PHYSICAL REVIEW B VOLUME 54, NUMBER 2 1 JULY 1996-II

Electronic structure of the 1×1 $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ superlattice: A local-spin-density approximation with on-site Coulomb interaction

M. Biagini, C. Calandra, and Stefano Ossicini
Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Modena,
via Campi 213/A, I-41100 Modena, Italy

(Received 2 November 1995)

We performed self-consistent linear muffin-tin orbital atomic sphere approximation calculations of the electronic structure of the 1×1 $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ (YBCO/PBCO) superlattice, based on the local-spin-density approximation with on-site Coulomb correlation. From our results, we can exclude that the experimentally observed depression of the critical temperature is originated intrinsically by a modification of the electronic structure of the CuO_2 planes. We find that the charge transfer between YBCO and PBCO layers is one order lower than the value required to explain the strong depression of both the critical temperature T_c(onset) and the zero-resistance transition temperature T_c^0, within the hole-filling model. [S0163-1829(96)01226-X]

I. INTRODUCTION

The compounds $(R)Ba_2Cu_3O_7$ present high superconducting transition temperatures when R stands for most of the rare-earth elements or for Y. A notable exception is the nonsuperconducting $PrBa_2Cu_3O_7$ (PBCO), which experimentally has an insulating character. From the theoretical point of view, the electronic structure of PBCO is still under debate, the main issue being how to account for the nonsuperconducting and the insulating character.

Recently, Fehrenbacher and Rice[1] have proposed a model which predicts that the insulating character of PBCO is due to extrinsic mechanisms such as defects in the CuO chains. While the CuO chains are metallic at the microscopic level, it is assumed that the macroscopic insulating behavior of this compound is due to its extreme sensitivity to disorder or defects in the chains. In this model the absence of superconductivity is ascribed to the existence of a local Pr $4f$ hybridized state which binds doped holes to Pr sites. The Fehrenbacher-Rice model is consistent with many experimental properties and is supported by light scattering,[2] positron annihilation,[3] and magnetotransport experiments.[4,5]

Electronic-structure calculations based on the local-spin-density approximation (LSDA) fail to reproduce the antiferromagnetic ground state of PBCO. Very recently,[7] we calculated the PBCO electronic structure within the local-density approximation with on-site Coulomb interaction.[8] This approach includes the leading terms for the on-site Coulomb and exchange interactions U and J, corresponding to Cu $3d$ electrons. We found Cu local moments in good agreement with experiments, in contrast with the LSDA results. Besides, the inclusion of the on-site Coulomb repulsion strongly suppresses the metallic character of the planar Cu(2) ions. On the other hand, an intermediate oxidation state for the Cu(1) ion, between Cu^{I} and Cu^{II}, was obtained and the metallic character of the CuO chains was preserved, in agreement with several experimental results.[2–5] Liechtenstein and Mazin[6] have calculated the electronic structure of PBCO, by taking into account the Coulomb correlations on the Pr site. From their calculations, they have derived a tight-binding model which accounts for the dependence of the suppression of superconductivity in the mixed rare-earth compounds $R_{1-x}Pr_xBa_2Cu_3O_7$ on the rare-earth component. However, since they do not consider the on-site correlation of Cu $3d$ electrons, they find that both the metallic character of the CuO_2 planes and the Cu spin moments are not modified with respect to the LSDA results.

The nonsuperconducting character of PBCO has stimulated much interest in the electrical transport properties of $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ (YBCO/PBCO) superlattices.[9] In fact, from such systems one can obtain important information about the role of interlayer coupling in high-T_c superconductivity. This is a central problem in the theory of high-T_c superconductivity. Actually, it is generally accepted that the still unknown microscopic superconducting mechanism in cuprate superconductors takes place in the CuO_2 planes, which is a common feature of all such materials. Experiments have revealed a strong anisotropy between the in-plane and the off-plane directions in their physical properties such as the normal-state resistivity,[10] the upper critical field,[11] the thermal conductivity,[12] etc. These results suggest a weakly coupled layered structure for the above materials. Nevertheless, it is not established to what extent the superconducting properties are bound to the two dimensionality of the CuO_2 planes, and how they are affected by the interaction between adjacent CuO_2 planes.

