

Could the relaxed and the O-deficient CrO₂(100) surface retain half-metallicity?

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(Received 27 June 2005; accepted 24 February 2006; published online 20 March 2006)

We report the results of a first principles study on the clean and the reduced CrO₂(100) surface. It is shown that both surfaces retain the half-metallicity because they share a common feature: the surface Cr atom also behaves like an isolated ion. Thus, the half-metallicity of the CrO₂ surfaces can be qualitatively understood by a simple model based on Hund's rule. © 2006 American Institute of Physics. [DOI: 10.1063/1.2188045]

The possibility of CrO₂ as a half-metallic material with a 100% spin polarization (SP) was theoretically predicted about 20 years ago.¹ However, it did not attract particular attention until the emergence of its potential applications to spintronics and magnetoresistive devices.² Despite the many experimental and theoretical investigations about properties of bulk CrO₂, only a few studies on its surfaces have been done,³ since a pure CrO₂ surface is difficult to realize.⁴⁻⁶ Furthermore, apparent contradiction exists: An early spin-resolved photoemission measurement showed a 100% SP for electrons with binding energies in the range of 2 eV below the Fermi level, but only negligible electron density near the Fermi level,⁷ whereas recent measurements confirmed the half-metallicity (HM) of CrO₂.^{8,9} A high-spin polarization experiment demonstrated that upon sputtering and annealing, the SP of CrO₂(100) could be recovered from 10% to 85%, which was attributed by the authors to surface quality.¹⁰ In spite of its importance, relatively little is known about the surface-dependence SP of CrO₂.

By using first principles calculations we demonstrate that the ionic feature of Cr in CrO₂ plays a crucial role in qualitatively explaining the HM of CrO₂. The calculations were performed in the framework of spin density functional theory implemented in the VASP package.¹¹ The wave functions were expanded in a plane-wave basis set with an energy cutoff of 500 eV. The interaction between atoms and electrons was described by the projector augmented plane-wave method.^{12,13} We used the generalized gradient approximation for exchange-correlation effect.^{14,15} To simulate surfaces we used a slab model, which contained nine principle CrO₂ layers. The *k* points were sampled on a 4×4 mesh in the surface Brillouin zone (SBZ). The vacuum thickness was kept larger than 15 Å. All atoms, except for the atoms in three center layers of the slab, were relaxed until the Hellmann-Feynman forces on them became smaller than 0.03 eV/Å. The total energy convergence is thus better than 0.01 eV. The parameters of the unit cell were determined by total energy minimizing. It is obtained *a*=*b*=4.425 Å, *c*=2.920 Å and *u*=0.303, in good agreement with experimental values, 4.419, 2.912 Å and 0.303.¹⁶

Figure 1 shows the density of states (DOS) of the bulk CrO₂. In the figure, the upper and the lower panel are for

majority (spin-up) and minority (spin-down) electrons, respectively. The O 2*p* states (mixed with few Cr 3*d*) extend between -1.5 and -7.5 eV, while the Cr 3*d* states (mixed with few O 2*p*) spread cross the Fermi level. There is a prominence separating near -1.5 eV, which corresponds to a pseudogap to separate the O 2*p* and Cr 3*d* bands in the majority bands. The 2*p* and 3*d* bands slightly overlap; thus, the separating is closed near the Γ point in the majority bands (note that the Γ point has the maximum phase factor), inconsistent with an early linear muffin-tin orbital calculation.¹⁷ The LMTO calculation showed a gap of about 2 eV to separate the *p* and *d* bands in the whole Brillouin zone. In the minority bands the lowest *d* band is shifted up above the Fermi level due to the *d-d* exchange interaction of Cr, leading to a gap of 1.4 eV, in good agreement with previous studies.^{1,18,19} However, it is inconsistent with an early experimental study using spin-resolved photoemission, which could not detect a sharp Fermi edge and showed the 100% spin-polarized electrons occurring only below -2.0 eV.⁷

