Electron-hole liquids in transition-metal oxide heterostructures

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Appropriately designed transition-metal-oxide heterostructures involving small band-gap Mott insulators are argued to support spatially separated electron and hole gasses at equilibrium. Spatial separations and carrier densities favoring the formation of excitonic states are achievable. The excitonic states may exhibit potentially novel properties. Energetic estimates are given, candidate material systems are discussed, and the possibility of large photovoltaic effects is mentioned.

Electron-hole bound states are a topic of longstanding importance in condensed matter physics and play a crucial role in solar-energy conversion. Excitons dynamically generated by incident photons dominate the optical response of many materials including organic compounds such as carbon nanotubes[1–3] and transition-metal oxides[4] such as Cu_2O. A dense gas of excitons may Bose condense or form a Wigner crystal.[5,6] Excitonic condensed states are of interest because the excitons may be spin singlet or triplet, or have more complicated properties in the presence of spin-orbit coupling[7] and in a topological insulators,[8] and also couple via dipolar interactions.[9]

Considerable effort has been invested over the years in optically generated electron-hole liquids[4,10,11] but creating and manipulating a sufficiently high-density optically excited particle-hole gas while preventing it from recombining has proven challenging. An alternative route, proposed by Zhu *et al.*[12] is to construct a double quantum well system in which one quantum well contains holes and the other contains electrons. The spatial separation prevents recombination while if the quantum wells are close enough the electrons and holes may interact.

Double quantum wells can be fabricated in semiconductor systems such as (Al,Ga)As but perhaps because of the large band gap it has not been possible to bias these systems strongly enough to create significant equilibrium electron and hole populations. Eisenstein and co-workers have created double-well systems in which each well was tuned to the $\nu = 1/2$ quantized Hall state, thereby producing a Bose condensate with highly unusual and still incompletely understood properties including nearly dissipationless transport characterized by counterflowing currents in the two layers.[13,14] Recent theoretical papers have raised the possibility of similar effects occurring in graphene bilayers.[15–17] Excitonic instabilities have also been considered in intrinsically compensated materials with coexisting electron and hole bands[18] including high-T_c cuprates.[19]

In this Brief Report we propose a different route to the formation of proximal electron and hole liquids. The basic idea is sketched in the middle panel of Fig. 1: an oxide heterostructure involving a thin layer of narrow gap correlated (Mott) insulator (labeled as B in the figure) sandwiched between two possibly different wide-band-gap insulators (labeled as A and C in the figure). If the AB and AC interfaces are polar, then in the absence of charge reconstruction[20,21] an

internal electric field will be generated, leading to a potential drop which scales linearly with the thickness of the correlated material (top panel of Fig. 1). The potential drop causes band bending (shown in the lower panel of Fig. 1) which, if large enough, pushes the conduction band below the Fermi level on one side of the structure and the valence band above the Fermi level on the other side, leading to electron and hole accumulation respectively. If the band gap of the inner material (B) is smaller than the band gaps of the outer materials ("A" and "C") and the heterojunctions have type-I band offsets then the electron and hole gasses will remain within layer B.

The idea is a variant of the proposal of Ref. 12. The importance of polar-discontinuity fields and the possibility of exciton formation was previously noted in the context of the non-Mott $LaAlO_3/SrTiO_3$ interface by Bristowe *et al.*[22] However, several features, apparently not previously noted, make the "tricolor" oxide heterostructures involving Mott insulators particularly attractive candidates. First, Mott insulators often have relatively small gaps $2\Delta \sim 0.3–2$ eV (Ref. 23) so that the electric fields required to produce the needed band bending need not be prohibitively large. Second, the
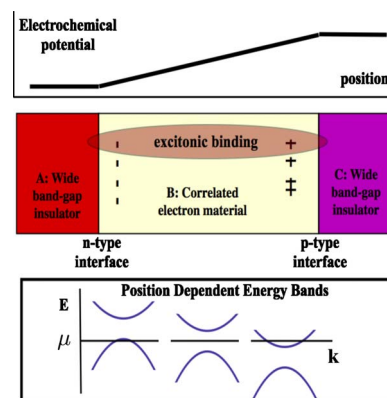

