

## Atomic substitutions in $\text{YBa}_2\text{Cu}_3\text{O}_7$ : Modification of the electronic structure

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We have performed semiempirical tight-binding calculations of the electronic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , with  $d$  and  $s$  orbitals included for all the metal atoms and  $p$  and  $s$  orbitals for the oxygen. Here we report studies of the following atomic substitutions: Al, Fe, Co, Ni, and Zn replacing Cu; Sr and La replacing Ba; Tl, Pb, and Bi replacing Y; and F and N replacing O. In each case, the modification of the local densities of states, the atomic valences, and the Fermi energy was calculated.

### I. INTRODUCTION

Since the discovery of the new high- $T_c$  superconductors,<sup>1,2</sup> there have been many studies of changes in the superconducting properties of these materials induced by replacement of the original atomic species. The studies of the 1:2:3 material  $\text{YBa}_2\text{Cu}_3\text{O}_7$  have provided valuable experimental information and some additional understanding of this material. The replacements of Y by rare-earth atoms showed only a very small effect on  $T_c$ ,<sup>3-8</sup> indicating a remarkable insensitivity of the relevant electronic and structural properties to the species on this site. In particular, the magnetic moment of the substituted atom does not appear to affect the superconducting transition temperature,<sup>7,8</sup> indicating that this site is isolated from the superconducting region of this material.

Replacement of Ba by Sr was found to yield a depression of  $T_c$  which is linear in the Sr concentration, and which was attributed to lattice distortions in the neighborhood of the Sr atom.<sup>9,10</sup> Substitution of La onto the Ba site leads to a more rapid decrease of  $T_c$ , with a sudden loss of superconductivity in  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_7$  for  $x > 0.4$ .<sup>11,12</sup> This effect was attributed to charge compensation for the donated electron of La by a reduction of the copper valence or by an increase in the oxygen content.<sup>12</sup> Further studies of the substitution of the rare earths Nd, Sm, Eu, Gd, and Dy onto both the Y and Ba sites indicate a strong suppression of  $T_c$  in  $\text{R}\text{Ba}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$ , with a loss of superconductivity for  $x > 0.5$ .<sup>13</sup>

Substitutions on the Cu sites lead to a particularly dramatic lowering of  $T_c$ . The substitution of Al onto the Cu(1) chain site in single-crystal  $\text{YBa}_2\text{Cu}_{3-x}\text{Al}_x\text{O}_7$  leads to a rapid decrease in  $T_c$  for  $x > 0.1$ , with a complete loss of superconductivity for  $x > 0.22$ .<sup>14</sup> This supports the critical function of the Cu(1)-O(1) chains for high-temperature superconductivity. For the 3d transition metals, substitution in polycrystalline  $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_7$  for  $x \leq 0.3$  yields a strong depression of the transition temperature.<sup>15-19</sup> Note particularly that nonmagnetic Zn suppresses  $T_c$  more than magnetic Fe or Co. Replacement of Cu by Ag also leads to a decreased transition temperature.<sup>20,21</sup>

Replacement of oxygen with sulfur in  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$  appears to enhance the Meissner effect, while leaving  $T_c$  unaffected at 90 K.<sup>22</sup> The substitutions of fluorine<sup>23</sup> and

nitrogen<sup>24</sup> into the 1:2:3 material, presumably onto the oxygen sites, have produced conflicting and irreproducible results. Lack of single-crystal measurements to confirm the location of these substituted atoms allows much speculation on the possible electronic or structural effects.

We have examined a series of substitutions in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  to determine the modification of the local densities of states, the atomic valences, and the Fermi energy. Some of these results have been presented in an earlier form.<sup>25</sup>

### II. METHOD

We previously calculated the electronic structure, the local densities of states, and the atomic valences for the superconducting oxide  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in the one-electron approximation using a semiempirical tight-binding model, with  $p$  and  $s$  orbitals included for the O atoms, and  $d$  and  $s$  orbitals for all of the metal atoms.<sup>26</sup> Good agreement was found with the results of other calculations for bandwidths and densities of states.<sup>27-29</sup> Using this same model, we now consider the effects of replacing Y, Ba, Cu, and O. For simplicity, we employ a periodic substitution scheme, with the substituted atom occupying the same location within each unit cell throughout the material. We neglect the small changes which occur in the lattice constants due to differences in covalent radii of the substituted atoms. Although such changes in the lattice parameters are observed, and may have a role in the superconductivity of these materials, they nevertheless have only a minor effect on the electronic structure of the material. The parameters needed for the electronic structure calculation of Ref. 26 are provided in Table I. Starting with these parameters for Y, Ba, Cu, and O, we take the differences in atomic energies for substitutional atoms from a standard table.<sup>30</sup> Where  $\epsilon_d$  or  $\epsilon_s$  is not given in this table, we have simply extrapolated from the nearest atom for which a value is given. We have also included the valence  $p$  orbitals for Tl, Pb, and Bi, although the original calculation neglected the unoccupied  $p$  orbitals on Y.