The dashed and dotted curve in Fig. 1 represent the number of electrons *Q*, which are obtained by integrating density of states (DOS) up to energy *E*, for spin-up *Q*^{up}(*E*) and spin-down *Q*^{dw}(*E*), respectively. At -1.29 eV both curves almost overlap and their sum is 32 e, indicating that four *d* electrons per Cr transfer to the O 2*p* bands. The difference between the two curves at this energy is 0.06 e, implying that the electrons filling below this energy have only a weakly ferromag-

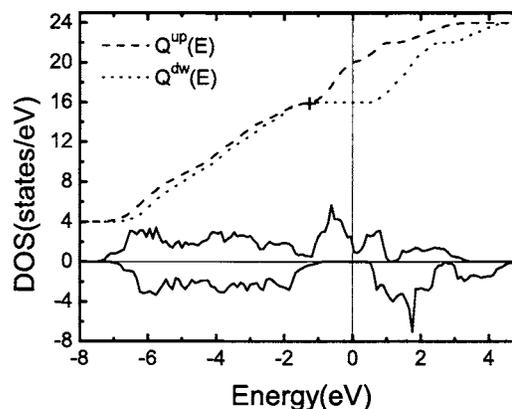


FIG. 1. Density of states (DOS) and integrated DOS for bulk CrO₂.

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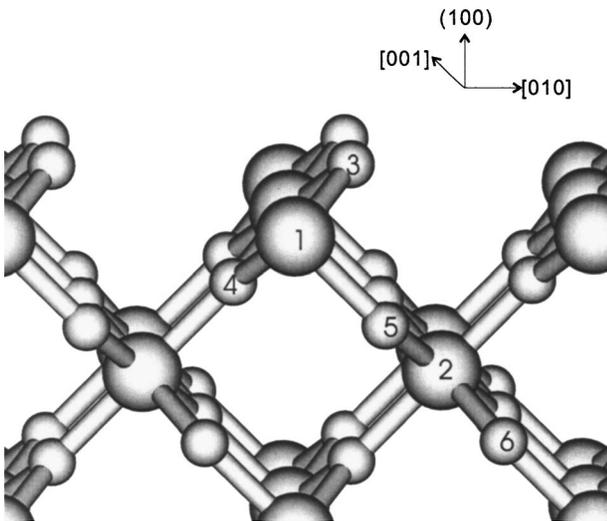


FIG. 2. Perspective view of the $\text{CrO}_2(100)$ surface. The big and small balls denote Cr and O atoms, respectively.

netic effect. Therefore, the filling above the pseudogap mainly determines the magnetic feature of CrO_2 .

It is well known that the $3d$ orbitals in an octahedral crystal field (CF) are split into a t_{2g} triplet and an e_g doublet.²⁰ They are split further by the distortion of the octahedra and disperse with the wave vectors. We can identify that the order of the splitting ($d_{xy}, d_{xz}, d_{yz}, d_{z^2}$ and $d_{x^2-y^2}$) in energy is the same as that of d orbitals of an ion splitting in a distorted octahedra CF.²⁰ This important feature, together with the pseudogap, supports the assumption that Cr is in the d^2 configuration of an isolated ion, Cr^{4+} .

According to Hund's rule, d electrons of an isolated ion in its ground state fill in the d orbitals with a maximum possible spin. The filling depends on the competition between the orbital splitting and the d - d on-site exchange energy of Cr. We determine that the splitting of the occupied d bands is 1.29 eV. The exchange energy (note that the d - d on-site exchange energy is different for the exchange splitting) is difficult to calculate, but it could be estimated to be larger than the exchange splitting, which can be obtained by comparing the lowest t_{2g} level for spin up and spin down from our calculated band structure. We estimate that the exchange energy might be larger than the exchange splitting of 1.9 eV, in good agreement with the previous calculation.¹⁸ Thus, the lowest unoccupied minority band must be pushed up above the Fermi level, leading to a gap in the minority bands. We find that it is true: The total magnetic moment for the unit cell is an integral number, $4\mu_B$, that is, $2\mu_B$ per formula unit, very close to the previous investigations.^{1,18,19}

The above picture shows that the ionic feature of Cr plays a crucial role in understanding the HM of CrO_2 in two aspects: (1) The HM of CrO_2 can be traced to the nature of the d electrons of the Cr ion; and (2) Hund's rule has already included complex effects such as exchange and correlation interactions, since the rule was concluded based on many experimental observations. However, in principle it is available for an isolated atom or ion.

