Spin, Orbital, and Charge Order at the Interface between Correlated Oxides

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The collective behavior of correlated electrons in the VO_2 interface layer of the $LaVO_3/SrTiO_3$ heterostructure is studied within a quarter-filled t_{2g}-orbital Hubbard model on a square lattice. We argue that the ground state is ferromagnetic, driven by the double-exchange mechanism, and is orbitally and charge ordered due to a confined geometry and electron correlations. The orbital and charge density waves open gaps on the entire Fermi surfaces of all orbitals. The theory explains the observed insulating behavior of the *p*-type interface between $LaVO_3$ and $SrTiO_3$.

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The recent progress in manufacturing and experimental studies of heterostructures and superlattices based on the transition metal oxides has lead to the discoveries of a number of novel physical phenomena and new electronic states emerging at the interfaces [1–9]. The formation of a high-mobility electron gas [4], the quantum Hall effect [5], and, remarkably enough, even a superconducting state [6] have been observed at the interfaces between insulating oxides. At the interface between nominally nonmagnetic oxides, magnetic effects have also been detected [7]. The physical properties of interfaces may largely differ from and can even be orthogonal to those of bulk materials, due to an ''electronic reconstruction'' phenomenon [10].

In correlated oxide heterostructures, electronic reconstruction involves not only charge but also spin [8] and, in particular, the orbital degrees of freedom [9,11,12] since electronic orbitals are highly sensitive to the local environment. Such a multifaceted response of correlated electrons gives rise to the rich interface physics that may form a basis for future device applications.

The recent work of Ref. [13] added a new puzzle into this field. Two types of interfaces between a Mott insulator $LaVO_3$ and a band insulator $SrTiO_3$ have been investigated: (i) the $VO_2/LaO/TiO_2/SrO$ interface with *n*-type polar discontinuity and (ii) the $LaO/VO_2/SrO/TiO_2$ with a *p*-type one (formed by inserting a ''metallic'' $SrVO_3$ unit into the *n*-type interface). In bulk compounds, the VO_2 (LaO) layers have a $-e$ ($+e$) charge per unit cell, while TiO_2 and SrO layers are neutral. In such systems, a polar discontinuity triggers the doping of an interface layer to resolve the polar catastrophe [14]: In the *n*-type interface the TiO_2 layer receives a $-e/2$ charge, while in the *p*-type interface a $-e/2$ charge is taken away from the VO_2 layer. This leads to a formal valence state $d^{0.5}$ of Ti and $d^{1.5}$ of V at the *n*- and *p*-type interface layers, respectively. The resistivity measurements have shown that the *n*-type interface is metallic and the *p*-type interface is insulating. The metallic character of the TiO_2 interface layer is not surprising and confirms existing theoretical results [10]. However, an insulating behavior of the hole-doped VO_2 interface layer is at odds with expectations and is striking, given that $SrVO_3$ is a good metal and already 18% Sr doping is sufficient to convert bulk $LaVO_3$ into a metal, too [15]. In this Letter, we present a theory resolving this puzzle. In short, the contrasting behavior of TiO_2 and VO_2 interfaces originates from their different spin and orbital structure. Indeed, while a TiO_2 layer with Ti^{3+}/Ti^{4+} states represents a diluted quantum $S = 1/2$ system (like high-T_c cuprates), a VO_2 interface layer is made of V^{3+} $S = 1$ and V^{4+} $S = 1/2$ states—a canonical background for the double-exchange (DE) physics. Once spins of the VO_2 layer are polarized by the DE mechanism, the system is effectively *half-filled*, and hence collective orbital and charge instabilities are triggered at the interface. We argue that these cooperative orderings of correlated electrons are responsible for the insulating character of the *p*-type interface.