The local density of states for both spins is calculated from

$$\rho_0(E) = -\frac{2}{\pi} \text{Tr} \text{Im} G_0(E), \quad (1)$$

TABLE I. "Atomic energies" in eV.

	$\epsilon_s$	$\epsilon_p$	$\epsilon_d^a$
Al	-10.1	-4.9	...
Fe	-11.6	...	-10.4
Co	-11.7	...	-11.6
Ni	-11.9	...	-12.8
Cu <sup>b</sup>	-12.0	...	-14.0
Zn	-13.5	...	-15.2
Ba	-4.5	...	-6.6
Sr	-5.0	...	-6.8
La	-4.9	...	-6.6
Y	-5.5	...	-6.8
Tl	-9.9	-4.6	-14.7
Pb	-12.1	-5.8	-16.1
Bi	-14.2	-7.0	-17.5
O	-29.0	-14.0	...
N	-23.0	-11.5	...
F	-36.0	-17.0	...

<sup>a</sup>For the 3d metals,  $r_d = 0.95 \text{ \AA}$ ;  $r_d(\text{Y, Ba, Sr, La}) = 1.6 \text{ \AA}$ ;  $r_d(\text{Tl, Pb, Bi}) = 1.0 \text{ \AA}$ .

<sup>b</sup>Parameters fitted in Ref. 26.

where Tr indicates a trace over those orbitals associated with a given site. The Green's function is given by

$$G_0(E) = \frac{1}{N} \sum_{\mathbf{k}, n} \frac{\psi(\mathbf{k}, n) \psi^\dagger(\mathbf{k}, n)}{E - E(\mathbf{k}, n) + i\delta}, \quad (2)$$

where  $E(\mathbf{k}, n)$  and  $\psi(\mathbf{k}, n)$  are the electronic energy and wave function (in a tight-binding representation) for the  $n$ th band and one of the  $N$  sample wave vectors  $\mathbf{k}$  within the irreducible  $\frac{1}{8}$  of the Brillouin zone. In the present calculations  $N = 64$ . A finite value  $\delta = 0.2 \text{ eV}$  was used to smooth the results. The Fermi energy is calculated by integrating the total density of states up to the total number of valence electrons for each particular material. The valence for each atom, defined to be the number of electrons lost by the atom when it is bonded in the solid, is cal-

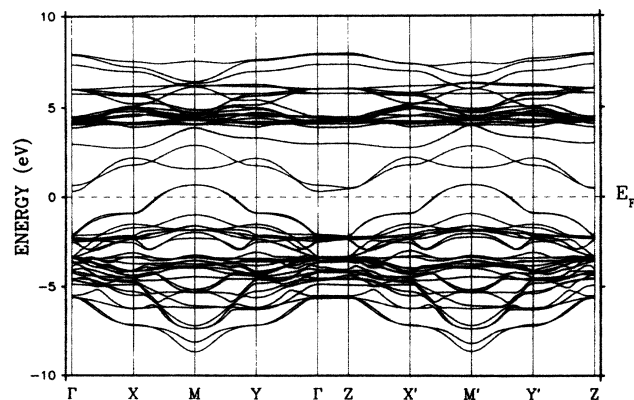


FIG. 1. Electronic structure of  $\text{YBa}_2\text{Cu}_2\text{AlO}_7$  for Al replacing the chain Cu.

culated from

$$\Delta n_i = n_i - \frac{2}{N} \sum_{\mathbf{k}, \alpha, E_n \leq E_F} |\psi_i^\alpha(\mathbf{k}, n)|^2, \quad (3)$$

where  $n_i$  is the number of valence electrons on the free atom  $i$ ,  $\psi_i^\alpha(\mathbf{k}, n)$  is the component of the eigenfunction corresponding to the valence orbital  $\alpha$  on this atom, and the summation is over the  $N$  sample wave vectors  $\mathbf{k}$ .