FIG. 1. (Color online) Middle panel: sketch of heterostructure configuration in which narrow-gap insulator (for this paper, a correlated electron compound) is placed between two wide band-gap semiconductors. Left panel: potential drop across heterostructure created by polarization discontinuities at AB and AC interfaces. Right panel: band bending presented as energy E vs momentum k plots at three positions across the heterostructure with chemical potential μ indicated.
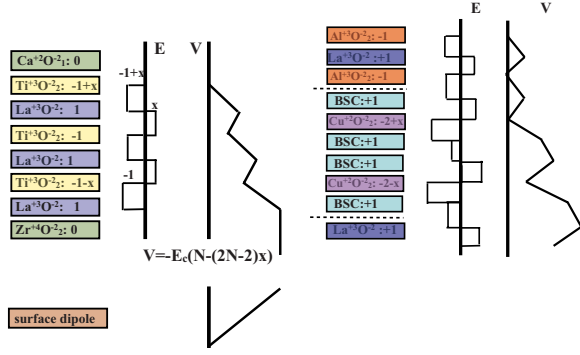
FIG. 2. (Color online) Electrostatics of electron-hole liquid formation. Upper panel: $N=3$ layers of polar correlated insulator such as LaTiO$_3$, LaVO$_3$, or LaCoO$_3$ inserted in hypothetical wide bandgap nonpolar insulating host (here CaZrO$_3$) with sheet charge density (in carriers per unit cell) indicated in the ionic picture, along with the induced electric field and the electrostatic potential (in units of the energy E_c defined in the main text. Also shown is the surface dipole required for electrostatic equilibrium, lower panel: $N=3$ layers of a nonpolar correlated insulator such as an infinite-layer cuprate inserted in a polar host with electric field and potential drop indicated. The final surface dipole layer is not shown.

physics of correlated materials is local: the relevant length scales for charge phenomena are of the order of a unit cell while interlayer couplings are either intrinsically weak (as in the case of insulating parent compounds of high-T_c materials) or can be made to be weak by appropriately induced orbital order. Third, the polarization discontinuities characteristic of many oxide interfaces produce substantial internal fields,[24] corresponding in the ideal case to sheet charge densities of one-half electron per ~ 16 Å^2. With a typical transition-metal oxide dielectric constant of order 10 for short-length scale phenomena,[25–27] this corresponds to an electric field of order 0.25–0.5 eV/Å so the polar discontinuity voltage drop across even a few-unit-cell-thick Mott channel would create enough band bending to establish proximal electron and hole liquids without the application of externally applied voltages. We also note that even though most Mott and charge-transfer insulators exhibit strongly particle-hole asymmetric doping properties, charge neutrality requires that in the absence of chemical defects the densities of electrons and holes must be equal, Of course, in practice the presence of defects means that an external voltage will have to be applied to balance the system but the voltages required need not be large.

We now use an energy minimization argument similar to those presented by Nakagawa *et al.*[28] and Bristowe *et al.*[22] to estimate the density of electrons and holes induced on opposite sides of an oxide heterostructure. We consider two representative heterostructures sketched in Fig. 2. The left panel shows case P: a perovskite oxide with a polar (001) surface embedded in a nonpolar host. Specific examples might be $ReXO_3$ with Re a 3$^+$ rare earth such as La and X a transition metal such as Ti,, V, Cr, Fe, Co, or Ni. The lower panel shows case NP: a perovskite-related oxide with a nonpolar (001) surface embedded in a host with a polar (001) surface. Examples would include La$_2$CuO$_4$ or one of the bismuth-strontium-calcium-copper-oxide materials. Viewed along the

(001) direction the materials consist of planes, which we idealize as having negligible thickness and a definite charge per unit area as shown in Fig. 2. The potential arising from the polar discontinuity may cause the transfer of a sheet carrier density of x electrons per unit cell from one side of the structure to the other.[20,21] (Charge neutrality requires that the number of electrons removed from one side equals the number of electrons added to the other). We determine x by minimizing the sum of the electronic charging energy cost to add electrons or holes to the correlated insulator and the volume integral of the electric field energy density $E^2/(8\pi\epsilon)$. We express the field energy in terms of the basic scale $E_c = \frac{e^2}{\epsilon a}\frac{d}{a}$ with a the in-plane lattice constant, ϵ the dielectric constant, and d the distance between the charge blocks shown in Fig. 2; in the situations considered here $d \approx a/2$. Using $a \approx 4$ Å and estimating $\epsilon \sim 10$ from previous analyses of oxide heterostructures[27] and from calculations of the screening of local interactions[25,26] we obtain $E_c \approx 0.15$ eV. For simplicity we neglect the energy cost of the dipole layer needed to remove the potential step shown in the left panel of Fig. 2; including it would increase the density of the electron and hole gasses. We also assume that the transferred layer is one unit cell thick so that x electrons per unit cell are transferred from the correlated electron layer nearest the interface on one side of the structure to the correlated electron layer nearest the interface on the other side. We find

