Ref. 3.

volved. For Cu^{2+}, Cu^{1+}, and O^{2-}, the values of γ_∞ of -25.0, -17.0, and -13.8, respectively, available in the literature[26,27] were used. For the O^- ion, an estimated value of -9.7 was used for γ_∞ which is about 30% smaller than that for the more deformable O^{2-} ion. From Table I, strong differences are observed between the point-ion values and the results of our UHF cluster calculation and experimental results for the e^2qQ of both ^{63}Cu(1) and ^{63}Cu(2) nuclei as well as the ^{17}O(4) nucleus. This testifies to the importance of including covalency effects in a first-principles manner. Similar quantitative disagreement between the predictions of the point-ion model and experimental values of e^2qQ have also been found in a number of other ionic crystals.[5,12-15]

Our results for e^2qQ for the ^{63}Cu and ^{17}O nuclei obtained from first-principles electronic structure investigations for Cu(1), Cu(2), O(2), and O(4) ions are seen from Table I to be in good agreement with experiment.[2,3] The e^2qQ for ^{63}Cu(2) is found to be substantially larger than for ^{63}Cu(1) in agreement with the trend from experiment,[2] the experimental results for both nuclei being about 30% smaller than theory. For the ^{17}O nuclei, the experimental trend in e^2qQ from O(2) to O(1) is again in agreement with that from our theoretical results. Additionally, the experimental ratio[3] of 1.28 of the e^2qQ for O(4) and O(2) is in excellent agreement with the theoretical value of 1.30, the corresponding values[2] for Cu(1) and Cu(2) being 1.63 and 1.69, respectively. As in the case of the ^{63}Cu nuclei, there is again about a 30% difference in magnitudes between the experimental and theoretical values of e^2qQ. The electronic environment around the ^{63}Cu(2) nucleus comes out as nearly axially symmetric from the results of our investigation, as seen from the small value of about 0.04 for η in Table I, which is in good agreement with the experimental result[2] of 0.02. The electronic environment around the ^{63}Cu(1) nucleus however departs substantially from axial symmetry as indicated by our result for η of about 0.3, which is however smaller than the experimental result[2] close to unity. For ^{17}O(4), our calculated asymmetry parameter of 0.20 is small, but indicates some asymmetry in the electronic environment, while the experimental value[3] of η is close to zero. For ^{17}O(2), while the asymmetry is not as pronounced as for ^{63}Cu(1), the calculated value of $\eta=0.27$ is significant in size, in keeping with expectations from experiment which suggests[3] an upper limit of 0.2 for η.

Thus there is good agreement between the experimental NQI data[2,3] and the results of our first-principles electronic-structure investigations. Theory is able to explain all the important observed trends[2,3] including the substantially larger ^{63}Cu(2) coupling constant as compared to ^{63}Cu(1), the larger ^{17}O(4) coupling constant compared to that for ^{17}O(2), the axial symmetry of NQI tensor for ^{63}Cu(2), the presence of significant asymmetry for ^{63}Cu(1), and the tendency towards asymmetry in the electronic environment of ^{17}O(2). There is also satisfactory agreement between theory and experiment from a quantitative point of view for both sets of ^{17}O and ^{63}Cu nuclei for which experimental data are available, the significant difference being mainly in the value of η for ^{63}Cu(1). It is hoped that the direct incorporation of the actual charge distributions of the Ba^{2+} and Y^{3+} neighbors by including their electrons in the cluster investigations, (especially the Ba^{2+} ions, since the Y^{3+} ions are believed to be rather ionic), would resolve the remaining quantitative differences between theory and experiment. Such calculations will be rather time consuming, but would be desirable to perform in the future. It would also be important to carry out investigations in the future on the role of many-body effects,[28,29] which are expected to be equally extensive and time consuming. While many-body effects have not been found to be particularly important for NQI in atomic systems,[30] they may be more important in molecular and solid-state systems due to smaller energy differences between the ground and excited states.

The NQI at a nucleus is a good probe for studying the anisotropy of the charge distribution around the nucleus. The anisotropy in ionic systems is of course strongly dependent on the covalent bonding between neighbors. The fact that satisfactory agreement has been obtained for the NQI of a number of nuclei in $YBa_2Cu_3O_7$ through our first-principles UHF cluster investigation lends support to our conclusions regarding the charge distributions in this system, particularly the effective charges on the ions [Eq. (5)] and the strong covalent bonding between Cu(1) and its O(4) neighbors. In this connection, it will be very useful to carry our similar investigations as in the present work on hyperfine data for ^{57m}Fe in the $YBa_2Cu_3O_7$ system, which are available from Mössbauer measurements.[4,5] In addition to the NQI, isomer shift and magnetic hyperfine data are also available in these systems. These properties provide information on the isotropic part of the charge densities as well as the isotropic and anisotropic components of the difference in electronic densities associated with opposite spins, thus complementing the information about the anisotropy of the charge densities associated with the NQI, providing a more complete test of the accuracy of calculated electron densities.