In the case of YBCO/PBCO superlattices, PBCO has lattice constants a and b 1.5% larger than in YBCO but the same orthorhombic structure as superconducting YBCO. It is then reasonable to expect that a variation of the number of PBCO layers can modify the coupling between YBCO layers without changing significantly their structural properties. Besides, interdiffusion between the two layers is negligible in these systems, as is proven by the different behavior of the superlattices from the one of random alloys of the same average composition.[13]

The superconducting properties of the above systems are a function of both YBCO and PBCO layer thicknesses. The zero-resistance transition temperature T_c^0 decreases as the YBCO layer thickness is decreased or as the PBCO layer thickness is increased, but for all YBCO layer thicknesses, including layers one unit cell thick, the superconducting transition temperature saturates at nonzero values.[9,14] The widths of the superconduction transitions are large, with $\Delta T_c \approx 37$ K for one unit cell thick YBCO layers isolated in a PBCO matrix.[15] Several different models have been proposed in order to explain such a behavior, which are based upon Kosterlitz-Thouless transition and charge redistribution effects,[16–19] interlayer coupling,[20,21] proximity effect,[22–25] and hole filling.[26,27]

In a recent work,[28] we performed self-consistent electronic band-structure calculations for YBCO/PBCO superlattices with different PBCO layer thickness, within the local density approximation (LDA). We found no relevant charge transfer between the YBCO and PBCO layers. On the other hand, the LDA gives a strong metallic character for the CuO_2 planes in PBCO, in contradiction with experiments. It is then important to establish how our previous results are affected from the above deficiency of the LDA. In the present work, we include the on-site Coulomb and exchange interactions on the Cu(2) sites in the PBCO layer. This method (LSDA$+U$) has provided a better description of the electronic structure of PBCO, with respect to the LDA results.[7] In order to better understand the effect of the on-site correlation in PBCO, we also present LSDA$+U$ results for $YBa_2Cu_3O_6$ (YBCO6). The insulating antiferromagnetic ground state of YBCO6 is in fact well described within LSDA$+U$. On the other hand, the CuO_2 planes in YBCO6 and PBCO are experimentally very similar.

Our goal is to study the effect of the PBCO layer on the electronic structure of the superconducting CuO_2 planes in the YBCO layer and to investigate quantitatively charge transfer effects. The knowledge of charge transfer effects can allow one to confirm or exclude models based on hole-filling mechanisms; on the other hand, if the YBCO electronic structure is severely modified by an adjacent PBCO layer, all theories based upon interlayer coupling and proximity effect become unreliable, since the above modification could strongly lower the critical temperature. This possibility was suggested by Lowndes *et al.*[14] by observing that the critical temperature T_c^0 increases strongly with the number of YBCO layers; indeed, T_c^0 is very close to the bulk value when only four YBCO layers are included in a thick PBCO matrix.

II. METHOD

Self-consistent electronic structures were calculated using the linear muffin-tin orbital method (LMTO) with the atomic sphere approximation (ASA).[29] The LMTO-ASA method has been used in several high-T_c^0 superconductor band-structure calculations and is found to give very similar results to those obtained using more elaborate methods such as the full-potential linear augmented plane-wave (LAPW) method.[30–32] In our calculations, all electrons are separated into either core or band electrons. The core electron wave functions are calculated by solving the relativistic Dirac equation at every self-consistent iteration, while the spin-orbit coupling is neglected for the valence electrons. All calculations were performed for the orthorhombic structure with lattice constants and atomic position parameters for YBCO and PBCO taken, respectively, from Refs. 33 and 34. In the case of the c-axis superlattice the a and b lattice constants were calculated as an average of the bulk values. Since YBCO and PBCO have very similar lattice constants, the superlattice values of a and b differ from the bulk values by less than 0.6%. We believe that the above small strain cannot affect significantly the superconducting properties of the system; this may be argued from the experimental observation of critical temperatures practically coincident with the bulk values for superlattices with 4 unit cell YBCO layers and 16 unit cell PBCO layers, where the strain is larger than the one corresponding to the systems studied in the present work. The length of the c axis has been chosen according to Vegard's law, so that both YBCO and PBCO cell volumes are kept equal to their bulk value. This procedure has allowed us to fix the atomic sphere radii to the same value in the bulk and in the superlattice. An empty sphere has been put along the x axis as described in Refs. 30,31. The basis functions for Y, Pr, and Ba were s,p,d,f LMTO's, and s,p,d for the Cu, O, and empty spheres. We used 100 k points within the irreducible wedge of the Brillouin zone in the self-consistent calculations of the YBCO and PBCO electronic structures, while 50 k points were used for the superlattice.

