# Electronic and magnetic structure of CrO_{2}-RuO_{2} interfaces

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*Abstract*

CrO$_2$ and RuO$_2$ share the same (rutile) crystal structure and have similar lattice constants. We have used Density Functional Theory (DFT) within the generalized gradient approximation (GGA) to calculate the electronic and magnetic structure of CrO$_2$, RuO$_2$ and their interfaces. We also used DFT-GGA to investigate the electronic and magnetic structure of CrO$_2$ and RuO$_2$. Consistent with previous calculations and experiment we find that the CrO$_2$ Fermi energy lies in a band gap for the minority channel. RuO$_2$, in agreement with experiment, is predicted to be a nonmagnetic. We find relatively good matching between the majority energy bands of CrO$_2$ and both RuO$_2$ channels in the (100), (110) and (001) directions. For (100) interfaces, we find a small induced Ru moment oriented opposite to that of the Cr moments. We study the change in energy as a function of the angle between the interfacial and bulk Cr magnetic moments. We investigate both sharp and mixed (100) - and (110) -oriented CrO$_2$-RuO$_2$ interfaces with a supercell approach. We investigate the origin of the large negative moment that forms when a Ru ion substitutes for a Cr ion. We speculate that weakened inter-ionic exchange interactions, non-collinear spins and induced moments at interfaces may be a common problem in oxides that may be a challenge to overcome for achieving large GMR and TMR effects.

## 1. Introduction

The goal of spintronics is to envision and fabricate devices that utilize the electron's spin degree of freedom as well as its charge. The operation of most spintronic devices is based on the difference in electronic structure and transport properties of the majority and minority spin channels of ferromagnetic metals. The most extreme difference between spin

channels is obtained in "half-metals," i.e. materials in which one channel is metallic and the other is insulating or semiconducting. Such materials should be ideal for spintronic applications. To date, however, the success of half-metals in spintronic applications has been limited.
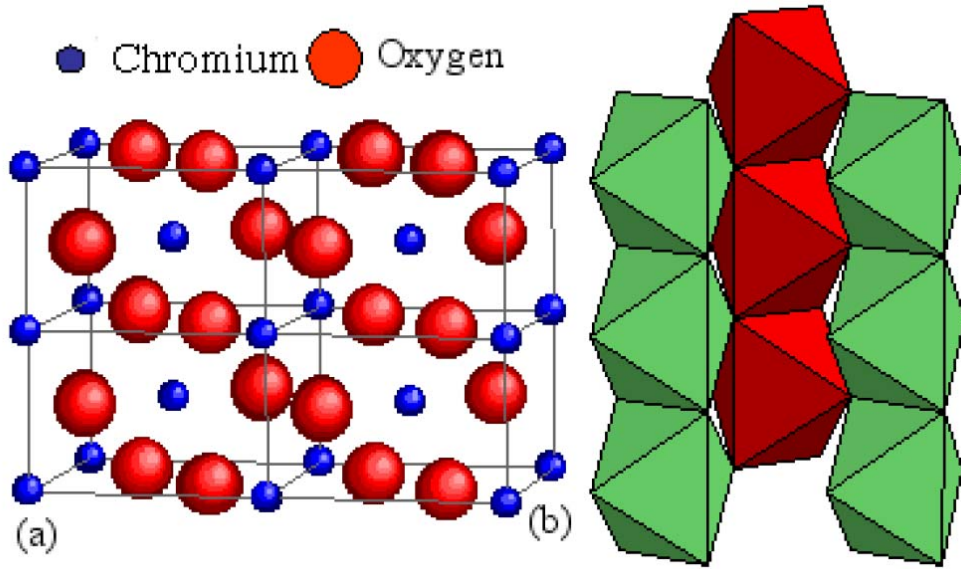


Figure 1: (Color online) Rutile structure. For $CrO_2$-$RuO_2$, we use $a = 4.42$ and $\frac{c}{a} \approx 0.670$.

In particular, $CrO_2$, which is the only material for which there exists definitive experimental evidence for a half-metallic electronic structure,[1,2,3,4,5,6] and which (among known half-metals) has the largest gap in the non-metallic spin channel, has shown only minimal spintronic effects.[7,8,9] $CrO_2$ also appears to be unique among the half metals currently known in that its surface is also predicted to be half-metallic.[10] One could also argue that in addition to being the "best" half metal (for the reasons mentioned above) it is also the "simplest" in the sense that it consists of only two elements and has a robust structure, e.g. it is highly unlikely that the Cr and O ions can exchange positions. Against this structural simplicity, one must balance the possible complications that may arise from electron-electron correlations which may be more important in these transition metal oxides than in the transition metals and their alloys.

