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Phys. Rev. B 87, 161119 — Published 26 April 2013
DOI: 10.1103/PhysRevB.87.161119
Dimer Mott Insulator in an Oxide Heterostructure

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(Dated: April 15, 2013)

We study the problem of designing an artificial Mott insulator in a correlated oxide heterostructure. We consider the extreme limit of quantum confinement based on ionic discontinuity doping, and argue that a unique dimer Mott insulator can be achieved for the case of a single SrO layer in a GdTiO$_3$ matrix. In the dimer Mott insulator, electrons are localized not to individual atoms but to bonding orbitals on molecular dimers formed across a bilayer of two TiO$_2$ planes, and is analogous to the Mott insulating state of Hubbard ladders, studied in the 1990s. We verify the existence of the dimer Mott insulator through both ab initio and model Hamiltonian studies, and find for reasonable values of Hubbard $U$ that it is stable and ferromagnetic with a clear bonding/anti-bonding splitting of order 0.65eV, and a significant smaller Mott gap whose size depends upon $U$. The combined effects of polar discontinuity, strong structural relaxation and electron correlations all contribute to the realization of this unique ground state.

PACS numbers:

Recently, the growth techniques from semiconductor physics, such as Molecular Beam Epitaxy (MBE), have been increasing applied to transition metal and rare earth materials to create correlated heterostructures. The resulting atomic layer control promises the ability to design orbital, spin, and charge states, create new emergent phenomena, and study fundamental physics of correlated quantum states in unprecedented new ways. A first step in this direction would be the creation of the simplest and most dramatic manifestation of electron-electron interactions: the formation of a Mott insulators, a system which would be a metal according to band theory, but in which instead electrons localize because their motion is jammed by their mutual short-range Coulomb repulsion.

Mott insulators occur only when the electron density is commensurate with the underlying lattice, and typically an (odd) integer number of electrons per atom is required. A charge density of one electron per atom is enormous, reaching of order $n_{2d} \approx 7 \times 10^{14}$cm$^{-2}$ for a typical perovskite structure even if these electrons are confined to a single atomic layer. This provides a challenge for heterostructures, as this $n_{2d}$ is already an order of magnitude larger than can be achieved in the highest density semiconductors, and even if it is created, the electron density per atom will be greatly reduced by the electrons tendency to spread out in the third dimension. In this paper, we show that these difficulties can be overcome by judicious design of a Dimer Mott Insulator (DMI), a state envisioned decades ago in the context of one-dimensional Hubbard ladders, and created here in two dimensions at a single monolayer of SrO embedded in a GdTiO$_3$ matrix. In the DMI, the requisite high charge density is achieved by combining ionic discontinuity doping, quantum confinement, and the formation of electronic dimers. The dimers are bonding orbitals on electron pairs, to which electrons are Mott localized instead of to individual atoms. Dimer formation halves the charge density needed to reach the Mott state, relative to the usual single atom localization, and is crucial to the success of our scheme. We combine ab initio and model calculations to establish the existence and nature of the DMI state theoretically.

The starting point for our work is the polar/ionic discontinuity, which induces a large net charge, typically half an electron per planar unit cell, at a polar to non-polar interface. The polar discontinuity has been identified as a possible mechanism of doping in many oxide interface studies, but has only recently been quantitatively verified systematically. In MBE grown heterostructures of GdTiO$_3$ and SrTiO$_3$, a carrier density of $n_{2d} = 3.5 \times 10^{14}$cm$^{-2}$ (=1/2 e$^-$ per planar unit cell) for each GdTiO$_3$/SrTiO$_3$ interface has been systematically observed by Hall coefficient measurements. These electrons fall into the empty $d$ states of the SrTiO$_3$, and consequently high 3d carrier density can be achieved by confinement in narrow quantum wells of SrTiO$_3$ embedded in thicker GdTiO$_3$, with $n_{3d}=n_{2d}/w$, where $w$ is the well width. Recent transport experiments showed that such wells with a width of a few SrTiO$_3$ unit cells are indeed strongly correlated metals with ultra-high carrier density $n_{2d} \approx 7 \times 10^{14}$cm$^{-2}$ arising from two interfaces, corresponding to 1/2 + 1/2 = 1e$^-$ per planar unit cell.

