

Turning a Nickelate Fermi Surface into a Cupratelike One through Heterostructuring

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Using the local density approximation and its combination with dynamical mean-field theory, we show that electronic correlations induce a single-sheet, cupratelike Fermi surface for hole-doped 1/1 LaNiO₃/LaAlO₃ heterostructures, even though both e_g orbitals contribute to it. The Ni $3d_{3z^2-1}$ orbital plays the role of the axial Cu $4s$ -like orbital in the cuprates. These two results indicate that “orbital engineering” by means of heterostructuring should be possible. As we also find strong antiferromagnetic correlations, the low-energy electronic and spin excitations in nickelate heterostructures resemble those of high-temperature cuprate superconductors.

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The discovery of high-temperature superconductivity (HTSC) in hole-doped cuprates [1] initiated the quest for finding related transition-metal oxides with comparable or even higher transition temperatures. In some systems, such as ruthenates [2] and cobaltates [3], superconductivity has been found. However, in these t_{2g} systems superconductivity is very different from that in cuprates, and transition temperatures (T_c 's) are considerably lower.

As it became possible to grow transition-metal oxides in heterostructures, this quest got a new direction: Novel effectively two-dimensional (2D) systems could be engineered. But which oxides, besides cuprates, are most promising for getting high T_c 's?

The basic band structure of the hole-doped cuprates is that of a single 2D Cu $3d_{x^2-y^2}$ -like band which is less than half filled (configuration d^{9-h}). In this situation, antiferromagnetic fluctuations prevail and are often believed to mediate the superconductivity. The Fermi surface (FS) from this $x^2 - y^2$ band has been observed in many overdoped cuprates and found to agree with the predictions of local density-functional (LDA) band theory.

Recently the following idea for arriving at a cupratelike situation in nickelates was presented [4]: Bulk LaNiO₃ (d^7) has one electron in two degenerate e_g bands, but sandwiching a LaNiO₃ layer between layers of an insulating oxide such as LaAlO₃ will confine the $3z^2 - 1$ orbital in the z direction and may remove this band from the Fermi level, thus leaving the electron in the $x^2 - y^2$ band. The possibility of finding bulk nickelates with an electronic structure analogous to that of cuprates was discarded a while ago [5], but heterostructures offer new perspectives.

Indeed, a major reconstruction of orbital states at oxide interfaces may recently have been observed [6], and this kind of phenomenon could lead to novel phases not present in the bulk. Extensive theoretical studies of mechanisms for orbital selection in correlated systems [7] have revealed the complexity of this problem, where details of the electronic structure and lattice distortions play decisive roles. It

is therefore crucial to examine nickelate heterostructures by means of state-of-the-art theoretical methods and find the optimal conditions for $x^2 - y^2$ orbital selection.

In this Letter we present results of electronic-structure calculations using the merger [8] of LDA band theory, which provides an *ab initio* description of the materials chemistry, and the dynamical mean-field theory (DMFT) [9], which includes electronic correlations. We find that the hopping between the $x^2 - y^2$ and $3z^2 - 1$ orbitals substantially reduces the effects of correlations in the $3z^2 - 1$ orbital. In this respect, e_g electrons behave very differently than the t_{2g} electrons, which have *no* interorbital hopping on a square lattice. Nevertheless, we do find that the correlations may sufficiently shift the bottom of the hybridizing e_g bands relatively to each other to yield a FS with only *one* sheet. This sheet has predominantly $x^2 - y^2$ character and a shape like in the cuprates with the highest $T_{c\max}$ (T_c at optimum hole doping) [10], but even more extreme. Moreover, stretching the in-plane lattice constants by suitable choice of substrate reduces the correlation strength needed to produce a single-sheet FS. Since we also find strong antiferromagnetic fluctuations, somewhat larger than in the cuprates, nickelate heterostructures hold the basic ingredients for high-temperature superconductivity.