The notation for the atomic sites places Cu(1) in the CuO chain, separating the BaO layers, and Cu(2) in the  $\text{CuO}_2$  planes, adjacent to the Y atom. Oxygen site O(1) lies within the CuO chain; O(2) and O(3) lie within the  $\text{CuO}_2$  planes, with the Cu(2)-O(3) in-plane bond approximately parallel to the CuO chains; and O(4) lies in the BaO layer separating the CuO chain and the  $\text{CuO}_2$  plane. Our notation in labeling the substituted atoms parallels this form; e.g., Al(1) refers to an aluminum atom which replaces the chain copper atom.

### III. RESULTS AND DISCUSSION

The substitution of Al onto the Cu(1) site shows a dramatic effect on the band structure of  $\text{YBa}_2\text{Cu}_2\text{AlO}_7$ , shown in Fig. 1, as compared with that of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>26</sup> In particular, the conduction state associated with the Cu( $d$ )-O( $p$ ) antibonding band of the one-dimensional chain is completely removed from the structure, indicating a complete loss of metallic conductivity for this region. However, the two-dimensional nature of the electronic structure is maintained, as demonstrated in Fig. 1 by the similarity of the two wave-vector paths which trace the edge of the rectangular  $\frac{1}{4}$  of the Brillouin zone in the  $z = 0$  and  $z = \frac{1}{2}$  planes. The density of states of the Al-doped material is shown in Fig. 2. Note that the Al( $p$ ) bands lie about 6 eV above  $E_F$ , leading to weak interactions with the neighboring chain oxygens. Additionally, the calculated valences in Table II show only very minor effects on the  $\text{CuO}_2$  plane regions. This indicates that Al substitution leads to a localized destruction of conduction

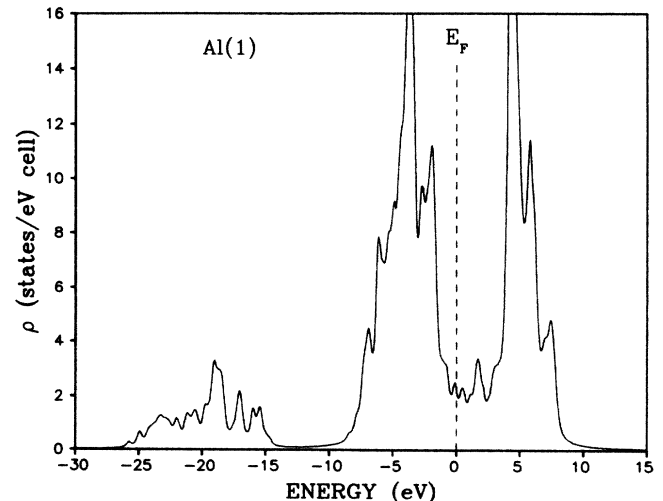


FIG. 2. Density of states of  $\text{YBa}_2\text{Cu}_2\text{AlO}_7$ .

TABLE II. Valences for  $\text{YBa}_2\text{Cu}_2\text{MO}_7$ .

<i>M</i>	Cu(1)	Cu(2) <sup>a</sup>	O(1)	O(2) <sup>a</sup>	O(3) <sup>a</sup>	O(4)
Al(1)	2.46	0.94	-1.59	-1.10	-1.11	-1.50
Fe(1)	3.24	0.38	-1.13	-1.30	-1.31	-1.19
Fe(2)	0.67	1.61	-1.35	-1.15	-1.16	-1.30
Co(1)	2.03	0.67	-1.10	-1.17	-1.17	-1.14
Co(2)	1.03	1.10	-1.18	-1.04	-1.06	-1.25
Ni(1)	1.12	0.99	-1.12	-1.07	-1.07	-1.18
Ni(2)	1.31	0.89	-1.12	-1.04	-1.05	-1.23
Cu <sup>b</sup>	1.34	0.98	-1.12	-1.09	-1.11	-1.21
Zn(1)	1.41	1.02	-1.33	-1.07	-1.07	-1.25
Zn(2)	1.37	1.09	-1.11	-1.15	-1.17	-1.23

<sup>a</sup>Averaged over sites in unit cell.