$$E_{field}^P = 4\pi(N-1)E_c(1-2x+2x^2), \qquad (1)$$

$$E_{field}^{NP} = 4\pi(N-1)E_c\left(\frac{11}{4}-3x+3x^2\right). \qquad (2)$$

The electronic charging energy is the sum of the gap energy $\Delta_{a=el,hole}$ and the "compressibility" energy $\kappa^{-2} = \partial\mu/\partial n$, Defining $\kappa^{-2} = (\kappa_e^{-2}+\kappa_h^{-2})/2$ and gap $2\Delta = \Delta_e+\Delta_h$ we get

$$E_a = 2\Delta x + \kappa^{-2}x^2. \qquad (3)$$

κ^{-2} is expected to be enhanced in correlated materials relative to its band theory value ~ 0.7 eV/unit cell; an estimate,[29,30] for parameters reasonable for lightly doped high-T_c superconductors is ≈ 4 eV/unit cell.

Minimizing the sum of the two terms gives

$$x = \frac{1}{2}\frac{(N-1)E_c - 2\dfrac{\Delta}{\Lambda\pi}}{(N-1)E_c + \dfrac{\kappa^{-2}}{\Lambda\pi}} \qquad (4)$$

with $\Lambda=4$ for the polar case and six for the nonpolar case. The condition $(N-1)E_c = 2\Delta/(\Lambda\pi)$ is the condition that the band bending is larger than the gap. The numerical estimates indicate that a two layer system suffices to produce electron and hole gasses if the gap $2\Delta \lesssim 2$ eV. Note also that the large value of κ^{-2} expected in Mott insulators means that the density rises relatively slowly above its onset. An example, using the gap $2\Delta=1.75$ eV appropriate to the high-T_c case, and the E_c and κ^{-2} estimates given above, is shown in Fig. 3.

While the arguments given above relate directly to the polar discontinuity route to charge accumulation, other
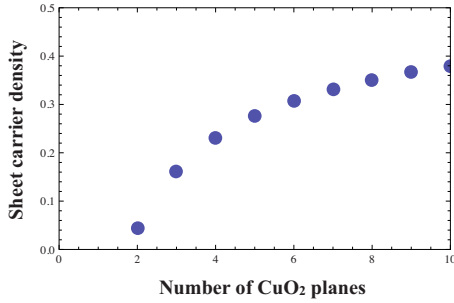
FIG. 3. (Color online) Sheet carrier density in units of holes per in-plane unit cell as function of number of Mott insulator layers, computed using parameters appropriate to CuO_2 case.

mechanisms are possible, including the application of an electric field,[31,32] a polarization discontinuity at the interface with an appropriately polarized ferroelectric[32] or a combination of the two. Such methods have been proposed and used previously to enhance high-temperature superconductivity[31–33] and if care is taken to equalize the density of electrons and holes may also be useful in achieving the proximal electron and hole liquids needed for exciton formation.

The next question is whether excitionic binding may occur. For weakly correlated systems binding occurs if the interparticle distance in one plane is greater than to the spacing between planes, or alternatively if the binding energy is larger than the Fermi energy.[12] The issue is more subtle in the doped Mott insulator case because one must address the question whether one counts carriers with respect to the half filled insulator or the full and empty bands. A detailed analysis requires a full many-body treatment of the interplay of binding and many-body physics which is not yet available. Here we argue that the "kinetic energy" associated with the "Drude" (zero-frequency-centered) component of the optical conductivity gives the delocalization energy of the doped holes or electrons. For high-T_c materials the Drude kinetic energy per dopant has been determined.[34,35] Using this information and our computed electron densities we plot in the two panels of Fig. 4 the interparticle spacing and kinetic energy, as well as the interplane distance and the Coulombic binding energy. One sees that two or three layer systems are most likely to exhibit excitonic binding.

Excitonic binding, if it occurs, will have interesting consequences. The Mott insulating channel material is likely to have a nontrivial magnetic structure, which the excitons will inherit. For example, Ribeiro *et al.*[36] and Han and Jia[37] modeled an electron-hole bilayer in a correlated bilayer by coupled t-J models and found regimes of novel magnetic behavior. But many more situations are possible. Wigner crystallization[12] and a Wigner supersolid[6] of excitions have been theoretically predicted, and may coexist with the "stripe" formation which is ubiquitous in lightly doped transition-metal oxides. Further, one may imagine a d^2 system or a manganite-based system) where each transition metal ion is in a high-spin configuration. If the system adopts a "layer antiferromagnetic" ground state (as occurs in some members of the 'Colossal' magnetoresistance manganite family[23] and may with appropriate orbital order occur in other systems) and if the number N of layers of correlated material is even, then in the ground state the exciton carries a spin, and exciton motion will lead to spin transport without charge transport.

