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Theory for the electronic charge distribution in $YBa_2Cu_3O_7$ and $PrBa_2Cu_3O_7$ a-axis superstructures and alloys

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Using a Hubbard Hamiltonian containing all Y, Cu, and O sites we determine the electronic charge distribution in a-axis-oriented $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ superlattices and $Y_{1-x}Pr_xBa_2Cu_3O_7$ alloys within the Hartree-Fock and the tight-binding approximations. We find that the local hole concentration in the CuO_2 planes of $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ superstructures reflects the modulation wavelength of the respective a-axis superlattice and peaks in the center of the $YBa_2Cu_3O_7$ layers. We discuss the correlation of the superconducting transition temperature with the hole concentration in the CuO_2 planes and the density of states at the Fermi level.

I. INTRODUCTION

In contrast to other rare-earth dopants,[1] praseodymium suppresses superconductivity in the high-T_c cuprate $YBa_2Cu_3O_7$. Also, doping with Pr increases the normal-state resistivity of $YBa_2Cu_3O_7$, which becomes insulating for large Pr concentrations. Consequently, there is considerable interest in both the superconducting and normal-state properties of $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ (YBCO/PBCO) superlattices and $Y_{1-x}Pr_xBa_2Cu_3O_7$ alloys.

Recently, a-axis-oriented YBCO/PBCO superlattices have been investigated by Eom *et al.*[2] These superstructures are of particular interest for several reasons. First, the a-axis superlattice mismatch at the YBCO/PBCO interface is significantly smaller than the mismatch for c-axis superlattices. Second, the same CuO_2 plane can be locally superconducting and insulating, depending on whether the neighboring rare-earth atoms are Y or Pr. Third, a change from two-dimensional to one-dimensional superconducting behavior is expected if the width d_Y of the YBCO layers is decreased below the coherence length ξ_{ab}. Finally, the mechanism for the suppression of superconductivity due to doping with Pr is not completely understood.[3-5]

In this paper we study the electronic charge distribution in YBCO/PBCO a-axis superstructures and alloys, which is important for various properties of these compounds. In particular, we would like to understand whether the decrease of T_c in $Y_{1-x}Pr_xBa_2Cu_3O_7$ with increasing x is a consequence of the depletion of holes in the CuO_2 planes. In order to determine the charge distribution we use a Hubbard Hamiltonian that contains all Y, Cu, and O sites and calculate the local densities of states and occupation numbers of the various electronic orbitals self-consistently in the Hartree-Fock approximation and also in a simple tight-binding approach.

Our results show that the number of holes in the CuO_2 planes decreases as the Pr content in $YBa_2Cu_3O_7$ is increased. Furthermore, the local number of holes in the planes of an YBCO/PBCO compound depends on the surrounding rare-earth atom and increases if one approaches the center of a YBCO supercell. An increase of the modulation wavelength λ at constant Pr content essentially leads to an increase of the number of YBCO unit cells (within one YBCO layer) with a relatively high hole content, but does not change the hole concentration in the central YBCO unit cells. The correlation of the superconducting transition temperature T_c with the hole concentration in the CuO_2 planes agrees well with experiment and a crude estimate of T_c as a function of the density of states at the Fermi level gives the correct trend.

II. THEORY

In order to calculate the charge distribution in $YBa_2Cu_3O_{7-x}$ as a function of x we use the Hubbard Hamiltonian

$$H = \sum_{i,\alpha,\sigma} \varepsilon_{i\alpha\sigma} c^{\dagger}_{i\alpha\sigma} c_{i\alpha\sigma} + \sum_{\substack{i,j,\alpha,\beta,\sigma \\ (i\neq j)}} t_{i\alpha\sigma;j\beta\sigma} c^{\dagger}_{i\alpha\sigma} c_{j\beta\sigma} + \frac{1}{2} \sum_{\substack{i,\alpha,\beta,\sigma,\sigma' \\ [(\alpha,\sigma)\neq(\beta,\sigma')]}} U_{i\alpha\sigma;i\beta\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} \,. \tag{1}$$