Both $CrO_2$ and $RuO_2$ are good metals, especially at low temperature and are thus appropriate candidates for a GMR device. As a step towards the application of half-metals to spintronic devices, we attempt to understand the electronic structure of $CrO_2$-$RuO_2$ interfaces.
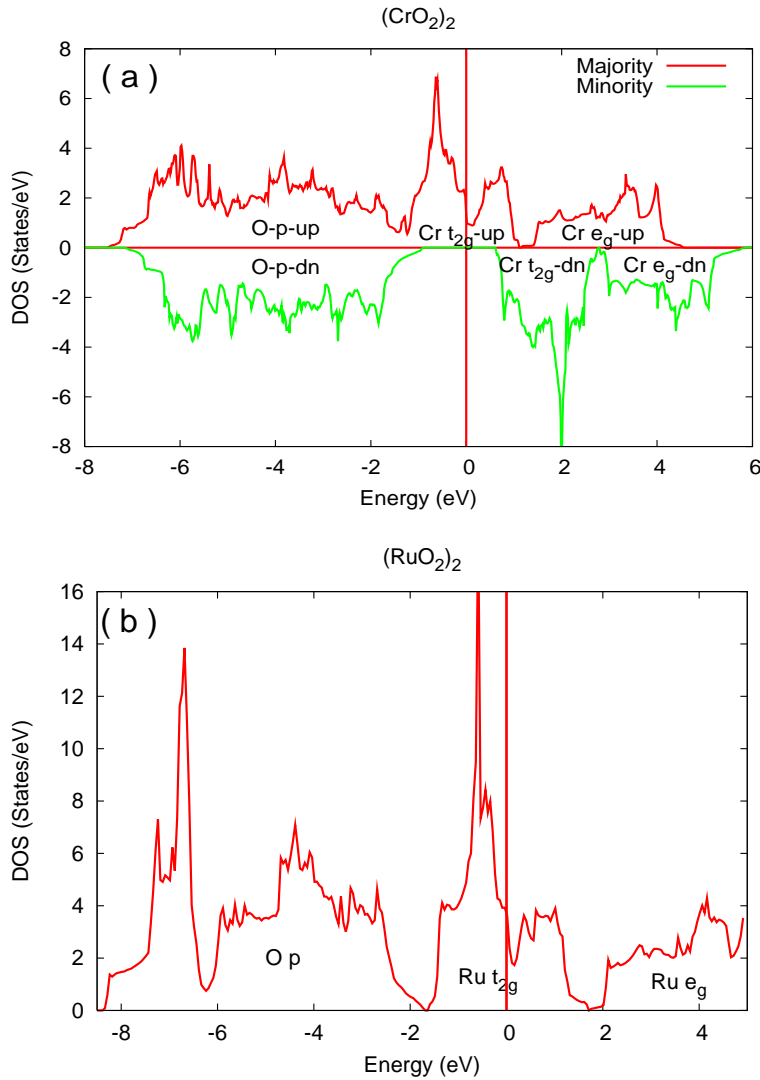
Figure 2: (Color online) Electronic density of states obtained within GGA calculations for (a) $CrO_2$, (b) $RuO_2$ (majority and minority spin channels are identical). For both cases we report the number of states per unit energy in a tetragonal cell containing 6 atoms. For $CrO_2$, the majority DOS is shown as positive and the minority as negative.

## 2. Electronic Structure of $CrO_2$ and $RuO_2$

$CrO_2$ is a ferromagnetic half-metal with the rutile crystal structure (Figure 1). Figure 2 shows our calculated electronic density of states for $CrO_2$ and $RuO_2$. Our results are in general agreement with previous first-principles electronic structure calculations. [1,11,12] The electronic structure calculations presented in this paper were performed using the VASP code with the generalized gradient approximation (GGA) for the exchange-correlation functional.[13,14]

In the rutile-structure transition metal oxides, six oxygen ions form a distorted octahedron surrounding each transition metal cation. It is useful to separate the electronic states into three groups as indicated in Figure 2. The lowest energy group, consisting of three states per O-ion per spin, (labeled "O-p" in Figure 2) have wave functions that are primarily of O-p character with some admixture of cation-d. The O-p states are filled in both $CrO_2$ and $RuO_2$. The O-s states are also filled (and lie about 20 eV below the Fermi energy) so that if we consider the electrons in the O-p states to "belong" to the O ion, they will have a total of 8 electrons per ion so that the O ions are in the -2 valence state. Correspondingly, in this picture, the cations in $CrO_2$ and $RuO_2$ will be in the +4 valence state each metal atom having "lost" 4 electrons to the surrounding O ions. Although this picture provides a useful shorthand for describing these oxides it should be remembered that it is an approximation. Both the "O-p" bands and the "cation-d" bands are hybridized and there may be no sensible way to apportion the charge density between the O ions and the cations that would give them charges equal to their nominal valence states.

The other two groups of states are primarily derived from the cation d-states and consist of a lower energy group of 3 states per transition metal cation (labeled "$t_{2g}$") that are derived from d-wave functions having $xy$, $yz$ or $zx$ symmetries relative to the axes of the distorted octahedron and a higher energy group consisting of 2 states per transition metal cation (labeled "$e_g$") derived from d-functions having $x^2$-$y^2$ and $3z^2$-$r^2$ symmetries. Although these states are nominally cation d-states they are hybridized with the O-p states.

Using the ionic picture we can say that there are two occupied Cr-d states per Cr ion and 4 occupied Ru-d states per Ru ion. In $CrO_2$ the system energy is reduced by the generation of spin-polarization which shifts the majority Cr-d states down and the minority d-states up resulting in both of the occupied Cr-d states being majority. For $RuO_2$, the gain in exchange energy from spin-polarization is insufficient to off-set the concomitant cost in kinetic energy so that there is no spin-polarization and there are two occupied majority states per Ru and two occupied minority states.

