PHYSICAL REVIEW B VOLUME 41, NUMBER 13 1 MAY 1990

# Electronic structure of undoped and doped $La_2CuO_4$: A Hartree-Fock cluster study

P. Saalfrank, M. A. Abdel-Raouf, J. Ladik, and R. F. Wood*

*Chair for Theoretical Chemistry, Friedrich-Alexander-University Erlangen-Nürnberg, Egerlandstrasse 3,*
*D-8520 Erlangen, Federal Republic of Germany*

(Received 27 December 1989)

By use of the *ab initio* Hartree-Fock method, $La_2CuO_4$ in undoped and doped form is studied by cluster calculations that take the La atoms explicitly into account. In these computations the important effects of the crystal field are studied in detail. Density-of-states curves are computed and compared with experiment and other calculations. The charge and spin distributions and the extent of covalent bonding in $La_2CuO_4$ are examined: We have found the bonding to be nearly ionic. Covalency becomes more important if one La atom in $La_2CuO_4$ is replaced by one of the alkaline-earth elements (Ba, Sr, Ca, or Mg). This "doping" produces holes in the $CuO_2$ planes that are mainly oxygenlike and are of $\sigma$ symmetry. The alkaline-earth atoms are fully ionized, thus suggesting that theoretical models based on the polarizability of these substituents may not be valid.

## I. INTRODUCTION

The discovery of high-temperature superconductivity in copper oxide ceramics by Bednorz and Müller[1] has led to the development of numerous theories concerning this phenomenon.[2] However, the validity of none of these has been unambiguously established up to the present time, although it seems rather probable that standard phonon-mediated BCS theory[3] does not hold. The most essential information for developing and verifying theoretical concepts undoubtedly comes from the detailed knowledge of the electronic structure of these materials. Extensive band and cluster calculations on the new materials have already been reported.[4] However, even among those numerous calculations that are described as "first principles" and that begin from the same starting point, the results are frequently quite different and often even contradictory.

Then too there is the difficulty of knowing just what the starting point should be. For example, it is now well established that there are long-range two-dimensional (2D) antiferromagnetic (AF) fluctuations within the $CuO_2$ planes of stoichiometric $La_2CuO_4$, $YBa_2Cu_3O_{7-x}$ for certain values of $x$, and presumably in the other copper oxide superconductors. Conventional, i.e., non-spin-polarized band calculations are unable to give this ordering and even those few spin-polarized calculations that have appeared give conflicting results. Similarly, the outcome of "first-principles" cluster calculations depends strongly on the initial assumptions about the *type* of calculation that is needed, as well as the many approximations that must subsequently be made in order to actually carry out the calculations. In this latter category fall such questions as the following: (i) How should the core of heavy ions such as Cu, La, Sr, etc., be treated? (ii) How extensive must the basis set be? (iii) What constitutes an adequate treatment of the crystal field, e.g., how many point charges must be included?

In our own work on the high-$T_c$ materials, we have tried to emphasize a systematic approach to determining the level of approximations that are needed to give reliable results. Thus, in this paper, we concentrate on Hartree-Fock calculations of relatively small clusters (the largest cluster is $LaBaCuO_4$) with the objective of answering some of the following questions. Given a particular cluster how many and what distribution of point charges are required to adequately represent the crystal field? At what level of complexity must one approximate the cores of heavy ions (essentially all ions but oxygen in these materials) in order to obtain reliable results? What do we know about the choice of basis sets, e.g., the use of minimal versus double-$\zeta$ sets? In connection with this last question, it must also be considered whether or not it is adequate simply to take over basis sets from calculations on small molecules or must the basis orbitals be reoptimized for the solid-state calculations. A prime example of this problem is the $O^{2-}$ ion which, of course, is unstable in free space but is stabilized by the crystal field in alkaline-earth and transition-metal oxides.

The paper is organized as follows. In the next section we give a brief review of some of the experimental and theoretical work that is particularly relevant to the calculations of Sec. IV. In Sec. III we describe briefly the numerical techniques and approximations used in the calculations. These are generally well known to quantum chemists, but may not be familiar to many solid-state physicists.

In a lengthy Sec. IV, we examine several clusters within $La_2CuO_4$. First the stability of different oxidation states of a single oxygen atom in different point-charge environments is studied.

A second subsection deals with $[CuO_6]^{9-}$ (oxidized cluster), which is examined with and without point charges. The influence of the crystal field on the density of states (estimated via one-particle level histograms) is considered. In a third subsection the electronic structure of a "stoichiometric" cluster, $La_2CuO_4$, is investigated. We emphasize charge and spin distributions, compute covalent bond orders, and discuss the influence of the crystal field.

Finally, we replace one La atom by various alkaline-earth elements (Ba, Sr, Ca, Mg). Lattice relaxation effects are also roughly taken into account. Some suggestions about hole formation are given and nonstoichiometry is simulated via modifications of the crystal field.

In the final section, the most important results are summarized, some conclusions are given, and the future direction of our program of calculations is briefly outlined.

## II. REVIEW OF SELECTED EXPERIMENTAL AND THEORETICAL RESULTS

In attempting to formulate and evaluate mechanisms of high-$T_c$ superconductivity one is particularly interested in (i) the density of states (DOS), (ii) the charge and spin distribution on various atoms, and (iii) details of hole formation due to cation alloying in the case of $La_2CuO_4$ (from now on 2:1:4), or variation of oxygen content in $YBa_2Cu_3O_{7-x}$ (from now on 1:2:3).

The density of states is of central importance even in standard BCS theory.[3] Photoelectron spectroscopy provides the information that there is a valence-band region $\approx 8$ eV wide in both the 2:1:4 and 1:2:3 superconductors.[4] The states in this region are strongly dominated by Cu 3*d* and O 2*p* orbitals. Additionally, the DOS peaks at a binding energy around 12 eV below the Fermi level. This peak has been identified as Cu 3*d* like.[4] Several band-structure calculations of the density-functional type[4] and within the framework of extended Hückel theory[5] have been performed to reproduce the experimental DOS. Cluster calculations followed the same line.[6,7] Rough agreement between theory and experiment is found, although some discrepancies must be noted:[8] (i) The computed valence-band region is shifted to 1–2 eV lower binding energies with respect to photoemission data; (ii) the calculated DOS near the Fermi level is too high; (iii) the $-12$ eV satellite cannot be reproduced. Fujimori *et al.*[8] attribute shortcomings to the neglect of correlation effects. Performing configuration-interaction (CI) calculations on a $[CuO_6]^{10-}$ cluster they were able to match the experimental DOS curve. However, the CI matrix elements in this work are not determined via first principles, but taken as parameters to fit the experimental results.