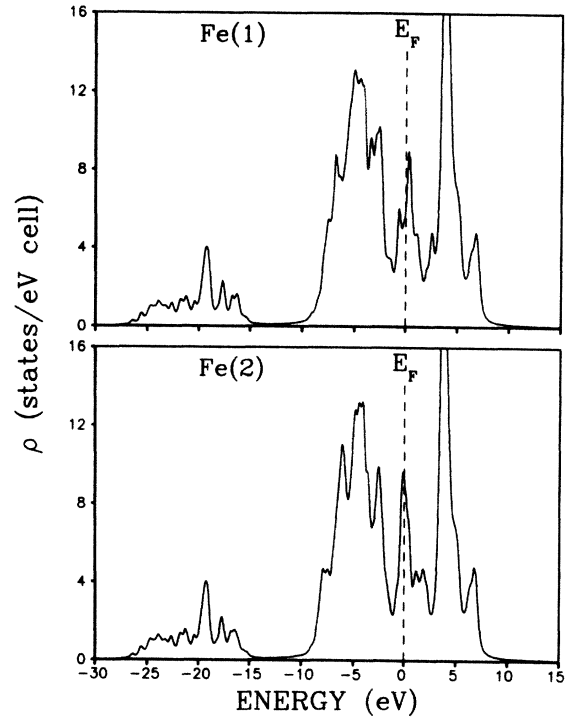
<sup>b</sup>Results from Ref. 26.

states and hole carriers within the one-dimensional chains, substantially suppressing superconductivity in this region.<sup>14</sup> The shift of the Fermi energy due to the substitution of Al, along with the total density of states at  $E_F$ , is given in Table III. Our calculated density of states at  $E_F$  for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is 3.2 states/eV cell.<sup>26</sup>

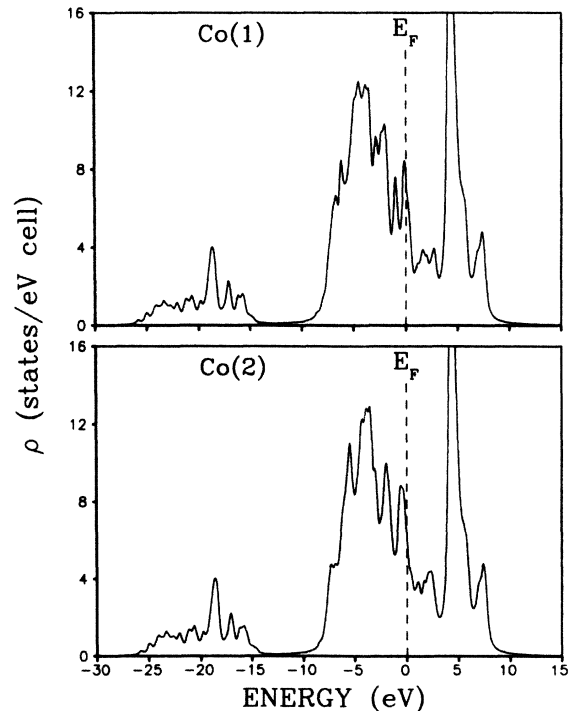
For the transition-metal substitutions, we considered both Cu(1) and Cu(2) sites within  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and performed the calculation independently for each of these substitution sites. The densities of states for the transition-metal substitutions are shown in Figs. 3–6, with the valences presented in Table II. Note that there is a strong dependence on the substitution site for both the metal and oxygen valences. The Fe and Co results in Table II show drastic changes in  $\rho(E_F)$  for both sites. We note that the Fermi energy is pinned near the peak of the Fe or Co *d*-state energy, so that  $\rho(E_F)$  is insensitive to small variations of the parameters  $\epsilon_d(\text{Fe})$  or  $\epsilon_d(\text{Co})$  in Table I, but for the same reason  $\Delta E_F$  is somewhat sensitive to these values. We also recognize that the large metal valences in Table II may be due to the simplified treatment of *d* orbitals for these atoms. However, these substitutions do strongly disrupt the character of the Cu(*d*)–O(*p*) antibonding state at  $E_F$ , which may explain the large decrease in  $T_c$  seen for Fe and Co substitution.<sup>15,16</sup> Replacement of Cu by Ni shows a smaller change in  $\rho(E_F)$  and in the atomic valences. This may explain the

