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Electronic structure of $Bi_4Sr_4Ca_{2-x}Y_xCu_4O_{16}$ ($x=0$ and 1)

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Electronic-structure calculations of $Bi_4Sr_4Ca_{2-x}Y_xCu_4O_{16}$ for the superconducting phase ($x=0$) and the nonsuperconducting phase ($x=1$) with use of the linearized muffin-tin orbital method with the atomic-sphere approximation are reported. No dramatic difference in their electronic structures is found except that the number of holes per CuO_2 unit (an important parameter in theories for high-T_c superconductivity) is about $0.27(-e)$ smaller in the nonsuperconducting phase. The application of directional stress along the c direction for constant unit-cell volume does not cause the number of holes in the Cu-O planes to change but the density of states at the Fermi energy does. Since T_c is strongly related to the value of the density of states at the Fermi energy in conventional superconductors, this implies that the corresponding experiment would be helpful for understanding the mechanism responsible for superconductivity.

I. INTRODUCTION

Since the number of known high-T_c superconductors continues to grow, it is a challenge to find out which characteristics are important for the superconductivity mechanism in these very complex materials. To aid in this task, we report calculations for two members of the class of bismuth copper oxides $Bi_4Sr_4Ca_{2-x}Y_xCu_4O_{16}$, namely, the $x=0$ superconductor and the yttrium-substituted nonsuperconductor ($x=1$). The idealized crystal structure of $Bi_2Sr_2CaCu_2O_8$ is shown in Fig. 1. The full unit cell consists of two primitive unit cells, one on top of the other and shifted by $(\frac{1}{2}, \frac{1}{2}, 0)$ with respect to each other. This shift creates a twofold screw axis in the c direction. The idealized crystal structure of the bismuth and thallium (2:2:1:2) superconductors, $Bi_2Sr_2CaCu_2O_8$ ($a=3.83$ Å, $c=30.89$ Å) and $Tl_2Ba_2CaCu_2O_8$ ($a=3.855$ Å, $c=29.33$ Å) (Ref. 1) have the same symmetry: body-centered tetragonal, space group $I4/mmm$. Both have the same coordination number of nearest neighbors for corresponding atoms except that the Bi planes are more separated in the bismuth compound than are the corresponding Tl planes in the other compound. This leads probably to the observed modulations in the real crystal structure of the former. As a result, the local positions of the atoms are slightly different[2] than their average values assumed in the idealized structure. The c/a ratio for the thallium compound is smaller (7.608) than that for the bismuth compound (8.063). In the present work, we consider the consequences of the modification of the structure of the bismuth compound by varying the c/a ratio or by replacing Ca atoms by Y atoms (to form the $x=1$ member of the class).