Interest in the charge and spin distribution in copper oxides arises for many reasons. First one wants to quantify the balance between ionic and covalent bonding in these materials. Secondly several theories of high-$T_c$ superconductivity restrict their attention to the $CuO_2$ plane—consequently, the effective charge in this plane must be known. Moreover, some investigators are interested in the charge of atoms other than Cu and O; e.g., Ronay and Newns[9] assume that the alkaline earth atoms in high-temperature superconductors are not fully ionized and consequently their high polarizability screens the Coulomb interaction thus effecting $T_c$. Finally, the interest in the spin distribution is strongly motivated by the remarkable magnetic behavior of these materials that has given rise to several theoretical concepts based on exchange interactions (direct or via intermediate ions).[10]

From core-level spectroscopy[11] it is found that the high-$T_c$ superconductors are highly ionic. Particularly, Cu seems to be in the $+2$ state even in the doped or oxidized systems, though this statement has been questioned, especially in early studies.[12] Furthermore, oxygen seems to be in the $-2$ state; doping or oxidation, however, leads to $O^-$ (see below). For atoms other than Cu and O the experimental data are less condensive. Viswanathan *et al.*[13] find some evidence for two inequivalent Ba ions from photoelectron spectroscopy measurements in $NdBa_2Cu_3O_{7-x}$, but the nature of these ions is not specified further. By neutron diffraction Vaknin *et al.*[14] identify a superlattice reflection resulting from planar antiferromagnetic ordering of Cu spins in 2:1:4. The Néel temperature $T_N$ seems to be very sensitive to the level of doping with divalent alkaline-earth elements (for details see Ref. 4).

Several theoretical investigations try to elucidate the questions concerning charge and spin distribution and bonding character. The more or less generally accepted picture is that there are strong ionic regions near somewhat covalent ones, the latter being identified with the $CuO_2$ planes.[4] Density-functional computations appear to some extent contradictory: Chen and Callaway[15] have studied the cluster $Ba_4Cu_2O_7$ (modeling a chain segment in 1:2:3) to show that the ionicity of the copper oxides is not very strong. Krakauer *et al.*,[16] using a similar technique within the framework of a band calculation, advocate the opposite. The amount of charge transfer has been the subject also of some extended Hückel studies on several $[CuO_m]^{n-}$ clusters.[17] The theoretical predictions of spin distribution were not very successful. Spin density band theory with local exchange fails to stabilize the observed antiferromagnetic ordering.[4] Even the location of spins seems to be controversial: Weinert and Fernando,[18] treating a $CuO_2$ plane in this approximation, arrive at the conclusion that "an important possible antiferromagnetic state of $CuO_2$ planes has the moments on the O, rather than the Cu, sites."

The question about charge and spin distribution is closely related to the third feature of interest mentioned above—the problem of hole formation, distribution, and symmetry in doped (2:1:4 system) and oxidized (1:2:3 system) superconductors. From Hall-effect measurements[19] we know that the charge carriers are positive (if we forget the new electron-type superconductors[20] for a moment). All the models developed emphasize that $T_c$ is a function of the hole concentration.[21] There is also agreement that holes are created in the $CuO_2$ planes. Several theoretical concepts use this fact together with assumptions about the symmetry of hole containing orbitals to explain normal and superconducting state properties of the ceramics.[22]

Among the experimental studies on hole formation, electron-energy-loss spectroscopy[23] and optical experiments[24] indicate that the holes are in the $CuO_2$ plane on the oxygen sites. In Ref. 23 arguments are given for the pure $p_x$ and $p_y$ character of the holes, while Ref. 24 argues for a small amount of $p_z$-like behavior. In any case the $p_{x,y}$ symmetry turns out to be dominant but it remains unclear whether the dopant holes are $p\sigma$ type or $p\pi$ type, i.e., whether the corresponding orbitals are collinear with the Cu—O bonds or perpendicular to them.

Cluster calculations have been performed to attempt to clarify the symmetry question and the hole distribution in general. Guo *et al.*[7] apply the so-called generalized-valence-bond (GVB) technique to several clusters modeling the 2:1:4 and 1:2:3 superconductors to show that holes are initially created at oxygen sites and are of $\pi$ symmetry. Since local density band calculations identify the holes as $\sigma$ like,[4] Guo *et al.* conclude that the one-electron picture is insufficient and that correlation effects have to be taken into account. Eto *et al.*,[25] using the multiconfiguration self-consistent-field method with configuration interaction (MCSCF-CI) to include correlation, find that oxidation of a $[Cu_2O_{11}]^{18-}$ cluster produces holes mainly on the bridging oxygen site of $\sigma$ symmetry. Martin and Saxe[26] perform CI calculations on a $[Cu_4O_{12}]^{n-}$ cluster ($n=15$ and 16), oxidized and nonoxidized systems) and associate the ground state with a hole on Cu rather than on oxygen. One recognizes that Refs. 7, 25, and 26 present contradictory results though the methods used are potentially highly accurate, i.e., they are free of experimental parameters, they treat exchange in a nonlocal manner, and they take correlation corrections into account. Looking for possible sources of errors we note the following: (i) In none of the above publications were atoms other than Cu and O considered; (ii) the crystal field is simulated by only a few hundred point charges; (iii) in Refs. 25 and 26 correlation effects are calculated with a minimal basis set although it is known that for transition metals a high-quality basis set is required to reach the Hartree-Fock limit;[27] (iv) in Ref. 7 energy differences of some meV are given significance, though the Ar core of Cu is replaced by an effective potential. There is, however, general agreement[28] that 3*s* and 3*p* orbitals are crucial for a really accurate description of transition elements.

There are many other investigations on hole creation, distribution, and symmetry, and on other effects due to cation alloying.[4] For example, the hole distribution is treated within a purely ionic (and semiclassical) model in Ref. 29.