Here we give results for the simplest, 1/1, superlattice LaNiO₃/LaAlO₃ = LaO-NiO₂-LaO-AlO₂ shown in the left-hand side of Fig. 1. For the in-plane lattice constant a we first took that of SrTiO₃, often used as substrate, whereby the Ni-O and Al-O distance in the x and y directions became $x_{\text{Ni-O}} = 1.95$ Å, not far from the value in pseudocubic LaNiO₃. The lattice constant c we took as the sum of those of pseudocubic LaNiO₃ and LaAlO₃, whereafter the position of apical O was relaxed within the LDA [11] to yield $z_{\text{Ni-O}} = 1.91$ Å, i.e., 2% smaller than $x_{\text{Ni-O}}$. Next, we expanded the LaNiO₃/LaAlO₃ heterostructure in the x and y directions by 3%, as might be achieved by growing LaNiO₃/LaAlO₃ on a PrScO₃ substrate, to yield

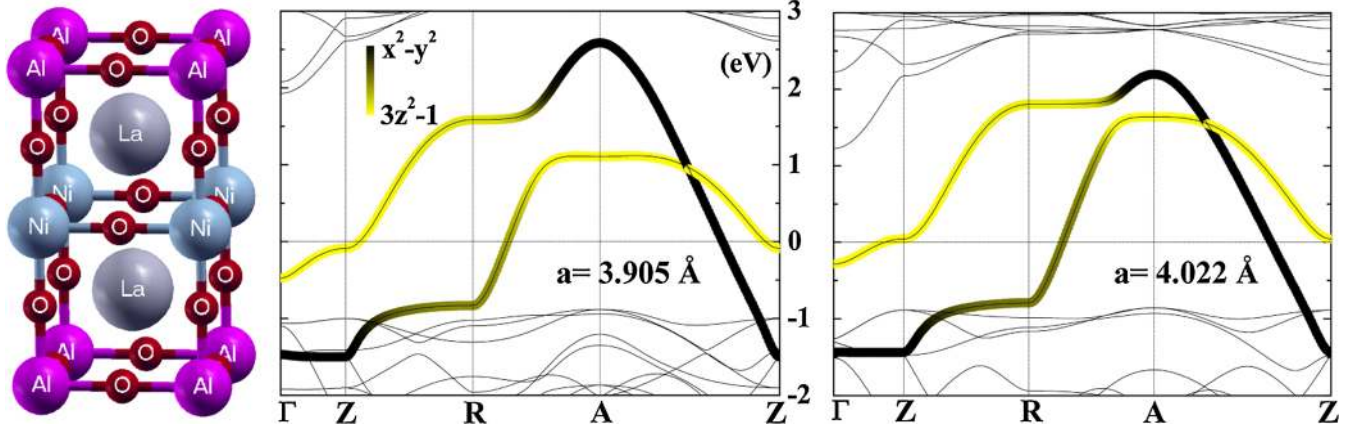


FIG. 1 (color online). The 1/1 LaNiO₃/LaAlO₃ heterostructure (left) and its LDA (NMTO) band structures without (center) and with (right) strain. The Bloch vector is along the lines $\Gamma(0, 0, 0) - Z(0, 0, \frac{\pi}{c}) - R(0, \frac{\pi}{a}, \frac{\pi}{c}) - A(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{c}) - Z(0, 0, \frac{\pi}{c})$. The shading gives the $x^2 - y^2$ vs $3z^2 - 1e_g$ Wannier-function character.

$x_{\text{Ni-O}} = 2.01 \text{ \AA}$. With the concomitant 6% contraction in the z direction, relaxation of the apical-oxygen position within the LDA finally lead to $z_{\text{Ni-O}} = 1.81 \text{ \AA}$.

