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

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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 \cite{1, 2, 3, 4, 5, 6, 7, 8}. A formation of a high-mobility electron gas \cite{4}, quantum Hall effect \cite{5} and, remarkably enough, even a superconducting state \cite{6} have been observed at the interfaces between insulating oxides. At the interface between nominally non-magnetic oxides, magnetic effects have also been detected \cite{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 \cite{10}.

In correlated oxide heterostructures, electronic reconstruction involves not only charge, but also spin \cite{8} and, in particular, the orbital degrees of freedom \cite{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 \cite{13} added a new puzzle into this field. Two types of interfaces between a Mott insulator LaVO\textsubscript{3} and a band insulator SrTiO\textsubscript{3} have been investigated: (1) the VO\textsubscript{2}/LaO/TiO\textsubscript{2}/SrO interface with n-type polar discontinuity, and (2) the LaO/VO\textsubscript{2}/SrO/TiO\textsubscript{2} with p-type one (formed by inserting a "metallic" SrO\textsubscript{2} unit into the n-type interface). In bulk compounds, the VO\textsubscript{2} (LaO) layers have a \(-e/2\) (+\(e\)) charge per unit cell, while TiO\textsubscript{2} and SrO layers are neutral. In such systems a polar discontinuity triggers the doping of an interface layer to resolve the polar catastrophe \cite{13}: In n-type interface the TiO\textsubscript{2} layer receives a \(-e/2\) charge while in p-type interface \(-e/2\) charge is taken away from the VO\textsubscript{2} layer. This leads to a formal valence state \(\text{V}\) of Ti and \(\text{O}\) of V at the n- and p-type interface layers, respectively. The resistivity measurements have shown that the n-type interface is metallic and p-type interface is insulating. The metallic character of TiO\textsubscript{2} interface layer is not surprising and confirms existing theoretical results \cite{10}. However, an insulating behavior of hole doped VO\textsubscript{2} interface layer is at odds with expectations and is striking, given that SrVO\textsubscript{3} is a good metal and already 18\% Sr-doping is sufficient to convert bulk LaVO\textsubscript{3} into a metal, too \cite{15}. In this Letter, we present a theory resolving this puzzle. In short, the contrasting behavior of TiO\textsubscript{2} and VO\textsubscript{2} interfaces originates from their different spin and orbital structure. Indeed, while TiO\textsubscript{2} layer with Ti\textsuperscript{3+}/Ti\textsuperscript{4+} states represents a diluted quantum S=1/2 system (like high-T\textsubscript{c} cuprates), VO\textsubscript{2} interface layer is made of V\textsuperscript{5+}/V\textsuperscript{4+} S=1/2 states – a canonical background for the double-exchange (DE) physics. Once spins of the VO\textsubscript{2} layer are polarized by the DE mechanism, 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 hole doped VO\textsubscript{2} layer within a multi-orbital Hubbard model for d-electrons \cite{16} on a square lattice:

\[
H = - \sum_{i,j} t_{ij,\alpha} d_{i\alpha}^\dagger d_{j\alpha} + U \sum_{i,\alpha} n_{i\alpha} n_{i\alpha\downarrow} + U' \sum_{i,\alpha<\beta} \left( S_{i\alpha}^z S_{i\beta}^z + \frac{1}{4} \right) n_{i\alpha} n_{i\beta} + V \sum_{\langle ij \rangle} n_{i\alpha} n_{j\beta}.
\]

The three-fold degenerate \(t_{2g}\) states \(d_{yz}, d_{xz}\), and \(d_{xy}\) are labeled by orbital index \(\alpha = 1, 2, 3\), respectively. The \(\bar{S}_{i\alpha}\) and \(n_{i\alpha} = n_{i\alpha\uparrow} + n_{i\alpha\downarrow}\) correspond to the spin and density of electrons in \(\alpha\) orbital. The first term in \(H\) describes an electron hopping between the nearest neighbor (NN) sites \cite{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. \(1\alpha\). While the \(d_{xy}\) orbital still forms a two-dimensional (2D) band: \(t_{ij,3} = t\). In momentum space the hopping term reads as \(\sum_{k_x, k_y} \epsilon_{k_x, k_y} d_{k_x, k_y}^\dagger d_{k_x, k_y}\), where \(\epsilon_{k_x}(1) = -2t \cos k_x(y)\) and \(\epsilon_{k_x}(2) = -2t \cos k_x + \cos k_y\). The interaction part of \(H\) consists of an on-site intra- and inter-orbital Coulomb repulsions, \(U\) and \(U'\), respectively. The latter term is further split by the Hund’s coupling \(J_H\) into an interorbital spin triplet \((U'-J_H)\) and singlets \((U'+J_H)\), such that \(S = 1\).
state with electrons residing on different orbitals is favored. It is this 2$J_H$ splitting between the high/low spin states that promotes a global ferromagnetic (FM) state by virtue of the DE mechanism in the present states that promotes a global ferromagnetic (FM) state. It is this state with electrons residing on different orbitals is favored.

**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 $U > V > t$. In a symmetry broken state the system is insulating at any values of $U$ and $V$.

deal with interacting spinless fermions with orbital flavors only. In this case the Hamiltonian (1) reduces to

$$H = -\sum_{i,j,\alpha} t_{ij,\alpha} d_{i\alpha}^\dag d_{j\alpha} + \bar{U} \sum_{i,\alpha<\beta} n_{i\alpha} n_{i\beta} + V \sum_{\langle ij \rangle} n_{i\alpha} n_{j\beta},$$

where $\bar{U} = U' - J_H = U - 3J_H$ (using well-known relation $U' = U - 2J_H$) is an effective Hubbard repulsion in the FM state. Optical data in cubic vanadates [21] suggests the high-spin transition at $\bar{U} \sim 2$ eV $\sim 10t$ but we will consider $\bar{U}$ 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).