## III. COMPUTATIONAL DETAILS

As mentioned above, for our calculations we use the HF scheme. For clusters with an odd number of electrons the frequently used different orbitals for different spins (DODS) technique (which is an unrestricted variant of the HF method) leads to a large spin contamination due to the fact that the wave function is not an eigenfunction of $\hat{S}^2$. To avoid this in the present calculations, the annihilated DODS (ADODS) method developed by Kovár[30] was applied: Here in each cycle of the iteration procedure the next higher spin component to the desired one is annihilated using the appropriate factor of the spin projection operator.[31] In the case of $La_2CuO_4$ (odd number of electrons; desired spin state: doublet) we obtain the exact expectation value of $\langle \hat{S}^2 \rangle = 0.75$ in this way $[\langle \hat{S}^2 \rangle = S(S+1) = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}]$.

To reduce the computational effort and to include relativistic effects for the heavy atoms (La, Ba, Sr, and Ca), we used the quasirelativistic pseudopotentials given by Preuss *et al.*[32] In this approach the (chemically almost inert) core electrons are replaced by effective potentials; relativistic corrections are included approximately by fitting the core potential parameters to the results of quasirelativistic all-electron HF calculations. Quasirelativistic here means that only a one-component wave function is used, but the most important relativistic corrections (mass velocity term, Darwin-spin-orbit term) are included in the Hamiltonian.[32] For La (atomic number 57), only 5*s*, 5*p*, 5*d*, and 6*s* orbitals are explicitly taken into account and for the heavy alkaline-earth elements only the outermost *s* functions.

All calculations were performed with basis sets of double-$\zeta$ quality, i.e., each atomic orbital is represented by two contractions (see Ref. 36). Preliminary computations[33] indicated that, particulary for Cu, a minimal-basis (MB) set[34] (one contraction per atomic orbital) is entirely insufficient. For example, the potential curve for CuO is completely wrong. Even worse, results for molecules containing Cu depend strongly on the copper MB set used, i.e., whether this basis set is optimized for the atomic $^2S$ or for the atomic $^2D$ state, while a double-$\zeta$ basis is not so sensitive to such differences.

For Cu we used a double-$\zeta$ basis optimized for the atomic $^2D$ state[35] (contraction scheme[36] $(14s\ 8p\ 5d)/[8s\ 4p\ 2d]$), for oxygen, Dunning's widely used double-$\zeta$ basis[37] ($(9s\ 5p)/[4s\ 2p]$), and for Mg, Clementi's double-$\zeta$ basis.[38] For La ($(6s\ 4p\ 4d)/[4s\ 2p\ 2d]$), and the heavier alkaline-earth ($(4s)/[2s]$), the basis sets of Preuss *et al.*[32] were adopted.

## IV. RESULTS AND DISCUSSION

### A. Oxygen in the crystal field of 2:1:4

Free $O^{2-}$ is unstable, but in an ionic crystal it is stabilized by the crystal field. Here we want to consider the field produced by the 2:1:4 superconductor and how it can be approximated by arrays of point charges. To do this we compared the total energies of O, $O^-$, and $O^{2-}$ in successively more and more realistic crystalline environments as simulated by increasing numbers of point charges. Figure 1 illustrates the layer structure of 2:1:4, the numbers in parentheses being indices for the positions of layers relative to the reference plane $CuO_2(0)$.

First we considered only this single reference plane to examine the horizontal or in-plane convergency behavior. Oxygen was put in the middle of squares built up from $CuO_2$ units (with a Cu—O distance of 1.89 Å). The latter were represented by point charges ($+2$ for Cu, $-1$ for O) to ensure charge neutrality of the stoichiometric point-charge distribution. Charge neutrality here is necessary to prevent the total energies from diverging as increasing numbers of point charges are taken into account—so horizontal convergence can be studied. The relative ener-

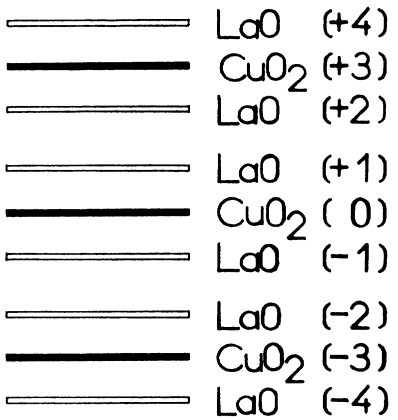

FIG. 1. Schematic representation of the layer structure of $La_2CuO_4$, showing $CuO_2$ planes (solid lines) and LaO sheets (empty lines). The numbers in parentheses indicate the position of the layers relative to the reference layer $CuO_2(0)$.

gies of the three oxidation states of oxygen are given in Table I. This table has to be understood as follows: The first column gives the number of point charges, where $\frac{2}{3}$ of them are for oxygen and $\frac{1}{3}$ of them are for copper. The second column gives the length in Å of the edge of the point-charge square around the site O, while the third and fourth columns list the energies of O, and $O^{2-}$ relative to that of $O^{-}$.

In the case of isolated oxygen (no point charges, first row of Table I) we see that the most stable state is $O^{-}$ (due to the positive electron affinity of O, but the negative electron affinity of $O^{-}$), the neutral and doubly charged negative oxygens being 2.08 and 12.93 eV higher in energy, respectively. If we take successively more point charges into account we find that the ordering of O and $O^{2-}$ is reversed, while $O^{-}$ stays lowest in energy in all cases. The quality of convergence is moderate since a 60.48 Å square still does not give full convergency—but the trend is clear.

Next the influence of neighboring planes was examined. Up to nine layers in total (see Fig. 1) were taken into account. The horizontal point-charge distribution was fixed at a square edge length of 30.24 Å. Moreover, as a first approximation the charges around the oxygen were assumed to be formal ones, i.e., +3 for La, +2 for Cu, and −2 for O, again to make the charge cage neutral. From Table II it can be seen as expected, that $O^{2-}$ has the largest (most negative) total energy, when neighboring layers are included, i.e., the second additional electron of $O^{2-}$ also becomes bound. Furthermore, one recognizes that the convergence behavior in the three-dimensional case is even worse than in the two-dimensional one.