The molecular orbitals associated with p states of the oxygen ions correspond to the highest occupied energy levels for the Cu_3O_{12} cluster we have studied. This fact along with the absence of any evidence for Cu^{3+} ions, and the presence of O^-, lends support to theories[31,32] for the origin of superconductivity requiring holes located on oxygen ions. Further, the results of our electronic-structure calculations show that there is strong localization of the spin distribution on the two Cu(2) ions, each one carrying an unpaired spin electron population of 0.95. This is in keeping with recent conclusions from the analysis of ^{63}Cu spin-lattice relaxation data.[33] Also the strong covalency between the Cu(1) and its two O(4) neighbors suggest that the unit O(4)—Cu(1)—O(4) could provide the medium for a superexchange between localized spins on the Cu(2) ions leading to the observed[34] antiferromagnetism in $YBa_2Cu_3O_6$. This mechanism of superexchange is also crucial for a recent hole-spin interaction theory[32] for superconductivity in the 1:2:3 systems.

IV. CONCLUSION

The first-principles UHF cluster investigations in this work have yielded electron distributions over the copper and oxygen ions in the $YBa_2Cu_3O_7$ system that provide satisfactory explanation of the available ^{63}Cu and ^{17}O nuclear quadrupole interaction data[1-3] as well as XPS data.[10] This leads us to conclude that the present investigations provide a reasonably accurate description of the electron distributions in these systems, which while supportive of the premises of recent theories[31-32] based on holes on oxygen ions and particularly one[32] involving hole-spin interactions, can also be of use in the analysis of other theories for the origin of superconductivity in high-T_c systems.

ACKNOWLEDGMENTS

The authors want to acknowledge very helpful discussions with Professor D. Brinkmann of the University of Zürich, Switzerland.

---

[1] H. Lütgemeier and M. W. Pieper, Solid State Commun. **64**, 267 (1987): I. Furo, A. Jánossy, L. Mihály, P. Bánki, I. Pócsik, I. Bakonyi, I. Heinmaa, E. Joon, and E. Lippmaa, Phys. Rev. B **36**, 5690 (1987); M. Mali, B. Brinkmann, L. Pauli, J. Roos, and H. Zimmermann, Phys. Lett. A **124**, 112 (1987); H. Riesemeier, Ch. Grabow, E. W. Scheidt, V. Mueller, and K. Lueders, Solid State Commun. **64**, 309 (1987); R. E. Walstedt, W. W. Warren, Jr., R. F. Bell, G. F. Brennert, G. P. Espinosa, J. P. Reimeika, R. J. Cava, and E. A. Rietman, Phys. Rev. B **36**, 5727 (1987); W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, G. P. Espinosa, and J. P. Remeika, Phys. Rev. Lett. **59**, 1860 (1987); Y. Kitaoka, S. Hiramatsu, T. Kondo, and K. Asayama, J. Phys. Soc. Jpn. **57**, 30 (1988); W. W. Warren, Jr., R. E. Walstedt, R. F. Bell, G. F. Brennert, R. J. Cava, G. P. Espinosa, and J. P. Remeika, Physica **153-155C**, Part I, 79 (1988); A. J. Vega, W. E. Farneth, E. M. McCarron, and R. K. Bordia, Phys. Rev. B **39**, 2322 (1989); C. H. Pennington, D. J. Durand, C. P. Slichter, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, *ibid.* **39**, 2902 (1989).

[2] C. H. Pennington, D. J. Durand, C. B. Zax, C. P. Slichter, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **37**, 7944 (1988); T. Shimizu, H. Yasuoka, T. Imai, T. Tsuda, T. Takabatake, Y. Nakazawa, and M. Ishikawa, J. Phys. Soc. Jpn. **57**, 2494 (1988).

[3] C. Coretsopoulos, H. C. Lee, E. Ramli, L. Reven, T. B. Rauchfuss, and E. Oldfield, Phys. Rev. B **39**, 781 (1989).

[4] P. Boolchand, R. N. Enzweiler, I. Zitkovsky, R. L. Meng, P. H. Hor, C. W. Chu, and C. Y. Huang, Solid State Commun. **63**, 521 (1987); Z. Q. Qui, Y. W. Du, H. Tang, J. C. Walker, W. A. Bryden, and K. Moorjani, J. Magn. Magn. Mater. **69**, L221 (1987); H. Tang, Z. Q. Qui, Y. W. Du, G. Xiao, C. L. Chien, and J. C. Walker, Phys. Rev. B **36**, 4018 (1987); R. A. Brand, Ch. Sauer, H. Lütgemeier, B. Rupp, and M. Zinn, Physica C **156**, 539 (1988); T. Tamke, T. Komai, A. Ito, Y. Maeno, and T. Fujita, Solid State Commun. **65**, 43 (1988); Q. A. Pankhurst, A. H. Morrish, M. Raudsepp, and X. Z. Zhou, J. Phys. **21C**, L7 (1988); E. R. Bauminger, M. Kowitt, I. Felner, and I. Novik, Solid State Commun. **65**, 123 (1988).