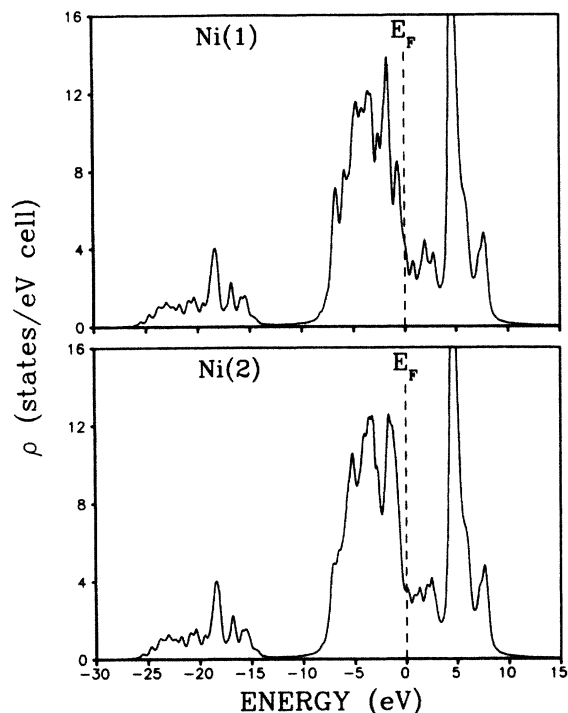
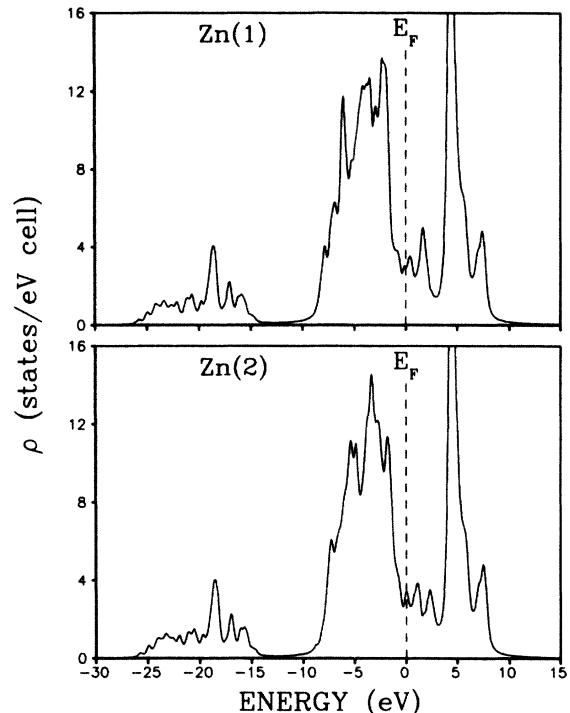
TABLE III. Shift in  $E_F$  and density of states for  $\text{YBa}_2\text{Cu}_2\text{MO}_7$ .

<i>M</i>	$\Delta E_F$ (eV)	$\rho(E_F)$ (states/eV cell)
Al(1)	0.15	2.4
Fe(1)	0.79	6.3
Fe(2)	0.78	9.3
Co(1)	0.22	7.5
Co(2)	0.16	6.3
Ni(1)	-0.12	4.2
Ni(2)	-0.08	3.5
Zn(1)	0.16	3.0
Zn(2)	0.08	3.3

FIG. 3. Density of states of  $\text{YBa}_2\text{Cu}_2\text{FeO}_7$ .

more moderate decrease in  $T_c$  for this case.<sup>15–17</sup> The Zn substitution shows only minor changes in valences and the density of states, in contrast to the large decrease in  $T_c$  seen experimentally.<sup>15</sup> We note that the lack of resonance of the Zn(*d*) states with the O(*p*) states leads to a lowering of the *d*-state character at the Fermi energy for this

FIG. 4. Density of states of  $\text{YBa}_2\text{Cu}_2\text{CoO}_7$ .

FIG. 5. Density of states of  $\text{YBa}_2\text{Cu}_2\text{NiO}_7$ .FIG. 6. Density of states of  $\text{YBa}_2\text{Cu}_2\text{ZnO}_7$ .

case. Nevertheless, the present results indicate that the direct electronic effect of Zn should be less than that of, e.g., Fe. We therefore suggest that the dramatic effect of Zn substitution observed experimentally must be attributed to some structural modification. Note that the shift in  $E_F$  in Table III is relatively site independent for all the transition-metal substitutions, indicating the dopant origin of the shift, while the density of states at  $E_F$  is strongly site dependent, except in the case of Zn.