Figure 1 shows the LDA energy bands for the two differently strained heterostructures in a 5-eV region around the d^7 Fermi level ($\equiv 0$). The two solid bands are the 1/4 full Ni-O $pd\sigma$ antibonding e_g bands, which are pushed up above the less antibonding Ni-O $pd\pi$ t_{2g} bands (thin bands) lying below -1 eV and well above the Ni-O, Al-O, and La-O bonding bands below the frame of the figure. The antibonding Al-O and La-O bands (thin bands above 1–2 eV) lie, respectively, 9 and ~ 5 eV above their bonding counterparts, and as a result there is a comfortable 2–3 eV gap above the top of the antibonding t_{2g} bands in which the two antibonding e_g bands reside.

The shading (coloring) of the e_g bands gives the relative $x^2 - y^2$ and $3z^2 - 1$ characters in the Wannier-function representation of these two bands, as calculated with the N th-order muffin-tin-orbital (NMTO) method and $N = 2$ [12]. We see that in the “nodal” $k_x = k_y$ plane containing the ΓZ and AZ lines, the $x^2 - y^2$ ($|m| = 2$) and $3z^2 - 1$ ($m = 0$) Wannier orbitals cannot mix [13]. The bottoms of both bands are along ΓZ , i.e., for $k_x = k_y = 0$. That of the $x^2 - y^2$ band is at -1.5 eV and does not disperse with k_z , while that of the $3z^2 - 1$ band is at -0.5 eV at Γ and disperses upwards to -0.1 eV at Z . The bottom of the $3z^2 - 1$ band is thus $1 \text{ eV} \approx 1/4e_g$ bandwidth above that of the $x^2 - y^2$ band. Straining by 3% is seen to shift the bottom of the $3z^2 - 1$ band up by further 0.2 eV. The LDA FS thus has *two* sheets, and reducing it to one would require moving the $3z^2 - 1$ band above the $x^2 - y^2$ band at Γ by an additional 0.5 eV for the unstrained and by an additional 0.3 eV for the strained superlattice.

The fact that the $x^2 - y^2$ Wannier orbital is more populated than $3z^2 - 1$ (the ratio is 70/30 for the unstrained superlattice) is mainly due to the *confinement* in the z direction. Consider for simplicity the dispersions in the $k_x = \pm k_y \equiv k$ planes where the $3z^2 - 1$ and $x^2 - y^2$ orbi-

tals do not hybridize: In cubic, bulk LaNiO₃, $\varepsilon_{3z^2-1}(k, k_z) \approx -\cos ak - 2\cos ak_z$, with respect to the center of the e_g band and in units of $|t_{dd\sigma}|$, while $\varepsilon_{x^2-y^2}(k, k_z) \approx -3\cos ak$ independently of k_z because $t_{dd\delta}$ is negligible. This means that both bands extend from $-3|t_{dd\sigma}|$ at $(0, 0, 0)$ to $+3|t_{dd\sigma}|$ at $(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$ in the bulk. Substituting now every second LaNiO₃ layer by an “insulating” LaAlO₃ layer forces the Bloch waves to have nodes approximately at the AlO₂ planes, so that only waves with $k_z \gtrsim \frac{\pi}{2a} \sim \frac{\pi}{c}$ are allowed. As a consequence, the bottom of the $3z^2 - 1$ band is pushed up by $\sim 2|t_{dd\sigma}|$, i.e., by $\sim 1/3$ the e_g bandwidth. The exact position of the nodes, and hence the upwards shift of the $3z^2 - 1$ band, depends on the scattering properties of the insulating layer. This suggests that the band structure can be tuned by choice of the insulating layer.

A further factor influencing the orbital separation is the tetragonal Jahn-Teller (JT) distortion of the nickel-centered oxygen octahedron. Since the $x^2 - y^2$ and $3z^2 - 1$ Wannier orbitals antibond with oxygen, flattening the octahedron ($z_{\text{Ni-O}} < x_{\text{Ni-O}}$) moves the energy of the former orbital down, and that of the latter up. However, this crystal-field splitting is little effective in achieving orbital separation for configuration d^{7-h} because the e_g Bloch sums at the *bottom* of the cubic band at $(0, 0, 0)$ have *no* oxygen character, so only energies higher up in the e_g band are effected. For JT flattening to be effective, confinement is therefore a prerequisite. This is clearly seen from the LDA bands for the 3% strained superlattice on the right-hand side of Fig. 1: Whereas the strain moves the top of the $x^2 - y^2$ band down and that of the $3z^2 - 1$ band up, the bottom of the $x^2 - y^2$ band is *not* affected, and that of the $3z^2 - 1$ band is shifted up only because it has antibonding oxygen character corresponding to $k_z \sim \frac{\pi}{2a}$ rather than to $k_z = 0$.