In the simplest model of the electronic structure of the interface in which the bulk electronic structures are used with matching Fermi energies, we would expect very little reflection of majority electrons at the $CrO_2$-$RuO_2$ interface. This is illustrated in Figure 3 where we show the majority bands near the Fermi energy of both $CrO_2$ and $RuO_2$ calculated in the (100), (110) and (001) directions. For the minority channel, the bands of $RuO_2$ are the same as for the majority, but for $CrO_2$, there are no minority bands. One would expect for such similar majority electronic structures that, if a sandwich structure were constructed in

which two $CrO_2$ electrodes are separated by a $RuO_2$ spacer layer, there should be a large conductance between the $CrO_2$ electrodes when the moments are aligned and essentially no conductance when they are anti-aligned. In fact, this expected large GMR has not yet been observed experimentally. One of the main conclusions of this paper is that, within density functional theory, this "simplest model" is not adequate to describe the electronic structure of the interfaces even if they are structurally perfect.

Usually, these interfaces are not perfect. In $CrO_2$ –$RuO_2$ multilayered structures grown in the (100) direction by chemical vapor deposition, no significant GMR effects were observed[9] for either CPP or CIP (current in the plane).[9] It was observed that the $CrO_2$ layer intermixed with the $RuO_2$ layer at the interface.[9] First-principles calculations of $CrO_2$ and $CrO_2$-$RuO_2$ interfaces in the (100) and (110) directions were conducted in order to determine whether non-collinear spins at the interface could form, thereby eliminating the GMR effect.

### 3. Exchange in $CrO_2$-$RuO_2$

We performed calculations in which the directions of the magnetic moments were constrained using VASP on (100)- and (110)-oriented $CrO_2$-$RuO_2$ interfaces to understand the likely magnetic orientation of the Cr ions at the interface. In this method, the magnetic moment of each ion was constrained along a certain direction in a manner analogous to applying an external magnetic field. As shown in Figure 4(a), a (100)-oriented $CrO_2$-$RuO_2$ sharp interface was modeled by putting two unit cells of $CrO_2$ and $RuO_2$ side by side. The termination of the rutile oxide surface along the (100) and (110) directions is well understood,[15] and the $RuO_2$ structure fits very well with the terminated surface of $CrO_2$ along both the directions. To simulate a mixed (100)-oriented $CrO_2$-$RuO_2$ interface, we replaced the corner Cr ions at the interface with Ru ions and the body centered Ru ion in the $RuO_2$ cell
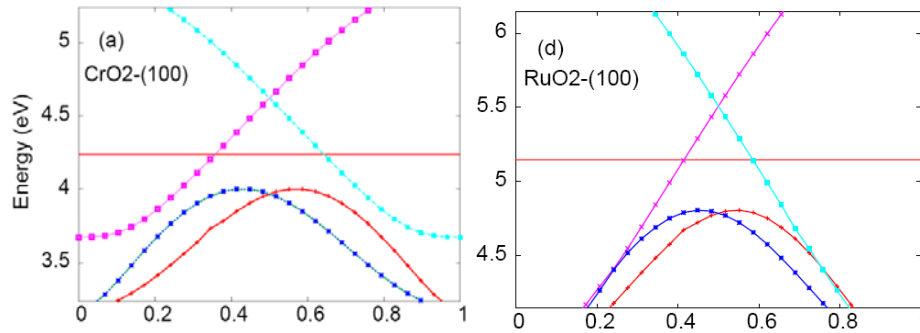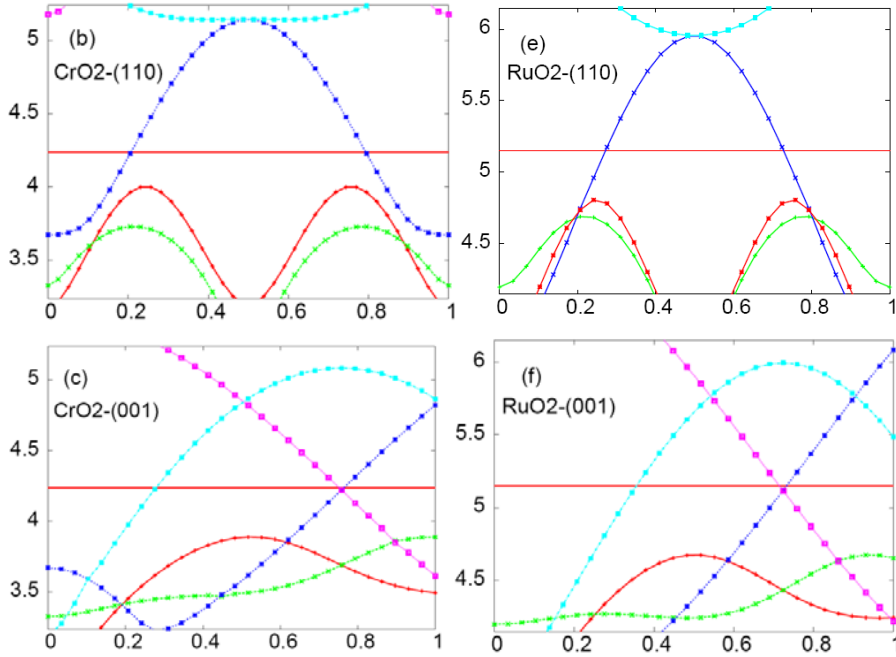
Figure 3: (Color online) Majority band structure near the Fermi energy for $CrO_2$ (no minority bands) and $RuO_2$ (minority bands are identical to majority) for, (a-c): (100), (110), and (001) directions for $CrO_2$ and (d-f): (100),(110), and (001) directions for $RuO_2$.

