Theory of nuclear quadrupole interactions of ^{135}Ba and ^{139}La in $YBa_2Cu_3O_6$ and La_2CuO_4

S. B. Sulaiman, N. Sahoo, and T. P. Das
Department of Physics, State University of New York at Albany, Albany, New York 12222

O. Donzelli
Department of Physics, University of Ferrara, I-44100, Ferrara, Italy
(Received 12 August 1991)

The electric-field gradients at ^{135}Ba in $YBa_2Cu_3O_6$ and ^{139}La in La_2CuO_4 have been investigated using the first-principles Hartree-Fock cluster procedure. The calculated electric-field gradients at these nuclei lead to nuclear quadrupole coupling constants in very good agreement with experiment. The significance of this good agreement is discussed.

I. INTRODUCTION

The electronic structures of high-T_c systems are of great interest for a number of reasons. The first and most important reason is that quantitative theories for the origin of superconductivity have to take account of the electron distributions associated with the electronic wave functions for the systems. Second, one needs a knowledge of the electronic structure to understand the measured properties, especially spectroscopic, for the normal and superconducting states of these systems.

The properties of interest in the present investigation are those associated with hyperfine interactions in the copper-oxide superconducting systems which have been studied by a number of different techniques, among them magnetic resonance, Mössbauer effect, perturbed angular correlation, and muon spin rotation. The hyperfine properties provide particularly useful probes of the electron distribution because they involve the inner regions of the ions involved, namely, the vicinity of the nuclei where the hyperfine interactions occur, as well as the surrounding environment which leads to the charge and spin distributions that are responsible for the observed nuclear quadrupole and magnetic hyperfine interactions. The procedure for using these probes to investigate electron distributions is to use the latter, calculated by first-principles procedures, to study hyperfine properties quantitatively and compare with observed data to test the accuracy of the theoretically obtained electronic structures.

In our program of investigations on the hyperfine properties of these systems, we have been utilizing the Hartree-Fock (HF) cluster procedure[1] using as large a representative cluster as is possible, with the influence of the rest of the lattice ions included by treating them as point charges and incorporating their Coulomb potentials in the HF Hamiltonian.[1,2] We have so far studied[3-5] the nuclear quadrupole interactions of ^{63}Cu and ^{17}O nuclei in the $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, and La_2CuO_4 systems and the hyperfine field at the ^{63}Cu nucleus in the antiferromagnetic state of the latter system. These earlier HF cluster results[3-5] have provided satisfactory explanations of the trends in experimental properties. However, they have led to overestimates in the magnitudes of the quadrupole coupling constants e^2qQ, by as much as 40% in the case of 1:2:3 compounds[3,4] and somewhat lower,[5] about 25%, for the lanthanum system. For the hyperfine field at the ^{63}Cu site in the latter case, the calculated result[5] is also about 25% larger in magnitude than experiment. While the cause for these differences in the nature of agreement between theory and experiment for the two systems is not totally understood, it is possible that they could be attributed to the difference in the nature of many-body effect that are related to the origin of the superconductivity in La_2CuO_4 and $YBa_2Cu_3O_7$.

Since the superconductivity seems to be associated with the copper and its neighboring oxygen atoms, it is interesting to explore the hyperfine properties of nuclei outside the "range" around the copper-oxygen systems that seem to be important for the superconductivity. This has been our motivation for studying the ^{139}La and ^{135}Ba nuclear quadrupole interactions, which is the topic of the present paper. If, indeed, the range of influence of the superconducting mechanism does not extend as far as the lanthanum and barium ions, one would expect that many-body effects related to these mechanisms would not be important for the ^{139}La and ^{135}Ba nuclear sites and one should have better agreement with experiment as compared to hyperfine effects for the ^{63}Cu and ^{17}O nuclei.

Section II presents briefly the procedure used for calculation of electronic structures and the associated e^2qQ and asymmetry parameter η. Section III presents the results and discussion.