For the undoped (d^9) cuprates, the LDA band structures are roughly similar to this, but the antibonding $3z^2 - 1$ band is now full and lies in the region of the t_{2g} bands.

Filling this band has annihilated the $pd\sigma$ bond to apical oxygen and thereby caused $z_{\text{Cu-O}}$ to increase well beyond $x_{\text{Cu-O}}$, whereby the antibonding pushup of the $3z^2 - 1$ band has been lost. The half full $pd\sigma$ antibonding $x^2 - y^2$ band lies a bit lower with respect to the O and cation bands than in the nickelates because the position of the $3d$ level in Cu is lower than in Ni. However, the shape of this cuprate conduction band near half filling is not unlike that of the lowest e_g band in the nickelate heterostructures, in particular, for the cuprates with the highest $T_{c\text{max}}$. Specifically, LDA calculations for a large number of cuprate families have revealed that, whereas the dispersion along the nodal direction (ZA) is always the same, the energy of the saddle points at $(\frac{\pi}{a}, 0)$ and $(0, \frac{\pi}{a})$, i.e., at R , depends on the material and is lower for materials with higher $T_{c\text{max}}$ [10]. The reason for this correlation is not understood, but the reason for the change of band shape is clearly that the $x^2 - y^2$ orbital is hybridizing with a material-dependent *axial* ($|m| = 0$) orbital whose energy lies ~ 10 eV above the Fermi level, but falls for cuprates with increasing $T_{c\text{max}}$. This axial orbital is essentially the antibonding linear combination of Cu $4s$ and apical O $2p_z$, so that its energy falls if their interaction decreases, e.g., by increasing $z_{\text{Cu-O}}$. Concomitant with this change of band shape is a concentration of the conduction-band Wannier function onto the CuO_2 layer, away from the perpendicular direction. Instead of using the energy of the axial orbital as band-shape parameter, one uses [10] a dimensionless parameter, r , which for materials with low $T_{c\text{max}}$ (< 50 K) becomes the ratio t'/t of the second- to the first-nearest-neighbor hopping integral. The cuprates with the highest $T_{c\text{max}}$ (~ 140 K) have $r \sim 0.4$. If one could lower the energy of the axial orbital right down to the Fermi level, r would have the value $1/2$.

This axial-orbital model also applies to the e_g bands of nickelate heterostructures, but due to the short distance to apical oxygen, the axial orbital is now essentially the antibonding linear combination of Ni $3d_{3z^2-1}$ and apical O $2p_z$. Its energy is that of the $3z^2 - 1$ band at Γ , and since this is *below* ϵ_F for the LDA bands shown in Fig. 1, they have $r > 1/2$. Engineering these heterostructures should presumably first aim at reducing r towards that (~ 0.4) of the cuprates with the highest $T_{c\text{max}}$, i.e., at moving the energy of the second band at Γ well above ϵ_F . This requires

increasing the interaction between Ni $3d_{3z^2-1}$ and apical O $2p_z$, e.g., by reducing $z_{\text{Ni-O}}$. As we shall see, this is helped by the electronic correlations, but does not necessarily lead to HTSC, because although the same value of r gives the same band shape for nickelates and cuprates, their conduction-band Wannier orbitals are not identical.