Here, i and j refer to Y, Cu(1), Cu(2), O(1), O(2), O(3), and O(4) (apex) sites, and $c^{\dagger}_{i\alpha\sigma}$ ($c_{i\alpha\sigma}$) are the usual creation (annihilation) operators of an electron at site i in the orbital α with spin σ. We consider five different d orbitals on Y and Cu sites, three p orbitals on oxygen, and neglect the spin degrees of freedom. The Pr and Ba ions are considered as purely ionic with a total charge $q(\mathrm{Ba}) + q(\mathrm{Pr}) = 5.75$. This assumption leads to a half-filled band for pure PBCO (which is an insulator) and will be discussed in detail in Sec. III. The on-site energies $\varepsilon_{i\alpha}$ and the hopping integrals t_{ij} which describe hopping processes up to third-nearest neighbors are taken from a tight-binding fit[6] to the local-density-approximation (LDA) band structure calculated by De Weert, Papaconstantopoulos, and Pickett.[6] The Hubbard U is treated in the Hartree-Fock approximation ($n_i n_i \simeq n_i\langle n_i\rangle + \langle n_i\rangle n_i - \langle n_i\rangle\langle n_i\rangle$, where $n_i \equiv c_i^\dagger c_i$). Note that we use $U_d = 9$ eV on all copper sites and $U_p = 6$ eV on all oxygen sites. The interorbital repulsions on a copper or oxygen site are fully taken into account. However, in view of the uncertainty of the used parameters we have neglected the intersite Coulomb repulsion U_{pd}, which is of the order of 1 eV.[7]

From this Hamiltonian we determine the local Green's function $G_{i\alpha,i\alpha}$ on each orbital using Haydock's recursion method[8] with a cluster of at least 13 × 13 × 7 unit cells and 11 levels in the continued fraction. Note that each unit cell contains 41 electronic orbitals. Thus we obtain the local density of states $\varrho_{i\alpha}(\epsilon) = -(1/\pi)\lim_{\eta\rightarrow+0} \mathrm{Im} G_{i\alpha,i\alpha}(\epsilon + i\eta)$ and the corresponding electron occupation numbers $n_{i\alpha}$ of the various orbitals. This procedure is performed self-consistently within the Hartree-Fock approximation. More details about these calculations can be found in a previous paper by the present authors.[9]

The calculations are done for pure YBCO, pure PBCO, and various $Y_{1-x}Pr_xBa_2Cu_3O_7$ alloys using the single-site coherent-potential approximation (CPA).[10] Furthermore, we generate a-axis-oriented YBCO/PBCO superlattices with (3 unit cells)/(3 unit cells), (3 unit cells)/(6 unit cells), (6 unit cells)/(3 unit cells), and (6 unit cells)/(6 unit cells) multilayers and calculate the density of states and the occupation numbers of the electronic orbitals in the various inequivalent unit cells.

III. RESULTS AND DISCUSSION

First we discuss our assumptions that Pr can be considered as purely ionic and that the total charge[11] of Pr and Ba amounts to 5.75. The Pr-O anf Pr-Cu overlap should be much weaker than the Y-O and Y-Cu overlap, since the $4f$ electrons in Pr are more localized than the $4d$ electrons in Y. For simplicity, we then neglect the overlap of the Pr ions with the CuO_2 planes and consider Pr as purely ionic. Concerning the charge state of Pr, there is no clear experimental evidence. High-temperature susceptibility measurements[12] support the hypothesis that praseodymium occurs in a Pr^{4+} configuration. Photoemission experiments[13] suggest that Pr is in a 3+ state and that the charge of the BaO planes changes due to doping with Pr. The x dependence of the ^{63}Cu Knight shift and of the spin-lattice relaxation rate at Cu in the normal state of $Y_{1-x}Pr_xBa_2Cu_3O_7$ is similar to the y dependence of the ^{63}Cu Knight shift and the relaxation rate in $YBa_2Cu_3O_{7-y}$.[14] These results indicate that the substitution of Pr for Y leads to the depletion of holes in the CuO_2 planes.

Since the individual charge states of Ba and Pr are not important for our calculations, we consider only the total charge $q_{\text{tot}} = q(\text{Ba}) + q(\text{Pr})$, choosing $q_{\text{tot}} = 5.75$. This leads to a half-filled band for pure PBCO in the Hartree-Fock approximation and accounts for both the observation of an insulating state induced by Pr doping and the depletion of holes found in NMR experiments.