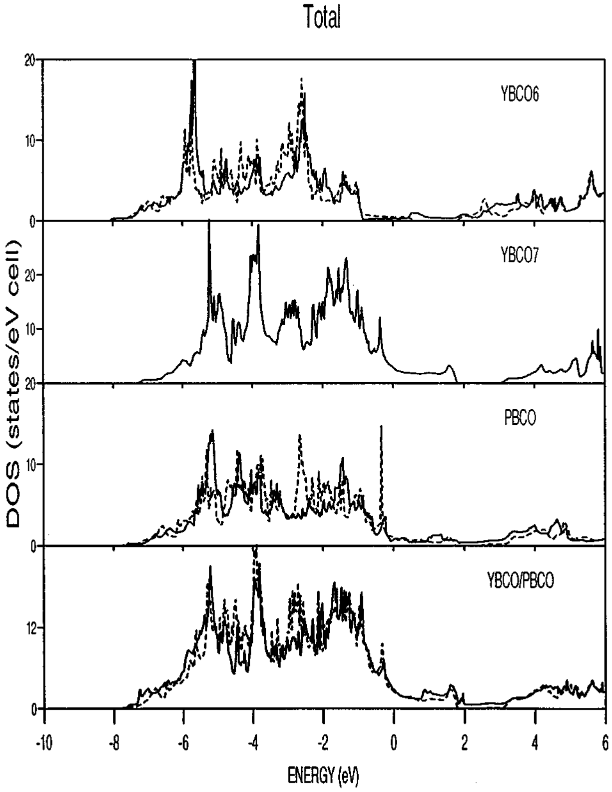

FIG. 1. Total density of states of YBCO6, YBCO7, PBCO, and 1×1 YBCO/PBCO superlattices: The solid and dashed lines correspond, respectively, to the minority and majority spin components, except the YBCO7 results, in which densities of states are not spin decomposed.

The calculations were performed within the density-functional formalism, in the local-spin-density approximation with on-site Coulomb repulsion (LSDA$+U$).[8] The following functional was used for the energy:

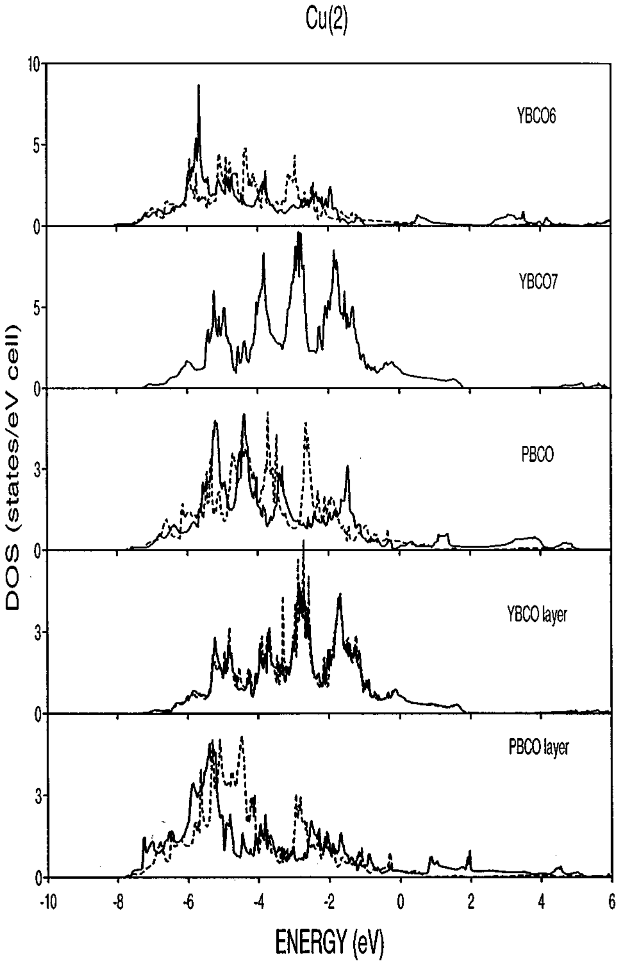

FIG. 2. Partial density of states projected on the Cu(2) site of YBCO6, YBCO7, PBCO, and 1×1 YBCO/PBCO superlattices: The solid and dashed lines correspond, respectively, to the minority and majority spin components, except the YBCO7 results, in which densities of states are not spin decomposed.