II. PROCEDURE

The HF cluster procedure employed in this work has been used recently by our group for investigation of the nuclear quadrupole interactions of ^{63}Cu and ^{17}O nuclei in yttrium–barium–copper-oxide systems[3,4] and ^{63}Cu in the lanthanum copper-oxide system[5] as well as the magnetic hyperfine interaction in the latter case. In addition to these high-T_c systems, it has been applied successfully for the study of magnetic and nuclear quadrupole hyperfine interactions in a number of other systems including impurity atoms in semiconductors[6] and a number of ionic crystal systems.[7] As in all these other investigations,

Gaussian basis functions were used, with the oxygen basis functions being obtained using for the O^{2-} ions a Watson sphere model[8] to include the influence, on these very diffuse negative ions, of the potential due to the neighboring positive ions. For the La^{3+} ion we have used the available[9] Gaussian-type functions (GTF) contracted to 6*s* (432222), 4*p* (4222), and 3*d* (411) basis functions. For the Ba^{2+} ions, the corresponding basis functions[9] consisted of 6*s* (432222), 4*p* (4222), and 2*d* (42). For the oxygen negative ions, we have used a basis set[10] consisting of 8*s* and 4*p* GTF contracted to 2*s* (44) and 1*p* (4) basis functions. All computations were carried out utilizing the GAUSSIAN88 program.[11]

The ^{135}Ba nuclear quadrupole interaction has been investigated in the present work in the $YBa_2Cu_3O_6$ system because experimental data[12] are available for this system. The geometrical parameters used for our investigation were taken from the available[13] crystal structure data. From the structure shown in Fig. 1 it can be seen that the immediate neighbors of Ba (denoted by *A*) consist of four oxygen ions of the type O(4) denoted by *B*, *C*, *D*, *E* in the figure, leading to a $Ba^{2+}(O^{2-})_4$ as the appropriate cluster to choose for our calculations. It can be seen from Fig. 1 that the next larger cluster would have to involve an additional eight copper ions, four of them of the Cu(1) type and four of the Cu(2) type. This would be a rather large cluster and involve substantially larger computational effort. Our earlier investigation[5] on NQI for ^{63}Cu in the La_2CuO_4 system, where a corresponding larger cluster was investigated in addition to the basic $Cu^{2+}(O^{2-})_6$ one, suggests that the influence of the additional copper neighbors in the present calculations would not be too significant. However, the influence of the ions in the rest of the lattice outside the chosen cluster was incorporated as in our earlier investigations[3-5] by augmenting[1,2] the Hartree-Fock potential with the Coulomb potential due to these external ions. The charges on the copper, oxygen, barium, and yttrium ions were taken to be the formal charges of 1+ [Cu(1)], 2+ [Cu(2)], 2−, 2+, and 3+, respectively. For the copper and oxygen ions we have also used the charges obtained from our earlier cluster calculations[3] concerned with ^{63}Cu hyperfine properties. The influence of using these latter charges as compared to the formal charges was found to be not very important. This process of including environmental effects could be considered as essentially allowing one to deal with the infinite lattice in studying the hyperfine properties of a particular nucleus, in this case, the ^{135}Ba at the center of the chosen cluster. For the ^{139}La nucleus in La copper oxide, the appropriate cluster, as can be seen from the crystal structure[14] in Fig. 2, is a $La^{3+}(O^{2-})_5$ one involving the La ion *A* and the oxygen ions *B*, *C*, *D*, *E*, and *F*.