To know if the HM retains for a CrO_2 surface, we need to check if the surface Cr behaves like an isolated ion, and also if the orbital splitting induced by the surface is larger than the exchange energy. Figure 2 shows the geometric structure of $\text{CrO}_2(100)$. When the CrO_2 bulk is cut to form a

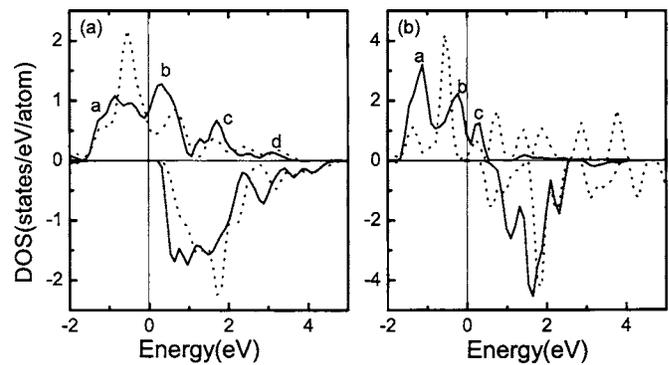


FIG. 3. Local density of states for the clean $\text{CrO}_2(100)$ surface (a) and the reduced Local density $\text{CrO}_2(100)$ surface (b). The dashed curves are for LDOS of the center Cr.

clean (100) surface, compared with the bulk the surface Cr (No. 1 in the figure) shifts 0.12 \AA along the $[010]$ direction, while two oxygen atoms, Nos. 3 and 4, shift -0.26 and -0.12 \AA along $[010]$, and lift up about 0.10 \AA along $[100]$, respectively, and the O (No. 5) shifts slightly 0.03 \AA along $[100]$ and $[010]$. This means that the surface Cr atom prefers a coordination of a rectangular cone.

From $Q(E)$ for the clean $\text{CrO}_2(100)$ surface, we find that the number of electrons filling up to -1.40 eV is 144 e. The difference of the number between spin-up and spin-down electrons is only 0.68 e, indicating that these electrons have only little contribution to ferromagnet. The electron number of 144 implies that the surface Cr atom also transfers four electrons to the p bands (note the slab with nine principle layers of CrO_2) and behaves like an isolated ion. It is reasonable, since compared with the bulk case, the surface Cr loses one bond to the apex O of the bulk case; however, the surface O (No. 3) also loses one bond to Cr at the same time. That is, creating the surface in the (100) orientation does not change the stoichiometry of CrO_2 . Therefore, the surface Cr is still in the d^2 configuration of Cr^{4+} .

The validity of the ionic picture for the surface Cr can also be seen from the splitting of its d orbitals in the CF, as shown in Fig. 3(a). Compared with the bulk case, the splitting between the d_{z^2} and $d_{x^2-y^2}$ orbitals (peaks c and d) increases. The order of $d_{xz}+d_{yz}, d_{xy}, d_{z^2}$ and $d_{x^2-y^2}$ (peaks a, b, c and d) has the feature of d electrons in the CF of a distorted tetrahedral cone. Thus, the surface Cr can keep much of its ionic character.

The width of the d bands driven by the surface Cr, in which the d electrons of Cr ions should fill, increases about 0.11 eV compared with the bulk case, implying that the surface existence does not greatly change the splitting width. This allows us to conclude that, although the surface exists, if the surface Cr still behaves like an ion and the surface induced splitting is not too large (depending on the change of the crystal field), Hund's rule is still available and the $\text{CrO}_2(100)$ surface still keeps the HM. Here we suppose that the exchange energy is unchanged. The calculated magnetic moment for the slab is $18\mu_B$, meaning $2\mu_B$ contributed by the surface Cr, just the same as that of the bulk.