The results above are true within the Hartree-Fock approximation and under assumption of formal oxidation numbers. Basis set effects are small: Adding one more diffuse $p$ function (exponent 0.059) to the double-$\zeta$ basis set does not affect the qualitative features. We conclude that as expected the crystal field of 2:1:4 tends to stabilize the more ionic oxygen states but the convergence behavior, especially perpendicular to the layers, is poor. These results emphasize that great care must be exercised in incorporating crystal-field effects into cluster calculations.

### B. Electronic states of $[CuO_6]^{9-}$

The distorted $CuO_6$ octahedron is a structural segment of the 2:1:4 superconductor (see Fig. 2). The square $CuO_4$ unit represents the in-plane atoms (Cu-O distance 1.89 Å), while the two apical oxygens (Cu-O distance 2.43 Å) belong to La-O sheets. Since $O^{2-}$ is unstable as a free species, the influence of the crystal field on the highly charged cluster $[CuO_6]^{9-}$ is expected to be even stronger than in Sec. IV A. The cluster $[CuO_6]^{9-}$ was chosen instead of the cluster $[CuO_6]^{10-}$ in order to model the system with a positive hole, e.g., when $La_2CuO_4$ is doped by alkaline-earth atoms (see below).

Two calculations were performed to verify the expected crystal-field effects, one without and one with point charges. In the latter case, a point-charge distribution similar to the above nine-layer charge distribution (see last row of Table II) was used. Of course to realize the $CuO_6$ cluster, some point charges had to be replaced by real atoms. The whole system (cluster +1505 point charges) was stoichiometric and neutral.

In Fig. 3(a) we give the molecular-orbital energy histogram of the cluster without charges. The histogram, in which levels belonging to 0.2 eV wide intervals are distributed in "boxes," serves as an approximate representation of the DOS. The highest occupied molecular orbital (HOMO) is set to zero. One can see that the major fraction of the states considered falls in the energy region 0–4 eV. They are essentially (Cu 3$d$)-like and/or (0 2$p$)-like in character. In agreement with the band calculations discussed in Sec. II, the DOS seems to be shifted to lower binding energies compared to experiment. In particular, the DOS near the Fermi level (energy zero) is too

TABLE I. Variation of the energies of O and $O^{2-}$ with the horizontal crystal field in $La_2CuO_4$ (see text). Energies are given relative to that of $O^{-}$.

| Number of point charges | Edge length | Relative energies (eV) O | $O^{2-}$ |
|---|---|---|---|
| 0 | | +2.08 | +12.93 |
| 60 | 15.12 | +12.69 | +3.03 |
| 216 | 30.24 | +13.24 | +2.48 |
| 468 | 45.36 | +13.43 | +2.35 |
| 816 | 60.48 | +13.54 | +2.24 |

TABLE II. Similar to Table I, but for an increasing number of planes in the vertical direction. Here the second column gives the numbers of planes considered for an in-plane point-charge square of 30.24 Å on an edge.

| Number of point charges | No. of layers | Relative energies (eV) O | $O^{2-}$ |
|---|---|---|---|
| 0 | | +2.08 | +12.93 |
| 216 | 1 | +13.24 | +2.48 |
| 504 | 3 | +24.70 | −9.39 |
| 1512 | 9 | +28.35 | −13.33 |

high. This seems to support the statement cited in Sec. II,[8] that correlation effects are responsible for the deviation of theory and experiment. The other proposed indicator for the importance of correlation, the −12 eV peak in the DOS,[8] however, can be observed for oxidized $CuO_6$ on the HF level: There is a nonvanishing DOS in the −10 to −12 eV energy region. The corresponding states are strongly (Cu 3*d*)-like, as observed experimentally.

Switching on the crystal field gave the approximate DOS in Fig. 3(b). The main differences compared to the former case occur in the valence-band region: There is some shift of the density of states to higher binding energies, especially in the lower-energy region. This implies that the DOS curves calculated here and given in the literature might be wrong not only due to the use of the one-particle picture, but also to some extent because the crystalline field was not properly included.

The $[CuO_6]^{9-}$ system (even number of electrons) models the oxidized ("doped") 2:1:4 system. Though the significance of the virtual states in the HF approximation should not be overemphasized, looking at the lowest unoccupied molecular orbital (LUMO) gives some idea of the nature of the hole orbitals. The LUMO of $[CuO_6]^{9-}$ consists of Cu $3d_{x^2-y^2}$ and O $2p_x$ and O $2p_y$ orbitals which interact in an antibonding manner. So the $p\sigma$-type holes seem to be favored. The antibonding $\pi$-type orbital (consisting mainly of O $2p_x$ and O $2p_y$ orbitals and a very small amount of Cu $3d_{xy}$) occurs according to these computations in the $\approx -3$ eV range.

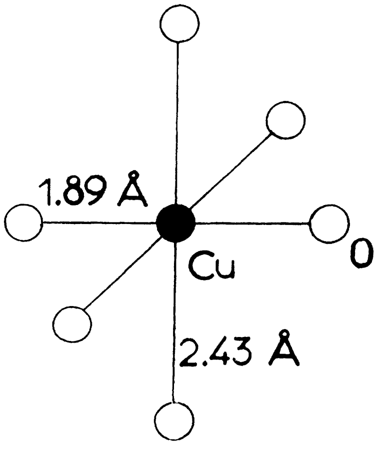

FIG. 2. Geometry used for the $[CuO_6]^{9-}$ cluster.

### C. Electronic properties of an $La_2CuO_4$ cluster

$CuO_6$ is a somewhat unrealistic cluster for 2:1:4, since (i) only oxygen and copper are involved and (ii) the Cu to O ratio is $\frac{1}{6}$ compared to the real ratio $\frac{1}{4}$. So in a next step we have treated the more realistic cluster $La_2CuO_4$ (see Fig. 4). Due to the demonstrated importance of the crystal field, we again performed the calculations with 1505 point charges (representing 215 units corresponding to the chemical formula) which were arranged in nine planes as before. Note that the cluster has been chosen in such a way that its components resemble the real system: Two LaO units are attached to a $CuO_2$ unit according to the real stoichiometry. The aim of this investigation was to gain insight into questions of charge and spin distribution and the nature of the bonding.