Once the electronic structure is obtained, one can determine the components V_{ij} of the electric-field-gradient (EFG) tensor including contributions from the electrons and nuclear charges within the cluster and the ionic charges outside, using the procedure described in our earlier work[4] on high-T_c systems. The EFG tensor can be diagonalized to obtain the principal components V_{xx}, V_{yy}, and V_{zz}, the labeling of principal axes being done in keeping with the convention commonly used in the literature,[15] namely, $|V_{xx}| < |V_{yy}| < |V_{zz}|$. The EFG parameter $q = V_{zz}$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ are ones that are derived from experiment and have to be compared with theory. Since the present calculations are all electron in nature including the core electrons, Sternheimer antishielding effects on

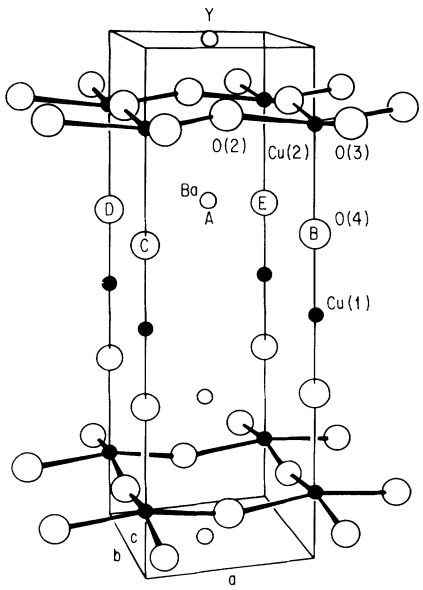

FIG. 1. Crystal structure of $YBa_2Cu_3O_6$. The ions included in the cluster BaO_4 used the present HF calculation are indicated in the figure as *A*, *B*, *C*, *D*, and *E*.

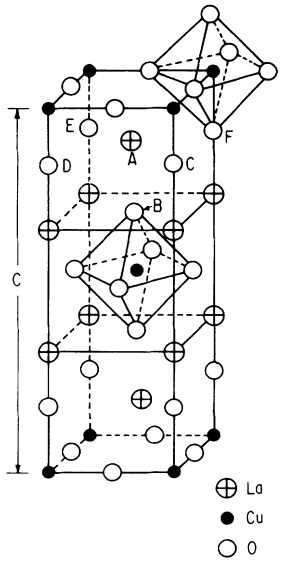

FIG. 2. Crystal structure of La_2CuO_4 in the tetragonal phase which is similar to the orthorhombic structure used in this work. The relation between the two phases is explained in Ref. 14. The ions included in the cluster LaO_5 used in the present investigation are indicated in the figure as *A*, *B*, *C*, *D*, *E*, and *F*.

the components of the EFG tensor are automatically included.[3-5]

III. RESULTS AND DISCUSSION

As in the case of our earlier investigations[3-5] on ^{63}Cu and ^{17}O nuclear quadrupole interactions, we shall present our results for the EFG tensor components in terms of the electronic contributions from within the cluster, the nuclear charge contribution from within the cluster, and external contributions from the charges outside the cluster. For the ^{135}Ba nucleus, there is axial symmetry about the c axis. For the total EFG tensors, one has therefore only to present the largest component q of the EFG tensor in the principal axis system which is along the c axis, the other two components perpendicular to the c axis being $-q/2$ each. The electronic, nuclear charge, and external contributions to q are found, in atomic units ea_0^{-3}, to be

$$q_{\rm el}=1.4581,\quad q_{\rm nuc}=-0.2050,\quad q_{\rm ext}=-0.0299\ , \tag{1}$$

adding up to a total value of q of

$$q=1.2232\ . \tag{2}$$

The external contribution $q_{\rm ext}$ is quite small but, in fact, it is subjected to a sizable antishielding effect which is already included in $q_{\rm el}$ through the incorporation of the potential due to these ions on the electrons in the cluster as explained in Sec. II. There are a number of different values of $Q(^{135}\text{Ba})$ available[16] in the literature which have significant differences from each other. An approximate mean[16,17] of these values is 0.18 b with an uncertainty of about 10%. Using this mean value of $Q(^{135}\text{Ba})$ and our calculated value of q in Eq. (2), one gets a net quadrupole coupling constant of 51.7 MHz. This is to be compared with the experimental magnitude[14] from nuclear quadrupole resonance of 54 MHz. Thus, our value is in satisfactory agreement with the experimental value within the range of uncertainty of $Q(^{135}\text{Ba})$. The value of q has also been obtained through a recent band-structure calculation by the linearized augmented-plane-wave (LAPW) procedure. Using the same value of $Q(^{135}\text{Ba})$ as we have used, the band-structure value[18] of q leads to an e^2qQ of 47.9 MHz, somewhat smaller than our results. But, considering the fact that the two calculations involve rather different methods, ours involving the HF cluster approach while the band-structure result involves the LAPW procedure using the local-density approximation to the Hartree-Fock exchange potential, the nature of agreement between the two theoretical results is quite satisfactory.