Using the localized spherical-wave method, van Leuken and de Groot reported the electronic structure of $\text{CrO}_2(001)$ and concluded that the HF character of the surface was maintained.³ However, neither atomic relaxation nor O deficiency at the surface was taken into account in their calculation. Downloaded 21 Mar 2006 to 202.120.224.18. Redistribution subject to AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

tions. Therefore, they did not find a gap near E_F for majority spins in the local electronic structure at the $\text{CrO}_2(001)$ surface, which is induced by an unusual geometry at the surface.²¹ In contrast to their work, we deal with the relaxed $\text{CrO}_2(100)$ above and now turn to study the O-deficient $\text{CrO}_2(100)$ surface, which is formed by removing one O (No. 3 in Fig. 2) from the clean $\text{CrO}_2(100)$, since it was found experimentally that the SP depends on surface quality.¹⁰ Our results show that the reduced $\text{CrO}_2(100)$ surface is still half-metallic. Similar to the case of the CrO_2 bulk and the $\text{CrO}_2(100)$ surface, the slab has precisely an integral number of Bohr magnetons, $22 \mu_B$. Therefore, we would like to know if each surface Cr atom contributes $4 \mu_B$ and its HM could be understood by the above picture.

The $Q(E)$ curves for the reduced $\text{CrO}_2(100)$ surface indicate that the electron number for spin-up and spin-down electrons integrated up to $E = -1.56$ eV is $128 e$. Different to the case of the clean $\text{CrO}_2(100)$, the surface Cr here transfers only two electrons to O. These 128 electrons contribute only little to the magnetic properties of $\text{CrO}_2(100)$ either. We find that the difference of electron number between spin up and spin down is $0.57 e$.

Losing two electrons of the surface Cr can be understood by analyzing electron transfer of Cr in the octahedra. In the bulk, one Cr atom is surrounded by six O atoms in the octahedral configuration. Two O atoms at the apex of octahedra share with two neighbor octahedra, and two of four O atoms at one side of the square in the equatorial plane share with one neighbor octahedra. Therefore, Cr, which formally loses four electrons, transfers on average one electron to each apex O and 0.5 electrons to each corner O. For the case of the reduced $\text{CrO}_2(100)$ surface, since the surface Cr loses three O atoms, Cr formally transfers 0.5 electrons to two corner O each and one electron to one apex O. Therefore, the surface Cr loses two electrons and might be in the d^4 configuration of Cr^{2+} .

However, removing one O (No. 3) distorts the structure greatly, leading to that the surface Cr atom shifts -0.14 \AA along $[010]$ and -0.21 \AA along $[100]$ compared with the bulk, while two O atoms (Nos. 4 and 5) shift -0.34 and -0.06 \AA along $[010]$, as well as 0.61 and 0.11 \AA along $[100]$, respectively. This means that three surface O atoms form a triangle and the surface Cr is above the triangle plane.

The local density of states (LDOS) for the surface Cr at the M point (0.5,0.5) is shown in Fig. 3(b). Through analyzing the orbitals we can find some traces of the splitting by using the crystal field theory: The d_{z^2} orbital (peak a), whose lobes point to the center of the triangle along the z axis, shift to lower in energy due to no negative point charge

at the center. For the same reason, the d_{yz} and d_{xz} orbitals (peaks a and b) are also lower. Because the triangle is not equilateral and the surface Cr is placed above the triangle, the orbitals are affected differently: The d_{xz} is split into two peaks (peaks a and b), whose center lies near the energy position of the d_{yz} , whereas the d_{xy} (peak b) and $d_{x^2-y^2}$ (peak c), whose lobes lie in the plane parallel to the triangle, overlap slightly with O. Compared with the bulk case, these levels split little and distribute in a narrow region. Therefore, although four d electrons fill in these orbitals, the width of the occupied bands is only 1.59 eV, still smaller than the exchange splitting, 1.9 eV, meaning that the HM of the reduced $\text{CrO}_2(100)$ surface could still be explained by the ionic picture. Thus, the magnetic moment of $4 \mu_B$ per surface Cr mentioned above can be attributed to the four d electrons of the surface Cr ion, Cr^{2+} .

This work is supported by the National Natural Science Foundation of China.

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