Table III (first row) gives the effective charges on the various atoms of $La_2CuO_4$ obtained by Mulliken's population analysis.[39] The charge of the LaO sheets is +0.91 and that of the $CuO_2$ layer is −1.82; the values expected for the purely ionic system using formal oxidation numbers would be +1.0 and −2.0, respectively. Due to the odd number of electrons in the system, one spin remains unpaired. Population analysis gives the information that the spin is strongly localized on the Cu site (Table III, second row). The difference between the numbers of $\alpha$ spins and $\beta$ spins is 0.96 for the Cu site, while the spin

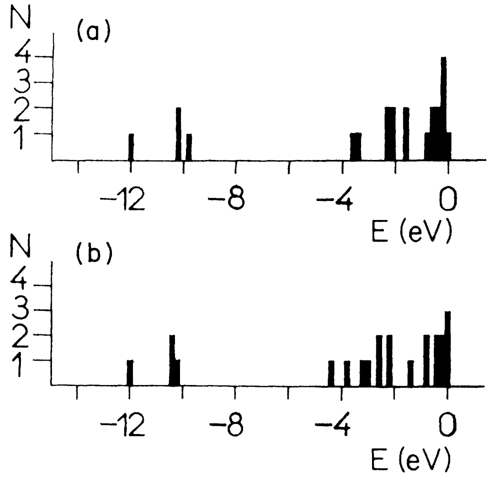

FIG. 3. One-electron energy-level histograms for $[CuO_6]^{9-}$ without any point charges (a) and with 1505 point charges (b). *N* counts the number of states per 0.2 eV.

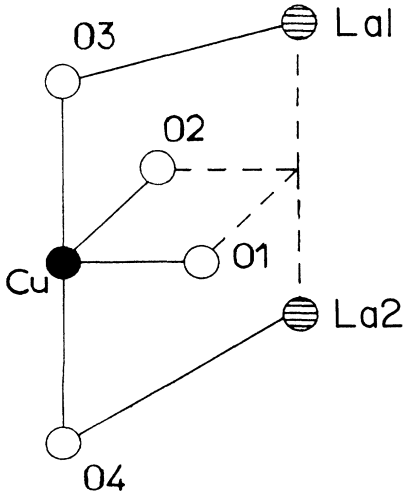

FIG. 4. Geometry and labeling of atoms for the $La_2CuO_4$ cluster.

densities of the other atoms are very small; at least if one neglects (as we did) the exchange potential produced by the crystalline environment. Since we considered only a single chemical unit explicitly, conclusions about collective magnetic phenomena cannot be drawn. (Results of calculations with a double chemical unit using the DODS formalism will be reported shortly in another paper.) The observations above indicate that ionic bonding in $La_2CuO_4$ dominates, at least when the realistic case of a nonvanishing crystal field is considered. On the other hand, high effective charges do not automatically exclude considerable regions of covalent contributions. To quantify this for 2:1:4 we used the concept of valencies and bond indices introduced by Wiberg[40] in the improved *ab initio* form of Mayer.[41] The valency of an atom $A$, $V_A$, gives a measure of its capacity for covalent bonding. It is defined as (see notation in Ref. 39 for Mulliken's population analysis)

$$V_A = 2 \sum_{\mu\in A} \Big( \sum_{\nu} P_{\mu\nu} S_{\nu\mu} - \sum_{\lambda \notin A} (\underline{\underline{P}}\,\underline{\underline{S}})_{\mu\lambda} (\underline{\underline{P}}\,\underline{\underline{S}})_{\lambda\mu} \Big) . \tag{1}$$

The bond index (or bond degree) $B_{AB}$ between two atoms $A$ and $B$ counts the covalent bonds between pairs of atoms:

$$B_{AB} = 2 \sum_{\mu\in A} \sum_{\lambda\in B} (\underline{\underline{P}}\,\underline{\underline{S}})_{\mu\lambda} (\underline{\underline{P}}\,\underline{\underline{S}})_{\lambda\mu} . \tag{2}$$

Using these definitions, the valency of La in $La_2CuO_4$ is $\approx 0.5$ and the bond indices between La1 and O3 (or La2 and O4, see Fig. 4) are $\approx 0.2$, indicating weak covalency. There is also some degree of covalent bonding between La and the oxygen atoms in the $CuO_2$ plane (O1 or O2): The bond index is 0.1, a value very nearly equal to that found for Cu and O1 (O2). So the Cu—O bonds are nearly fully ionic. It will turn out in the next section that doping enhances the covalency character of the in-plane copper-oxygen bonds. Though population and bonding analyses always entail some uncertainties, we conclude this section with the following statements about undoped $La_2CuO_4$: (i) The system behaves as strongly ionic; (ii) the small amount of covalency does not bind the atoms in the $CuO_2$ plane to each other more strongly than it couples the LaO plane with the $CuO_2$ layer. The ionicity of the $CuO_2$ layer is not smaller than that of other regions in $La_2CuO_4$. The latter statement somewhat contradicts the picture given in Sec. II, that the $CuO_2$ planes are "islands of covalency" in otherwise ionic 2:1:4.

### D. Doping with alkaline-earth atoms

This final section deals with effects due to the replacement of one La atom (La1 in Fig. 4) by one of the alkaline-earth elements Ba, Sr, Ca, or Mg. In particular, we were interested in hole creation, distribution and symmetry, in the charge distribution (especially in the charge of the alkaline-earth elements) and in possible trends as the alkaline-earth ion is changed.