To maximize the 3d electron density and approach the Mott limit, we take this approach to its logical end and consider the case of a single SrO layer embedded in GdTiO$_3$. However, even in this case of ultimate confinement, we do not achieve a 3d density of 1 e$^-$ per atom. This is because the doped electrons go symmetrically into the two interfaces TiO$_2$ layers on either side of the SrO plane. While this situation appears unfavorable for the formation of a Mott insulator, all is not lost. On fundamental grounds, the condition for the formation of a Mott...
state depends only on the charge per unit cell defined by the translational symmetry of the system. Here the two interface planes form a bilayer, with translational symmetry only within the plane, and there is indeed a unit charge per planar unit cell. This indicates that a Mott state is possible in principle. To realize it, we must somehow induce the two Ti atoms in a unit cell to act as a single ‘superatom’.

It is instructive to view the bilayer on its side, with the Ti atoms projected into an x-z plane (here we use standard cubic coordinates for the perovskite structure, and z is the growth direction). The Ti-O-Ti network then forms a ladder with Ti-O-Ti bonds between the two interfaces making the rungs of the ladder, and intra-plane bonds projecting to the ladder’s legs. In a Hubbard model description, symmetry dictates that the hopping amplitude for electrons along the legs, t, and along the rungs, $t_{\perp}$, are unequal. Correlated electron ladders were studied intensively in the 1990s, and in particular it was shown when $t_{\perp}/t$ is sufficiently large (approximately $t_{\perp}/t > 1$ for the one-dimensional Hubbard ladder), electrons form an unconventional Mott state of bonding orbitals on the rungs of the ladder - the one dimensional analog of the DMI. Qualitatively, we anticipate the same physics applies to the Hubbard bilayers, provided $t_{\perp}/t$ is sufficiently large.

Hopping parameters in transition metal oxides are largely controlled by the metal-oxygen-metal bond angle, due to the directionality of $d$ and $p$ orbitals, and are generally largest when the bond angle is closest to $180^\circ$. Intuitively, we expect that the interlayer Ti-O-Ti bonds are the most SrTiO$_3$-like, while those within the TiO$_2$ planes conform more closely to those of the GdTiO$_3$. Since SrTiO$_3$ is nearly perfectly cubic, while GdTiO$_3$ is one of the most highly distorted titanates, this appears quite favorable. We checked this intuition with \textit{ab initio} density functional theory (DFT) calculations for periodic superlattices of the single SrO layer, (SrTiO$_3$)$_n$(GdTiO$_3$)$_n$, with $n=3,5$. Calculations were performed in the Wien2k implementation and the generalized gradient approximation\(^7\) (GGA). An RKmax parameter 7.0 was chosen with RMTs of 1.91 a.u., 1.69 a.u., 2.29 a.u. and 2.27 a.u. for Ti, O, Sr and Gd, respectively. The DFT calculation is carried out in a $\sqrt{2}a \times \sqrt{2}a \times c$ unit cell to allow for the possibility of octahedral tilts, where $a$ is set to be the value of the experimental SrTiO$_3$ lattice constant, 3.905 Å (see the Supplemental Material for additional details). The structural optimization is done both on the atomic coordinates and $c/a$ ratio, within the GGA + U approximation. We focus on $U_{\text{eff}}=U-J=4$ eV on the Ti $d$ orbitals, an acceptable value for the titanates\(^9\). In addition, we further add $U_{\text{eff}}=U-J=8.5$ eV on the Gd $f$ orbitals since the energy of the occupied Gd $f$ bands lie much lower than the Fermi energy in practice. This value will not affect the relevant electronic properties.

We now discuss the key features of the relaxed structure, which becomes independent of $n$ for $n \geq 3$, and is shown in Fig. 1. First, relaxation is significant at the two interface layers, but decays quickly into the GdTiO$_3$ region. Second, the Ti-O-Ti bond angles are highly direction dependent near the interface, as shown in Fig. 2. The “vertical” Ti-O-Ti bond connecting the two interfaces is slightly distorted, with a $160^\circ$ angle. The next vertical Ti-O-Ti bond away from the interface is already highly distorted, with only a $3^\circ$ angular difference from that of bulk GdTiO$_3$, and more distant bonds are nearly indistinguishable from bulk. On the other hand, the in-plane bonds are distorted but different from the bulk even in the interfacial layers, with bond angles of about $153^\circ$. Third, the Ti-O bond length varies by only 6% between the longest and shortest bonds in the entire superlattice, and is less significant compared to the dramatic bond angle variations.