In order to determine the number of holes in the CuO_2 planes of the various inequivalent unit cells in a YBCO/PBCO superlattice, we use symmetrized unit cells (see Fig.1). For example, the number of holes in the CuO_2 plane of the central YBCO unit cell of the (12 Å)/(12 Å) structure shown in Fig. 1 is given by

$$n_h = n_h(\text{O}^a(2)) + 0.5[n_h(\text{Cu}^a(2)) + n_h(\text{Cu}^b(2))] \\ +0.5[n_h(\text{O}^a(3)) + n_h(\text{O}^b(3))]\,.$$

These unit cells have the same symmetry as the YBCO/PBCO superlattices.

Our results for the hole count in the CuO_2 planes of different a-axis-oriented YBCO/PBCO superstructures and for $Y_{1-x}Pr_xBa_2Cu_3O_7$ alloys (calculated by using the single site CPA) are shown in Tables I and II and in Fig. 2. The Hartree-Fock results were obtained using $U_d = 9$ eV and $U_p = 6$ eV and the tight-binding approximation refers to setting $U_p = U_d = 0$. In $Y_{1-x}Pr_xBa_2Cu_3O_7$ *alloys* the number of holes decreases continuously with increasing x. This results from the additional electrons injected into the compound due to doping with Pr.[15] Note that the tight-binding and the Hartree-Fock approximations give very similar results for this case. For the a-axis *superlattices* we also find a continuous decrease of the average hole concentration in the CuO_2 planes (averaged over all the inequivalent YBCO and PBCO unit cells) with increasing Pr content for both approximation schemes. However, there are significant differences between the two approximations regarding the distribution of the holes among the YBCO and PBCO unit cells. In the Hartree-Fock approximation we obtain an almost uniform distribution of the holes within the compound. By contrast, in the tight-binding approximation we find a strong decrease of the number of conducting holes if we go from the center of the YBCO layers to the center of the PBCO layers. For example, in the (12 Å)/(12 Å) superlattice (corresponding to three unit cells YBCO and three unit cells PBCO) there are 1.305 holes per CuO_2 unit cell in the central YBCO cell compared with 1.046 in the central PBCO unit cell.[16] The hole concentration in the inner YBCO unit cells of the (24 Å)/(24 Å) superstructures is not larger than that in the central unit cell of the (12 Å)/(12 Å) superlattices. However, in this case there are four connected YBCO

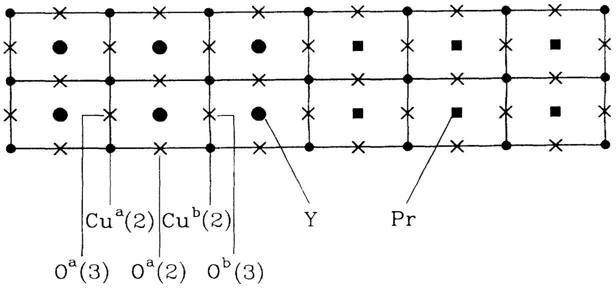

FIG. 1. The CuO_2 planes and the Y/Pr planes of a (3 YBCO unit cells)/(3 PBCO unit cells) superstructure as seen from above.

TABLE I. Numerical results for the number of the holes (n_h) in the CuO$_2$ planes of $Y_{1-x}Pr_xBa_2Cu_3O_7$ as a function of x calculated by using the CPA. We compare the tight-binding results with the results obtained within the Hartree-Fock approximation.

x	n_h (tight binding)	n_h (Hartree-Fock)
0.00	1.45	1.45
0.20	1.35	1.35
0.33	1.27	1.28
0.40	1.22	1.24
0.50	1.16	1.18
0.66	1.06	1.09
1.00	0.88	1.00

TABLE II. Numerical results for the number of holes (n_h) in the CuO$_2$ planes of the inequivalent YBCO and PBCO unit cells in YBCO/PBCO superlattices with (3 unit cells)/(3 unit cells), (6 unit cells)/(6 unit cells), (6 unit cells)/(3 unit cells), and (3 unit cells)/(6 unit cells) multilayers. We compare the tight-binding results with the results obtained within the Hartree-Fock approximation.