Having studied the materials dependence of the LDA band structures, and having found that the conduction bands in the paramagnetic phase are well separated from all other bands, we can study the effects of Coulomb correlations in the nickelate heterostructures using the two-band Hubbard Hamiltonian:

$$\hat{H} = \sum_{\mathbf{k}, mm', \sigma} H_{mm'}^{\mathbf{k}} \hat{c}_{m\sigma}^{\dagger} \hat{c}_{m'\sigma}^{\mathbf{k}} + U \sum_{i,m} \hat{n}_{m1}^i \hat{n}_{m1}^i + \sum_{i, mm', \sigma \sigma'} (V - \delta_{\sigma \sigma'} J) \hat{n}_{m\sigma}^i \hat{n}_{m' \neq m \sigma'}^i.$$

Here, the on-site Coulomb terms, namely, the intraorbital and interorbital Coulomb repulsions, U and $V = U - 2J$, as well as Hund's exchange J , have been added to the LDA e_g Wannier-function Hamiltonian, $H_{mm'}^{\mathbf{k}}$. This Hubbard Hamiltonian we solve for $1/4$ filling in the single-site DMFT approximation for the paramagnetic phase and at a temperature so high (1160 K = 0.1 eV/ k_B) that we can afford to use the Hirsch-Fye quantum Monte Carlo method.

Our DMFT calculations confirm the common expectation that, for a metallic multiband system, the main effect of the Coulomb correlations is to enhance the splitting between the subbands such as to reduce the density of states at the Fermi level. Specifically, for the undoped superlattice with $J = 0.7$ eV and U increasing, we find that the bottom of the $3z^2 - 1$ band is driven up and passes the Fermi level when U exceeds 6.4 eV for the unstrained and 5.7 eV for the strained structure. Hereafter the FS has only one sheet, a large $(\frac{\pi}{a}, \frac{\pi}{a})$ -centered hole cylinder whose shape can be seen from Fig. 2 to be similar to that found in the cuprates with the highest $T_{c\text{max}}$, but even more extreme. It is, of course, possible that the strong nesting of this FS makes it unstable with respect to spin- or/and charge-density waves with $q_x \sim \frac{\pi}{2a}$ and $q_y \sim \frac{\pi}{2a}$, similar to what has been found in cuprates. At the point where the second FS sheet disappears, $r = 1/2$, and the ratio between the $x^2 - y^2$ and $3z^2 - 1$ populations has increased to $80/20$ for the unstrained—and beyond that for the

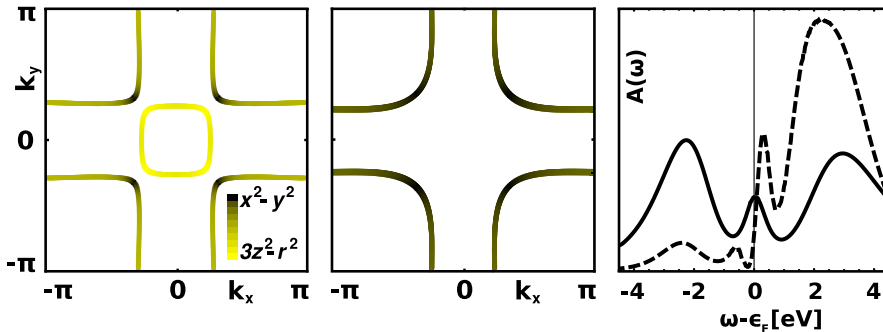


FIG. 2 (color online). Cross section of the FS with the $k_z = 0$ plane for the unstrained $1/1$ heterostructure. Left: LDA. Middle: LDA + DMFT ($U = 6.7$ eV). Right: LDA + DMFT k -integrated spectral functions (in arbitrary units) projected onto the $x^2 - y^2$ (full) and $3z^2 - 1$ (dashed) Wannier functions.