First we performed calculations with the same point-charge distribution as in Sec. IV C for $La_2CuO_4$. Table IV gives the Mulliken effective charges of the alkaline-earth "doped" systems. Immediately one recognizes that the alkaline-earth atoms are fully ionized: Their charge is practically $+2$. Combining this information with the result of the preceding section about the charge on La ($\approx +2.8$) tells us that $\approx 0.8$ holes are formed (the terminology "hole" means hole with respect to the undoped system) when one La is replaced by one alkaline-earth atom. Sheetwise population analysis furthermore indicates that the holes are created nearly exclusively in the $CuO_2$ plane [the effective charge of the $CuO_2$ layer changes from $-1.82$ (Table III) to $-1.00$ (Table IV)]. Some charge is removed from the Cu sites ($\approx 0.2$); the major fraction, however, leaves the oxygen positions ($\approx 0.6$). The hole symmetry cannot be directly taken from our cluster results, but some information again may arise from the inspection of the symmetry properties of the LUMO. As in the case of $CuO_6$ one finds that it is the $\sigma^*$ orbital, again favoring the hypothesis of $p\sigma$-like holes. The $\pi^*$ orbital, as before, is found $\approx 3$ eV below

TABLE III. Effective charges (first row) and spin densities (second row) on the atoms of $La_2CuO_4$ in a crystal field accordingly to Mulliken's population analysis. The labeling of atoms is the same as in Fig. 4. The last two columns give effective charges (first row) and spin densities (second row) of the $CuO_2$ and LaO planes, respectively.

| $Q_{Cu}$ | $Q_{La}$ $(=Q_{La2})$ | $Q_{O1}$ $(=Q_{O2})$ | $Q_{O3}$ $(=Q_{O4})$ | $Q_{CuO_2}$ | $Q_{LaO}$ |
|---|---|---|---|---|---|
| +1.79 | +2.77 | −1.81 | −1.86 | −1.82 | +0.91 |
| +0.96 | 0.00 | +0.02 | 0.00 | +1.00 | 0.00 |

TABLE IV. Mulliken effective charges of La$E$CuO$_4$ ($E$=Ba, Sr, Ca, and Mg). Labeling of atoms as in Fig. 4 ($E$ replaces La1).

| System | $Q_{\mathrm{Cu}}$ | $Q_{\mathrm{La2}}$ | $Q_E$ | $Q_{\mathrm{O1}}$ ($=Q_{\mathrm{O2}}$) | $Q_{\mathrm{O3}}$ | $Q_{\mathrm{O4}}$ | $Q_{\mathrm{CuO_2}}$ | $Q_{\mathrm{LaO}}$ |
|---|---|---|---|---|---|---|---|---|
| LaBaCuO$_4$ | +2.01 | +2.83 | +1.97 | −1.50 | −1.92 | −1.88 | −1.00 | +0.95 |
| LaSrCuO$_4$ | +2.02 | +2.83 | +1.97 | −1.51 | −1.92 | −1.88 | −1.00 | +0.95 |
| LaCaCuO$_4$ | +2.02 | +2.84 | +1.97 | −1.51 | −1.92 | −1.88 | −1.00 | +0.95 |
| LaMgCuO$_4$ | +2.02 | +2.83 | +1.94 | −1.51 | −1.91 | −1.88 | −0.99 | +0.95 |

the highest occupied molecular orbital, and again $\pi^*$ is more oxygenlike than $\sigma^*$.

Study of the computed bond indices reveals an interesting feature: The bond degree between Cu and the nearest (in-plane) oxygen atoms is enlarged from $\approx 0.1$ to $\approx 0.5$, while the bonding between La and its neighbors is almost unaffected (there is a small increase in ionicity). So we conclude that, for these calculations at least, "doping" tends to make the CuO$_2$ layer more covalent (metallic). This can be understood if indeed the states near the Fermi level are (i) built up from Cu 3$d$ and O 2$p$ orbitals in the CuO$_2$ plane and (ii) are antibonding in character. Oxidizing the system then means removing an electron from an antibonding orbital. Hence the antibonding character in the CuO$_2$ plane will be reduced, which is synonymous with the statement that covalency will increase. The lower lying Cu 3$d$ and O 2$p$ orbitals remain occupied and so they will not strongly affect the character of bonding.

We have already seen that the alkaline-earth atoms are fully ionized according to our results. This seems to rule out models based on not completely ionized, highly polarizable alkaline-earth elements—at least at the present level of approximation and for the 2:1:4 system. On the other hand, up to now we have considered only "rigid" lattices, i.e., lattices not allowed to relax despite substitution of ions of quite different sizes. To include relaxation effects, at least in an approximate way, we performed a series of calculations in which the alkaline-earth ions were allowed to displace along the $c$ axis of the crystal (perpendicular to the layers) by $\approx \pm 1.5$ Å; Ba, Sr, and Ca were considered. In this way, we found that the oxidation number of the alkaline-earth atoms is not influenced by these displacements.

Due to possibly large differences in the polarizabilities of incompleted ionized alkaline-earth ions, theoretical concepts based on these polarizabilities might have given a natural explanation for the fact that $T_c$ strongly depends on the kind of atom substituted for La.[9] Since our calculations indicate that the residual valence-electron charges on the alkaline-earth atoms are extremely small, and hence the polarizabilities too, we need to seek an alternative property to explain the observed behavior.

One could think of differences in the DOS. Figures 5(a) and 5(b) show the DOS curves for LaBaCuO$_4$ and LaSrCuO$_4$. They are nearly identical: A more accurate examination shows that the maximal difference in the energy of the one-particle states considered here is 0.04 eV; in many cases the difference is still smaller and therefore negligible. The DOS patterns of the other alkaline-earth elements (Ca and Mg), not given here, show also no significant differences.

However, substituting one La atom with one alkaline-earth atom again seems to be unrealistic. Superconductivity in La$_{2-x}$E$_x$CuO$_4$ ($E$ stands for an alkaline-earth atom) only occurs for not too large $x$, the optimal value (with respect to $T_c$) being $x \approx 0.15$ [for $E$=Sr (Ref. 4)]. It is impractical for us at the present time to compute clusters large enough to describe an appropriate supercell. On the other hand, at least the crystal field (modeled by point charges) can be rearranged such that nonstoichiometry is included. So we replaced 32 +3 point charges (representing La$^{3+}$) by +2 point charges (representing $E^{2+}$) randomly; this fraction corresponds fairly well to a "doping value" of $x=0.15$. As we saw, doping leads mainly to the oxidation of CuO$_2$ plane oxygens. To account for this and to ensure charge neutrality, 64 point charges representing O ions in the three CuO$_2$ layers considered (see Fig. 1) were randomly "oxidized" from −2.0 to −1.5. Repeating the calculations on the Ba and the Sr doped systems with this "realistic charge distribution" we obtained the DOS histograms shown in Figs. 6(a) and 6(b), respectively. In contrast to the small differences found with the "stoichiometric point-charge distribution" remarkable deviations between Ba and Sr are realized now. Especially in the low-energy interval (−8 to −12 eV) shifts of the order of electron volts are found in the DOS histrogram. The significance of this feature is not clear due to the simplicity of the model used, but it again suggests the importance of crystal-field effects.