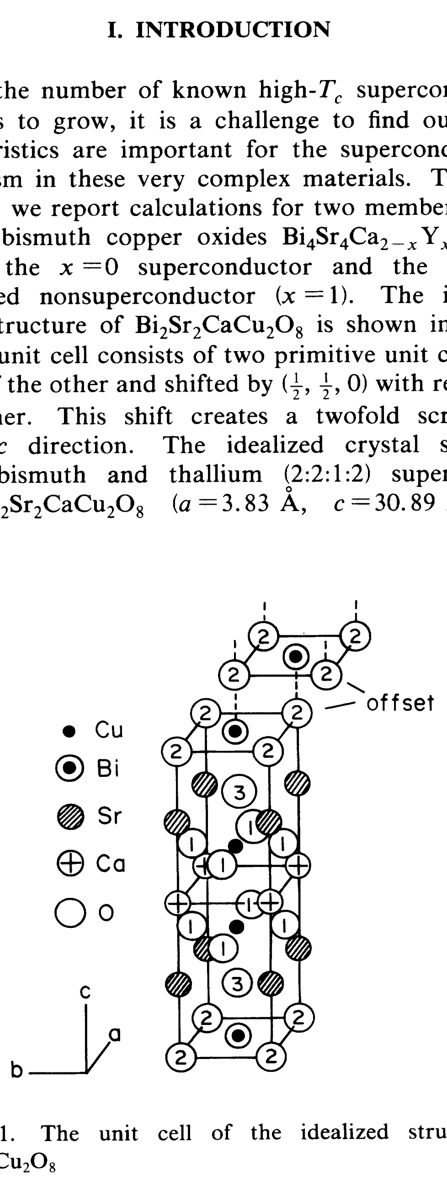

FIG. 1. The unit cell of the idealized structure for $Bi_2Sr_2CaCu_2O_8$

Band-structure information by means of angle-resolved photoemission[3] as well as several band-structure calculations[4–7] are now available for $Bi_2Sr_2CaCu_2O_8$. All of these calculations were performed for the idealized structure (Fig. 1). The main feature (which is characteristic for all the known high-temperature superconductors) are copper-oxygen bonding bands, which are the lowest in energy, and the antibonding copper-oxygen band crossing the Fermi energy. The new feature in the band structure is additional bands of p electrons of bismuth in the region of the antibonding copper-oxygen band. There is general agreement among various band-structure calculations;[4–7] however, closer inspection shows that there are differences at the X point (1,1,0). In some of the calculations[4,5] no band crosses the Fermi energy there, and in others[6,7] there is a band-touching or -crossing at the X point. The experimental results[3(a),3(b)] show a flat band very close to the Fermi energy at that point.

In all the theoretical data[4–7] the antibonding $dp\sigma$ band crosses the Fermi energy between the X and Γ points, where the experimentally observed[3(a),3(b)] band crosses it. The calculated electron pocket of bismuth and oxygen p electrons [D point (1,0,0)] is not present in the experimental results. It is possible that if calculations were performed for a crystal structure (for "first-principles" methods this would require an enormous amount of memory and computer time), which takes into account the observed modulation in the Bi-O layers,[2] the Bi-O electron pocket (at D) would be shifted to higher energies above the Fermi energy and the agreement with experiment would be improved.

It was very encouraging when the first angle-resolved photoemission experiment[3(a)] demonstrated that the high-T_c superconducting materials are marginal Fermi liquids because one band crossed the Fermi surface. However, the experimental results for the (2:2:1:2) bismuth compound[3(a),3(b)] show a much lower dispersion of the bands then predicted computationally and observed experimentally in $YBa_2Cu_3O_7$.[3(c)] The lower dispersion of the bands means that the third band below the Fermi energy is separated from the upper two bands by a gap (1 eV) that would be rather more in agreement with our previous calculations for doped isolated planes[8] than for these full structure calculations. Before we conclude that for full understanding of these superconductors the corrections to the local spin density (LSD) method (which would lead to higher localization of electrons in the Cu-O planes) are necessary, we would like to consider other possibilities such as the influence of structural effects.

In this paper we present results of our theoretical calculations within the linearized muffin-tin-orbital method with the atomic-sphere approximation[9] (LMTO-ASA), for this compound for both pressed and nonpressed structures and doped (superconducting) and undoped (nonsuperconducting) phases. Since the present understanding of high-temperature superconductivity requires doped copper-oxygen planes for superconductivity, the substitution of yttrium (valence equal to three) for calcium (valence equal to two) is particularly interesting as it has been shown experimentally to suppress superconductivity for substitutions larger than 50%.[10]

II. LMTO-ASA ELECTRONIC STRUCTURE CALCULATIONS

Before we present our results, it is fair to say that the LMTO-ASA method is less accurate than the highly precise full-potential linearized augmented-plane-wave method (FLAPW).[11] However, it is quite encouraging to see how well it mimics the FLAPW results. The LMTO-ASA method has the advantage that it is computationally very efficient, and thus it can be used economically for larger unit cells and larger number of **k** points. In the present calculations we used 56 **k** vectors per irreducible wedge of the Brillouin zone. Self-consistency has been obtained, with frozen core and semicore electrons, for valence electrons with wave functions expanded up to $l=2$ (d electrons). The assumed atomic sphere radii for different sites are shown in Table I.

