Orbital ordering induced ferroelectricity in SrCrO$_3$

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Using density functional theory calculations, ultrathin films of SrVO$_3$(d$^1$) and SrCrO$_3$(d$^2$) on SrTiO$_3$ substrates have been studied as possible multiferroics. Although both are metallic in the bulk limit, they are found to be insulating as a result of orbital ordering driven by lattice distortions at the ultrathin limit. While the distortions in SrVO$_3$ have a first-order Jahn-Teller origin, those in SrCrO$_3$ are ferroelectric in nature. This route to ferroelectricity (FE) results in polarizations comparable with conventional ferroelectrics.

Recent advances in the growth of oxide thin films have allowed one to engineer both electronic and magnetic functionalities in oxides, very different from their bulk counterparts[1–5]. This additional dimension of oxide research has opened up the possibility of generating cross-correlated electronic couplings which could be interchangeably controlled by both electric as well as magnetic fields, generating new classes of multiferroics. In contrast, there are very few examples among bulk materials which are both magnetic as well as ferroelectric. This is because FE is usually found in d$^0$ systems and d$^0$-ness is not compatible with magnetic order [6]. There are examples of systems which exhibit both orders among finite d$^n$ systems, however the magnitudes of polarization are usually small in such cases.

An avenue that has been quite successful as a route to new ferroelectrics in thin films is one where substrate strain and overlayer thickness have been used as handles to modify properties resulting in behavior very different from the bulk. The work by Haeni et al. [7] showed that substrate strain could be used to engineer a ferroelectric ground state in SrTiO$_3$, a d$^0$ paraelectric. While it was not obvious that this route should work for multiferroics also, first-principles calculations [8] predict that the strain induced by merely depositing the room-temperature ferrimagnetic double perovskites Bi$_2$NiReO$_6$ and Bi$_2$MnReO$_6$ on a substrate should turn their antipolar bulk ground state into a ferroelectric one. S. Bhattacharjee et al. [9] showed theoretically that by increasing the lattice constant of CaMnO$_3$, a polar mode becomes soft and almost degenerate with an antipolar mode. Similar observations were made in epitaxially strained simple binary oxides such as BaO, EuO [10] as well as BaMnO$_3$ [11], SrMnO$_3$ [12] and EuTiO$_3$ [13–14], none of which are examples of bulk ferroelectric materials. All these examples were band insulators. Therefore, Jahn-Teller effects were irrelevant in these systems, allowing, under strain, for the manifestation of the pseudo Jahn-Teller effects, which are usually associated with non-centrosymmetric distortions. An important consequence of these studies was that ferroelectric polarization as large as that found in d$^0$ ferroelectrics was predicted in these oxides. In contrast the observed ferroelectric polarization in most multiferroics is at least one or more orders of magnitude lower [15–17]. This route to a high polarization and possibly magnetism associated with the same atom opens up interesting possibilities.

Orbital ordering has recently emerged as an alternate route to FE. This was recently realized in films of doped manganites on a high-index surface of the substrate [18] where orbital ordering with an axis tilted away from the substrate normal was found. This led to off-centring. Again in this case the examples considered were bulk insulators, which we show in the present work need not be a limitation in the choice of materials. We start by considering the example of SrVO$_3$ and SrCrO$_3$, both of which are metallic in the bulk. In this work we explore a new route to non-d$^0$ FE through ultrathin films of transition metal oxides which, as discussed earlier, were found to be insulating. In contrast to the examples listed above, in the cases we investigate, the transition-metal cation is Jahn-Teller active in bulk. A further important difference is that strain (although it could be present) does not play a crucial role in the induced FE.

Ultrathin films (just two monolayers(MLs)) of SrVO$_3$ on SrTiO$_3$ (001) as well as films comprising of two MLs of SrCrO$_3$ on SrTiO$_3$ (001) are considered. Examining the electronic structure theoretically, we find both systems to be insulating, both arising from an orbital ordering at the surface, driven primarily by structural distortions. While SrVO$_3$ favors Jahn-Teller distortions, SrCrO$_3$ favors a ferroelectric ground state, with a large contribution to the energy lowering in the insulating state derived from these distortions. Our detailed analysis shows that the modifications of the crystal field at the surface associated with a missing apical oxygen allow for the observed FE in SrCrO$_3$ (and possibly in other non-d$^0$ transition metal compounds). These distortions at the surface survive even for the thicker films. The calculated polarization is found to be large, comparable to that in bulk d$^0$.
ferroelectrics.

