Surface Enhanced Covalency and its Effect on the Surface States of $d$-Band Metal Oxides

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Abstract. The effect of electron-electron interactions on the surface states of ionic $d$-band oxides is reported. The local density of states of surface cations in the valence band region is significantly increased when surface states occur in the band gap. Coulomb repulsion associated with this surface enhanced covalency tends to force surface states out of the band gap. These results suggest an explanation of recent experiments on SrTiO$_3$ and TiO$_2$.

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The $d$-band transition metal oxides are of interest because of their catalytic [1] and electrocatalytic properties [2, 3]. Theoretical calculations [4–6] have suggested that highly localized $d$-electron surface bands should occur in the band gap region of insulating SrTiO$_3$ and TiO$_2$. These states are of importance because of their possible role in surface reactions [5]. Recent photoemission experiments on surfaces of reduced SrTiO$_3$ by Powell and Spicer [7], and on TiO$_2$ and SrTiO$_3$ by Henrich et al. [8, 9] may be summarized as follows: 1) cleaved (or fractured) surfaces of TiO$_2$ or SrTiO$_3$ do not have surface states in the band gap; 2) well ordered SrTiO$_3$ surfaces that have been cut, polished, etched and annealed in vacuum do possess band gap surface states, but similarly prepared TiO$_2$ surfaces show no band gap states; 3) band gap surface states appear for both TiO$_2$ and SrTiO$_3$ when the surfaces are bombarded with Ar-ions; 4) exposure to oxygen removes the band gap states; and 5) LEED patterns indicate that cleaved or fractured surfaces of SrTiO$_3$ or TiO$_2$ are more disordered than surfaces annealed in vacuum.

In this paper we present theoretical results which suggest an explanation for many of these experimental observations. We have calculated the local density of states (LDS) of surface cations including Coulomb repulsion among $d$-electrons [10]. We find the LDS of a surface cation is enhanced in the filled valence band region when surface states occur in the band gap. This phenomenon of surface enhanced covalency introduces additional Coulomb repulsion among $d$-electrons, which tends to forbid self-consistent surface state solutions in the band gap. We then suggest that surface vacancies and/or electron screening effects could stabilize band gap surface states.

We make use of the LCAO model for perovskites described in detail in our previous papers [4–6]. The model provides an excellent representation of the near-band-gap electronic structure of SrTiO$_3$ and a more qualitative description of other $d$-band oxides such as TiO$_2$ or Ti$_2$O$_3$. The LCAO model energy bands are shown in Fig. 1. The $\sigma^*$, $\sigma^0$ bands are derived from admixtures of $e_g$ cation $d$-orbitals and oxygen $p$-orbitals which form sigma bonds. $\sigma^0$ is a non-bonding $p$-band. The three $t_{2g}$ $d$-orbitals and six (per unit cell) $p$-orbitals which can pi-bond form six bands; three equivalent lower conduction bands ($\pi^*$) and three equivalent upper valence bands ($\pi$). There are also three non-bonding $\pi^0$-bands. Analytical expressions for all of these bands have been given elsewhere [4, 6]. The bands
associated with the A-ion of an ABO$_3$ perovskite lie much further from the band gap and will be omitted in our discussion.

Of particular interest here is the surface band in Fig. 1 which lies in the band gap between the $\pi^*$ and $\pi$-bands. The position of this band depends upon the effective ionization energy of the surface cations and is directly related to the change in the Madelung potential, $AV_M$, at the surface. For an ideal (001) surface of SrTiO$_3$, $AV_M$ is about 2 eV [11] and the lower edge of the surface state band is 1.5 eV below the $\pi^*$-band edge [5].

In this paper we investigate the effect of electron-electron interactions on the one-electron results just described. We limit our initial discussion to the pi-bands and indicate later the role of the sigma-bands. First, we note that the d-orbitals of cations are partially filled with electrons even for insulators such as SrTiO$_3$ or TiO$_2$ because the wave functions of the filled valence bands are admixtures of p and d-orbitals. This covalency effect reduces the formal ionic charges on both the cations and anions and therefore reduces the Madelung potentials. If covalent mixing is assumed to be increased at the surface there would be two opposing effects. The effective ionization energy would be increased because of the reduction in the repulsive Madelung potential at a cation site. This is opposed by Coulomb repulsion among the extra d-electrons.

We have derived expressions for the local density of states (LDS) including a parameter $\Delta E_t$ which accounts for the change in the effective ionization energy of surface cations

$$\Delta E_t = -AV_M + (U_a - C_M)\Delta n_a. \quad (1)$$

Here $-AV_M$ is the reduction in the Madelung potential at a surface cation site with all formal ion charges equal to their bulk values [11]. $\Delta n_a$ is the change in the electron occupancy of a surface cation and $U_a$ is the Coulomb repulsion integral. A term of the form $U_a\Delta n_a$ can be derived from the Anderson model [10] assuming non-magnetic states. The quantity $-C_M\Delta n_a$ approximates the change in the surface Madelung potential due to changes in the surface ion charges [12]. The free-ion value of $U_a$ based on ionization energy differences between Ti$^{+2}$ and Ti$^{+3}$ is about 19 eV [13]. From Madelung sums [11] we estimate $C_M$ to be about 11 eV. Both $U_a$ and $C_M$ will be reduced by screening and polarization in the solid by an amount that is not known precisely. Herring [14] has discussed these effects for transition metals and concludes that a reduction by a factor of two is not unreasonable. N-type SrTiO$_3$ will have smaller electron screening than a typical metal but polarization should be larger. Therefore, in the absence of detailed information we shall assume that the ionic value of $U_a - C_M$ is reduced from 8 eV to 4 eV. The qualitative results do not depend upon the precise value chosen.

The self-consistency condition for the model is

$$\Delta n_a = \int_{-\infty}^{E_f} dE [\varphi_d(0,E) - \varphi_d(\infty,E)], \quad (2)$$

where $\varphi_d(0,E)$ is the LDS for a surface cation and $\varphi_d(\infty,E)$ is that for a distant interior ion, and $E_f$ is the Fermi energy. These functions (including spin degeneracy) are given by

$$\varphi_d(0,E) = (6/2\pi^2)(E - E_d)K \left[ \sqrt{1 - (\varepsilon/4)^2} \right] / (pdn)^2,$$

$$\varphi_d(\infty,E) = (2/2\pi^2)(E - E_d)K \left[ \sqrt{1 - (\varepsilon/4)^2} \right] / (pdn)^2 + (4/\pi\pi) |(E - E_d)| \Im \{G_d(E)\} / (pdn)^2,$$

$$\varepsilon = [((E - E_d)(E - E_t - \Delta E_t))/(pdn)^2] - 4,$$

$$\varepsilon' = [((E - E_d)(E - E_t - \Delta E_t))/(pdn)^2] - 4, \quad (3)$$

where K is the complete elliptic integral of the first kind, $E_t$ and $E_d$ are the energies of the bottom of the $\pi^*$-band and the top of the $\pi$-band, respectively and $(pdn)$ is the LCAO transfer integral ($\sim$ 1 eV) for pi-bonding. The

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**Fig. 1.** Illustration of LCAO model energy bands for a perovskite structure. Analytic expressions for the energy bands are given in [4] and [6].