To make comparison easier between $Bi_4Sr_4Ca_{2-x}Y_xCu_4O_{16}$ for $x=1$ and 0 we performed calculations for the full unit cell presented in Fig. 1. In Fig. 2 we present the band structure of $Bi_2Sr_2CaCu_2O_8$ for the normal structure ($c/a=8.065$) (Ref. 1) and a structure squeezed along the c direction ($c/a=7.065$). Our results for nondeformed $Bi_2Sr_2CaCu_2O_8$ are in essential agreement with the calculations of Hybertsen and Mattheiss[4] who used the same LMTO-ASA method.[9] Some delicate differences are due to the fact that in the present calculations we consider the full unit cell with the twofold screw axis, which doubles the size of the primitive unit cell in the z direction.[1] As a result of the unit cell doubling, these bands are folded back in the center of the Brillouin zone (Γ point). At the surface of the Brillouin zone the bands stick together as has been discussed in the general case for a screw axis,[12] and our results are the same as for the primitive unit cell.[4]

TABLE I. The variation of the electron occupation number (Δn) and the density of states at the Fermi energy ($\Delta\rho$) with c/a. S is the atomic-sphere radius.

Atom	S (a.u.)	Δn	$\Delta\rho$ (states/Ry atom)
Cu	2.550	−0.02	1.59
O(1)	2.450	0.00	0.52
Bi	3.562	0.01	1.03
O(2)	2.450	0.00	0.48
Sr	3.609	0.04	0.16
O(3)	2.450	−0.02	0.84

When we apply stress along the c direction, while keeping the volume ca^2 constant (with the same atomic sphere radii), c and c/a decrease, while $a=b$ increases. Examination of Fig. 2 indicates that there is some narrowing of

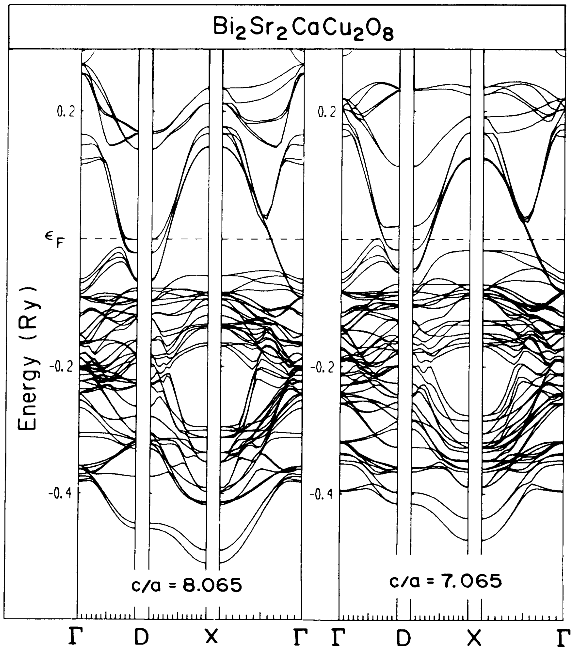

FIG. 2. Band structure for $Bi_2Sr_2CaCu_2\ O_8$ along significant symmetry directions [$\Gamma=(0,0,0)$, $D=(1,0,0)$, and $X=(1,1,0)$ in units of π/a)] for $c/a=8.065$ (left-hand side) and $c/a=7.065$ (right-hand side).