The model.—We describe the physics of the hole-doped VO_2 layer within a multiorbital Hubbard model for *d* electrons [16] on a square lattice:

$$H = -\sum_{i,j}\sum_{\alpha,\sigma} t_{ij,\alpha} d^{\dagger}_{i\alpha\sigma} d_{j\alpha\sigma} + U\sum_{i,\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \sum_{i,\alpha<\beta}\left[U' - 2J_{\mathrm{H}}\left(\vec{s}_{i\alpha}\vec{s}_{i\beta} + \frac{1}{4}\right)\right] n_{i\alpha} n_{i\beta} + V\sum_{\langle ij\rangle} n_i n_j. \quad (1)$$

The threefold degenerate t_{2g} states d_{yz}, d_{xz}, and d_{xy} are labeled by orbital index $\alpha = 1$, 2, and 3, respectively. The $\vec{s}_{i\alpha}$ and $n_{i\alpha} = n_{i\alpha\uparrow} + n_{i\alpha\downarrow}$ correspond to the spin and density, respectively, of electrons in the α orbital. The first term in H describes an electron hopping between the nearest-neighbor (NN) sites [17] and is diagonal in orbital space. The peculiarity of a t_{2g} system on a planar geometry is that the orbitals d_{yz} and d_{xz} become one-dimensional (1D). They have a finite hopping amplitude only along the one particular direction $t_{ij,1(2)} = t$ for $ij \parallel x(y)$ and zero otherwise [see Fig. 1(a)], while the d_{xy} orbital still forms a two-dimensional (2D) band: $t_{ij,3} = t$. In momentum space, the hopping term reads as $\sum_{\mathbf{k}\alpha\sigma}\epsilon_{\mathbf{k}\alpha} d^{\dagger}_{\mathbf{k}\alpha\sigma} d_{\mathbf{k}\alpha\sigma}$, where $\epsilon_{\mathbf{k}1(2)} = -2t\cos k_{x(y)}$ and $\epsilon_{\mathbf{k}3} = -2t(\cos k_x + \cos k_y)$. The

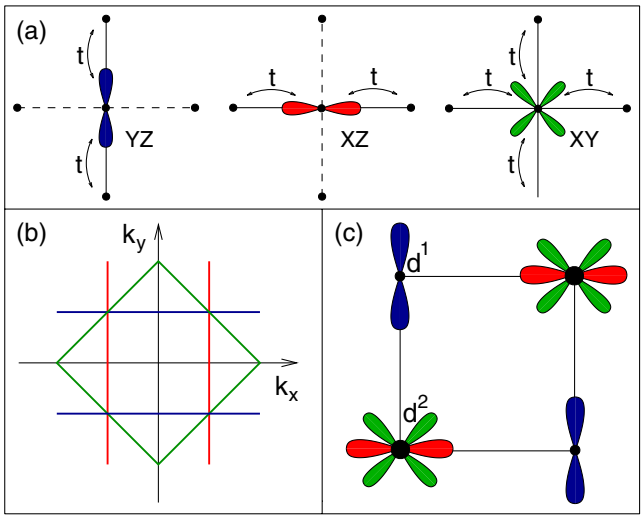

FIG. 1 (color online). (a) The hopping amplitudes of t_{2g} electrons on a square lattice. (b) The Fermi surfaces for d_{yz} (horizontal lines), d_{xz} (vertical lines), and d_{xy} (square) electrons in the ferromagnetic state. (c) A sketch of the orbital and charge-ordered state for $U > V \gg t$. In a symmetry broken state, the system is insulating at any values of U and V.

interaction part of H consists of on-site intra- and interorbital Coulomb repulsions U and U', respectively. The latter term is further split by the Hund's coupling $J_{\rm H}$ into an interorbital spin triplet ($U' - J_{\rm H}$) and singlets ($U' + J_{\rm H}$), such that the $S = 1$ state with electrons residing on different orbitals is favored. It is this $2J_{\rm H}$ splitting between the high- or low-spin states that promotes a global ferromagnetic (FM) state by virtue of the DE mechanism in the present $V^{3+/4+}$ mixed-valent system. We have also included NN repulsion V, which is relevant for charge ordering [19]. We consider quarter-filled t_{2g} bands ($d^{1.5}$ configuration) to model an interface VO_2 layer with formal valency $V^{3.5+}$.

