Low Photoemission Intensity near $E_F$ Induced by the Surface Relaxed Structure of CrO$_2$(001)

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Based on first principles calculations we find that CrO$_2$(001) will form a relaxed structure at its surface, at which each surface Cr atom is surrounded by four oxygen atoms in a distorted tetrahedral configuration. This tetrahedral environment has important effects on the electronic structure, leading to an inversion of the $t_{2g}$-$e_g$ splitting of Cr 3d orbitals. Two 3d electrons of the surface Cr ion will fully occupy the doublet $e_g$, which becomes lower in energy than the $t_{2g}$, leaving the $t_{2g}$ orbitals empty. The consequence is that the Fermi level lies in a gap between the $e_g$ and $t_{2g}$ for a local electronic structure at the surface. This finding is consistent with and explains the extremely low photoemission intensity near $E_F$ at CrO$_2$(001) [Kämper et al., Phys. Rev. Lett. 59, 2788 (1987)].

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The fact that CrO$_2$ is theoretically predicted to be at 100% spin polarization near the Fermi level ($E_F$), that is, its half-metallic (HM) nature, makes CrO$_2$ a promising material for magnetoelectronic devices, see, e.g., Refs. [1–3]. However, in contrast to theoretical predictions, an early photoemission measurement on CrO$_2$(001) found an extremely low intensity near $E_F$ [4], inconsistent with its metallic behavior even though CrO$_2$ is known as a bad metal at high-$T$ [5]. However, most photoemission measurements on CrO$_2$ displayed a small but finite intensity near $E_F$ [6,7]. A recent study on CrO$_2$(100) by the same group found a weak but finite intensity near $E_F$ [8]. Considering this controversy, the group deduced that the vanishing of photoemission intensity near $E_F$ at the CrO$_2$(001) surface found by their early work [4] was likely due to defects such as an oxygen deficiency at the surface [8,9].

Ferromagnetic and metallic behaviors are rarely found together for 3d transition metal oxides and are therefore important for applications of CrO$_2$. Motivated by this controversy, a collection of experimental and theoretical investigations has been devoted to understanding the physics of CrO$_2$. A local spin-density approximation study considering Hubbard splitting of d bands by $U$ (LSDA + $U$) [10] explained why CrO$_2$ is not a Mott insulatinglike material, in contrast to many 3d transition metal oxides, despite a large Coulomb interaction. This could be attributed to the fact that a strong hybridization of O $2p$ and Cr 3d bands dilutes the on-site $d$-$d$ Coulomb interaction [10]. Such an explanation was supported by experiments of core level spectroscopy and photoemission measurement [6,7,11], as well as by x-ray absorption spectroscopy and x-ray magnetic circular dichroism [12]. Recently, based on a combination of LSDA calculations with dynamical-mean-field theory (LSDA + DMFT), Craco et al. extended the LSDA + $U$ calculations and argued that the HM of CrO$_2$ can be understood as manifestations of a collective orbital Kondo effect in the $t_{2g}$ [13]. However, since many experimental and theoretical investigations showed CrO$_2$ to be a half-metallic ferromagnet with substantial correlation effects, the question about the very low photoemission intensity at $E_F$ still remains open after almost 20 years and needs unambiguous clarification.

In this Letter, we demonstrate that a tetrahedral structure at the CrO$_2$(001) surface is mainly responsible for this rather peculiar observation of the photoemission measurement. Our finding was obtained by spin-density functional approximation (LSDA) implemented in the VASP package [14]. 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 [15,16]. The generalized gradient approximation for exchange-correlation effects was used [17,18]. To simulate surfaces we used a slab model, which contained nine principle CrO$_2$ layers. The $k$ points were sampled on a $4 \times 4$ mesh in the surface Brillouin zone (SBZ). The vacuum thickness was kept larger than 15 Å. All atoms, except for atoms in three center layers of the slab, were relaxed until the Hellmann-Feynman forces on them being smaller than 0.03 eV/Å. The total energy convergence is better than 0.01 eV.

CrO$_2$ crystallizes in a rutile structure with a tetragonal unit cell consisting of 2 formula units, each of which has one Cr octahedrally surrounded by six O. The parameters of the unit cell were determined by total energy minimizing, $a = b = 4.425$ Å, $c = 2.920$ Å, and $u = 0.303$, in good agreement with experimental values, 4.419 Å, 2.912 Å, and 0.303 [19]. The ration of $c/a$ is 0.660, compared with the value of the rutile structure with perfect octahedrons, 0.586. Hence, the octahedron is distorted.