with a Cr ion as shown in Figure 4(b). In the intermixed region, the Cr ion is surrounded by Ru ions, and we expected that the exchange interaction between two Cr ions mediated by the Ru ion might cause an antiferromagnetic or even noncollinear spin alignment in the intermixed region. The $CrO_2$ structure was relaxed using the GGA to optimize the lattice parameter and the atomic positions. The calculated lattice parameters were $a=b=4.66$Å and $c=2.968$Å, which are very close to the experimental values.[16] Considering the relative thickness of electrode and spacer layer in a GMR stack, we set the $RuO_2$ cell's in-plane lattice parameters to that of our relaxed $CrO_2$, creating in-plane strain at the interface. The magnetic moments of the fixed-moment-direction Cr atoms were aligned in the $z$ direction, and the magnetic moment of the Cr atoms at the interface were rotated through 180º, starting parallel to the fixed moments.
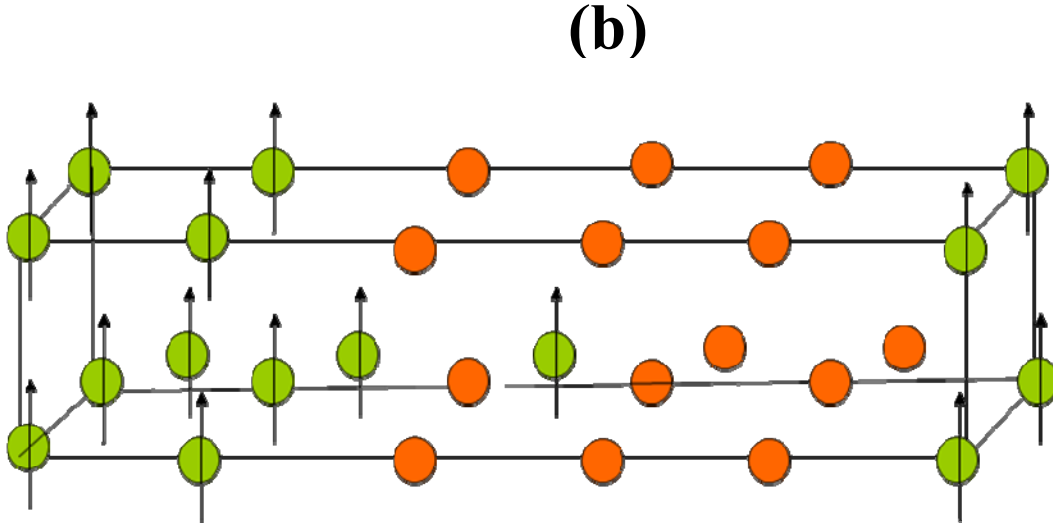
**(a)**

**(b)**
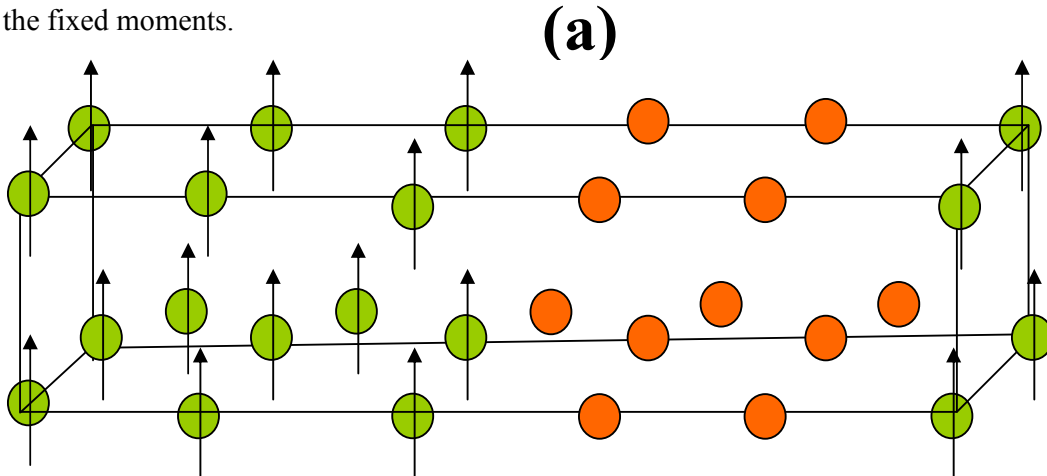


Figure 4: (Color online) (100) oriented $CrO_2$-$RuO_2$ interface (a) sharp interface (b) mixed interface. Oxygen ions are omitted for clarity.