x	n_h (tight binding)	n_h (Hartree-Fock)
(3 YBCO unit cells)/(3 PBCO unit cells)		
1. YBCO	1.24	1.23
2. YBCO	1.30	1.24
3. YBCO	1.24	1.23
1. PBCO	1.11	1.23
2. PBCO	1.05	1.24
3. PBCO	1.11	1.23
(6 YBCO unit cells)/(6 PBCO unit cells)		
1. YBCO	1.23	1.22
2. YBCO	1.30	1.23
3. YBCO	1.31	1.24
4. YBCO	1.31	1.24
5. YBCO	1.30	1.23
6. YBCO	1.23	1.22
1. PBCO	1.12	1.22
2. PBCO	1.03	1.23
3. PBCO	1.04	1.23
4. PBCO	1.04	1.23
5. PBCO	1.03	1.23
6. PBCO	1.12	1.22
(6 YBCO unit cells)/(3 PBCO unit cells)		
1. YBCO	1.29	1.30
2. YBCO	1.35	1.32
3. YBCO	1.36	1.32
4. YBCO	1.36	1.32
5. YBCO	1.35	1.32
6. YBCO	1.29	1.30
1. PBCO	1.16	1.30
2. PBCO	1.09	1.30
3. PBCO	1.16	1.30
(3 YBCO unit cells)/(6 PBCO unit cells)		
1. YBCO	1.19	1.15
2. YBCO	1.25	1.16
3. YBCO	1.19	1.15
1. PBCO	1.07	1.16
2. PBCO	0.99	1.17
3. PBCO	0.98	1.13
4. PBCO	0.98	1.13
5. PBCO	0.99	1.17
6. PBCO	1.07	1.16

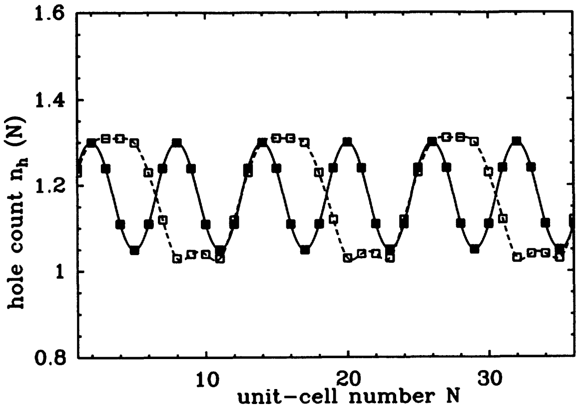

FIG. 2. Numerical results for the spatial variation of the hole concentration along the a axis in a 36-unit-cell section of (3 YBCO unit cells)/(3 PBCO unit cells) superstructures (filled squares) and (6 YBCO unit cells)/(6 PBCO unit cells) superstructures (empty squares) as obtained from the tight-binding approximation. Note that the leftmost layer is of YBCO type in both cases. Lines are guides to the eye.

cells with a large hole content compared to only one unit cell for the smaller superlattice.

The large hole concentration within the YBCO layers is due to the Y-O and Y-Cu hybridizations which lead to a transfer of electrons from the CuO$_2$ planes to the Y atoms. This effect may be overestimated in our study, since we neglect the much smaller Pr-Cu and Pr-O hopping elements. However, this simplification can be justified, because we also neglect the interatomic Coulomb repulsion, which causes an increase of the hole energies in the CuO$_2$ planes close to a Pr ion and further reduces the hole concentration in these planes.

In general, our results reflect the well-known fact that the inclusion of correlations within the self-consistent Hartree-Fock approximation overestimates the rearrangement of charges due to doping. Hence, correlations suppress charge differences and spatial variations of the hole concentration. This is especially true for superstructures. The tight-binding calculations (resulting from setting $U = 0$) drive charge rearrangement to a lesser extent. They may be physically more appropriate, since they lead to a more localized behavior of the holes as would be expected from the treatment of strong correlations beyond the Hartree-Fock approximation. Note that the Hartree-Fock results for the superstructures can also be improved by taking into account the Madelung energy of the system, since a large hole concentration in a CuO$_2$ plane close to a Pr ion would then be energetically unfavorable.