Even if excitonic binding does not occur, the properties can be of interest. The slow rise to saturation of the transferred charge shown in Fig. 3 implies that a typical structure will have a non-negligible internal electric field. In a structure of thickness $N > 2$ the intermediate layers will be in the insulating configuration. Absorption of incident light at frequencies of order the Mott gap will produce particle-hole pairs which will be rapidly dissociated by the internal field, leading (if the electron or hole layers are mobile) to a large photocurrent. If the Mott insulator is magnetic, then the electron and hole currents will each be spin polarized.

Significant difficulties are likely to arise in attempts to put into practice the ideas proposed here. The length scales required are extremely short, but hybridization between the electron and hole layers should be minimal, placing stringent requirements on sample fabrication and measurement techniques. Further, we assume that the polar discontinuity fields are resolved by electronic reconstruction; of course in practice ionic and chemical effects such as interdiffusion and vacancy formation are likely to be important and must be carefully controlled. Finally, the subject of excitonic pairing in a strongly correlated background is in its infancy. Theoretical investigation of this issue is warranted, both in gen-
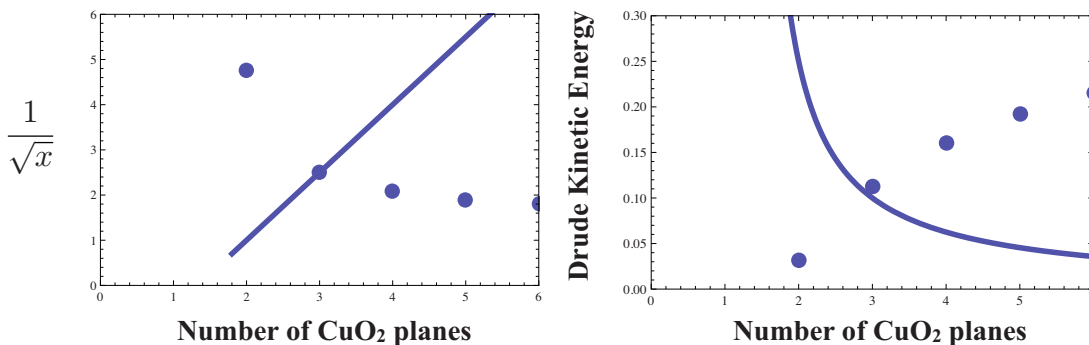

FIG. 4. (Color online) Criteria for exciton binding. Left panel: comparison of mean interparticle spacing of electron or hole gas (solid points) computed using bandgap $2\Delta = 1.75$ eV appropriate for high-T_c cuprates. Solid line: interplane distance (assuming interblock spacing is one half of in-lane lattice constant). Right panel: comparison of Drude kinetic energy vs doping (solid points, taken from data summarized in Ref. 35 and Coulomb interaction at scale of interplane spacing $E_c a / d_{interplane}$.

eral and in connection with the interplay of excitonic and superconducting pairing.

Potentially the most serious difficulty is that while a number of reports have appeared of electron conduction at oxide interfaces,[24,38–42] hole conduction seems to be difficult to achieve in many of the ABO_3 perovskite systems which have been the prime focus of study so far.[43] High-T_c cuprate systems may be more appropriate choices although the "colossal" magnetoresistance manganites also present interesting possibilities. $La_{1-x}A_xMnO_3$ has been reported in both electron-doped (A=Ce) and hole-doped (A=Ca) forms and a p-n junction comprised of these two constituents has been constructed.[44] Magnetic ground states are ubiquitous in the manganite materials, providing the possibility of spin-polarized excitons, and orbital ordering may be exploited to

weaken the hybridization between electron and hole layers. However, it seems to us that the most attractive choice for initial investigation is a member of the infinite layer family of high-T_c cuprates $ACuO_2$ with A=Ca, Sr, or Ba. While most crystal structures support either electron or hole liquids (but not both), n-type[45] and p-type[46] superconductivities have both been reported in the infinite-layer material. These systems also exhibit very weak interlayer coupling which is important for the spatial segregation of the electron and hole gasses.

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