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Surface States and Catalysis on d-Band Perovskites*

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It is demonstrated that surface states derived from the lower conduction band of d-band perovskites produce a square-root singularity peak in the density of surface states at energies which lie in the forbidden gap. These surface states are highly localized and have nearly pure d-state character. It is suggested that these surface states provide the necessary orbitals to facilitate an important class of symmetry-forbidden chemical reactions.

Considerable attention has been focused recently on transition-metal oxides of the perovskite structure because of their possible utility as catalysts. Pedersen and Libby[1] suggested that the rare-earth cobalt oxides $R\text{CoO}_3$ (R = La, Nd, and Dy) might provide an inexpensive substitute for platinum-based catalysts for the oxidation of pollutants in auto exhaust. More recently, Voorhoeve[2] reported success in oxidizing carbon monoxide and reducing the oxides of nitrogen using transition-metal oxides such as $(\text{La}_{1-x}\text{Pb}_x)\text{MnO}_3$ and $(\text{Pr}_{1-x}\text{Pb}_x)\text{MnO}_3$ which also have the cubic perovskite structure. Although it is generally believed that the catalytic properties of these materials are associated with the d electrons, the detailed mechanisms of catalysis are not well understood.

We had suggested previously[3] that the d-band perovskite insulators such as SrTiO_3 would be simple model materials with which to initiate studies of the catalytic properties of the d-band perovskites since the d-band surface states in these materials are normally empty but may be populated in a controlled manner by photoexcitation. Theoretical calculations by Wolfram, Kraut, and Morin[3] have established that a reasonably realistic, analytical model for the d bands in the perovskites could be derived from a very simple linear-combination-of-atomic-orbitals (LCAO) energy band calculation. The utility of this model was demonstrated by Wolfram[4] who showed that analytic expressions derived for the density of states of the lower conduction bands were in *quantitative* agreement with detailed calculations of Mattheiss.[5] The model has also been used to derive exact expressions for the surface energy bands and wave functions.[3]

In this Letter we demonstrate that (001) surface states derived from the lower conduction bands produce a square-root singularity peak in the density of states in the band gap and that these surface states are of nearly pure d character. We suggest that these states are capable of providing the necessary orbitals to facilitate an important class of symmetry-forbidden chemical reactions.

In a previous Letter,[4] we showed that the lowest conduction bands of a number of d-band perovskites were dominated by the two-center transfer (resonance) integral ($pd\pi$) which mixes the t_{2g} d orbitals of the transition-metal ion with the p orbitals of the oxygen. These three bands are described to a very good approximation by the simple expression

$$E(k)=\tfrac{1}{2}(E_t+E_p)+\{[\tfrac{1}{2}(E_t-E_\perp)]^2+4(pd\pi)^2(S_\alpha^{\,2}+S_\beta^{\,2})\}^{1/2}, \quad (1)$$

where the parameters are described in detail in Refs. 3 and 4. The energies E_t and $E_\perp$ refer to diagonal d and p matrix elements including Madelung and crystalline field potentials. The dispersion of these bands is determined by $S_\alpha=\sin(k_\alpha a)$ and $S_\beta=\sin(k_\beta a)$, where $\alpha\beta=xy$, xz, and yz, k_α is the αth component of the wave vector, and a is the transition-ion–oxygen distance. Each of these bands depends only on two components of the wave vector and, therefore, possesses two-dimensional character. It was shown[4] that this feature leads to discontinuities in the density of states at the conduction band edges and a logarithmic singularity in the center of the band. These properties also lead to structure in the joint density of states, dielectric function, and reflectivity which is in qualitative agreement with experiments by Cardona.[6]