Is the bond angle difference, together with other minor structural relaxation effects sufficient to promote a DMI? We first check the electronic structure within...
the GGA+U approximation using the relaxed structure. Searching for possible magnetic structures, we obtained the lowest energy for a state with ferromagnetic alignment of Ti spins within each TiO$_2$ plane, with interfacial Ti spins antiparallel to those in the GdTiO$_3$ region (energy difference compared to parallel to those in the GdTiO$_3$ region is small). With this configuration, and $U_{\text{eff}} = 4 \text{eV}$, the interfacial and bulk density of states (DOS) is shown in Fig. 3. We observe a bulk gap of 1.25eV, comparable to theoretical values in the literature, but remarkably a much reduced but still non-zero gap at the interface of approximately 0.2eV. This is a signature of the DMI state. Within GGA+U, the DMI persists for $U_{\text{eff}} \geq 3.5 \text{eV}$, with both bulk and interfacial gaps reduced for smaller $U$. To see the DMI more directly, we decomposed the DOS by Ti site and the 3 octahedral rotations. The anti-bonding state, centered $\approx 0.8 \text{eV}$, is again mainly composed of $m_{xz}$ orbitals of the DMI state. Within GGA+U, the DMI persists for smaller $U_{\text{eff}}$ = 4 \text{eV}, comparable to theoretical values in the literature, but remarkably a much reduced but still non-zero gap at the interface of approximately 0.2eV. This is a signature of the DMI state. Within GGA+U, the DMI persists for $U_{\text{eff}} \geq 3.5 \text{eV}$, with both bulk and interfacial gaps reduced for smaller $U$. To see the DMI more directly, we decomposed the DOS by Ti site and the 3 octahedral rotations. The anti-bonding state, centered $\approx 0.8 \text{eV}$, is again mainly composed of $m_{xz}$ orbitals of the DMI state. Within GGA+U, the DMI persists for smaller $U_{\text{eff}}$. The separation (of subband centers) from the Fermi energy is set to zero.

47% for Ti at sublattice a, similar to in bulk GdTiO$_3$.

To study the DMI state more explicitly, we constructed a model extended Hubbard Hamiltonian by extracting hopping parameters from the ab initio calculations. Using the optimized structure obtained within GGA+U, a pure GGA calculation was carried out. The eigenvalues of the $f$ states of Gd were shifted manually away from the Fermi energy. We constructed 30 maximally localized Wannier functions\textsuperscript{10,11} (MLWF) around the Fermi energy, with the 3 $t_{2g}$ orbitals forming the basis. The hopping parameters were then calculated by evaluating the matrix element of the MLWF. Including these hopping parameters, the tight-binding model of the bilayer takes the form

$$H_{\text{tb}} = \sum_{(ij)} \sum_{m,n,\alpha} t_{ij}^{mn} c_{i m \alpha}^{\dagger} c_{j n \alpha}$$

(1)

where $i$ and $j$ are nearest neighbor sites, $m$ and $n$ are orbital indices and $\alpha$ is the spin index. The hopping parameters for the two interfacial Ti layers are tabulated in Table 1, which contains the full orbital dependence of the hopping terms. The maximum intra-plane and inter-plane hopping matrix elements are $t \sim 0.35 \text{eV}$, $t_{\perp} \sim 0.63 \text{eV}$, respectively, which gives strong support for the DMI picture. The separation energy between bonding and anti-bonding state is consistent with this magnitude inter-plane hopping.

We supplement these hopping parameters with interactions\textsuperscript{9,12} to form the effective Hamiltonian

$$H = H_{\text{tb}} + H_{\text{int}}$$

$$H_{\text{int}} = \sum_{i} \sum_{m} U n_{im\uparrow} n_{in\downarrow} + U' \sum_{m \neq n} n_{im\uparrow} n_{in\downarrow} + \frac{1}{2} (U' - J) \sum_{m \neq n, \alpha} n_{ima} n_{ina} + J \sum_{m \neq n} c_{im\uparrow}^{\dagger} c_{in\downarrow} c_{in\uparrow}^{\dagger} c_{jm\downarrow}$$

$$+ J' \sum_{m \neq n} c_{ima}^{\dagger} c_{ina}^{\dagger} c_{ina} c_{jmb}$$

(2)

where $U$ and $U'$ represent on-site intra-orbital and inter-orbital Coulomb repulsion between up and down spin, respectively, and $J$ is the Hund coupling. We will not

\begin{table}[h]
\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
$(im; jn)$ & $[1, 1, 0]$ & $[-1, 1, 0]$ & $(im; jn)$ & $[0, 0, 1]$ \\
\hline
$(1ayz; 1byz)$ & 0 & -0.35 & $(0ayz; 1ayz)$ & -0.6 \\
$(1ayz; 1bzx)$ & 0.14 & 0.14 & $(0ayz; 1axz)$ & 0 \\
$(1axz; 1byz)$ & -0.12 & -0.12 & $(0axz; 1ayz)$ & 0 \\
$(1axz; 1bzx)$ & 0 & 0.14 & $(0axz; 1axz)$ & 0.14 \\
$(1axy; 1bry)$ & -0.34 & -0.34 & $(0axy; 1axy)$ & 0 \\
\hline
\end{tabular}
\end{center}
\end{table}
restrict the condition to Slater-Kanamori interaction parameter $U' = U - 2J$ and $J = J'$, but rather simply assume $J = J'$ and explore the phase diagram by varying all the other parameters.