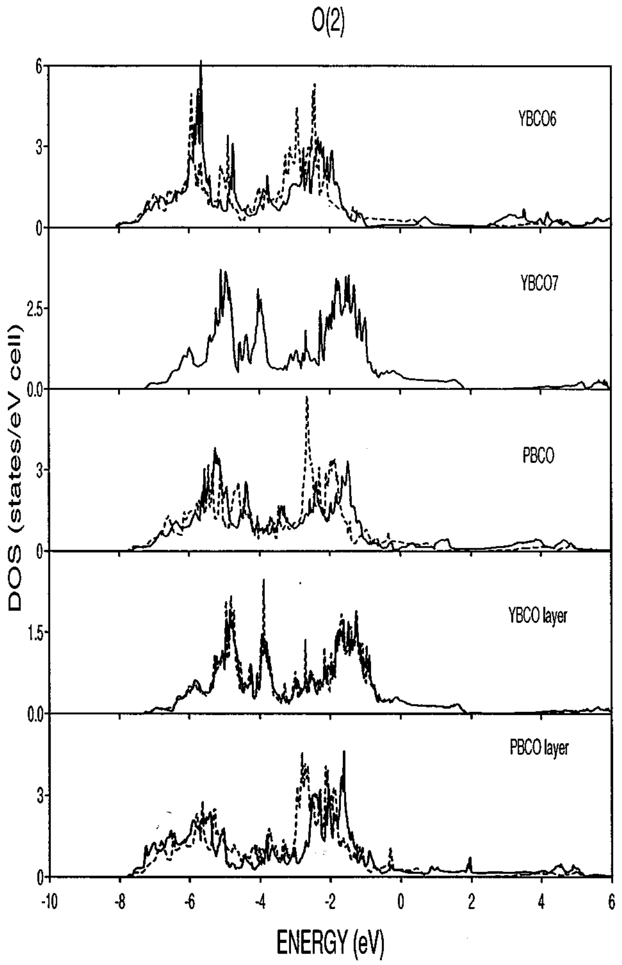

FIG. 3. Partial density of states projected on the O(2) site of YBCO6, YBCO7, PBCO, and 1×1 YBCO/PBCO superlattices: The solid and dashed lines correspond, respectively, to the minority and majority spin components, except the YBCO7 results, in which densities of states are not spin decomposed.

$$E^{\mathrm{LSDA}+U}=E^{\mathrm{LSDA}}+\frac{U}{2}\sum_{m,m',\sigma}(n_{m\sigma}-n_{\sigma}^{0})(n_{m'\sigma}-n_{\sigma}^{0})$$
$$+\frac{U-J}{2}\sum_{m,m',m\neq m',\sigma}(n_{m\sigma}-n_{\sigma}^{0})(n_{m'\sigma}-n_{\sigma}^{0}), \tag{1}$$

where $n_{m\sigma}$ are occupation numbers of the Cu d orbitals and $n_{\sigma}^{0}=\Sigma_{m}n_{m\sigma}/(2l+1)$. We have dropped site indices in U, J, $n_{m\sigma}$, and n_{σ}^{0} and in the summation over all sites. The functional derivative $\delta/\delta n(\mathbf{r})$ used in the density-functional theory to obtain the effective potential is generalized to the variation of the charge density of particular orbital $n_{m\sigma}(\mathbf{r})$. One then finds the effective potential

$$V^{\mathrm{LSDA}+U}(\mathbf{r})=V^{\mathrm{LSDA}}(\mathbf{r})-(U-J)(n_{m\sigma}-n_{\sigma}^{0}). \tag{2}$$