the bonding and antibonding Cu-O(1) bands due to the increased distance between Cu and O(1) atoms in the Cu-O(1) planes ($a=b$ increases in the deformation). In particular, the lowest occupied band, shown in Fig. 2, which is mainly copper-oxygen bonding, is very sensitive to the c/a value. This band is shifted to lower energy at the Γ point and to higher energy at the X point. There is much better agreement with experiment for the squeezed structure, and the flattening of the bands in the $\Gamma-D$ direction is particularly interesting. The band structure around the Fermi energy for $Bi_2Sr_2CaCu_2O_8$ with the smaller c/a ratio is in much better agreement with the experimental observations[3(a),3(b)] as the flat band at the X point and Bi-O electron pocket at the D point are pushed up to higher energies. For both c/a ratios the antibonding copper-oxygen band crosses the Fermi surface at about the middle of $\Gamma-X$ in agreement with experiment. It is interesting that the relative position of the bands on the energy scale agrees with experiment except for the antibonding BiO band, which is moved to higher energies by more then 1 eV.[3(b)] The position of this band at the Fermi energy is sensitive to structural deformation and modulation effects,[2] which might be crucial in describing this band properly. While the band structure for the smaller c/a ratio agrees better with experiment, the total energy is lower for the unsqueezed structure (experimental) by 0.04 Ry/unit cell.

It is worth noting that the shape of the bands is related to the c/a ratio and not to the volume of the unit cell, due to factorization of the LMTO-ASA Hamiltonian into a structure part (volume independent) and an energy part.[9] Because of the lack of information about changes of the local structure due to directional stress, we have assumed in the calculation that the relative positions of the atoms stay the same in both the deformed and undeformed structures.

In Fig. 3 we show the total and projected density of states (DOS) for both c/a ratios. Due to the two-dimensional character of these cuprates, it is of interest to examine the contribution of states in the a-b plane (shaded in the figure), which for a spherical potential are predominantly states corresponding to the maximum azimuthal orbital quantum number m_z ($m_z=2$ for d electrons and $m_z=1$ for p electrons). The unshaded part of the DOS are the out of plane states. The narrowing of the bandwidth of the planar contribution to the density of states is due to lowering of the overlap in the plane with increasing a ($=b$). Since the electron structure is highly two dimensional, the effective interaction between electrons is decreasing despite the decrease in the distance between atoms in the c direction, and therefore the total bandwidth is smaller in the squeezed structure. In this case, the highest occupied bands are closer to the Fermi energy and the density of states at the Fermi energy increases from 38.1 to 48.4 states/(Ry* primitive unit cell) as can be seen in Fig. 3. The increase in the density of states at the Fermi energy comes mainly from the in-plane states (shaded), while the contribution of the out-of-plane states unshaded is almost unchanged.

The most interesting result is that the number of electrons per Cu-O(1) plane or Bi-O(2) plane is independent of the c/a ratio (Table I). This implies that the number of holes in the Cu-O(1) planes does not change with the c/a ratio, provided that the structure is uniformly deformed in the c direction. However, we cannot rule out the possibility that if the relative distances between planes would be changed, the charge equilibrium would be broken and some charge transfer between planes would be possible, which might change the number of holes per [Cu-O(1)] plane unit.

It would be interesting to examine experimentally whether or not T_c is dependent on the c/a ratio. For the conventional mechanism for superconductivity (BCS theory), one would expect (changes) of T_c with varying c/a, since T_c is dependent on the DOS at the Fermi energy. As indicated in Table I, the DOS at the Fermi energy does vary strongly with the c/a ratio. For those theories that relate T_c to the number of holes in Cu-O(1) planes, the present results would imply that T_c should not change with c/a.