In Figure 5 we show the energy of the supercell shown in Figure 4 containing a (100) interface between $CrO_2$ and $RuO_2$. We show for both sharp and mixed interfaces, the calculated energy as the moments on the interfacial Cr ions are rotated relative to the moments of the bulk Cr ions. In the (100)-oriented sharp interfaces (no interdiffusion of Cr and Ru ions) ferromagnetic alignment of the Cr ions at the interface is energetically favorable. The energy of the $CrO_2$-$RuO_2$ system *vs*. angle between fixed and rotated moments curve fits approximately to a cosine function, indicating that it can be represented with a Heisenberg model as was found for bulk $CrO_2$[17]. The relatively strong ferromagnetic alignment at the interface reduces the probability of losing magnetoresistive signal due to interfacial spin-flip scattering. However, when Cr and Ru ions interdiffuse near the interface in (100) $CrO_2$-$RuO_2$, the strength of the interfacial exchange interactions is greatly reduced and the sign is opposite indicating that antiferromagnetic ordering between the interfacial and bulk Cr ions is more stable than ferromagnetic alignment. This is an undesirable effect for a GMR structure that may lead to increased spin-flip scattering and lower MR. We speculate that this effect may contribute to the low MR value observed in the (100)-oriented $CrO_2/RuO_2/CrO_2$ GMR structure.[9]

The calculated energy differences shown in Figure 5 correspond to a difference in

interfacial energy between interfacial Cr moments aligned and anti-aligned with the bulk Cr moments of 95.7 meV per supercell for the sharp interface and -25.6 meV per supercell for the mixed interface. The latter, antiferromagnetic, exchange interaction is in qualitative agreement with that reported in Sims et al.[17] For our model of the mixed interface, the interfacial Cr ion has only one Cr nearest neighbor (along (100)). Note that the energy difference reported in this work (-25.6 meV per supercell) contains a doubly-counted contribution from both the interfacial Cr and its neighbor along (100). Dividing this quantity in half yields a result that is similar to the $J_{100}$ exchange energy reported in Ref. [17]. Ref. [18] reports exchange energies for single layers of $CrO_2$ surrounded by multiple layers of $RuO_2$, whereas the interfaces in the present work consist of alternating regions of $CrO_2$ and $RuO_2$. As noted above, the exchange at the mixed interface (as well as the sharp interface) fits the Heisenberg model as in Ref. [17], while the Cr—Cr exchange in Ref. [18] follows an interlayer exchange model, mediated by the Ru ions.
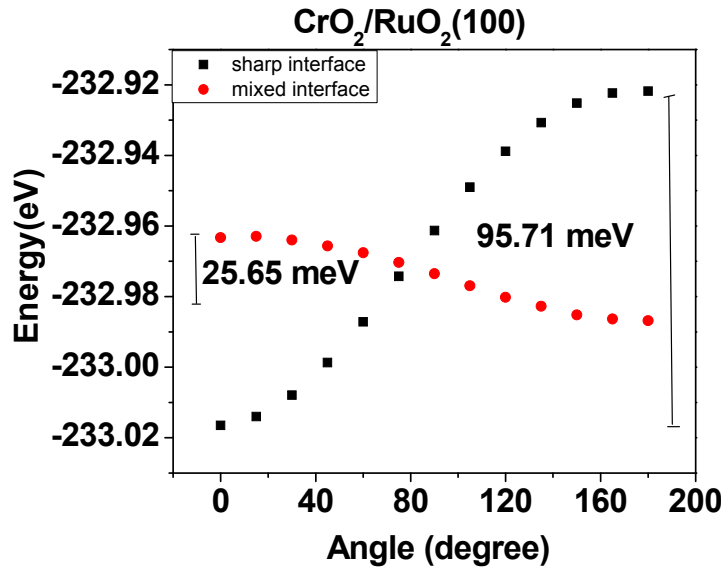


Figure 5: Energy of a supercell containing a $CrO_2$-$RuO_2$ interface oriented perpendicular to the (100) direction as a function of the magnetic moment direction (relative to that of the bulk Cr ions) of the interface Cr ions. The supercell energy differences due to the interfacial moments being rotated between 0 and 180 degrees correspond to energies of 95.7 meV for the sharp interface and -25.6 meV for the mixed interface.

Similar calculations were performed for (110)-oriented $CrO_2$-$RuO_2$ sharp and mixed interfaces. As shown in Figure 6(a) and (b), there are two cations and four anions per layer in the cell that we used to model these structures. For the sharp interface, the corner Cr ion and the face-centered Cr ion at the interface are rotated, while the moments of all other Cr ions