Substitutions on the Ba site were performed for  $\text{YBaSrCu}_3\text{O}_7$  and  $\text{YBaLaCu}_3\text{O}_7$ . For the case of Sr, little change is seen in direct electronic effects, as shown by the valences in Table IV and the shift of the Fermi energy and the total density of states at  $E_F$  in Table V. This is consistent with the experimental results and would support a purely structural effect for the observed decrease in the superconducting transition temperature.<sup>9,10</sup> Substitution of La does show shifts due to doping, resulting in fewer conduction holes within the material. We propose that the dominant effect of this substitution on the superconducting properties of  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_7$  is the destruction

of the charge carriers.

The replacement of Y by Tl, Pb, and Bi is performed on the single Y site within each unit cell. We chose these three atoms because their covalent radii and valences are not far from those of Y. Again, we neglect any lattice parameter shifts which might occur due to atomic size differences. The densities of states for the Y replacements are shown in Fig. 7. Note the empty  $p$  states introduced 4–6 eV above  $E_F$ . Only small changes in the densities of states are predicted for these substitutions, although  $d$ -state resonances with  $O(p)$  lead to additional structure in the density of states near  $E_F$ . Table IV lists the valences for each replacement, while Table V gives the change in the Fermi energy and the density of states at  $E_F$ . Note that the increase in the density of states at  $E_F$  for Bi is primarily due to the near coincidence of the Bi( $s$ ) energy with the Fermi energy. Introduction of Bi into the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  material on the La and Sr site does appear to increase  $T_c$  from 38 to 42 K, indicating that similar results might be expected for the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  material.<sup>31</sup>

TABLE IV. Valences for Ba and Y replacements.

	Ba <sup>a,b</sup>	Y <sup>c</sup>	Cu(1)	Cu(2) <sup>b</sup>	O(1)	O(2) <sup>b</sup>	O(3) <sup>b</sup>	O(4) <sup>b</sup>
Sr	1.43	1.77	1.34	0.98	-1.12	-1.09	-1.11	-1.20
La	1.94	1.76	1.30	0.71	-1.12	-1.19	-1.20	-1.23
Tl	1.42	2.57	1.23	0.92	-1.14	-1.21	-1.22	-1.25
Pb	1.42	3.22	1.24	0.72	-1.14	-1.27	-1.28	-1.25
Bi	1.42	3.83	1.21	0.53	-1.14	-1.31	-1.32	-1.26

<sup>a</sup>Undoped valence of Ba = 1.44 (Ref. 26).

<sup>b</sup>Averaged over sites in unit cell.

<sup>c</sup>Undoped valence of Y = 1.77 (Ref. 26).

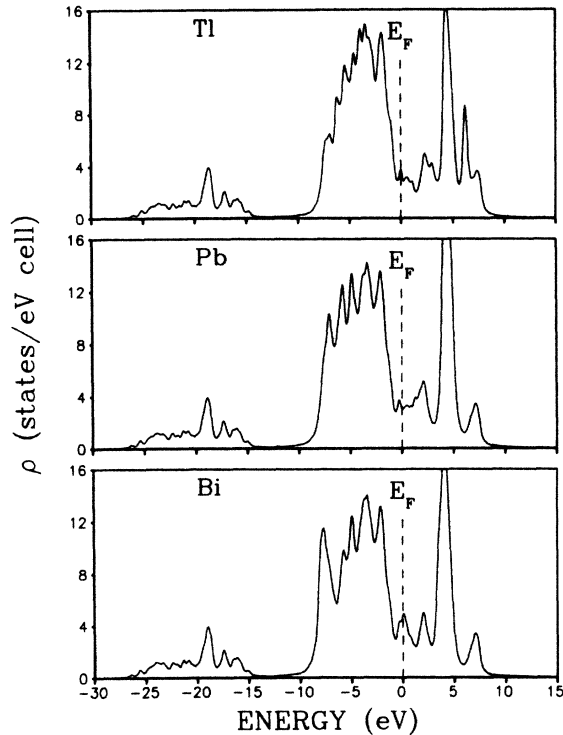


FIG. 7. Density of states of  $ABa_2Cu_3O_7$  for  $A = Tl, Pb, \text{ or } Bi$ .

