Turning a nickelate Fermi surface into a cuprate-like 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, cuprate-like Fermi surface for hole-doped 1/1 LaNiO3/LaAlO3 heterostructures, even though both ε_g orbitals contribute to it. The Ni 3d_{x^2−y^2} 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}−ε_g band which is less than half-filled (configuration d^8−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 density-functional (LDA) band theory.

Recently the following idea for arriving at a cuprate-like situation in nickelates was presented [4]: Bulk LaNiO3 (d^8) has one electron in two degenerate ε_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 density-functional (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, ε_g electrons behave very differently than the t_{2g} electrons, which have no inter-orbital hopping on a square lattice. Nevertheless, we do find that the correlations may sufficiently shift the bottom of the hybridizing ε_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_{Ni-O} = 1.95 Å, not far from the value in pseudo-cubic LaNiO3. The lattice constant c we took as the sum of those of pseudo-cubic LaNiO3 and LaAlO3, whereafter the position of apical O was relaxed within the LDA to yield: z_{Ni-O} = 1.91 Å, i.e. 2% smaller than x_{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 z_{Ni-O} = 2.01 Å. With the concomitant 6% contraction in the z-direction, relaxation of the
apical-oxygen position within the LDA finally lead to: $z_{\text{Ni-O}} = 1.81 \text{ Å}$. 

Fig. 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 $-1$ eV) lie respectively 9 and $\sim 5$ 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 Nth-order muffin-tin-orbital (NMTO) method and $N=2$ [12]. We see that in the "nodal" $k_z = k_y$ plane containing the $\Gamma Z$ and $A Z$ 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 $\Gamma Z$, i.e. for $k_z = k_y = 0$. 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 $\Gamma$ and disperses upwards to $-0.1$ eV at $Z$. The bottom of the $3z^2 - 1$ band is thus $1$ eV $\approx 1/4 e_g$ 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 $\Gamma$ by an additional $0.5$ eV for the unstrained and by an additional $0.3$ eV for the strained superlattice.

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 $k_z = k_y = k$ planes where the $3z^2 - 1$ and $x^2 - y^2$ orbitals do not hybridize: In cubic, bulk LaNiO$_3$, $\varepsilon_{3z^2-1}(k,k_z) \approx -3 \cos a k_z$ independently of $k_z$ because $t_{dd\sigma}$ 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 LaNiO$_3$ layer by an "insulating" LaAlO$_3$ layer, forces the Bloch waves to have nodes approximately at the AlO$_2$ planes, so that only waves with $k_z \approx \frac{\pi}{a} \sim \frac{\pi}{2}$ 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 $d^7-\pi$ 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 affected. 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 $k_z \approx \frac{\pi}{2}$ rather than to $k_z = 0$.

For the undoped ($d^9$) cuprates, the LDA bandstructures 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 push-up 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

![FIG. 1: The 1/1 LaNiO$_3$/LaAlO$_3$ heterostructure (left) and its LDA (NMTO) bandstructures without (center) and with (right) strain. The Bloch vector is along the lines $\Gamma (0,0,0) \rightarrow Z (0,0,\frac{\pi}{a}) \rightarrow R (\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}) \rightarrow A (\frac{\pi}{a}, \frac{\pi}{a}, 0) \rightarrow Z (0,0,\frac{\pi}{a})$. The shading gives the $x^2 - y^2$ vs $3z^2 - 1$ $e_g$ Wannier-function character.](image-url)
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 $T_c$ max. Specifically, LDA calculations for a large number of cuprate families have revealed that whereas the dispersion along the nodal direction (2A) is always the same, the energy of the saddlepoints at $(\pi, 0)$ and $(0, \pi)$, i.e. at R, depends on the material and is lower for materials with higher $T_c$ max. 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 $\sim 10$ eV above the Fermi level, but falls for cuprates with increasing $T_c$ 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 $z_{Cu\text{-O}}$. 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 a dimensionless parameter, $r$, which for materials with low $T_c$ max ($< 50$K) becomes the ratio $t'/t$ of the 2nd to the 1st-nearest-neighbor hopping integral. The cuprates with the highest $T_c$ max ($\sim 140$ 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 $\Gamma$, and since this is below $\varepsilon_F$ 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 ($\sim 0.4$) of the cuprates with the highest $T_c$ max, i.e. at moving the energy of the second band at $\Gamma$ well above $\varepsilon_F$. This requires increasing the interaction between Ni 3d_{3z^2-1} and apical O 2p_z, e.g. by reducing $z_{Ni\text{-O}}$. 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:

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

Here, the on-site Coulomb terms, namely the intra and inter-orbital Coulomb repulsions, $U$ and $V = U - 2J$, as well as the Hund’s exchange, $J$, have been added to the LDA $e_g$ Wannier-function Hamiltonian, $H_{mm'}$. 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 using the Hirsch-Fye Quantum Monte Carlo method.

![FIG. 2: Cross-section of the LDA (left) and LDA+DMFT (U = 6.7 eV) FS with the k_z=0 plane for the unstrained 1/1 heterostructure. e_g-orbital characters are coded as in Fig. 1.](image)

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. 1 to be similar to that found in the cuprates with the highest $T_c$ 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 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 for the strained – superlattice. Reasonable changes of $J$ slightly influence details of the Hubbard subbands, but not the physics of the transition.

The remaining half-full band undergoes a Mott-transition when $U$ exceeds 7.4 eV for the unstrained and 6.5 eV for the strained superlattice. 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 $r_{\text{LDA}}$ (unstrained) > $r_{\text{LDA}}$ (strained) ~ 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.

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

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 $H_{nm}^{kr}$, and truncation to a diatomic molecule directed along $x$. The energy levels are presented in Fig. 3 as functions of the the difference, $\Delta$, between the energies of the $3z^2 - 1$ and $x^2 - y^2$ Wannier orbitals. The ground state is always a spin singlet. Increasing $\Delta$ from 0 to $\infty$ 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 $J_{AF} \sim 0.2$ eV, i.e. somewhat higher than in cuprates.

Altogether, our analysis of the 1/1 LaNiO$_3$/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 $T_{c,max}$. 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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[1] J.G. Bednorz and K.A. Müller, Z. Phys B 64, 189 (1986).
[2] Y. Maeno et al., Nature 372, 532 (1994).
[3] K. Takada et al., Nature 422, 53 (2003).
[4] J. Chaloupka and G. Khaliullin, Phys. Rev. Lett. 100, 016404 (2008).
[5] N. Anisimov, D. Bukhvalov, and T.M. Rice, Phys. Rev. B 59, 7901 (1999).
[6] M. Katsnelson, Phys. Rev. B 79, 085127 (2007).
[7] See, e.g., V.I. Anisimov et al., Euro. Phys. J. B 25, 191 (2002); A. Koga et al., Phys. Rev. Lett. 92, 216402 (2004); R. Arita and K. Held, Phys. Rev. B 72, 201102(R) (2005); A.I. Poteryaev et al., Phys. Rev. B 76, 085127 (2007).
[8] V.I. Anisimov et al., J. Phys.: Condens. Matter 9, 7359 (1997); A.I. Lichtenstein and M.I. Katsnelson, Phys. Rev. B 57, 6884 (1998); G. Kotliar et al., Rev. Mod. Phys. 78, 865 (2006).
[9] W. Metzner and D. Vollhardt, Phys. Rev. Lett. 62, 324 (1989); A. Georges et al., Rev. Mod. Phys. 68, 13 (1996).
[10] E. Pavarini et al., Phys. Rev. Lett. 87, 047003 (2001).
[11] G. Kresse, J. Furumulter, Software VASP, Vienna (1999); P.E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[12] O.K. Andersen and T. Saha-Dasgupta, Phys. Rev. B 62, R16219 (2000).
[13] O.K. Andersen et al., J. Phys. Chem. Solids 56, 1573 (1995).
[14] T. Saha-Dasgupta (unpublished); see also H. Das and T. Saha-Dasgupta, Phys. Rev. B (accepted).