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

We discuss now the orbital and charge density waves (ODW and CDW) 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 $Q = (\pi, \pi)$. We introduce the orbital order parameters $\tau_{\alpha}$ as $\langle n_{\alpha \alpha} \rangle = n_3 + e^{iQR} \tau_{\alpha}$, where $n = 3/2$ is an average electron density. The corresponding CDW modulation is given by $\langle n_{\alpha \alpha} \rangle - n = e^{iQR} \delta$, 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 excitation 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 [22]. The ground state energy per site is expressed in terms of order parameters:

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

where $E_{\alpha} = \sqrt{\epsilon_{\alpha \alpha}^2 + \Delta_{\alpha}^2}$ with $\Delta_{\alpha} = U \tau_{\alpha} - (U - zV) \delta$, and $z = 4$ is a number of NNs. (The constant contribution $E_0 = \frac{1}{4} Un_z^2 + \frac{1}{2} zVn_z^2$ has been dropped.) Physically, $|\Delta_{\alpha}|$ represent band gaps. The minimization
of the energy $E$ gives the coupled integral equations
\[ \tau_a = \sum_k \Delta_k / E_{ka}, \]
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 $d_{xy}$ 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 is used). The staggered order of $d_{yz}$ and $d_{xz}$ orbitals is strong and weakly affected by $V$ (see the $\tau_1$ and $\tau_2$ curves). The strengths of $d_{xy}$ orbital ($\tau_3$) and charge ($\delta$) density waves decrease with $V$. Surprisingly, $\delta$ 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 different mechanism has been found within the two-orbital model for manganites [24].

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 (1) is then expressed in terms of $\tau_3$ only: $E = -U + J/2 + 2J\tau_2^2 - \frac{J}{2} \sum_k \sqrt{\epsilon_{ki}^2 + (4J\tau_3)^2}$, where $J = 4t^2 / U$. The minimization of $E$ gives a finite $\tau_3$ and non-zero CDW order parameter $\delta \approx \tau_3 - O(J/U)$, because of a singular response of the nested $d_{xy}$ Fermi surface at half-filling.

The orbital and charge density waves with $Q = (\pi, \pi)$ 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 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 $d_{xy}$ band is controlled by an effective coupling constant $\propto J$. In the “weak-coupling” limit $J \ll t$ (i.e. 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 $U_c \approx 2.4$ from the phase-I, sketched in Fig. 1(c), to the phase-II. In the latter $d_{yz}$ and $d_{xz}$ orbitals predominantly occupy one sublattice while the density of $d_{xy}$ orbital is higher at the other one. The ODW order parameters for $d_{yz}$ and $d_{xz}$ bands ($\tau_1$ and $\tau_2$) are controlled by $U$ and monotonically decrease with $U$. The non-monotonic behavior of $d_{xy}$ orbital and CDW order parameters is explained as follows. The effective coupling constant controlling them vanishes in the limits of small as well as of large $U$: being of the order of $U$ for $U \ll t$ and $\propto t^2 / U$ for $U \gg t$. For realistic values of model parameters the 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 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 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 charged ordered state: $J_{FM} \approx K / [2S(S+1)]$, where $K$ is a kinetic energy per site. Fig. 4 shows $K$ as a function of $V$. Considering a moderate value of $V = 2t \approx 0.4$ eV, we find $J_{FM} \approx 40$ meV. This suggests an onset of FM correlations at fairly high temperatures and explains insulating behavior of VO$_2$ interface in the experiment [13]. Further, we predict a transition to a metallic state and large magneto- resistivity effects at higher temperature 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
FIG. 5: (a) V\textsuperscript{3.5+}O\textsubscript{2} bilayer formed by replacement of a LaO (001) layer of LaVO\textsubscript{3} by SrO. (b) Spin structure of the V\textsuperscript{3.5+}O\textsubscript{2} bilayer. Large (small) circles and spins indicate cites where V\textsuperscript{3+}d\textsubscript{xy}/d\textsubscript{yz} (V\textsuperscript{4+}d\textsubscript{xz}/d\textsubscript{yz}) configuration is favored. The layers are coupled ferromagnetically via the DE between S=1 and S=1/2 states. (c) Periodic sequence of V\textsuperscript{3.5+}O\textsubscript{2} bilayers. Spin coupling through the intermediate V\textsuperscript{3+}S = 1 ions of VO\textsubscript{2} layer is antiferromagnetic (as shown here) if the charge ordering patterns of different bilayers are in-phase.

CDW-ordering patterns are in-phase (out-of-phase) \cite{10}. 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 \cite{27} and manganites \cite{28}, which have the same magnetic structure as in Fig. 5(e) 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\textsubscript{2} planes is varied, provided their V\textsuperscript{3+} spins stagger along the c axis as in YVO\textsubscript{3} at low-temperature \cite{21}.

To conclude, we have studied a Hubbard model for a quarter-filled t\textsubscript{2g} bands on a square lattice. Due to a confined geometry at the interface, at large enough Hund’s coupling (J\textsubscript{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\textsubscript{3}/SrTiO\textsubscript{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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