Our calculated properties of bulk CrO$_2$ are similar to most first principles calculations [2,3,10,20,21] and are briefly summarized in the following: (1) for spin-up electrons there is a pseudogap to separate O $2p$ and Cr 3d bands, which overlap near the $\Gamma$ point of the Brillouin zone (BZ), while for spin-down electrons the Cr 3d bands are fully separated from the O $2p$ bands and shifted up above $E_F$ due to the $d$-$d$ exchange interaction of Cr, leading to a gap of 1.4 eV; (2) four of six electrons per Cr atom transfer
to the O 2p bands, leaving two electrons in a $d^2$ configuration as a Cr$^{4+}$ ion, consistent with the x-ray absorption measurements, which indicated very atomlike behavior of the Cr 3d$^2$ ions [11]; and (3) the 3d orbitals of the Cr ion are split by an octahedral crystal field into a $t_{2g}$ triplet and an $e_g$ doublet with the $t_{2g}$ low lying [22]. The $t_{2g}$ orbitals are split further into a singlet, $d_{xy}$, and a doublet, $d_{x^2−y^2}$ and $d_{xz−yz}$. The doublet, $d_{x^2−y^2}$ and $d_{xz−yz}$, is half filled and the Fermi level lies in a pseudogap between them.

The optimized geometry of CrO$_2$(001), which is obtained by relaxing atoms until the Hellmann-Feynman forces on them being smaller than 0.03 eV/Å, is similar to that of TiO$_2$(001) [23], which crystallizes also in a rutile structure. The relaxed CrO$_2$(001) surface favors the ideal CrO$_2$(001) by 1.08 eV per surface unit cell in energy, in the same order as that of TiO$_2$(001) [23].

Like the bulk case, we find a local minimum density of states (DOS) at $−1.53$ eV for spin-up electrons of CrO$_2$(001), indicating a pseudogap to separate the O 2p and Cr 3d bands, in good agreement with UPS and BIS experiments [6] and calculations [2,10,20,21]. The electron number filling up to this local minimum is 144 $\epsilon$ (the slab with 9 CrO$_2$ layers), indicating that four 3d electrons of the surface Cr transfer also to the O 2p bands, leaving two electrons for the Cr in the $d^2$ configuration. The surface Cr also contributes to a magnetic moment with an integral number, 2$p_{2\mu_B}$, the same as that in the bulk case.

Because of its crucial role in electronic structures, we then take a close look at the geometric structure at the surface to understand the photoemission experiment of CrO$_2$(001). Figure 1(a) shows the ideal geometric structure of CrO$_2$(001). When CrO$_2$ is cut to form a clean CrO$_2$(001) surface, compared with the bulk, the surface Cr [No. 1 in Fig. 1(a)] shifts down $−0.24$ Å into the inner, while two O, No. 5 and 6, shift 0.23 Å along [110] close to the Cr, and lift up 0.20 Å along [001], respectively. The oxygen of No. 7 and 8 shift only slightly (0.03 Å) along the [100] and [010] directions. This relaxation is reasonable. We can understand it by taking the coordination change of the surface O into account. In the bulk, each O is threefold coordinated and its atomic orbitals form three $sp^3$ hybrids. Each of the three $sp^3$ hybrids bonds with one Cr atom and the bond angle for an ideal $sp^3$ hybridization is 120° [24]. Because of surface existence, the O (No. 5 and 6) loses one Cr to become twofold coordinated (to No. 1 and 2). The most favorable structure for the O would thus be a $sp^3$ hybridization in a tetrahedral configuration; that is, two of the four $sp^3$ hybrids bond with two Cr (No. 1 and 2), and the other two hybrids are filled by four electrons of the O to form two so-called lone pairs. An ideal $sp^3$ hybridization is tetrahedral with the bond angle being 109.5° [24]. Finally, the angle of the two O bonds to No. 1 and 2 therefore decreases by about 12°. This tendency induced by the changed coordination (from threefold to twofold) leads to the surface O relaxing out of the surface and the surface Cr relaxing down to the inner so that the surface Cr atom prefers a tetrahedral configuration (somewhat distorted), as shown in Fig. 1(b), which displays a real structure for a surface Cr atom and four surrounding O atoms.

In order to confirm if the $d$ orbital splitting of the surface Cr follows the features in a tetrahedral crystal field, we plot local density of states (LDOS) of the surface Cr in Fig. 2(a). It is clearly shown in Fig. 2 that like the bulk case, there is a gap crossing $E_F$ for spin-down electrons, implying 100% spin polarization at $E_F$. We can clearly identify the feature of an $e_g$-$t_{2g}$ splitting in the tetrahedral crystal field [22], which is that the $e_g$ ($d_{x^2−y^2}$ and $d_{xz−yz}$) is really low lying. There is an obvious gap between the $e_g$ and $t_{2g}$ ($d_{xy}$, $d_{xz+yz}$, and $d_{xz−yz}$) crossing the Fermi level. Two $d$ electrons of the surface Cr ion will completely occupy the $e_g$, leaving the $t_{2g}$ empty. The gap between $e_g$ and $t_{2g}$ explains why the photoemission measurement observed very low photoemission intensity near $E_F$ [4].