We consider a symmetric slab (see for instance Ref. [20]) consisting of 13 layers of SrO - TiO₂, terminating in a TiO₂ layer, to mimic the substrate. The in-plane lattice constant is fixed at the experimental value (3.905 Å) for SrTiO₃, while the out of plane lattice constant was varied. We allowed for tilts of the TiO₆ as well as MO₆ octahedra, a distortion observed in low temperature SrTiO₃ [21]. The electronic structure of these systems was calculated within VASP [22] using a k-point mesh of 6x6x1 using GGA+U scheme [24] with a Uₐₙₐ [25]/Cr. A vacuum of 15 Å was used to minimize interaction between slabs in the periodic supercell geometry. Internal positions were allowed to relax to their minimum energy value. We construct maximally localized Wannier functions (MLWF) and use the shifts of their centers in the ferroelectric phase with respect to the paraelectric one to calculate the ferroelectric polarization [19]. For this purpose, the electronic ground state for the relaxed structure was converged with the Full-Potential Linearized Augmented Plane-wave Method-based code FLEUR [20], in film geometry, on a 7x7 k-points mesh. MLWF were constructed with the Wannier90 code [27] and the interface between FLEUR and Wannier90 [28]. The advantage of the Wannier functions approach (over the Berry phase one) in the specific system where the ferroelectric polarization is not uniform is that the contributions of every layer/atom (see [28]) to the electronic polarization can be extracted.

We started by calculating the electronic structure of bulk SrVO₃ and SrCrO₃ within GGA+U. Both compounds were found to be metallic, consistent with experiment. Next, we performed similar calculations for two MLs of SrMO₃ (M = V, Cr) on SrTiO₃, and the ground state was in both cases found to be insulating.

Let us first examine in more detail the case of SrVO₃. Each VO₃ unit at the surface has in-plane V-O bondlengths (1.95 Å) longer than the out of plane one (1.91 Å). This could in principle result in a lower energy for the dₓᵧ orbital than for the doubly degenerate dᵧz and dₓz orbitals (Fig. 1(a)). As there is just one electron associated with the V⁴⁺ ion, in this case an insulating ground state is expected. However, since one of the apical oxygens is missing at the surface, this could result in a reversed ordering of the levels leading to a metallic state (Fig. 1(b)). Our calculations find the scenario discussed in Fig. 1(b) realized. However, on performing a complete structural optimization one finds an orbital ordering transition which has a Jahn-Teller origin with two elongated V-O (2.18 Å) and two contracted V-O bondlengths (1.78 Å) (see Fig. 1(c)). A ferromagnetic state is found to be favored by 60 meV/V at the two ML limit in contrast to the bulk which is paramagnetic.

To contrast the results for SrVO₃ films, we have also considered two MLs of SrCrO₃ on SrTiO₃ substrate. Here also the degeneracy lifting of the Cr t₂g levels is a consequence of the missing apical oxygen with the dₓz and dᵧz levels at lower energy than the dₓᵧ level. As there are two electrons in the d levels of Cr⁴⁺ ion, they occupy the doubly degenerate dₓz and dᵧz levels, leading to a band insulator. Interestingly, we find that carrying out complete structural optimization results in a strong modification of the in-plane Cr-O bondlengths from their starting values: while two of the bondlengths contract, the other two extend (Fig. 1(d)) [29]. The effect of this structural distortion is that the system has no inversion symmetry now and possesses a finite electric polarization. While in both SrVO₃ and SrCrO₃ the dominant energy lowering comes from the in-plane distortions, note the important difference: in SrCrO₃, the Jahn-Teller effect is quenched due to one additional electron on Cr⁴⁺ and to the modified crystal field at the surface (with respect to that of the bulk material), so the pseudo-Jahn-Teller effects become operative driving the system ferroelectric/polar. These results put ultrathin films of SrCrO₃ in the same category of band insulators turned ferroelectrics where orbital ordering drives the system insulating. Now every band insulator does not turn ferroelectric, so this immediately brings up the question of the microscopic interactions that are responsible for FE here. In the following, we investigate the origin of the observed ferroelectric distortions.