Ferromagnetism.—The large on-site repulsions U and U' suppress the high energy charge fluctuations $(d^2, d^1) \leftrightarrow (d^3, d^0)$, and only the low energy ones $(d^2, d^1) \leftrightarrow (d^1, d^2)$ are allowed. In the paramagnetic and orbital liquid state, all three bands are quarter-filled, and there are no apparent Fermi surface (nesting) related instabilities. However, there is a potential instability towards FM ordering because the Hund's coupling favors the high-spin state of a d^2 configuration and, together with the hopping term, induces the DE interaction. The critical value of Hund's coupling at which FM instability appears is estimated from a vanishing determinant of a two-component spin susceptibility for 1D and 2D bands:

$$\begin{vmatrix} 1 & -4J_{\rm H}\bar{\chi} \\ -2J_{\rm H}\chi & 1 - 2J_{\rm H}\chi \end{vmatrix} = 0, \qquad (2)$$

where $\chi = \rho(0)/2$ and $\bar{\chi} = \bar{\rho}(0)/2$ are uniform static magnetic susceptibilities for one- and two-dimensional bands, respectively, and $\rho(0)$ and $\bar{\rho}(0)$ are the corresponding density of states at the Fermi level. For an estimate we set $\rho(0) \simeq 1/W_1$ and $\bar{\rho}(0) \simeq 1/W_2$, where $W_1 = 4t$ and $W_2 = 8t$ are bandwidths of 1D and 2D bands, respectively. This gives a FM instability for $J_{\rm H} > 2(\sqrt{5} - 1)t \simeq 2.5t$. This inequality is well satisfied for the actual parameters $J_{\rm H} \simeq 0.7$ eV and $t \simeq 0.2$ eV [18,20]. We thus deal with interacting spinless fermions with orbital flavors only. In this case the Hamiltonian (1) reduces to

$$H = -\sum_{i,j,\alpha} t_{ij,\alpha} d^\dagger_{i\alpha} d_{j\alpha} + \tilde{U} \sum_{i,\alpha<\beta} n_{i\alpha} n_{i\beta} + V \sum_{\langle ij \rangle} n_i n_j, \qquad (3)$$

where $\tilde{U} = U' - J_{\rm H} = U - 3J_{\rm H}$ (using the well-known relation $U' = U - 2J_{\rm H}$) is an effective Hubbard repulsion in the FM state. Optical data in cubic vanadates [21] suggest the high-spin transition at $\tilde{U} \sim 2$ eV $\sim 10t$, but we will consider $\tilde{U}$ as a free parameter and denote it below simply as U. Each orbital band is half-filled, and the corresponding Fermi surfaces are fully nested; see Fig. 1(b). We discuss now the orbital and charge density waves (ODW and CDW, respectively) triggered by such a nesting.

Orbital and charge density waves.—Let us consider the instabilities towards the ODW and CDW with a modulation wave vector $\mathbf{Q} = (\pi, \pi)$. We introduce the orbital order parameters τ_α as $\langle n_{i\alpha} \rangle = n/3 + e^{i\mathbf{Q}\mathbf{R}_i}\tau_\alpha$, where $n = 3/2$ is an average electron density. The corresponding CDW modulation is given by $\sum_\alpha \langle n_{i\alpha} \rangle - n = e^{i\mathbf{Q}\mathbf{R}_i}\delta$, where $\delta = \sum_\alpha \tau_\alpha$. The order parameters are calculated within a mean-field approach. We consider a wide range of U and V, in order to see how the ODW/CDW orderings evolve from a weak-coupling regime to the limit of strong interactions $U \gg t$. While care must be taken in calculating excitation spectra, the mean-field method gives a reliable picture of the nature of the ordered phases and of the zero temperature properties of interest here [22] and, hence, is widely used to study similar problems (including multiorbital physics at interfaces [10]) even in a regime of strong correlations [23]. The ground-state energy per site is expressed in terms of order parameters:

$$E = -\frac{1}{2}\sum_{\mathbf{k}\alpha} E_{\mathbf{k}\alpha} + \frac{1}{2}U\sum_\alpha \tau_\alpha^2 + \frac{1}{2}(U - zV)\delta^2, \qquad (4)$$

where $E_{\mathbf{k}\alpha} = \sqrt{\epsilon^2_{\mathbf{k}\alpha} + \Delta^2_\alpha}$, with $\Delta_\alpha = U\tau_\alpha - (U - zV)\delta$, and $z = 4$ is a number of NNs. (The constant contribution $E_0 = \frac{1}{3}Un^2 + \frac{1}{2}zVn^2$ has been dropped.) Physically, $|\Delta_\alpha|$ represent band gaps. The minimization of the energy E gives the coupled integral equations $\tau_\alpha = \sum_{\mathbf{k}} \Delta_\alpha / E_{\mathbf{k}\alpha}$ solved numerically. For large U and V, one finds $\tau_3 \lesssim \tau_2 = -\tau_1 \simeq 0.5$. A sketch of a fully saturated version of the corresponding orbital and charge patterns is shown in Fig. 1(c). It consists of a staggered order of d_{yz}/d_{xz} orbitals, with the d_{xy} orbital being predominantly occupied at one of the sublattices. This results in a checkerboard charge-ordered pattern of d^2/d^1 states.

Shown in Fig. 2 are the ODW and CDW order parameters as a function of V at $U = 10$ (hereafter, the energy unit

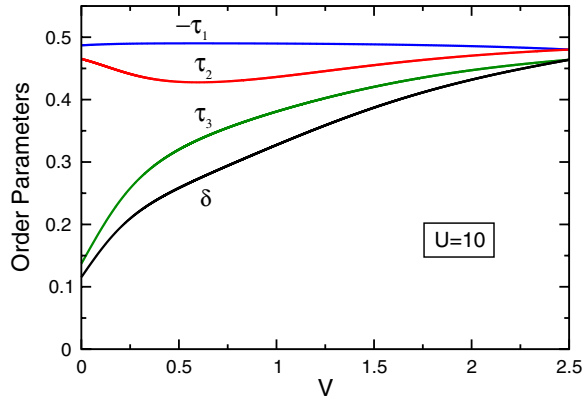

FIG. 2 (color online). Order parameters of the orbital ($\tau_{1,2,3}$ for $d_{yz,xz,xy}$ bands, respectively) and charge (δ) density waves vs nearest-neighbor repulsion V at large U.

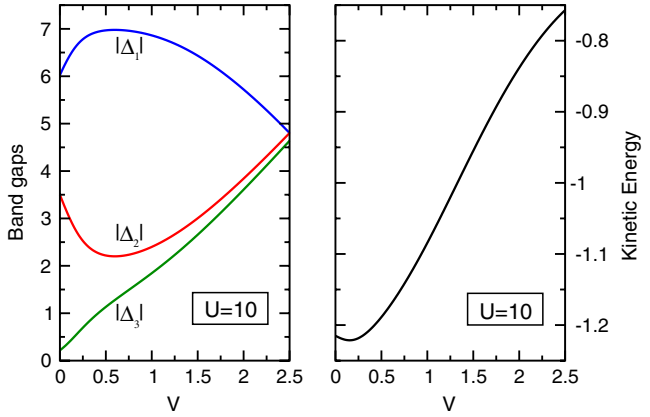

FIG. 3 (color online). Band gaps (left) and kinetic energy per site K (right) vs nearest-neighbor repulsion V.