This same model has been used to derive an exact expression for the surface states and their wave functions including spatial variations in the Madelung and crystalline field potentials, variation in the atomic layer spacing near the surface, and rotations of the oxygen–transition-metal bonds. The surface energy bands are given by the solutions of the transcendental equation

$$\Delta P+1/\Delta P=2+4S_\alpha^{\,2}-(\epsilon_t-\epsilon)(\epsilon_\perp-\epsilon), \quad (2)$$

$$\Delta P=(\Delta\epsilon_t+\epsilon_t-\epsilon)(\epsilon_\perp-\epsilon)-(\epsilon_t-\epsilon)(\epsilon_\perp-\epsilon)-(\epsilon')^2-4(\epsilon'')^2S_\alpha^{\,2}\frac{\epsilon_\perp-\epsilon}{\Delta\epsilon_\perp+\epsilon_\perp+\epsilon}+2+4S_\alpha^{\,2} \quad (3)$$

for a (001) surface containing oxygen and transition-metal ions.

Two equivalent sets of surface bands result ($\alpha=x$ and $\alpha=y$). The parameters in Eq. (3) are described in detail in Ref. 3. The energies are in dimensionless units [$\epsilon_t=E_t/(pd\pi)$, $\epsilon_\perp=E_\perp/(pd\pi)$, etc.]. The parameters $\Delta\epsilon_t$ and $\Delta\epsilon_\perp$ are the changes in the diagonal matrix elements ϵ_t and $\epsilon_\perp$ due to changes in the Madelung potentials and crystalline field. ϵ' is the ratio of the $(pd\pi)$ surface matrix element to the bulk value of $(pd\pi)$ and accounts for changes in the layer spacing. ϵ'' is a similar ratio which accounts for bond rotations on the surface. It is clear from Eq. (2) that these surface bands have a one-dimensional character in momentum space since they depend only on one component of the wave vector parallel to the surface. The density of surface states possesses square-root singularities near the top and bottom of the surface band as illustrated in Fig. 1. To demonstrate this property, consider the ideal surface for which the only important surface perturbation is the change of the surface electrostatic potential at the transition-metal site so that $\Delta\epsilon_t\neq 0$, $\Delta\epsilon_\perp=0$, $\epsilon'=\epsilon''=1$. Then the

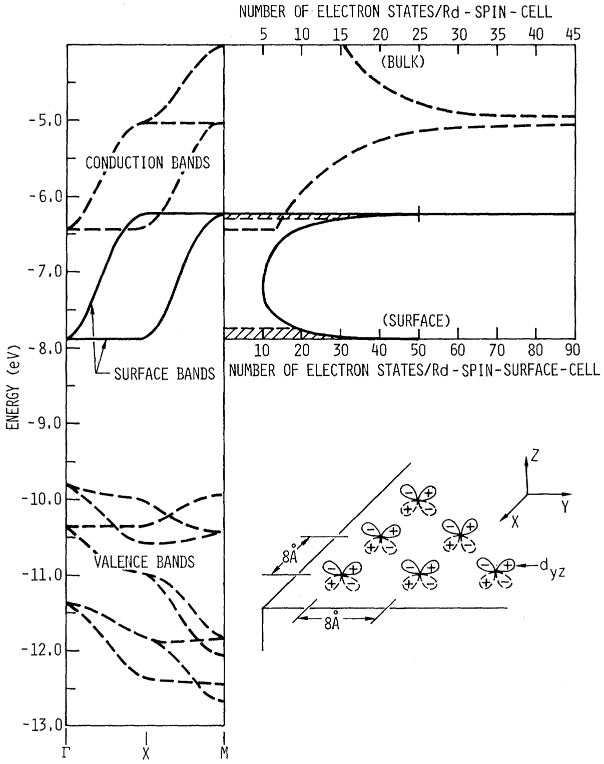

FIG. 1. Bulk and surface energy bands and density of states for $SrTiO_3$. The bulk and surface energy bands are shown on the left side along the lines ΓX ($0\leq k_x\leq\pi/2a$) and XM ($k_x=\pi/2a$, $0\leq k_y\leq\pi/2a$). The upper right portion is the density of bulk states of the lower conduction band and (below) the density of surface states. (Note different scales.) The bulk density has jump discontinuities at the bottom and top of the bulk band and a logarithmic discontinuity in the middle of the band. The surface density has square-root singularities at the band edges. The cross-hatched areas each contain 10% of the total surface state density (1.2×10^{14} states/cm^2). The lower right portion illustrates schematically the nature of one of the two equivalent pure d-orbital surface states near the bottom of the band. The parameters used are $(pd\pi)=1.34$ eV and $\Delta\epsilon_t(pd\pi)=-2$ eV and other parameters are given in Fig. 1 of Ref. 4.