are kept fixed. The intermixed region is modeled by replacing the corner Cr ions at the interface with Ru ions and replacing one face-centered Ru ion in the $RuO_2$ cell with a Cr ion. Figure 7 shows the energy as a function of the angle between the rotated and fixed Cr moments for both sharp and mixed interfaces. In both the sharp and intermixed (110) interface, ferromagnetic alignment is the energetically stable state. This may be viewed as an encouraging result, indicating that use of (110) oriented $CrO_2$-$RuO_2$-$CrO_2$ GMR structures, may reduce interfacial spin-flip scattering and point towards a potential path for achieving a larger magnetoresistive effect. We should caution, however, that this is only one of many possible ways the interface may be disordered. The exchange interactions between the neighboring spins in the (110)-oriented interface (measured in terms of the energy required to reorient the interfacial Cr ion moments from parallel to anti-parallel with the bulk) were 180meV for sharp interface and 46 meV for mixed interfaces.
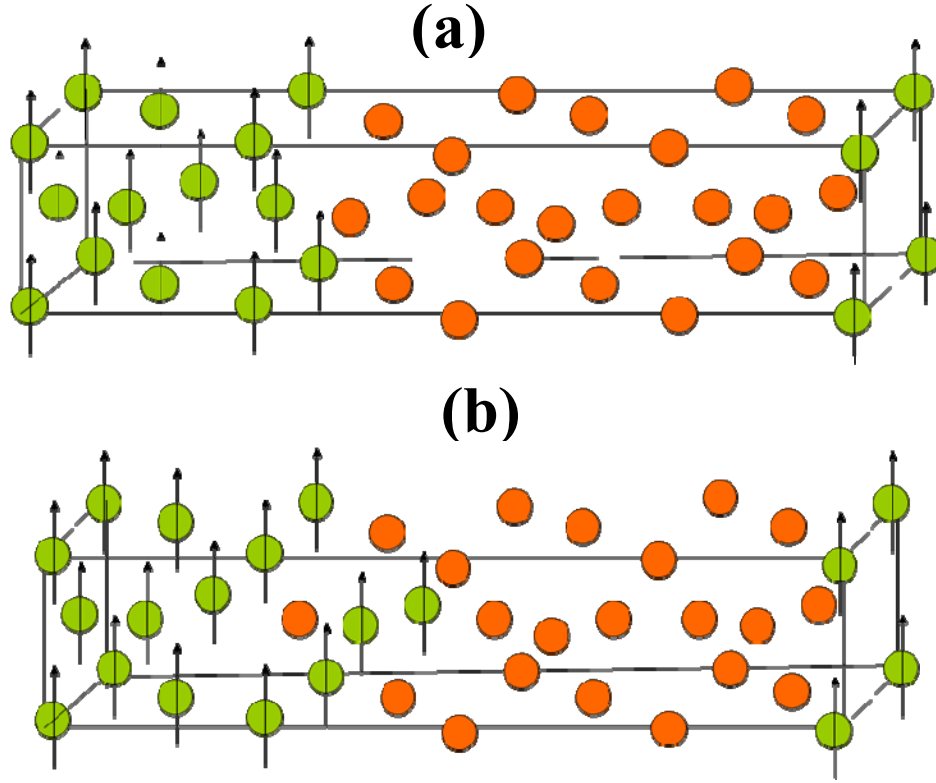
**(a)**

**(b)**



Figure 6: (Color online) (110) oriented $CrO_2$-$RuO_2$ interface (a) sharp interface (b) mixed interface. Oxygen ions are omitted for clarity.

## 4. Induced Moments on Ru ions in $CrO_2$-$RuO_2$

In the preceding calculations, small moments were found on Ru ions near the

interface. The moments were found to be larger for the mixed interface than for the sharp interface. For the (100) oriented $CrO_2$-$RuO_2$ sharp interface, a moment of -0.1 $\mu_B$ is induced in the Ru atom in the body centered position at the interface and in the corner atom next to the interface layer. For the mixed interface, the moment induced on the Ru atom in the intermixed region is -0.22 $\mu_B$ and -0.12 $\mu_B$ on the Ru atom in the next layer,. In the (110) $CrO_2$-$RuO_2$ sharp interface, the induced Ru moment was approximately -0.04 $\mu_B$, while the
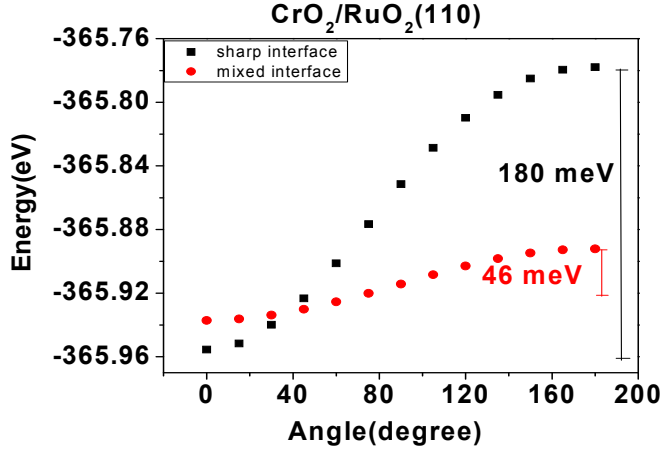


Figure 7: (Color online) Energy of a supercell containing a $CrO_2$-$RuO_2$ interface oriented perpendicular to the (110) direction as a function of the magnetic moment direction (relative to the bulk Cr ions) of the interface Cr ions. The supercell energy differences due to the interfacial moments being rotated between 0 and 180 degrees correspond to energies of 180 meV for the sharp interface and 46 meV for the mixed interface.