t is used). The staggered order of d_{yz} and d_{xz} orbitals is strong and weakly affected by V (see the τ_1 and τ_2 curves). The strengths of the d_{xy} orbital (τ_3) and charge (δ) density waves decrease with V. Surprisingly, δ remains finite down to $V = 0$; i.e., a charge modulation is present even in the case of local interactions only. A similar effect but with a different mechanism has been found within the two-orbital model for manganites [24]. The physics behind this unusual picture here is as follows. In the limit $U \gg t$, the orbital order parameters $\tau_{1,2}$ for 1D bands are nearly saturated and can be expanded in powers of t/U. The energy (4) is then expressed in terms of τ_3 only: $E = -\frac{1}{4}U - \frac{1}{2}J + 2J\tau_3^2 - \frac{1}{2}\sum_{\mathbf{k}}\sqrt{\epsilon_{\mathbf{k}3}^2 + (4J\tau_3)^2}$, where $J = 4t^2/U$. The minimization of E gives a finite τ_3 and nonzero CDW order parameter $\delta \simeq \tau_3 - O(J/U)$, because of a singular response of the nested d_{xy} Fermi surface at half filling.

The orbital and charge density waves with the $\mathbf{Q} = (\pi, \pi)$ modulation wave vector induce the gaps on the entire Fermi surfaces of all three bands and drive the system into the insulating state. In Fig. 3, the band gaps are plotted as a function of V at $U = 10$. At $V = 0$, the gaps in the d_{yz} and d_{xz} bands ($|\Delta_1|$ and $|\Delta_2|$, respectively) are large since they scale as U in the limit $U \gg t$, while the gap of the d_{xy} band is controlled by an effective coupling constant $\propto J$. In the "weak-coupling" limit $J \ll t$ (i.e., the strong-coupling $U \gg t$ limit in conventional language), it is exponentially small: $|\Delta_3| \sim t\exp[-t/4J]$ at $V = 0$. At large V, the expected $|\Delta_3| \sim 2V$ scaling is observed.

To complete our analyses, in Fig. 4 the dependence of the order parameters on U is presented for $V = 0$. The dashed line marks a first-order phase transition at around $U_c \simeq 2.4$ from phase I, sketched in Fig. 1(c), to phase II. In the latter, d_{yz} and d_{xz} orbitals predominantly occupy one sublattice, while the density of the d_{xy} orbital is higher at the other one. The ODW order parameters for d_{yz} and d_{xz} bands (τ_1 and τ_2) are controlled by U and monotonically decrease with U. The nonmonotonic behavior of the d_{xy} orbital and CDW order parameters is explained as follows. The effective coupling constant controlling them vanishes in the limits of small as well as large U: of the order of U for $U \ll t$ and $\propto t^2/U$ for $U \gg t$. For realistic values of model parameters, phase I, sketched in Fig. 1(c), is the ground state of the system. We emphasize that the system is insulating for any finite values of U and V.

Thus, we arrived at a rather unusual situation where DE-driven FM and insulating states coexist [25] and, moreover, are closely interrelated. In fact, the ODW and CDW states are stable only if the FM correlation length is large. In the DE system, a kinetic energy of electrons defines a stiffness of FM order. Along the same line, we estimate a FM coupling of neighboring $s = 1/2$ and $S = 1$ spins in the charge-ordered state: $J_{\mathrm{FM}} \simeq K/[2S(2s+1)]$, where K is the kinetic energy per site. Figure 3 shows K as a function of V. Considering a moderate value of $V = 2t \simeq 0.4$ eV, we find $J_{\mathrm{FM}} \simeq 40$ meV. This suggests an onset of FM correlations at fairly high temperatures and explains the insulating behavior of the VO_2 interface in the experiment [13]. Further, we predict a transition to a metallic state and large magnetoresistivity effects at higher temperature