In Fig. 3, we present the partial DOS for Cu d, Bi p, Sr

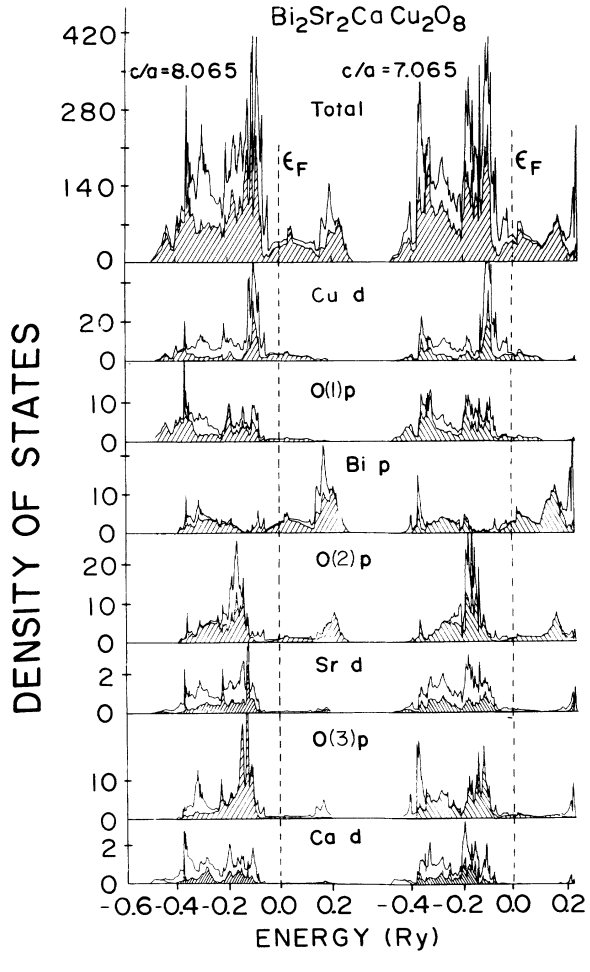

FIG. 3. Total and projected [Cu d, O(1) p, Bi p, O(2) p, Sr d, O(3) p, and Ca d] density of states (states/Ry atom) of electrons in $Bi_2Sr_2CaCu_2O_8$ for c/a equal to 8.065 (left-hand side) and 7.065 (right-hand side). The shaded areas correspond to states projected onto the a-b plane.

d, Ca *d* sites, and the various oxygen *p* sites. It should be noticed that the shape of each oxygen DOS is in concert with the shape of the DOS of the sharing atoms in the *a*-*b* plane. The positions of the maxima and minima in the partial DOS's coincide. The predominantly in-plane states at the Fermi energy are a demonstration of two-dimensionality and strong hybridization of the electrons of atoms in the same *a*-*b* plane. At the Fermi energy, the main contribution comes from strongly hybridized planar Cu *d*−O(1)*p* and Bi*p*−O(2)*p* states. Above the Fermi energy, the main contribution comes from Bi and O(2) *p* electrons.

It can be seen that the Sr *d* and Ca *d* contributions to the total density of states at the Fermi energy is negligible. The small component from out-of-plane states of the Sr-O(3) planar atoms possibly implies a very weak direct interaction between the Bi-O(2) plane and Cu-O(1) plane through these atoms.

The total energy for the squeezed structure is higher, and the Fermi energy is shifted up by 0.01 Ry. In general, both the experimental and squeezed partial DOS's look similar. There are, however, some differences, for example the density of states of Bi *p* electrons 0.1 Ry above the Fermi energy is strongly modified in the squeezed structure. There are also some new peaks with mainly out-of-plane character in the squeezed density of states; for example one at −0.4 Ry is particularly visible in the O(3) *p* electron DOS.