density of surface states is given by

$$N_S(E)=[2\pi(pd\pi)]^{-1}[(1/\Delta P^2-1)\Delta\epsilon_t+2\epsilon-\epsilon_t-\epsilon_\perp)](R_1R_2)^{-1/2}, \tag{4}$$

where $R_1=(\Delta P+1/\Delta P)+(\epsilon_t-\epsilon)(\epsilon_\perp-\epsilon)-2$ and $R_2=1-R_1/4$. It is easily shown that $N_S(E)$ possesses a square-root singularity at $k_\alpha=0$ or $k_\alpha=\pi/2a$ by expanding the surface energy in a power series about these points. From Eq. (2), we have

$$\epsilon_S(k_\alpha)\to\epsilon_S{}^0+\epsilon_1{}^0K_\alpha{}^2a^2, \tag{5}$$

$$\epsilon_1=\pm4[(1/\Delta P^2-1)\Delta\epsilon_t-(\epsilon_\perp+\epsilon_t-2\epsilon_S{}^0)]^{-1}, \tag{6}$$

where $K=k_\alpha$ or $\pi/2a-k_\alpha$, $\epsilon_S{}^0$ is the value of the surface state energy at $k_\alpha=0$ or $k_\alpha=\pi/2a$, ΔP is evaluated at the appropriate value of $\epsilon_S{}^0$, and the + (−) is for $K=k_\alpha$ ($K=\pi/2a-k_\alpha$). The density of surface states including both bands (i.e., $\alpha=x$ and $\alpha=y$) is

$$N_S(E)=[2/\pi(pd\pi)]|d\epsilon_S/d(k_\alpha a)|^{-1}\to[\pi(pd\pi)]^{-1}[(\epsilon_S-\epsilon_S{}^0)\epsilon_1]^{-1/2}. \tag{7}$$

The behavior of $N_S(E)$ given by Eq. (4) is shown in Fig. 1 for $SrTiO_3$ using the 2-eV decrease in Madelung potential at the surface[7] and the values of other parameters appropriate for $SrTiO_3$.[4] These surface states should be observable by a variety of experimental techniques including high-resolution reflectivity and thermally stimulated current.

The surface state charge density decreases as $(1/\Delta P)^{2n}$, where n is the number of layers in from the surface. For the case shown in Fig. 1, ΔP increases from 3.7 for $k_\alpha=0$ to 5.4 for $k_\alpha a=\pi/2$. This means that about 93% to 96% of the charge density is on the surface transition-metal ions. The surface states consist of nearly pure d orbitals near the bottom of the surface bands. The cross-hatched regions on the surface density of states each contain 10% of the total surface state density. For $SrTiO_3$, this means that about 1.2×10^{14} electron states cm^{-2} of nearly pure d character are contained in an energy interval of 0.13 eV at the bottom of the surface bands. A schematic of the surface wave function is shown in the lower right of Fig. 1 for one of the two equivalent wave functions. These states are normally empty in insulating perovskites such as $SrTiO_3$, $BaTiO_3$, or $KTaO_3$, but may be populated at will by photoexcitation and subsequent trapping of electrons from the valence band. In conducting perovskites and ReO_3, these surface states will be occupied. In the case of compounds, such as $(La_{1-x}Pb_x)MnO_3$, with several electrons in the d bands, correlation effects must also be considered. When the correlation energy is of the order of the bulk bandwidth, localization of the d electrons, rather than band formation, can occur. This circumstance does not invalidate the qualitative ideas utilized here, it simply means that the surface states will be even more highly localized than those predicted by our LCAO model.