It is known[17,18] that T_c correlates with the number of holes in the CuO$_2$ planes of $YBa_2Cu_3O_{7-y}$. This should also be the case in Pr-doped compounds. In a previous paper[9] we calculated the y dependence of the hole concentration in the conducting planes of $YBa_2Cu_3O_{7-y}$. Since the y-dependent superconducting transition temperatures of these compounds are well known from various experiments,[17,18] we are able to obtain a relation between T_c and the hole content in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

Here, we consider our previous CPA calculations only for $y \leq 0.4$ in order to avoid difficulties concerning the origin of the plateau behavior of T_c in $YBa_2Cu_3O_{7-y}$ for $0.4 < y < 0.5$. Thus, we are limited to larger hole concentrations corresponding to $T_c \geq 55$ K. We then find for $Y_{1-x}Pr_xBa_2Cu_3O_7$ that $T_c(x = 0.25) = 70$ K and $T_c(x = 0.35) = 58$ K, which agrees well with experimental results[12,19] and exhibits the above-mentioned behavior.

Concerning our tight-binding results for the a-axis superstructures we observe that there are four connected YBCO unit cells with $n_h = 1.3$ in the (24 Å)/(24 Å) superlattices. Hence, there is a region of four lattice constants along the a axis (which is comparable to the coherence length ξ_{ab}) with a hole concentration corresponding to a $T_c < 55$ K.[20] Experimentally, T$_c$ was determined[2] to be around 30 K in (24 Å)/(24 Å) superlattices. For the (12 Å)/(12 Å) superstructures the region with a hole concentration large enough to yield superconductivity consists of only one unit cell along the a axis. Therefore, one expects quasi-one-dimensional behavior and suppression of superconductivity for this compound, which indeed is found[2] to be nonsuperconducting.

Although the mechanism of superconductivity is still under debate[21] it might be interesting to see whether a simple BCS picture gives the observed trend for the transition temperature as a function of the Pr concentration x and the density of states at the Fermi level ε_F. For this we estimate T_c for the superconducting alloy $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_7$ via the BCS-type formula

$$k_B T_c(x) = 1.14\hbar\omega_0 \exp\frac{-1}{N_{\varepsilon_F}(x)V_{\text{eff}}} .$$

Here, the effective pairing interaction V_{eff} and the characteristic frequency ω_0 were computed from the experimental T_c at $x = 0.0$ ($T_c = 92$ K) and $x = 0.2$ ($T_c = 73.6$ K).[12] Note that this leads to reasonable characteristic frequencies $1.14\hbar\omega_0/k_B$ of 164 K (tight binding) and 193 K (Hartree-Fock), respectively. The obtained value for T_c (62 K, see Table III)—although quantitatively too large compared with experiment (50 K)—shows the observed decrease. The discrepancy between the theoretical and the experimental results might be due to the general overestimate of metallic behavior by our method.

TABLE III. Characteristic frequencies and superconducting transition temperatures T_c in the alloy $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_7$ for the tight-binding and Hartree-Fock calculations.

x	Tight binding	Hartree-Fock
$1.14\hbar\omega_o/k_B$ (K)	163.6	192.5
T_c (K)	62.9	62.2

Though we cannot rule out the possibility that pair breaking[19] also plays a role in the suppression of superconductivity in Pr-doped $YBa_2Cu_3O_7$, we conclude from our calculations that hole depletion in the CuO_2 planes can account for the behavior of T_c in these compounds. Furthermore, the assumption of a pair-breaking mechanism is not sufficient to explain the normal-state properties of $Y_{1-x}Pr_xBa_2Cu_3O_7$, such as the insulating behavior for large x.

Finally, an important difference concerning the theoretical description of a-axis- and c-axis[22–24]-oriented YBCO/PBCO superlattices should be pointed out. As the different layers in c-axis superlattices are coupled via the *nonmetallic* CuO chains, the determination of the hole distribution by minimization of the Madelung energy is justified in this case.[25] By contrast, *covalent* forces play a significant role in a-axis superlattices, where the inequivalent parts of the CuO_2 planes are directly linked to each other. Thus, in contrast to Wood's[25] argument for c-axis superlattices, the difference in the hole occupation numbers between different parts in the same symmetrized unit cell can even exceed the difference between neighboring layers. Therefore, an electronic theory for the charge distribution should be more appropriate in these systems.

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from 0.5 to 0.0). This is very similar to the behavior found in oxygen-deficient $YBa_2Cu_3O_{7-y}$ (Ref. 9) and confirms the Knight-shift results by Reyes *et al.* (Ref. 14).

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