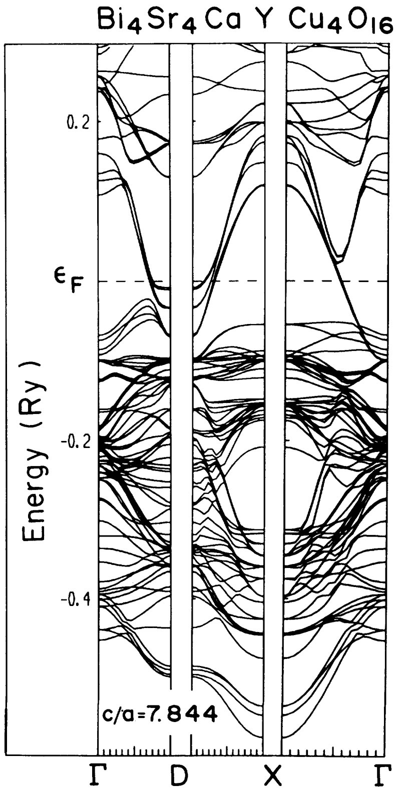

FIG. 4. Band structure for $Bi_4Sr_4CaYCu_4O_{16}$ ($c/a=7.844$) along significant symmetry directions [$\Gamma=(0,0,0)$, $D=(1,0,0)$, and $X=(1,1,0)$ in units of π/a].

The contribution of O(3) p_z electrons at the Fermi energy is negligible in comparison with that of oxygen atoms in the barium plane for $YBa_2Cu_3O_7$.[13] This is in agreement with recent electron-energy-loss spectroscopy (EELS) experiments[14] where holes with $2p_z$ symmetry have been observed on oxygen in the (1:2:3) compound but not in the (2:2:1:2) bismuth compound.

Since the (2:2:1:2) bismuth compound is a hole superconductor, it is important to examine the hole concentration and its influence on the superconductivity. One way

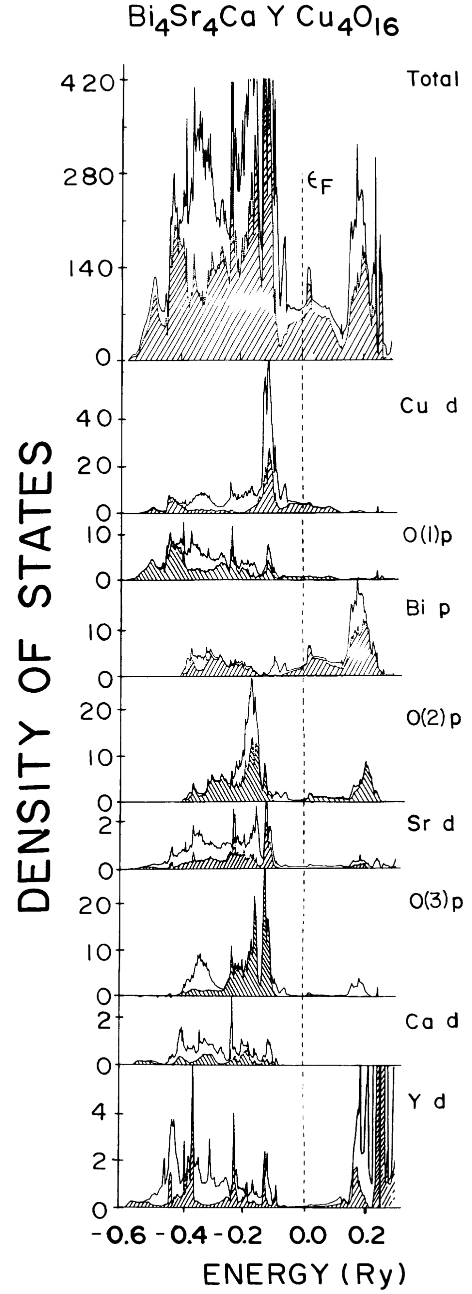

FIG. 5. Total and projected [Cu *d*, O(1) *p*, Bi *p*, O(2) *p*, Sr *d*, O(3) *p*, Ca *d*, and Y *d*] density of states (states/Ry atom) of electrons in Bi_4Sr_4 $CaYCu_4O_{16}$. The shaded area represents states projected onto the plane.

of doing this is by looking at the correlation between substitution by atoms with different valences and superconductivity. We considered the substitution of calcium by yttrium, since $Bi_4Sr_4Ca_{2-x}Y_xCu_4O_{16}$ with $x=1$ becomes nonsuperconducting and semiconducting.[10] It also exhibits antiferromagnetic ordering in the Cu-O planes as do other nonsuperconducting phases related to ceramic superconductors such as $YBa_2Cu_3O_6$. Comparison of Fig. 2 with Fig. 4 shows that there is not much change in the band structure (paramagnetic) due to the substitution by yttrium. The changes around the Fermi energy can be described in the rigid-band model by the shift of the Fermi energy to higher values due to the higher valency of yttrium. This causes the Bi-O pocket hole to deepen with substitution while the filling of the antibonding Cu-O band increases.