Interestingly enough, population analysis yields the information that the alkaline-earth atoms stay fully ionized, and that in general the sheet effective charges remain almost uneffected. There is, however, some redistribution

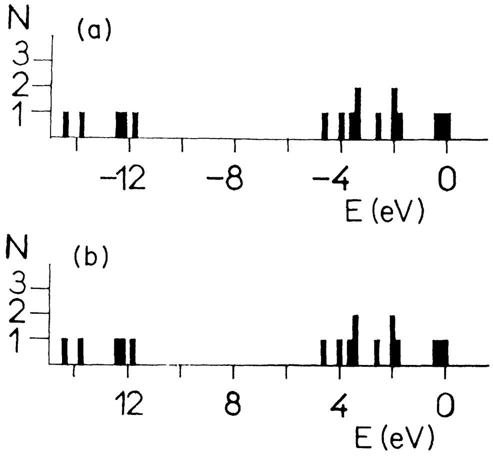

FIG. 5. One-electron energy-level histogram for LaBaCuO$_4$ (a) and LaSrCuO$_4$ (b).

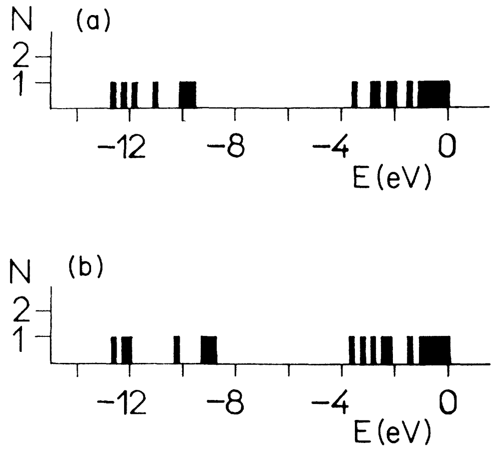

FIG. 6. The same as Fig. 5 in the case of a modified point-charge distribution modeling the real, nonstoichiometric crystal

of charge within the $CuO_2$ plane: Cu becomes more negative ($\approx +1.7$ instead $\approx +2.0$), while oxygen becomes more positive. This suggests that the oxygen character of holes becomes more important. One should be aware, however, again of the simplicity of our nonstoichiometric model and therefore the above-mentioned DOS difference between Ba and Sr must be proven in detail.

## V. CONCLUSIONS

In conclusion, these studies on nonoxidized and oxidized $La_2CuO_4$ have shown that the crystal field produced by surrounding ions is of central importance. We found $La_2CuO_4$ in the presence of the field to be highly ionic. Oxidation, which influences nearly exclusively the $CuO_2$ planes, strengthens covalency in these planes and produces holes of $\sigma^*$ symmetry, while the $\pi^*$ orbital remains occupied. Alkaline-earth atoms appear to be fully ionized. In general, the calculated effective charges are in reasonable agreement with the formal values expected for fully ionic $La_2CuO_4$. There is a charge transfer from the LaO planes to the central $CuO_2$ layer of $\approx 1.8$ electrons.

Our studies have been performed in the HF approximation. Though many of our results are encouraging, the importance of correlation effects for transition-metal compounds in general and hence the copper-based superconductors in particular must be stressed. As a consequence, inclusion of correlation corrections is in progress in our Institute. Furthermore, the important crystal-field effects were only considered in an approximate way. In this connection the main points one might criticize are as follows: (i) We used $\approx 1500$ point charges, but convergence is still not achieved; (ii) the values for these charges must be preassigned. To overcome both problems we are going to use the full (converged) Madelung potential (the lattice sums calculated by Ewald's technique) in a self-consistent form. With these methodological improvements we plan to extend our research to the 1:2:3 superconductor, to the Tl- and Bi-based species, and to the new electron-type superconductors.

After performing cluster calculations on all these systems including the appropriate DODS versions to describe their magnetic properties, we will calculate the band structure of the $CuO_2$ plane of the ceramics. In these computations (which are in progress) we take into account (i) the charge transferred from other planes to the $CuO_2$ plane and (ii) the correct Madelung potential of the system (preliminary *ab initio* HF calculations without taking into account these two effects have already been reported,[42] both in the restricted and unrestricted (DODS) case. After that we intend to correct the valence and conduction bands of the system for correlation[43,44] and calculate also correlated many-electron wave functions for them. In our opinion only after such "hard" calculations will it be possible to test the different theoretical models proposed for high-$T_c$ superconductivity, especially the "two-bands" model (one or several narrow and highly polarizable valence bands and a broad, partially filled conduction band) advocated by one of us a long time ago.[45]

## ACKNOWLEDGMENTS

We are very grateful to Professor H. Preuss and Professor H. Stoll for providing us with their core potentials and basis sets and explaining their use. One of us (P.S.) would like to express his gratitude for financial support from the Studienstiftung des Deutschen Volkes, which made it possible for him to perform this work. R.F.W. would like to express his special thanks to the Alexander von Humboldt Foundation for financial support, which made his stay in Erlangen possible. We should like to thank very much the Deutsche Forschungsgemeinschaft (Project No. La 371/24-1) for its financial support.

---

[*] Permanent address: Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] See, for instance, in *Theories of High Temperature Superconductivity*, edited by J. Woods Halley (Addison-Wesley, Redwood City, CA, 1988).

[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[4] A review of some experimental and many theoretical investigations on the electronic structure of high-$T_c$ superconductors is given by W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[5] E. Orti, Ph. Lambin, J.-L. Brédas, J.-P. Vigneron, E. G. Derouane, A. A. Lucas, and J.-M. André, Solid State Commun. **64**, 313 (1987); P. De La Mora and C. De Teresa, *ibid.* **70**, 745 (1989).

[6] H. Eschrig and G. Seifert, Solid State Commun. **64**, 521 (1987); K. Yamaguchi, Y. Takahara, T. Fueno, and K. Nasu, Jpn. J. Appl. Phys. **26**, L1362 (1987); **26**, L2037 (1987).