Ru ions in the mixed interface had an induced moment of -0.24 $\mu_B$ and the Ru in the next layer had a moment of -0.12 $\mu_B$. All of the moments quoted are within a sphere of radius 0.55 Å. This induced moment and its relevance to interlayer exchange in this same system was also discussed by Sims and Butler.[18] Ref. [18] reports that the Ru ions in the (100) interface acquire an induced moment of -0.2 $\mu_B$, which is consistent with the present results.
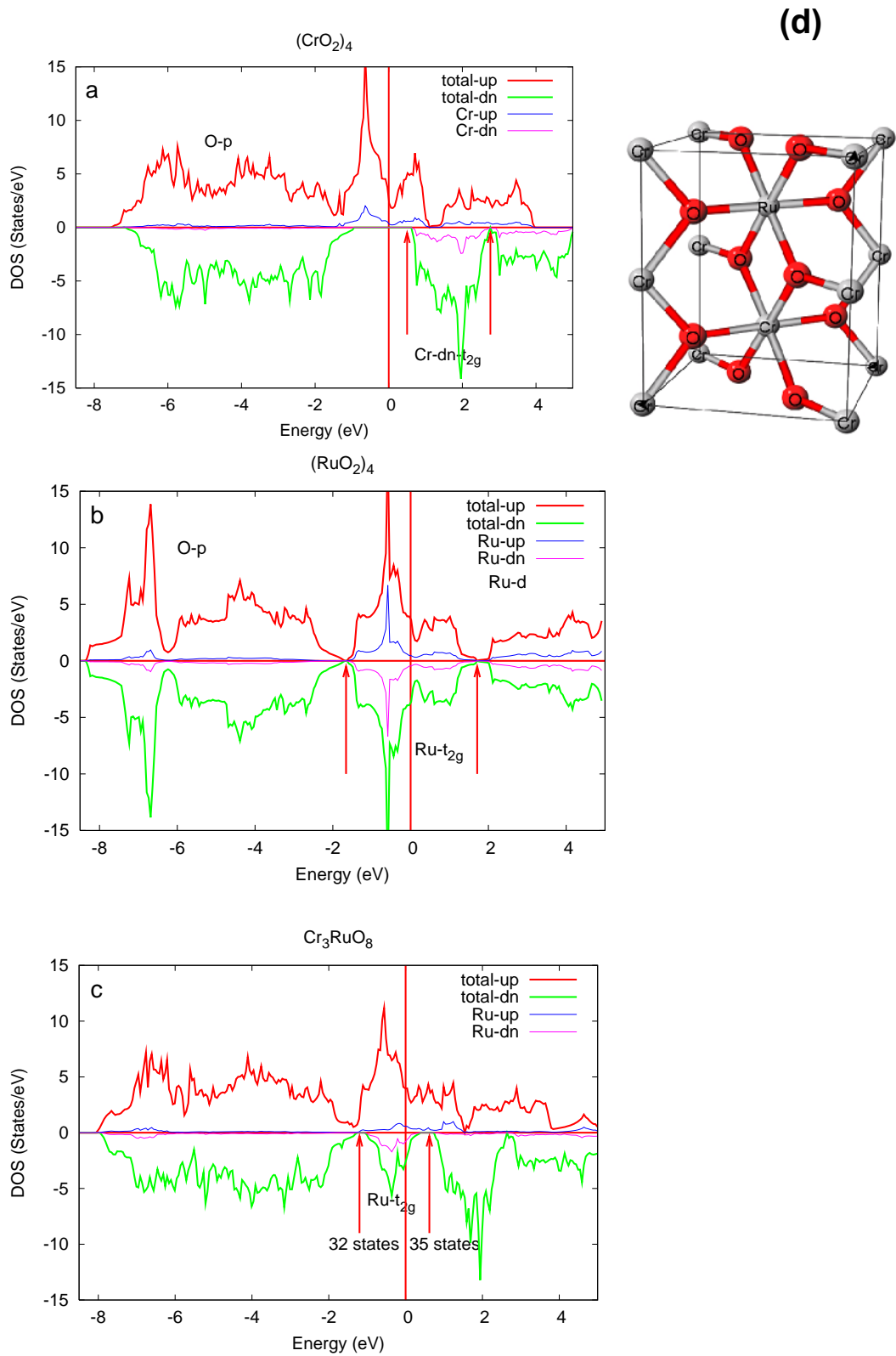
Figure 8: (Color online) (a) Total Density of States (bold lines) for a $CrO_2$ supercell containing 4 Cr ions. Thin curves indicate the DOS within a sphere of radius 0.55Å centered at a Cr ion position. (b) Total (bold lines) Density of States for an $RuO_2$ supercell containing 4 Ru ions. Thin curves indicate the DOS within a sphere of radius 0.55Å centered at a Ru ion

position. (c) Total (bold lines) Density of States for a supercell containing 3 Cr ions and a single Ru ion. Thin curves indicate the DOS within a sphere of radius 0.55Å centered at the Ru ion position. (d) Two unit cell rutile structure model for Ru impurity in $CrO_2$. One of 4 Cr cations is replaced by Ru. Two arrows in panels (a), (b) and (c) distinguish an energy interval containing exactly 3 states per cation.

We investigated the origin of this induced moment in interfacial Ru ions via another set of calculations within GGA using VASP. We calculated the density of states of $CrO_2$ (Figure 8a) and $RuO_2$ (Figure 8b). The panels also indicate the DOS within a sphere of 0.55 Å radius centered on one of the cations. The figures also label the O-p states and the Cr and Ru d-states.

Comparing panels (a) and (b) of Figure 8 we observe that the primary difference is that the Ru ion has four electrons compared to two for the Cr ion. The additional two electrons go into the minority d-band so that the Ru ion in $RuO_2$ has no moment. The two arrows in the panel indicate points of zero DOS that are useful for counting the number of states. Because of the approximate cubic symmetry of the oxygen octahedron surrounding each ion, the 5 d-states split into a low energy ($t_{2g}$) complex of three states per cation and a higher energy complex of two ($e_g$) states per cation. In the minority channel this splitting causes the DOS to go to zero between them so it is easy to identify the states. Thus the two arrows in each panel define an energy interval containing precisely 3 minority ($t_{2g}$) states per cation.