Fig. 4 shows the phase diagram as a function of $U$ and $U'$ obtained by the Hartree-Fock approximation, with fixed Hund's coupling $J = 0.6$ eV. When the Coulomb repulsion is small, the ground state is just paramagnetic metal. In the unphysical region where inter-orbital repulsion is dominant, $U' > U$, electrons reside in a single orbital per Ti and in fact charge order. Of most interest is the lower right part of the phase diagram, where $U > U'$. In this region, ferromagnetism arises for sufficiently large $U$. In the weak inter-orbital repulsion limit, the electrons are distributed in all three $t_{2g}$ orbitals. Under this condition, the system is always metallic or semi-metallic, since those electrons in $xy$ orbitals are non-bonding between layers and hence metallic. For sufficiently large $U'$, however, the inter-orbital repulsion eventually disfavors and empties the $xy$ states, in favor of the $xz/yz$ orbitals which have lower energy through inter-layer hopping. In this way the bonding state becomes fully occupied and a (ferromagnetic) DMI is achieved. Further increase of $U'$ enhances the gap and eventually prefers an antiferromagnetic DMI, since Hund’s coupling becomes ineffective if there is strictly one electron per site, and superexchange becomes dominant. For completeness, we also have tested $J=0.1$ eV, which shows the Hund’s coupling enhances the ferromagnetic insulating state. For our best guess at physically appropriate values, e.g. $U = 4.5$ eV and the Slater-Kanamori $U' = U - 2J$, the ferromagnetic DMI obtains. The Hartree-Fock results for these values for the band gap and orbital ordering are very similar to those of the previously discussed GGA+U calculations.

In summary, we have argued for the existence of a Dimer Mott Insulator (DMI) for a single SrO layer embedded in a thick GdTiO$_3$ matrix, using both ab initio and model calculations. The DMI state is unique to the bilayer TiO$_2$ structure created by a single SrO layers; we have indeed verified that a metallic state is obtained in GGA+U for the case of two SrO layers embedded in GdTiO$_3$ (see Supplemental Material). Insulating behavior in such structures experimentally should therefore be attributed to the combined effects of disorder (e.g. SrTiO$_3$ thickness fluctuations) and interactions. The DMI for a single SrO layer could be experimentally probed by many experiments, including transport, optical measurements of the gap and bonding-antibonding splitting, and angle-resolved photoemission. Observing the magnetic structure is more difficult, but might be possible with ferromagnetic resonance or optical dichroism. This work suggests many directions for future theoretical and experimental research.

We thank Jim Allen, Susanne Stemmer, Dan Ouellette, Pouya Moetakef and Chuck-Hou Yee for helpful discussions. We acknowledge support from the Center for Scientific Computing at UCSB: NSF CNS-0960316. This research is supported by DARPA grant No.W911NF-12-1-0574 (L.B. and R.C.) and the MRSEC Program of the National Science Foundation, Award No. DMR 1121053, NSERC, CIFAR (SB.L.).
1. J. Mannhart and D. Schlom, Science 327, 1607 (2010).
2. E. Dagotto and T. M. Rice, Science 271, 618 (1996).
3. N. Nakagawa, H. Hwang, and D. Muller, Nature materials 5, 204 (2006).
4. P. Moetakef, T. A. Cain, D. G. Ouellette, J. Y. Zhang, D. O. Klenov, A. Janotti, C. G. Van de Walle, S. Rajan, S. J. Allen, and S. Stemmer, Appl. Phys. Lett. 99, 232116 (2011).
5. P. Moetakef, C. A. Jackson, J. Hwang, L. Balents, S. J. Allen, and S. Stemmer, Phys. Rev. B 86, 201102 (2012).
6. P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties (Vienna University of Technology, Austria, 2001).
7. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
8. See Supplemental Material at (link) for (a) more DFT calculation details of the superlattices; (b) the ab initio results obtained for two SrO layers embedded in a GdTiO$_3$ matrix.
9. T. Mizokawa and A. Fujimori, Phys. Rev. B 54, 5368 (1996).
10. A. Mostofi, J. Yates, Y. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comp. Phys. Comm. 178, 685 (2008).
11. J. Kuneš, R. Arita, P. Wissgott, A. Toschi, H. Ikeda, and K. Held, Comp. Phys. Comm. 181, 1888 (2010).
12. M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).