In Fig. 2(a) we have plotted the partial density of Cr-d states for the structure in which the film is constrained to be centrosymmetric. A band gap barely opens up in this structure between the majority spin Cr dᵧz/dₓz states and the dₓᵧ states. The bandwidths associated with the dₓz, dᵧz orbitals are a factor of two less than the bandwidths associated with the dₓᵧ orbitals as a result of broken periodicity along the positive z-direction. Allowing for the constraint of centrosymmetry to be relaxed, we find that two of the in-plane Cr-O bondlengths become shorter and are equal to 1.78 Å while two others become longer and are equal to 2.15 Å, in contrast to their undistorted values of 1.95 Å. A part of the energy lowering in the process comes from the increased hopping interaction due to shorter Cr-O bonds. This is clearly seen in the increased separation of the bonding and antibonding states with dominant contribution from the dₓᵧ orbitals (Fig. 2(b)). The shorter Cr-O bondlengths also result in an increased repulsion between the electrons on Cr and O. This is partly overcome by the presence of the vacuum in the z-direction which allows the dₓz, dᵧz orbitals to extend into the vacuum region. This may be seen from the charge density plot associated with the antibonding states with dₓz/dᵧz character plotted in the inset of Fig. 2(b). The lobe of the d orbital closer to the longer Cr-O bond, extends further into the vacuum to compensate for the increased repulsion associated with the shorter Cr-O bonds. These results also provide us with design principles for generating multiferroic materials in which one has MO₃ structures resulting from MO₆ octahedra. In-
plane distortions as well as larger spacings in one of the z-direction in which the oxygen is absent could result in ferroic distortions.

In Fig. 3 we show the calculated values of the layer-resolved ferroelectric polarization for the case of two MLs of SrCrO$_3$ on SrTiO$_3$. The bars with vertical, (violet) pattern show the total (ionic plus electronic) polarization in CrO$_2$/TiO$_2$ layers, while the ones with the horizontal (green) pattern show the total polarization in SrO layers. The (gray) bars outlined with violet (CrO$_2$/TiO$_2$ layers) or (green) (SrO layers) indicate the electronic contribution to the total polarization in the respective layers. Note that the electronic contribution in CrO$_2$/TiO$_2$ layers is rather large. It constitutes about 50% of the total polarization, while in SrO layers it is smaller and negative. The polarization points in the <110> direction (in-plane) and is calculated per layer, i.e. instead of the unit cell volume that would be used to evaluate it in a bulk system, we use the volume of each layer, calculated as the product of the area of the in-plane unit cell and the sum of the half-distances to the neighboring layers on either side. The volume of the surface layer is taken to be equal to the one beneath it. While not ferroelectric in bulk, we find that a significant polarization is induced in high-k SrTiO$_3$ by the ferroelectric shifts of Cr$^{4+}$ ions at the surface. Note that the polarization in the center of the film is constrained to zero by the chosen geometry (in the calculation, the Cr$^{4+}$ ions move in the opposite directions on the opposite sides of the film) and its decay with the distance from the surface need not be as rapid in the case of a thicker substrate. A rough estimate of the energy for switching is found to be 42 meV [30], similar to other displacive ferroelectrics [31].

In SrCrO$_3$ the observed ferroelectric distortions were associated with the two MLs limit. However when an additional SrO ML was added, this led to the out-of-plane distortions becoming the largest distortions. The differing environments on either side of the surface CrO$_6$ octahedra lead to unequal bondlengths of 1.88 Å and 1.95 Å along the positive and negative z-direction. As a result, a finite dipole moment develops (though it is unswitchable by an electric field). Similar observations have been made on other interfaces [32]. The system still remains insulating at this limit. Adding another layer we find that the surface CrO$_2$ layer sustains ferroelectric distortions in addition to charge ordering. Cr in CrO$_2$ is found to have a negative charge transfer energy [32]. Here also we find this to be the case, and consequently some of the holes are localized on the oxygens. The surface Cr atoms are found to have a valency of d$^{3+6}$ and d$^2$ (Fig. 4 (a)-(b)), while the sub-surface Cr atoms have a breathing mode type distortion which leads to a valency of d$^{3-δ}$ and d$^2$ on these Cr atoms (Fig. 4 (c)-(d)). By comparing the total energy of several configurations we find a ferromagnetic coupling parameter in the surface Cr layer and an antiferromagnetic coupling in the sub-surface layer and between the layers.

In the preceding discussion the substrate imposed a tensile strain on the SrCrO$_3$ overlayers. It is impressive, however, that one finds that as a consequence of the large stabilization energy for the in-plane ferroelectric distortions, the films can sustain these distortions even for 2% compressive strain.