For the ^{139}La nucleus in La_2CuO_4, because of the slight orthorhombic distortion from tetragonal symmetry,[14] the V_{xx} and V_{yy} components of the EFG tensor are not equal. This leads to an asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$ determined from our calculation to be 0.02, which is small as expected, and in good agreement with the experimental value[19] of 0.024. The contributions to the net $q=V_{zz}$ broken down in the same manner as in Eq. (1) for ^{135}Ba are

$$q_{\rm el}=-2.4849,\quad q_{\rm nuc}=0.2898,\quad q_{\rm ext}=0.0508\ , \tag{3}$$

leading to a net q of $-2.1443ea_0^{-3}$. The value of $Q(^{139}\text{La})$ from the literature obtained through collinear fast-beam laser spectroscopy[20] is 0.20 b with an uncertainty of 5%. This value using our net calculated q leads to $e^2qQ=-100.8$ MHz, in good agreement, within the uncertainty in Q, with the experimental[19] value of 89.4 MHz. As far as we are aware, there is no other result in the literature from electronic structure calculations to compare with ours.

There is a point-ion model result for ^{139}La available[21] in the literature, where the Sternheimer antishielding factor[22] of -76 has been used and all the ions surrounding the La^{3+} ion under study have been handled as point charges corresponding to their formal charges. This point-ion value[23] for e^2qQ is -81.1 MHz, which is somewhat smaller than our calculated result. We have also made a point-ion calculation of the EFG for ^{135}Ba in the $YBa_2Cu_3O_6$ system, which, when combined with the value of $\gamma_\infty=-76.2$ for Ba^{2+} available in the literature,[24] leads to $e^2qQ=69.7$ MHz. This value, in contrast to the case of ^{139}La in La_2CuO_4, on the other hand, is somewhat larger than that obtained from our present electronic structure calculation by the HF cluster procedure. There can be a number of reasons for the difference between the point-ion results and those from detailed electronic structure calculations. One of these reasons is the occurrence of some local contribution arising from the departure from spherical symmetry of the electron distribution on the Ba^{2+} and La^{3+} ions due to the small but significant covalent bonding between the metal and oxygen ions as manifested by the departures of the calculated charges of 1.94 and 2.98 from the formal charges of 2 and 3. This local contribution is not included in the point-ion model. The other reason is that concerned with the uncertainty of the Sternheimer antishielding factors to be associated with the contributions to the EFG from the oxygen ions next to the metal ion due to the distributed nature of the overlapping electron densities on the former and the latter, as has been discussed in an earlier work[25] on Fe_2O_3 concerned with this question.

In concluding, it is important to point out that there is more satisfactory agreement between the results for ^{135}Ba and ^{139}La from our theoretical work using the HF cluster procedure as compared to the situation[3-5] for ^{63}Cu and ^{17}O nuclei. This would be considered as suggestive of the fact that many-body effects which could influence the calculated EFG and which could be related to the mechanisms for the origin of superconductivity in the copper-oxide superconductors are more important at the copper and its neighboring oxygen sites than at the barium and lanthanum sites which are more distant from the copper ions.

ACKNOWLEDGMENTS

A major part of the computation was carried out at Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering at Cornell University which receives a major funding from the National Science Foundation and IBM Corporation, with additional support from New York State and members of the Corporate Research Institute. One of us (O.D.) has been partially supported by Consiglio Nazionale delle Ricerche of Italy, Contract No. 90.01647.PF66.