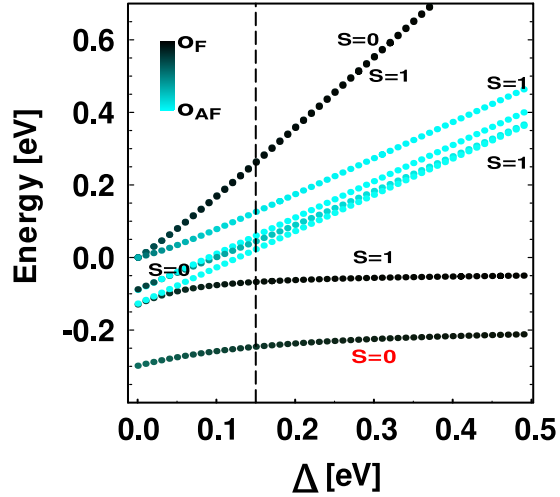


FIG. 3 (color online). Energy levels for the unstrained two-site model with $U = 6.4$ eV as a function of the splitting Δ between the energies of the $3z^2 - 1$ and $x^2 - y^2$ Wannier orbitals. The LDA value of Δ is indicated by the dashed line. O_F (O_{AF}) denotes a configuration with the same (different) orbital(s) on the two sites.

strained—superlattice. For slightly larger U , the upper quasiparticle band still exists above the Fermi level. This may be seen from the $3z^2 - 1$ projected \mathbf{k} -integrated spectral function in the right-hand side of Fig. 2. Reasonable changes of J slightly influence details of the Hubbard subbands, but not the physics of the transition.

When U reaches 7.4 eV for the unstrained and 6.5 eV for the strained superlattice, the lower quasiparticle band undergoes a Mott transition, at which point the peak seen at the Fermi level in the right-hand side of Fig. 2 disappears. For comparison, a half full cuprate band undergoes a Mott transition in DMFT for a critical value of U which increases with r and takes the value 4.5 eV for $r = 0.4$ [14]. This behavior for the cuprates is thus in line with what we find for the nickelate heterostructures where r_{LDA} (unstrained) $>$ r_{LDA} (strained) $\sim 1/2$, and this supports our hope that the nickelates can be engineered such that, like in the cuprates, hole doping will suppress the Mott transition and produce superconductivity. For nickelates there is even the possibility of engineering the e_g bands such that the real value of U falls between the one needed to reduce the FS to a single sheet and the one needed to eliminate this sheet by a Mott transition. If this can be achieved, superconductivity in the nickelates may occur even without doping. This is a remarkable result.

Next, we need to estimate the strength of antiferromagnetic correlations, which are believed to play a central role in the physics of the cuprates. Since our LDA + DMFT calculations would be prohibitively expensive for the study of low temperature magnetic properties, we merely diagonalized the two-site version of the Hubbard Hamiltonian obtained by Fourier transformation of $H_{mm'}^{\mathbf{k}}$ and truncation to a diatomic molecule directed along x . The energy levels

are presented in Fig. 3 as functions of the difference Δ between the energies of the $3z^2 - 1$ and $x^2 - y^2$ Wannier orbitals. The ground state is always a spin singlet. Increasing Δ from 0 to ∞ leads to demixing such that the orbital configuration changes from $3x^2 - 1$ to $x^2 - y^2$. For the LDA value, the orbital character is already close to $x^2 - y^2$. From the distance between the singlet ground state and the triplet first excited state, we estimate the magnitude of the antiferromagnetic coupling constant to be $J_{\text{AFM}} \sim 0.2$ eV, i.e., somewhat higher than in cuprates.

Altogether, our analysis of the 1/1 $\text{LaNiO}_3/\text{LaAlO}_3$ system shows that heterostructuring of d^7 nickelates is promising because their physics contains the main ingredients of high-temperature superconductivity. In particular, we find that electronic correlations reduce the FS to a *single* sheet whose shape is similar to the one in the hole-doped cuprates with the highest $T_{c\text{max}}$. This sheet has not only $x^2 - y^2$, but also $3z^2 - r^2$ character, and this gives a new twist to the intensive discussion of orbital-selective Mott-Hubbard transitions. Substrate-induced strain and/or use of insulating layers different than LaAlO_3 may tune the FS shape and may enable superconductivity without doping.

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