[5] Z. M. Stadnik, G. Stroink, and R. A. Dunlap, Phys. Rev. B **39**, 9108 (1989).

[6] P. Singh, M. N. Nyayate, S. H. Devare, and H. G. Devare, Phys. Rev. B **39**, 2308 (1989).

[7] F. J. Adrian, Phys. Rev. B **38**, 2426 (1988).

[8] R. Kamal, Loveleen, Sumanjit, B. R. Sood, and K. S. Sidhu, Phys. Rev. B **37**, 5928 (1988).

[9] E. A. Colbourn and J. Kendrick, in *Computer Simulation of Solids,* edited by C. R. A. Catlow and W. C. Mackrodt (Springer-Verlag, New York, 1982), p. 67.

[10] B. K. Chakraverty, D. D. Sarma, and C. N. R. Rao, Physica **156C**, 413 (1988).

[11] See for instance, N. Sahoo, S. K. Mishra, K. C. Mishra, A. Coker, T. P. Das, C. K. Mitra, L. C. Snyder, and A. Glodeanu, Phys. Rev. Lett. **50**, 913 (1983); N. Sahoo, K. C. Mishra, and T. P. Das, Hyperfine Interact. **32**, 601 (1986); N. Sahoo, K. C. Mishra, M. Van Rossum, and T. P. Das, *ibid.* **35**, 701 (1987).

[12] P. C. Kelires and T. P. Das, Hyperfine Interact. **34**, 285 (1987).

[13] P. C. Kelires, Ph.D. thesis, State University of New York at Albany, 1987 (unpublished).

[14] H. H. Klauss, N. Sahoo, P. C. Kelires, T. P. Das, W. Potzel, M. Kalvius, M. Frank, and W. Kreische, Hyperfine Interact. (to be published).

[15] J. Stein, N. Sahoo, S. B. Sulaiman, and T. P. Das, Hyperfine Interact. (to be published).

[16] R. Poirier, R. Kari, and I. G. Csizmadia, *Handbook of Gaussian Basis Sets* (Elsevier, Amsterdam, 1985).

[17] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[18] M. A. Beno, L. Soderholm, D. W. Capone II, D. G. Hinks, J. D. Jorgensen, J. D. Grace, I. K. Schuller, C. U. Segre, and K. Zhang, Appl. Phys. Lett. **51**, 57 (1987).

[19] T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic, New York, 1957).

[20] R. M. Sternheimer, Z. Naturforsch. **41a**, 24 (1986); T. P. Das and P. C. Schmidt, *ibid.* **41a**, 47 (1986).

[21] R. Bersohn, J. Chem. Phys. **29**, 326 (1958); R. R. Sharma and T. P. Das, *ibid.* **41**, 3581 (1964).

[22] R. Daudel, G. Leroy, D. Peeters, and M. Sana, *Quantum Chemistry* (Wiley, New York, 1983), p. 137.

[23] K. C. Hass, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, San Diego, 1989), Vol. 42.

[24] H. P. Schaefer III, R. A. Klemm, and F. E. Harris, Phys. Rev. **181**, 138 (1969).

[25] R. M. Sternheimer, Phys. Rev. **164**, 10 (1987).

[26] P. C. Schmidt, K. D. Sen, T. P. Das, and A. Weiss, Phys. Rev. B **22**, 416 (1980).

[27] R. E. Watson and A. J. Freeman, Phys. Rev. **131**, 250 (1963).

[28] Y. Guo, J. M. Langlois, and W. A. Goddard III, Science **239**, 896 (1988).

[29] J. E. Rodgers, T. Lee, and D. Ikenberry, Phys. Rev. A **7**, 51 (1973).

[30] J. E. Rodgers and T. P. Das, Phys. Rev. A **12**, 353 (1975); J. E. Rodgers, R. Ray, and T. P. Das, *ibid.* **14**, 1595 (1976).

[31] See Ref. 20 for a review of oxygen-hole based theories.

[32] S. Kurihara, Phys. Rev. B **39**, 6000 (1989).

[33] M. Horvatic, P. Segransan, C. Berthier, Y. Berthier, P. Butaud, J. Y. Henry, M. Couach, and J. P. Chaminade, Phys. Rev. B **39**, 7332 (1989).

[34] J. M. Tranquada, D. E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston, Phys. Rev. Lett. **60**, 156 (1988); J. Rossat-Mignot, P. Burlet, M. J. G. M. Jurgens, J. Y. Henry, and C. Vettier, Physica **152C**, 19 (1988).