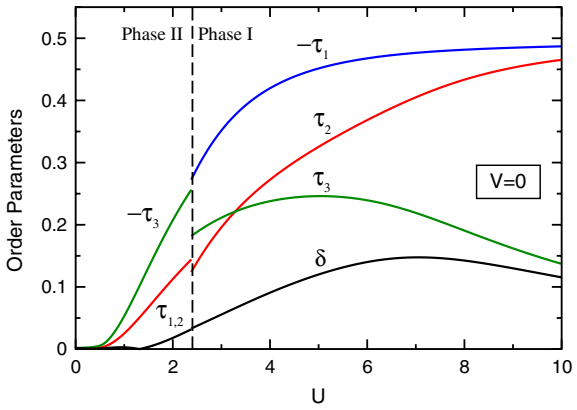

FIG. 4 (color online). Order parameters of the orbital ($\tau_{1,2,3}$) and charge (δ) density waves vs U. The dashed line marks a first-order phase transition (see text for details).

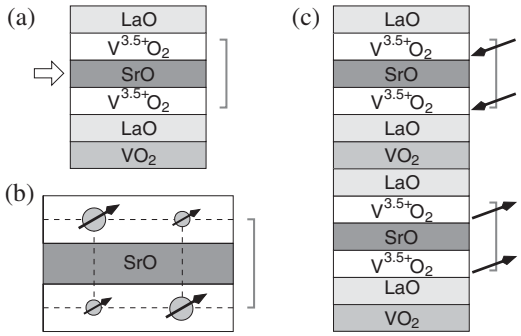

FIG. 5. (a) $V^{3.5+}O_2$ bilayer formed by replacement of a LaO (001) layer of $LaVO_3$ by SrO. (b) Spin structure of the $V^{3.5+}O_2$ bilayer. Large (small) circles and spins indicate sites where V^{3+} $d_{xy\uparrow}d_{yz\uparrow}$ (V^{4+} $d_{zx\uparrow}$) configuration is favored. The layers are coupled ferromagnetically via the DE between $S = 1$ and $S = 1/2$ states. (c) Periodic sequence of $V^{3.5+}O_2$ bilayers. Spin coupling through the intermediate V^{3+} $S = 1$ ions of VO_2 layer is antiferromagnetic (as shown here) if the charge-ordering patterns of different bilayers are in-phase.

when FM correlations are reduced. Apart from transport measurements, magnetic x-ray and optical studies may provide a crucial test for the theory.

The present work motivates an interesting idea of a superlattice depicted in Fig. 5. Here, insertion of SrO planes into $LaVO_3$ can be viewed as a ''spatially correlated doping'' that generates *two* $V^{3.5+}O_2$ planes—each midway between $Sr^{2+}O$ and $La^{3+}O$ layers—forming a ferromagnetic bilayer. Spins of different bilayers weakly couple antiferromagnetically (ferromagnetically) if their CDW-ordering patterns are in-phase (out-of-phase) [26]. Such a direct link between charge and spin structures suggests a magnetic control of charge sector and vice versa; e.g., a relatively weak magnetic field may lead to the CDW phase shift. In fact, the proposed superlattice is similar to the bilayer ruthenates [27] and manganites [28], which have the same magnetic structure as in Fig. 5(c) and show large magnetoresistivity and spin-valve effects. We notice also that the bilayer coupling may oscillate in sign as the number of intermediate VO_2 planes is varied, provided their V^{3+} spins stagger along the c axis as in YVO_3 at low temperature [21].

In conclusion, we have studied a Hubbard model for quarter-filled t_{2g} bands on a square lattice. Because of a confined geometry at the interface, at large enough Hund's coupling ($J_H \gtrsim 2.5t$) the correlated electrons develop a peculiar insulating ferromagnetic ground state accompanied by the orbital and charge density waves. This provides a natural explanation for an insulating behavior of the p-type $LaVO_3/SrTiO_3$ interface. The experimental and theoretical studies of superlattices like in Fig. 5, where a complex electronic reconstruction takes place coherently over many interfaces, remains a future challenge.

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