The above results are obtained without considering electronic correlation effects. Korotin et al. [10] concluded that the correlation effect can modify the electronic structure of CrO$_2$; the conduction bands shift to higher energy, leading to the occupied and unoccupied states being more widely separated. We then take the correlation effect within LSDA + $U$ into account. Compared with the results obtained by our LSDA calculations, the relaxed structure of CrO$_2$(001) is almost unchanged. Thus the surface Cr is also in a tetrahedron even for the LSDA + $U$ calculations. If LSDA + $U$ calculations are performed, the splitting between $e_g$-$t_{2g}$ in the LDOS of the surface layer will extend to about 1.2 eV, as shown in Fig. 2(b).

In our calculations, we set up the screened parameters $U = 3$ and $J = 0.87$ eV, as suggested by Korotin et al. [10]. We note that although small but finite density near $E_F$, can be found in the calculations of Korotin et al. using the same value, indicating that the correlation effect with this $U$ and $J$ value is not large enough to open the gap [10], since the $d$ orbital splitting of Cr in an octahedral crystal

![FIG. 1. (a) The geometric structure of CrO$_2$(001), and (b) a tetrahedral part selected from CrO$_2$(001). The big and small balls denote Cr and O atoms, respectively.](image-url)
field is $t_{2g}$ low lying. Korotin et al. found that for an insulating gap the $U$ should be larger than 6 eV. However, experiments found that a reasonable $U$ value is about 3 eV by comparing LSDA + $U$ calculations with experimental data of x-ray absorption measurement and of UPS-BIS spectra [6,12]. On the other hand, our LSDA + $U$ calculations with $U = 3.0$ eV and those of Korotin et al. [10] show that the on-site $d$-$d$ exchange-split energy is 4.4 and 4.5 eV, respectively, in good agreement with the experimental value of about 5 eV [6], indicating also that a reasonable $U$ value should be about 3 eV rather than $U > 6$ eV. In other words, a reasonable Hubbard splitting cannot open a gap near $E_F$ if $t_{2g}$ is low lying, as shown by the dashed line in Fig. 2(b), which corresponds to the LDOS of the centered Cr.

A small weight but finite intensity near $E_F$ found by photoemission measurements [6–8,12] did not contradict our conclusions, since the measurements were either for deeper layers due to bigger escape depth of higher photon energy or for surfaces not in the (001) orientation, in which the surface Cr is not in a tetrahedron. However, the photon energy of the early photoemission experiment on the CrO$_2$(001) is 21.2 eV [4] and very surface sensitive.

Thus, it is most likely that the vanishing of photoemission intensity near $E_F$ found by Kämper et al. [4] was a surface effect and is mainly caused by the tetrahedral structure at the CrO$_2$(001) surface.

In order to further reveal the inversion of the $e_g$-$t_{2g}$ splitting and the physics behind, the surface band structure of CrO$_2$(001) is calculated by LSDA + $U$ and shown in Fig. 3 for spin-up electrons. In this figure the band structure of bulk CrO$_2$ projected onto the surface Brillouin zone (SBZ) is given by the shaded areas. The solid and dashed curves represent the surface states, which are created by the surface Cr. There are two pseudogaps in the figure: one is near $E_F$ and the other is above $E_F$. The pseudogap above $E_F$, which corresponds to the local minimum near 1.3 eV for LDOS of the centered Cr as shown by the dashed line for spin-up electrons in Fig. 2(b), separates the $e_g$ and $t_{2g}$ bands of the bulk Cr, which slightly overlap each other near the $\Gamma$ point of SBZ. There are six surface state bands mainly contributed by the $t_{2g}$ ($d_x^2$, $d_{xz+y^2}$, and $d_{x^2-y^2}$) of the surface Cr in this pseudogap. The pseudogap near $E_F$ separates the $d_{xz+y^2}$ and $d_{x^2-y^2}$ bands, which also overlap near the $\Gamma$ point. Therefore, electronic intensity near $E_F$ is quite small in this orientation due to this pseudogap, which is in agreement with most photoemission measurements [6–8,12]. There are also two surface state bands in this pocket (the solid curves), which are mainly contributed by the $d_{x^2-y^2}$ of the surface Cr, while two surface state bands mainly contributed by the $d_{z^2}$ of the surface Cr lie below the pocket, as shown by the dashed curves in Fig. 3. Hence, the surface states in both pseudogaps indicate clearly that the $e_g$-$t_{2g}$ splitting is indeed inverted with the $e_g$ ($d_{x^2}$ and $d_{x^2-y^2}$) low lying, compared with the bulk case.