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

[8] A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, Phys. Rev. B **35**, 8814 (1987).

[9] M. Ronay and D.-M. Newns, Phys. Rev. B **39**, 819 (1989).

[10] P. W. Anderson, Science **235**, 1196 (1987); V. Emery, Phys. Rev. Lett. **58**, 2794 (1987); J. E. Hirsch, Phys. Rev. B **35**, 8726 (1987); R. F. Wood, M. Mostoller, and J. F. Cooke, Physica C **165**, 97 (1990); H. Kamimura, S. Matsumo, and R. Saito, Solid State Commun. **67**, 363 (1988); G. Chen and W. A. Goddard III, Science **239**, 899 (1987).

[11] See, for instance, M. S. Hegde and P. Ganguly, Phys. Rev. B **38**, 4557 (1988).

[12] B. Langeler, M. Wilhelm, B. Bobst, W. Schwaen, B. Seebacher, and U. Hillebrecht, Solid State Commun. **65**, 1545 (1989); N. T. Liang, K. J. Lie, Y. C. Chou, M. F. Tai, and T. T. Chen, *ibid.* **64**, 761 (1987).

[13] B. Viswanathan, R. Raman, N. S. Raman, and V. R. K. Murthy, Solid State Commun. **64**, 409 (1987).

[14] D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Phys. Rev. Lett. **58**, 2802 (1987).

[15] H. Chen, J. Callaway, and P. K. Misra, Phys. Rev. B **36**, 8863 (1987).

[16] H. Krakauer, W. E. Pickett, and R. E. Chohen, J. Supercond. **1**, 111 (1988).

[17] S. Saul, A. M. Llois, A. Levy Yeyati, and M. Weissmann, Solid State Commun. **66**, 491 (1988).

[18] M. Weinert and G. W. Fernando, Phys. Rev. B **39**, 835 (1989).

[19] See, for example, N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. McKonnon, Phys. Rev. B **35**, 8807 (1987).

[20] Y. Tokura, H. Takagi, and S. Uchida, Nature **337**, 345 (1989); H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).

[21] See, for example, M. Avignon and K. H. Bennemann, Solid State Commun. **69**, 999 (1989).

[22] J. E. Hirsch and S. Tang, Solid State Commun. **69**, 987 (1989).

[23] J. Fink, N. Nücker, H. Romberg, and J. C. Puggle, IBM J. Res. Dev. (to be published).

[24] F. J. Himpsel, G. V. Chandrasekhar, A. B. McLean, and W. Shafer, Phys. Rev. B **38**, 11 946 (1988).

[25] M. Eto, R. Saito, and H. Kamimura, Solid State Commun. **71**, 425 (1989).

[26] R. L. Martin and P. W. Saxe, Int. J. Quantum Chem. Symp. **22**, 237 (1988).

[27] See, for example, H. F. Schaefer III, J. Mol. Struct. **76**, 117 (1981).

[28] See, for example, P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985).

[29] L. F. Feiner and D. M. De Leeuw, Solid State Commun. **70**, 1165 (1989).

[30] T. Kovár, M.S. thesis, Chair for Organic Chemistry, University Erlangen-Nürnberg, 1986.

[31] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

[32] M. Dolg, H. Stoll, A. Savin, and H. Preuss, Theor. Chim. Acta **75**, 173 (1989).

[33] P. Saalfrank, M.S. thesis, University Erlangen-Nürnberg, 1988.

[34] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985).

[35] S. Huzinaga, in *Physical Science Data 16, Gaussian Basis Sets for Molecular Calculations,* edited by S. Huzinaga (Elsevier, New York, 1985), p. 192.

[36] A contraction scheme tells how a set of Gaussian functions ("primitives") is contracted by a linear combination with fixed coefficients to a smaller set of (usual) Slater-type orbitals ("contraction"). The above contraction scheme for Cu means that 14 *s*-type Gaussians are contracted to eight *s* functions, eight sets of *p*-type Gaussians are contracted to four sets of *p* orbitals, and finally five *d*-type Gaussian sets form two *d* orbitals.

[37] T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry,* edited by H. F. Schaeffer III (Plenum, New York, 1977), p. 1.

[38] R. Gomperts and E. Clementi, Documentation and user's guide Quantum Chemistry Program Exchange KGNMOL.

[39] In Mulliken's population analysis the effective charge of an atom $A$, $q_A$, is given by

$$q_A = Z_A - \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} S_{\nu\mu} ,$$

where $P$ and $S$ are the charge-density-bond-order and overlap matrices, respectively (Greek letters are atomic orbital indices), and $Z_A$ is the atomic number of atom $A$. The main disadvantage of Mulliken's analysis is that the so-called overlap population (sum of terms in which $\mu$ and $\nu$ belong to two different atoms) is equally distributed between pairs of atoms. In the case of ionic compounds (as $La_2CuO_4$) these overlap populations are quite small, however, and hence so are the errors introduced by this charge partitioning scheme.

[40] K. A. Wiberg, Tetrahedron **24**, 1083 (1968).

[41] I. Mayer, Chem. Phys. Lett. **97**, 270 (1983).

[42] J. J. Ladik, P. Saalfrank, and R. F. Wood, Int. J. Quant. Chem. **23**, 621 (1989).

[43] S. Suhai, Phys. Rev. B **27**, 3506 (1983); M. Vracko, C.-M. Liegener, and J. Ladik, Chem. Phys. Lett. (to be published); C.-M. Liegener and J. Ladik, Chem. Phys. **106**, 1339 (1986).

[44] J. Ladik and C.-M. Liegener, J. Mol. Struct. **200**, 245 (1989).

[45] J. Ladik, G. Biczó, and A. Zawadowski, Phys. Lett. **18**, 257 (1965); J. Ladik, G. Biczó, and J. Redly, Phys. Rev. **188**, 710 (1969); T. C. Collins, M. Seel, J. Ladik, M. Chandrasekhar, and H. P. Chandrasekhar, Phys. Rev. B **27**, 140 (1983); J. J. Ladik and T. C. Collins, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 181; T. C. Collins, A. B. Kunz, and J. J. Ladik, *ibid.*, p. 378.