In our LSDA+U calculations, we applied the potential (2) to planar Cu(2) atoms in the PBCO layer. We performed also calculations within the LSDA+U model for $\mathrm{YBa_2Cu_3O_6}$ (YBCO6), in order to make a comparison with the PBCO electronic structure. The parameters U and J were chosen to be 6.5 eV and 0.98 eV, respectively. These data were taken from Ref. 8, and they were succesfully applied to the calculation of the electronic structure of $\mathrm{La_2CuO_4}$ and $\mathrm{YBa_2Cu_3O_6}$.[35]

The valence state of the Pr ion was assumed to be 3+ and the Pr $4f$ electrons were treated as core states. Treating the Pr $4f$ states as band electrons does not modify significantly the density of states of PBCO in a LSDA+U calculation, as shown in Ref. 7. Therefore we expect that our results are not affected by our assumption of a Pr valence state of 3+. In our calculations we used a ferromagnetic ordering rather than the experimentally observed antiferromagnetic ordering. We expect that magnetic ordering contributes only a small energy with respect to the band energies, so that the above choice does not affect significantly the results of the electronic-structure calculations.

III. RESULTS AND DISCUSSION

In the present section we compare the results of four calculations: (i) LSDA+U electronic structure of YBCO6, (ii)

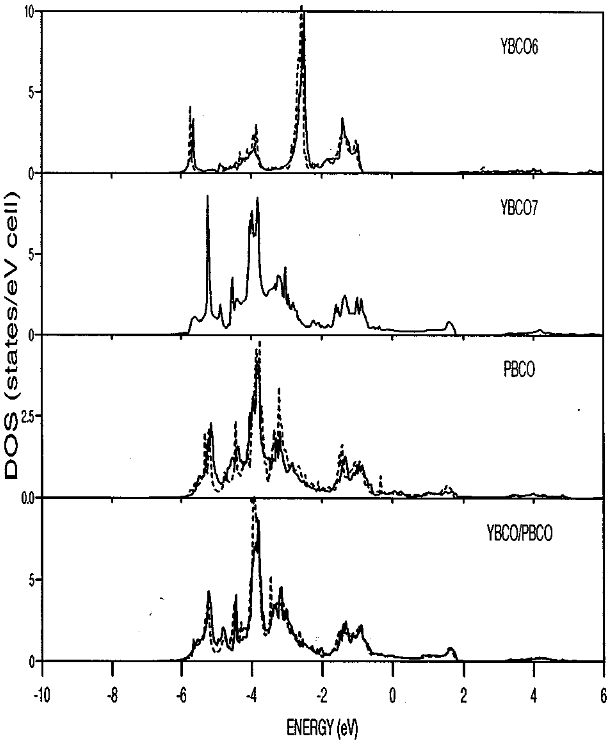

FIG. 4. Partial density of states projected on the Cu(1) site of YBCO6, YBCO7, PBCO, and 1×1 YBCO/PBCO superlattices: The solid and dashed lines correspond, respectively, to the minority and majority spin components, except the YBCO7 results, in which densities of states are not spin decomposed.

(LDA) electronic structure of YBCO7, (iii) LSDA+U electronic structure of PBCO, and (iv) LSDA+U electronic structure of the 1×1 YBCO/PBCO superlattice, with on-site Coulomb repulsion applied to the planar Cu(2) atoms in the PBCO layer. The total densities of states are represented in Fig. 1. In Figs. 2–5 the site-decomposed densities of states corresponding to Cu(2), O(2), Cu(1), and O(4) are represented, in order to understand the behavior of CuO planes and chains. The solid and dashed lines correspond, respectively, to the minority and majority spin components. Since the YBCO7 system is a paramagnetic metal, the corresponding densities of states are not spin decomposed.

The inclusion of the on-site Coulomb repulsion strongly modifies the electronic structure of both YBCO6 (Ref. 35) and PBCO (Ref. 7), with respect to the LSDA results. The Cu(2) upper Hubbard band lies about 1 eV above the Fermi level, indicating a Cu$^{\mathrm{II}}$ oxidation state. The density of states at the Fermi level for the planar Cu(2) sites is strongly reduced with respect to the LSDA values. From Figs. 2 and 3, one can see that the electronic structures of the CuO$_2$ planes in YBCO6 and PBCO are very similar. On the other hand, the electronic structures of the CuO chain in PBCO bear close resemblance to the one in YBCO7. These results are in qualitative agreement with recent experiments,[2–5] which support the assumption in PBCO of metallic CuO chains (similar to YBCO7) and insulating CuO$_2$ planes (similar to YBCO6).