The total DOS (to of Figs. 3 and 5) does not change much with substitution. Partially due to the change in the c/a ratio with substitution (from 8.065 for $x=0$ to 7.844 for $x=1$), the DOS at the Fermi energy is a bit higher and equals 39.6 states/(Ry* primitive unit cell). Yttrium atoms contribute more electrons to the conduction band than calcium atoms do, and the Fermi energy is shifted higher. The most important effect of substitution is that the number of electrons in the copper-oxygen planes is increased by $0.27e$ with substitution ($x=1$). Evidently about $0.3e$ per CuO_2 plane unit reduces the number of holes by an amount sufficient to destroy superconductivity.

In Fig. 5 the most important electron DOS (p on Bi and oxygen, d on Cu and Sr atoms) DOS are presented. The hybridization effect between the electrons of atoms in the same a-b plane is again visible and the energy position of corresponding peaks coincide. The intensities of the peaks show that the character of electrons varies very much with energy. For example, in the Bi-O plane, for higher energies we observe electrons to be predominantly of bismuth p character, while for lower energies we observe oxygen p character. The overall shape of the Bi(p) and Cu(d) DOS is very similar to that in the pure (2:2:1:2) bismuth compound. The predominant two-dimensional character of electrons around the Fermi energy is seen as discussed above. The d electrons of the Y, Ca, and Sr atoms make only small contributions (notice the different scales) to the density of states about 0.5 Ry below the Fermi energy. Thus they are highly ionic in these compounds. The different feature is a large DOS of yttrium above the Fermi energy, which is quite characteristic when alloying yttrium with transition metals.[15]

The next question is how these results would be modified when magnetic ordering is allowed. We performed *forced* spin-polarized ferromagnetic calculations for $Bi_2Sr_2CaCu_2O_8$ (where we kept the external field in order to stabilize the moment on Cu) (Ref. 13) and noticed that the number of holes per [Cu-O(1)] unit stays the same. Even if the local moment would persist in the superconducting phase, this result implies that to investigate the number of holes in Cu-O planes in this material it is sufficient to consider the paramagnetic case. This is a useful conclusion, since we know that within the LSD approximation it is difficult to stabilize magnetic ordering in these compounds and at best (metamagnetic solution) LSD predicts a stable local moment, which is usually half as large as measured.[16] It is quite surprising that in order to get the same moment on the planar copper atoms in $Bi_2Sr_2CaCu_2O_8$ and $YBa_2Cu_3O_7$, a 50% larger external field has to be used in the former compound than in the latter. This suggests that it would be even more difficult to obtain magnetic ordering in the LSD approximation for the bismuth (2:2:1:2) oxides than the (1:2:3) oxides.[16]

III. SUMMARY

From computer experiments on the electronic structure of these bismuth superconductors, we conclude that the number of holes in the [Cu-O(1)] planes is probably an important parameter in the search for the new high-T_c superconductors and the mechanism responsible for the observed superconductivity. An important result is that for uniform deformation of the structure along the c axis, the number of electrons per unit Cu-O plane does not change. The number of holes per copper-oxygen plane does change, however, when 50% substitution of calcium by yttrium occurs and superconductivity is destroyed. The directional stress applied in the c direction influences tremendously the value of the density of states at the Fermi energy. This effect in conventional superconductivity would lead to a strong dependence of the critical temperature on the c/a ratio. The corresponding experiment would be of value.

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