[1]K. 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.

[2]P. C. Kelires, Ph.D thesis, State University of New York at Albany, 1987; I. Q. Broughton and P. S. Bagus, Phys. Rev. B **30**, 4761 (1984).

[3]S. B. Sulaiman, N. Sahoo, Sigrid Markert, J. Stein, and T. P. Das, Bull. Mater. Sci. **14**, 149 (1991).

[4]N. Sahoo, Sigrid Markert, T. P. Das, and K. Nagamine, Phys. Rev. B **41**, 220 (1990).

[5]S. B. Sulaiman, N. Sahoo, T. P. Das, O. Donzelli, E. Torikai, and K. Nagamine, Phys. Rev. B **44**, 7028 (1991).

[6]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); S. B. Sulaiman, N. Sahoo, K. C. Mishra, T. P. Das, and K. Bonde Nielsen, Hyperfine Interact. **60**, 861 (1990).

[7]See, for instance, P. C. Kelires and T. P. Das, Hyperfine Interact. **34**, 285 (1987); P. C. Kelires, K. C. Mishra, and T. P. Das, *ibid.* **34**, 289 (1987); H. H. Klauss, N. Sahoo, P. C. Kelires, T. P. Das, W. Potzel, G. M. Kalvius, M. Frank, and W. Kreische, *ibid.* **60**, 853 (1990); J. Stein, N. Sahoo, S. B. Sulaiman, and T. P. Das, *ibid.* **60**, 849 (1990).

[8]R. E. Watson, Phys. Rev. **111**, 1108 (1950).

[9]J. Andzelm, S. Huzinaga, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, in *Gaussian Basis Sets for Molecular Calculations,* edited by S. Huzinaga (Elsevier, Netherlands, 1984).

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

[11]GAUSSIAN 88, M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, Q. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburg, PA.

[12]H. Lütgemeier, V. Florentiev, and A. Yakubovski, *Electronic Properties of High-T_c Superconductors and Related Compounds, Proceedings of the Conference at Kirchberg* (Springer-Verlag, Berlin, 1990).

[13]P. Bordett, C. Chaillout, J. J. Capponi, J. Chenavas, and M. Marezio, Nature (London) **327**, 687 (1987).

[14]J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 526 (1973); C. P. Poole, Jr., T. Datta, and H. A. Farach, *Copper Oxide Superconductors* (Wiley, New York, 1988).

[15]T. P. Das and E. L. Hahn, in *Solid State Physics, Suppl. 1,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1958).

[16]P. Raghavan, At. Data Nucl. Data Tables **42**, 249 (1989).

[17]H. Chihara and N. Nakamura, in *Nuclear Quadrupole Resonance Spectroscopy Data,* Landolt-Börnstein, New Series, Group III, Vol. 20a, edited by K.-H. Hellwedge and A. M. Hellwedge (Springer, Berlin, 1987).

[18]Karlheinz Schwarz, Claudia Ambrosch-Draxl, and Peter Blaha, Phys. Rev. B **42**, 2051 (1990).

[19]H. Lütgemier and M. W. Pieper, Solid State Commun. **64**, 267 (1987).

[20]P. Raghavan, At. Data Nucl. Data Tables **42**, 248 (1989).

[21]Frank J. Adrian, Phys. Rev. B **38**, 2426 (1988).

[22]R. E. Watson and A. J. Freeman, Phys. Rev. **135**, A1209 (1964).

[23]This value is obtained by adjusting the value of -85.4 MHz obtained by F. J. Adrian (Ref. 21) by the ratio of the ^{139}La quadrupole moment of 0.20 b (Ref. 20) that we have used to 0.21 b used in Ref. 21.

[24]P. C. Schmidt, K. D. Sen, T. P. Das, and Alarich Weiss, Phys Rev. B **22**, 4167 (1980).

[25]A. C. Beri, R. M. Sternheimer, T. Lee, and T. P. Das, Phys. Rev. B **28**, 2335 (1983).