The Cu spin moments obtained by our LSDA+U calculations are significantly improved with respect to the LSDA results. In PBCO, the Cu(2) moment increases from $0.16\mu_B$ to $0.41\mu_B$, to be compared to the experimental value of $\approx 0.7\mu_B$.[36] In YBCO6, we find a Cu(2) spin moment of $0.53\mu_B$, to be compared to the experimental value of $0.48\mu_B$.[37] In the YBCO/PBCO superlattice the spin moments in the PBCO layer are slightly increased ($0.45\mu_B$), and a small spin moment of $0.02\mu_B$ is obtained in the Cu(2) sites in the YBCO layer. No experimental value for the Cu moments in the superlattice is currently available.

The density of states of the CuO$_2$ planes in the YBCO layer in the superlattice is practically unchanged, with respect to the bulk. This proves that, in spite of the differences in the electronic structure between YBCO and PBCO, the PBCO layer has only negligible effects on the electronic structure of the superconducting planes. This fact can be explained by assuming that the CuO chains at the interface provide a metallic bath which shelters the internal CuO$_2$ planes. From our self-consistent calculations we can obtain direct information about charge tranfer processes between YBCO and PBCO layers. We find that the charge transfer in a single CuO$_2$ plane in the YBCO layer is equal to 0.002 a.u. These results are consistent with the ones we have very re-

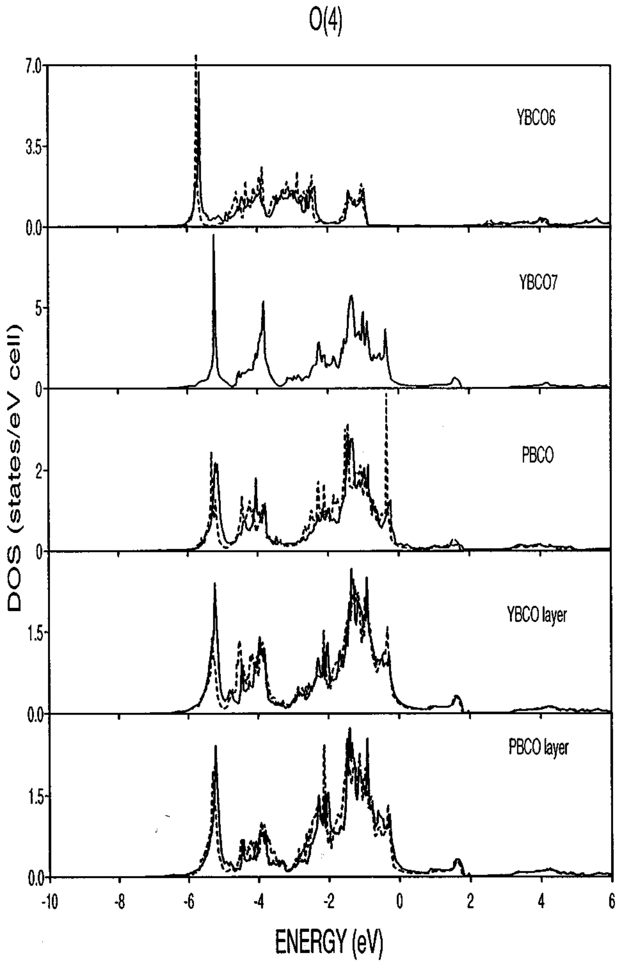

FIG. 5. Partial density of states projected on the O(4) site of YBCO6, YBCO7, PBCO, and 1×1 YBCO/PBCO superlattices: The solid and dashed lines correspond, respectively, to the minority and majority spin components, except the YBCO7 results, in which densities of states are not spin decomposed.

cently obtained from LDA calculations of the electronic structure of YBCO/PBCO superlattices.[28] The inclusion of the on-site Coulomb interaction strongly modifies the electronic structure of the CuO_2 planes in the PBCO layer but does not affect the CuO_2 planes in the YBCO layer.