Substitution of N or F for oxygen is complicated by the several distinct oxygen sites, along with the many possible combinations for multiple substitutions. However, we find that sites O(2) and O(3) in the  $CuO_2$  planes behave quite similarly in their electronic structure, as expected from the minor orthorhombic distortion of the structure.<sup>32</sup> We consider only single atom substitution of nitrogen for oxygen, but both single and double substitution in the case of fluorine.

Table VI gives the valences for the oxygen replacements. The strongest secondary valence effect occurs on the copper site nearest to the substituted atom, particularly for substitutions in the  $CuO$  chain. Table VII gives the shift in  $E_F$  and the density of states at  $E_F$  for the replacement of oxygen. We note that N acts primarily to lower the Fermi energy, while F raises it; i.e., N acts as an acceptor and F as a donor when replacing oxygen. Fluorine is found to have a larger effect on  $E_F$  than nitrogen.

TABLE V. Shift in  $E_F$  and density of states for Ba and Y replacements.

	$\Delta E_F$ (eV)	$\rho(E_F)$ (states/eV cell)
Sr	-0.01	3.2
La	0.31	2.8
Tl	0.16	3.7
Pb	0.41	3.0
Bi	0.49	4.8

TABLE VI. Valences for O replacements.

	Cu(1)	Cu(2) <sup>a</sup>	O(1)	O(2) <sup>a</sup>	O(3) <sup>a</sup>	O(4) <sup>a</sup>
N(1)	1.18	0.97	-0.89	-1.06	-1.08	-1.25
N(2)	1.24	1.06	-1.13	-1.05	-1.05	-1.25
N(4)	1.30	0.98	-1.14	-1.08	-1.09	-1.14
F(1)	0.81	1.00	-0.67	-1.08	-1.07	-1.28
F(2)	1.36	0.73	-1.11	-0.86	-1.16	-1.23
F(4)	1.26	0.78	-1.15	-1.16	-1.18	-0.87
F(1),F(2)	0.78	0.77	-0.67	-0.84	-1.12	-1.30
F(1),F(4)	0.79	0.76	-0.68	-1.16	-1.15	-0.93
F(2),F(2)	1.39	0.47	-1.10	-0.63	-1.21	-1.24
F(4),F(4)	0.98	0.69	-1.27	-1.19	-1.18	-0.61

<sup>a</sup>Averaged over sites in unit cell.

#### IV. CONCLUSIONS

In summary, calculations for the replacement of Y, Ba, Cu, and O with other elements have been performed. The results are in reasonable agreement with expected chemical trends. The strong correlation of Al substitution on the Cu(1) site with suppression of  $T_c$  is explained by the destruction of the conduction band within the  $CuO$  chain, clearly indicating the importance of the chains to the existence of superconductivity at temperatures near 90 K in  $YBa_2Cu_3O_7$ . The substitutions of transition metals for Cu also give results which are compatible with experiment, except in the case of Zn. We suggest that this group IIB element produces a structural modification when substituting for group IB Cu. Results from the replacement of Ba by Sr give support for a purely structural suppression of  $T_c$ , while we suggest that La substitution leads to filling of the hole charge carriers by the donor electrons, resulting in the destruction of superconductivity in this case. Our results for F and N substitutions on the oxygen sites show that the electronic structure of  $YBa_2Cu_3O_7$  may be affected by such replacements, but no obvious correlations to the superconducting properties have been seen.

*Note added in proof.* In the present paper, and earlier

TABLE VII. Shift in  $E_F$  and density of states for O replacements.

	$\Delta E_F$ (eV)	$\rho(E_F)$ (states/eV cell)
N(1)	0.02	5.0
N(2)	-0.06	3.7
N(4)	-0.08	4.8
F(1)	0.11	3.5
F(2)	0.14	3.0
F(4)	0.25	2.8
F(1),F(2)	0.27	2.7
F(1),F(4)	0.36	2.8
F(2),F(2)	0.34	2.0
F(4),F(4)	0.43	3.5

in Ref. 25, we considered the substitution of Tl, Pb, and Bi for Y even though such substitutions had not been previously reported, because we thought these substitutions should be possible and might prove interesting. Recently several new classes of high- $T_c$  superconductors have been reported,<sup>33,34</sup> involving substitution of Bi, (Pb,Bi), and Tl for Y.

#### ACKNOWLEDGMENTS

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