Having established FE at the ultrathin limit, we next went on to examine the magnetic properties as a function of thickness. The bulk is found to be an antiferromagnetic metal, consistent with experiment. At the ultrathin limit of two MLs the antiferromagnetic state is more stable than the ferromagnetic state by 45 meV/Cr atom corresponding to a nearest-neighbor coupling of $J = 11.25$ meV in a Heisenberg model. The stabilization of an antiferromagnetic state can be easily understood within a superexchange picture as there are channels for delocalization only for an antiferromagnetic arrangement of spins. This difference is enhanced at the three MLs limit to 52 meV/Cr atom. At the four MLs limit various magnetic configurations were considered, and we find that the surface layer becomes ferromagnetic while the subsurface CrO$_2$ layer becomes antiferromagnetic with the system found to be insulating. The closely competing configuration where both surface layer Cr atoms as well as the sub-surface layer Cr atoms are coupled antiferromagnetically is found to be 9 meV/Cr atom higher.

From a device perspective, the important question is whether there is a coupling between the electrical and magnetic degrees of freedom. We compute the magnetic crystalline anisotropy for the two MLs film of SrCrO$_3$ and find that the spin favors an in-plane orientation over an out-of-plane one by 128 μeV per Cr atom. Within the plane, the spin favors an orientation at 90° to the direction of the electric polarization by 14 μeV. We note that a similar arrangement was observed in BiFeO$_3$[34]. By Monte Carlo simulations on a Heisenberg model basis including single-ion anisotropy we find that the coupling between electric polarization and staggered-magnetization direction persists up to a temperature of 70 K after which short-range magnetic order is lost. Even if this temperature is considerably lower than room temperature, the novel mechanism that is revealed here could emerge in other materials at higher temperature provided that the exchange is stronger.

Ultrathin films of d$^1$ and d$^2$ transition metal oxides have been explored as possible candidates for multiferroicity. Orbital ordering allows one to realize an insulating surface even in systems where the bulk form is metallic. While these have a Jahn-Teller origin in the case of SrVO$_3$, pseudo Jahn-Teller effects result in sizeable ferroelectric distortions for SrCrO$_3$ which, even in the absence of strain, also turns out to be an antiferromagnetic insulator at this limit of two MLs. These distortions persist into the substrate and survive for the surface CrO$_2$ layer even for thicker films of four MLs opening up new possi-
bilities for non-\textit{d}^{0} multiferroics.

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FIG. 1: (Color online) Distortions and crystal field splitting of the $t_{2g}$ orbitals for (a) a $MO_6$ octahedron under tensile strain, (b) a surface $MO_5$ unit, where $M=$transition metal atom. The $M$-$O$ network in the x-y plane found in the presence of (c) Jahn-Teller distortions (seen in SrVO$_3$), (d) pseudo Jahn-Teller distortions (seen in SrCrO$_3$). Large(small) and grey(red) spheres denote M (O) atoms.
FIG. 2: (Color online) The majority spin $d_{xz}$, $d_{yz}$ and $d_{xy}$ projected partial density of states for a Cr atom in (a) bulk-like geometry, (b) in the optimised ferroelectric geometry for two MLs of SrCrO$_3$ films on SrTiO$_3$. The charge density associated with the antibonding states with $d_{xz}$, $d_{yz}$ character is shown in inset of panel (b). Vertical dashed lines indicate the valence band maximum and conduction band minimum of SrTiO$_3$. The zero of energy indicates the fermi energy.

FIG. 3: (Color online) The layer resolved polarizations for two MLs of SrCrO$_3$ on SrTiO$_3$. The bars with vertical, violet pattern show the total (ionic plus electronic) polarization in CrO$_2$ layers, while the ones with the horizontal green pattern show the total polarization in SrO layers. The gray bars outlined with violet (CrO$_2$ layers) or green (SrO layers) indicate the electronic contribution to the total polarization in the respective layers.
FIG. 4: The majority spin $d_{xz}$, $d_{yz}$ and $d_{xy}$ projected partial density of states for a Cr atom belonging to the surface layer ((a)-(b)), and to the sub-surface layer (panels (c)-(d)), of 4 MLs SrCrO$_3$ films on SrTiO$_3$. Vertical dashed lines indicate the valence band maximum and conduction band minimum of SrTiO$_3$. The zero of energy indicates the fermi energy.