In the case of the 1×1 YBCO/PBCO superlattice, both the zero-resistance transition temperature T_c^0 and the critical temperature T_c(onset) present a strong drop of about 15 K and 35 K, respectively.[15] On the other hand, from our calculations, it results that a single PBCO layer gives rise only to negligible modifications in the electronic structure of the superconducting CuO_2 planes, which cannot be ascribed as the origin of the above depression of the critical temperature. Moreover, the calculated charge transfer is one order lower than the value required to explain the reduction of both the critical temperature T_c(onset) and the zero-resistance temperature T_c^0, within the hole-filling model.

The lack of charge transfer in YBCO/PBCO superlattices is consistent with the experimental results found by Norton *et al.*[15] These authors investigated how the superconducting transitions of YBCO-based superlattices depend on the electronic properties of the barrier layers. They varied the hole concentration of the barrier layers by replacing Pr atoms with Ca atoms; they found that the superconducting transition width depends on the carrier density in the barrier layers, while T_c(onset) does not. These results seem to be inconsistent with the hole-filling model: In fact, one may expect that, if mobile holes are added to the PBCO layers, by doping with Ca atoms, charge transfer from the YBCO layers, and consequently T_c(onset) depression, is reduced.

In conclusion, we performed all-electron, self-consistent electronic-structure calculations for the 1×1 YBCO/PBCO superlattice, within the LSDA$+U$. From our results, we can exclude that the experimentally observed depression of the critical temperature is originated intrinsically by a modification of the electronic structure of the CuO_2 planes. Charge transfer effects between YBCO and PBCO layers have been proposed by many authors as the origin of the reduction of the critical temperature. From our calculations, we can confirm that the charge transfer is one order lower than the value required to explain the strong depression of both the critical temperature T_c(onset) and the zero-resistance transition temperature T_c^0, within the hole-filling model.

ACKNOWLEDGMENTS

This work was supported by Consiglio Nazionale delle Ricerche (CNR) Italy and the Human Capital and Mobility Psik Project (Contract No. ERBCHRX CT930369). The calculations have been performed at the Centro Interdipartimentale di Calcolo Automatico e Informatica Applicata (CICAIA), University of Modena, and at the Centro di Calcolo Interuniversitario (CINECA), Bologna.

---

[1] R. Feherenbacher and T. M. Rice, Phys. Rev. Lett. **70**, 3471 (1993).

[2] K. Takenaka, Y. Imanaka, K. Tamasaku, T. Ito, and S. Uchida, Phys. Rev. B **46**, 5833 (1992).

[3] L. Hoffmann, A. A. Manuel, M. Peter, E. Walker, M. Gauthier, A. Shukla, B. Barbiellini, S. Massidda, G. Adam, S. Adam, W. N. Hardy, and R. Liang, Phys. Rev. Lett. **71**, 4047 (1993).

[4] Y. Suzuki, J.-M. Triscone, C. B. Eom, M. R. Beasley, and T. H. Geballe, Phys. Rev. Lett. **73**, 328 (1994).

[5] M. Lee, Y. Suzuki, and T. H. Geballe, Phys. Rev. B **51**, 15 619 (1995).

[6] A. I. Liechtenstein and I. I. Mazin, Phys. Rev. Lett. **74**, 1000 (1995).

[7] M. Biagini, C. Calandra, and S. Ossicini, Phys. Rev. B **52**, 10 468 (1995).

[8] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[9] Q. Li, X. X. Xi, X. D. Wu, A. Inam, S. Vadlamannati, W. L. McLean, T. Venkatesan, R. Ramesh, D. M. Hwang, J. A. Martinez, and L. Nazar, Phys. Rev. Lett. **64**, 3086 (1990); T. Terashima, K. Shimura, Y. Bando, Y. Matsuda, A. Fujiyama, and S. Komiyama, *ibid.* **67**, 1362 (1991).

[10] J. Z. Wu, D. J. Hsieh, A. V. McGuire, D. L. Schmidt, L. T. Wood, Y. Shen, and W. K. Chu, Phys. Rev. B **44**, 12 643 (1991).

[11] T. T. M. Palstra, B. Betlogg, L. F. Schneemeyer, R. B. van Dover, and J. V. Waszczak, Phys. Rev. B **38**, 5102 (1988).

[12] C. Uher, J. Supercond. **3**, 337 (1990).