Korotin et al. found that crossing $E_F$, the delocalized $p$-$d$ states as electrons or holes reservoir in a self-doping mechanism played an important role to keep metallic for spin-up electrons of bulk CrO$_2$ despite a large $d$-$d$ on-site interaction of Cr [10]. The delocalized $p$-$d$ states caused a nonintegral occupation of the $d$ states and contributed to magnetic moments with $1\mu_B$ [10]. From Fig. 3 it can be

![FIG. 2.](image) (a) Local density of states for the surface Cr of the relaxed CrO$_2$(001) obtained by LSDA calculations, (b) similar to (a) but obtained by LSDA + $U$, (c) similar to (a) but for the unrelaxed CrO$_2$(001), and (d) similar to (a) but for the reduced CrO$_2$(001). The dashed lines in the figures are for the Cr in the center layer of the respective slab. Symbols $e_g$ and $t_{2g}$, see text.

![FIG. 3.](image) Surface band structure of CrO$_2$(001) for spin-up electrons.
seen that the dispersion of the occupied surface states is small, implying that these surface states are quite localized. Furthermore, we find that these surface states are contributed dominantly by Cr 3d orbitals, with little contribution by O 2p orbitals. This allows us to conclude that the role of the delocalized p-d states for the bulk case is weakened at the surface, which may be attributed to that the surface Cr loses two surrounding O compared with the bulk case.

We emphasize here the role of the relaxed structure in the surface layer. If we carry out the same LSDA calculations on a reduced CrO$_2$(001) surface, we cannot expect this kind of splitting. The splitting features, shown in Fig. 2(c), are similar to that of the Cr in the bulk. That is, the doublet $t_{2g}$, $d_{xz-2yz}$ and $d_{xz+yz}$, cross $E_F$. This can be expected, since in fact for an unreleased CrO$_2$(001) surface only two O in the equatorial plane are moved away from an octahedron. Compared with the bulk case, the interaction of $d_z^2$ with surrounding O is unchanged, while the interaction of the other $d$ orbitals are weaker due to the absence of two O atoms in the equatorial plane. Therefore, according to crystal field theory, the occupied states approximately wholly shift to lower energy relative to the LDOS in the Cr in the center layer [as shown by solid and dashed line in Fig. 2(c)]. We also calculate electronic structures of the unreleased CrO$_2$(001) with the same correlation effect, $U = 3.0$ and $J = 0.87$ eV, but no gap can be found near $E_F$ for local electronic structures at the surface layer.

The coordination of the surface Cr plays an important role in opening a gap as discussed above, since the crystal field of ligands will split the degenerated 3d orbitals of Cr and determine the degenerated degree of the highest occupied orbital. The CrO$_2$(001) is unique, with the surface Cr being fourfold coordinated among low-index orientations such as the (100), (110), (011), and (001) orientation. The surface Cr in the (100), (110), and (011) orientations are all fivefold coordinated. Therefore, we could not find a similar splitting for these orientations to explain the low electronic density of states near $E_F$.

Dedkov et al. [8,9] recently suggested that the very low photoemission intensity near $E_F$ may be induced by O deficiency at CrO$_2$(001). We thus also carry out calculations on a reduced CrO$_2$(001) surface in which one O atom [No. 6 in Fig. 1(a)] is moved from the surface unit cell. The calculated electronic structures show that the reduced CrO$_2$(001) surface does not destroy the half-metallic nature of CrO$_2$ and there is no gap crossing $E_F$ in the local electronic structure for the spin-up electrons of the surface Cr, as shown in Fig. 2(d). The detailed results will be published elsewhere.

In conclusion, from the detailed surface structure analysis based on first principles calculations a clarification about the question of the extremely low photoemission intensity near $E_F$ at CrO$_2$(001) is obtained. Our results show that the surface structure plays a crucial role in understanding the physics of the CrO$_2$ surface. The surface Cr atom at CrO$_2$(001) prefers a tetrahedral configuration, leading to the inversion of the $e_g$-$t_{2g}$ splitting of the $d$ orbitals of the surface Cr with the $e_g$ low lying. Thus, the two remaining $d$ electrons of the surface Cr will fully occupy the $e_g$, leaving the $t_{2g}$ empty. There is a gap crossing $E_F$ between the $e_g$ and $t_{2g}$ of the local electronic structure in the surface layer, consistent with the extremely low photoemission intensity near $E_F$ found by Kämper et al. [4].

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[24] The angles of the O-Cr bonds in the bulk are disrepanct to those of a perfect sp$^2$ hybridization (about 130°, 130°, 100°), while the angle of the O-Cr bonds at the surface is finally about 118°, since the O sp$^3$ hybridization is imperfect, whose two hybrids bond with two Cr (No. 1 and 2), the other two hybrids form two lone pairs.