The presence of a large density of localized electronic states of d symmetry may be a significant factor in accounting for the catalytic properties of the d-band perovskites. The reasons for this can be qualitatively understood in terms of molecular-orbital concepts.

When molecules come together and react to form a product, electrons flow between the reacting molecules and redistribute themselves in the molecular orbitals of the product. As the reactants approach each other, the molecular orbitals critical to the reaction are (energetically) the highest occupied and the lowest unoccupied molecular orbitals. These critical orbitals must bring occupied and empty states to within kT of each other. Therefore, for electron flow to occur, the initial orbitals must be near together in energy and must have a symmetry such that they experience a net positive orbital overlap. Furthermore, as Woodward and Hoffmann[8] have shown, for a reaction to go to completion in either direction in the ground state, orbital symmetry must be conserved along the reaction coordinate. Where a reaction cannot proceed because symmetry is lacking, and electrons are not available at an appropriate energy, it is the role of the catalyst to provide occupied surface states of such symmetry that an activated complex forms which allows the reaction to proceed with symmetry conservation. In the case of heterogeneous catalysis many reactions appear to be controlled by the chemisorption of one or more of the reactants. This implies the existence of occupied surface states whose symmetry permits a net positive overlap to occur between the surface states and the antibonding orbitals of the gaseous reactant. Thus electronic rearrangement may occur and a new set of molecular orbitals may be formed which include the wave functions both of the surface state and of the chemisorbed molecule. Without attempting to describe the chemisorption and desorption process, Mango[9] has shown how symmetry may be conserved along the reaction coordinate and electronic rearrangement facilitated for the dimerization of ethylene by constructing a set of molecular orbitals which include the π and π^* orbitals of two ethylene molecules together with the atomic d orbitals of a transition-metal catalyst. Mango's model may be used to describe the catalysis of many similar reactions including the hydrogenation of ethylene. The highly localized perovskite d-band surface states described above, when occupied, meet the requirements of that model. A more detailed model, which includes chemisorption and interaction among molecules on the surface, has yet to be developed. It is significant that the symmetry of low-lying empty states in a large variety of important molecules is the same as that of the d_{xz} and d_{yz} surface states depicted in Fig. 1. Examples are the empty σ_s^* orbital of H_2 and the pair of half-filled π_p^* orbitals of oxygen. When electrons are introduced into these orbitals from occupied d-band surface states, the molecules dissociate and chemisorb as atoms. Other examples are the lowest unoccupied states of CO which are a pair of π_p^* orbitals, and the single π_p^* orbital[10] in NO_2. Thus, it appears reasonable that oxidation of CO and the reduction of NO_2 may be initiated by a chemisorption step which includes the formation of a new set of molecular orbitals consisting of orbitals of the molecule and of the surface state.

The catalytic performance of the d-band perovskites is not expected to be highly sensitive to surface orientation or to surface irregularities. Crystal surfaces other than the (001) surface are expected to produce surface bands with more complex dispersion. The surface density of states may be less peaked than in the case discussed here but localized surface states with a high degree of d character will still be produced. The behavior of other materials, however, may be quite different with respect to surface irregularities. For example, recent work on CdS,[11] ZnO,[12] and Pt[13] has shown that the activity of a surface containing point defects or other irregularities is greatly enhanced over that of an atomically regular surface. We expect the intrinsic surface states of ZnO and CdS to be relatively inefficient for interactions with the gas phase because they are basically p character rather than d character. In addition to this, the fact that the density of states in the conduction band edge of ZnO and CdS is much smaller than that of $SrTiO_3$ suggests that the intrinsic surface states on ZnO and CdS are too diffuse to be capable of interacting efficiently with molecules from the gas phase. Surface irregularities, on the other hand, alter the ionic potential and thereby produce localized surface states which enhance surface activity.

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