[13] J.-M. Triscone, O. Fischer, O. Brunner, L. Antognazza, A. D. Kent, and M. G. Karkut, Phys. Rev. Lett. **64**, 804 (1990).

[14] D. H. Lowndes, D. P. Norton, and J. D. Budai, Phys. Rev. Lett. **65**, 1160 (1990); P. Monthoux, A. B. Balatsky, and D. Anes, *ibid.* **67**, 3448 (1991); Phys. Rev. B **16**, 14 803 (1992); N. E. Bickers, D. J. Scalapino, and S. R. White, Phys. Rev. Lett. **62**, 961 (1989).

[15] D. P. Norton, D. H. Lowndes, S. J. Pennycook, and J. D. Budai, Phys. Rev. Lett. **67**, 1358 (1991).

[16] M. Rasolt, T. Edis, and Z. Tesanovic, Phys. Rev. Lett. **66**, 2927 (1991).

[17] K.-M. Ham, R. Sooryakumar, I. Takeuchi, Z. Trajanovic, C. Kwon, Q. Li, and T. Venkatesan, Phys. Rev. B **50**, 16 598 (1994).

[18] M. Z. Cieplak, S. Guha, S. Vadlamannati, T. Giebultowicz, and P. Lindenfeld, Phys. Rev. B **50**, 12 876 (1994).

[19] D. Ariosa and H. Beck, Phys. Rev. B **43**, 344 (1991).

[20] A. K. Rajagopal and S. D. Mahanti, Phys. Rev. B **44**, 10 211 (1991).

[21] Q. Li, X. X. Xi, X. D. Wu, A. Inam, S. Vadlamannati, W. L. McLean, T. Venkatesan, R. Ramesh, D. M. Hwang, J. A. Martinez, and L. Nazar, Phys. Rev. Lett. **64**, 3086 (1990).

[22] J. Z. Wu, C. S. Ting, W. K. Chu, and X. X. Yao, Phys. Rev. B **44**, 411 (1991); J. Z. Wu, X. X. Yao, C. S. Ting, and W. K. Chu, *ibid.* **46**, 14 059 (1992).

[23] T. Koyama and M. Tachiki, Physica C **193**, 163 (1992); T. Koyama, N. Takezawa, and Y. Naruse, *ibid.* **194**, 20 (1992); N. Takezawa, T. Koyama, and M. Tachiki, *ibid.* **207**, 231 (1993).

[24] S. Theodorakis, Physica C **216**, 173 (1993).

[25] D. Feinberg, S. Theodorakis, and A. M. Ettouhami, Phys. Rev. B **49**, 6285 (1994).

[26] R. F. Wood, Phys. Rev. Lett. **66**, 829 (1991); Phys. Rev. B **50**,

13 688 (1994); R. F. Wood and M. A. Abdel-Raouf, *ibid.* **51**, 11 773 (1995).

[27] S. Tanaka and Y. Motoi, Phys. Rev. B **52**, 85 (1995).

[28] M. Biagini, C. Calandra, and S. Ossicini, Europhys. Lett. **31**, 317 (1995).

[29] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).

[30] G. Y. Guo and W. M. Temmerman, Phys. Rev. B **41**, 6372 (1990).

[31] W. M. Temmerman, Z. Szotek, P. J. Durham, G. M. Stocks, and P. A. Sterne, J. Phys. F **17**, L319 (1987).

[32] S. J. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).

[33] J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournrie, Europhys. Lett. **3**, 1301 (1987).

[34] E. Moran, U. Amador, M. Barahona, M. A. Alario-Franco, A. Vegas, and J. Rodriguez-Carvajal, Solid State Commun. **67**, 369 (1988).

[35] P. Wei and Z. Q. Qi, Phys. Rev. B **49**, 12 159 (1994).

[36] N. Rosov, J. W. Lynn, G. Cao, J. W. O'Reilly, P. Pernambuco-Wise, and J. E. Crow, Physica C **204**, 171 (1992).

[37] J. M. Tranquada, D. E. Cox, W. Kunnmann, H. Moudden, G. Shiraue, M. Suenaga, P. Zolliker, D. Vakin, S. K. Sinha, M. S. Aluarez, A. Jacobson, and D. C. Johnston, Phys. Rev. Lett. **60**, 156 (1988).