To understand why the Ru ion develops a moment and why it is opposite to that of the Cr ion, we imagine replacing a Cr ion by a Ru ion. As a first approximation, we could imagine taking ¾ of the $CrO_2$ DOS and adding to it, ¼ of the $RuO_2$ DOS. If this approximation were perfect, the number of majority electrons would not be affected, but we would have added 2 minority electrons so the total moment would decrease by $2\mu_B$. However, because we have added the Ru "$t_{2g}$" d-states into the minority gap of the $CrO_2$, this group of states will become narrower. The width of the d-bands is determined by the indirect interactions among the cation d-states mediated by the O-p states. Since there are no near-by d-states with which to interact, the 3 "$t_{2g}$" states narrow so that the fraction of the 3 states per Ru atom that is filled is greater than 2/3. Since the number of electrons must be conserved, the number of majority filled states must decrease by a corresponding amount. The net result is that the substitution of the Ru ion for a Cr ion adds more than 2 electrons to the minority channel and reduces the number of majority electrons. Our calculation shows a net reduction of spin moment of 3.4 $\mu_B$ when a Ru ion is substituted for a Cr ion in the two-cell structure.

In a simple picture in which the spin-moment is localized on the cations this would indicate a moment of -1.4 $\mu_B$ on the Ru ion. In fact, it is difficult to apportion the magnetization density unambiguously among the ions. This is particularly true of 4d impurities, which have more diffuse d-states than 3d transition metals. The moment observed within the 0.55Å radius sphere surrounding the Ru ion is only -0.5 $\mu_B$.
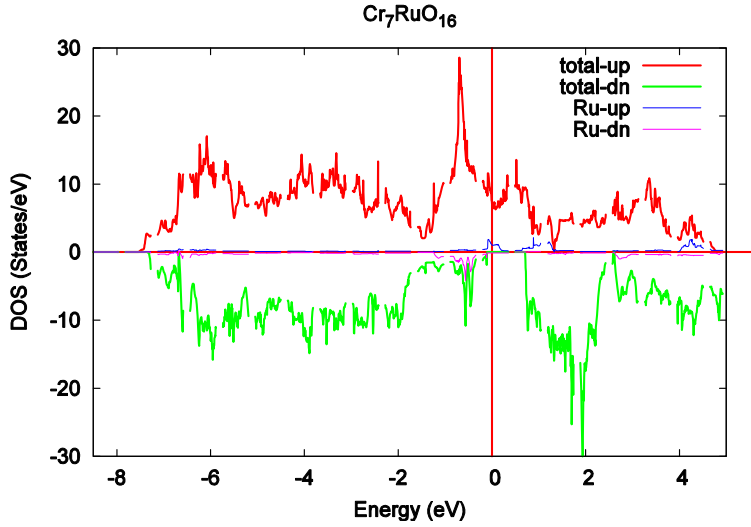


Figure 9: (Color online) Total (bold lines) Density of States for a supercell containing 7 Cr ions and a single Ru ion. Thin curves indicate the DOS within a sphere of radius 0.55Å centered at the Ru ion position.

In order to better model the dilute limit, we repeated the calculations with a four-unit-cell structure, containing 7 Cr ions and one Ru ion (i.e. one Cr ion is replaced with a Ru ion). The DOS of the Ru ion shows that the width of the band in the minority spin channel further shrinks, leaving no states at the Fermi level, as with an ordinary half-metallic system (Figure 9). The total spin magnetic moment of the supercell is reduced by 4 $\mu_B$ due to all three minority $t_{2g}$ Ru $d$-states falling below the Fermi energy. In order to conserve electrons the majority d-states must give up an electron so that the net change in moment is $4\mu_B$.

Although the ferromagnetic spin alignment of Cr ions at the (110)-oriented $CrO_2$-$RuO_2$ interface seems promising for achieving high MR in $CrO_2$-$RuO_2$ multilayers, the induced negative moment of Ru ions at the interface may be a serious issue that should be considered. Spin flip scattering resulting from the negative moment in Ru may significantly affect the transport properties of the device. XMCD (X-ray magnetic circular dichroism) or neutron reflectivity experiments could be designed to probe the interface moment of the ions in $CrO_2$-$RuO_2$ multilayers.

**Conclusions**

Although a simple model of a $CrO_2$-$RuO_2$-$CrO_2$ sandwich based on their bulk band structures with a common Fermi energy indicates a nearly ideal system for spintronic applications because of excellent matching in the majority channel, we show that the near-perfection of this model is spoiled by the development of moments on Ru ions, when they are in the vicinity of, or embedded in $CrO_2$. In addition, the inter-ionic exchange interactions among the Cr ions are degraded and may even change sign. Inter-diffusion of cations at the interfaces enhances this degradation. We find that (110) interfaces may show somewhat more robustness than (100) interfaces against this exchange degradation. We speculate that these observations may be indicative of a generic challenge that must be overcome before $CrO_2$ based spintronics can be widely successful.

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