

## Sulfur-induced occupation of $\bar{\Delta}$ Fe minority surface states in $c(2 \times 2)$ S/Fe(001)

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The poisoning of iron's catalytic value in the synthesis of hydrocarbons through contamination by small amounts of sulfur is a well-known, though poorly understood, phenomenon. Using results from our recent first-principles, full-potential linearized augmented-plane-wave study of  $c(2 \times 2)$  sulfur chemisorbed on magnetic Fe(001), we review a number of important adsorption-induced modifications of electronic and magnetic structure, which probably have bearing on this poisoning phenomenon. These include a significant reduction in the density of states (DOS) at  $E_F$ , and a narrowing and sharpening of various surface resonance states above  $E_F$ . The most prominent of these features involves a striking level repulsion of minority surface states (SS's), all along the  $\bar{\Delta}$  line of the  $c(2 \times 2)$  surface Brillouin zone, which is largely responsible for the decline in the DOS at  $E_F$ . At  $\bar{X}$ , this level repulsion leads to a large ( $\sim 1$  eV) upward shift of one of the two degenerate  $d(xz, yz)$  SS's, located 0.2 eV above  $E_F$ , accompanied by a downward shift of the remaining SS, which becomes occupied and remains highly localized all along  $\bar{\Delta}$ . We examine the origins of this effect and suggest various spin-polarized photoemission and inverse-photoemission experiments, which could provide independent confirmation of our prediction of this dramatic effect.

### INTRODUCTION

It is well known that the introduction of small amounts of a sulfur contaminant readily poisons the catalytic value of iron in the synthesis of hydrocarbons. However, not only is very little known about the origin of this poisoning phenomenon, at the microscopic level, surprisingly little is known about the interaction of sulfur with iron. The impact of sulfur contamination on the magnetic properties of iron is even less well understood.

In a recent study<sup>1</sup> of the electronic and magnetic structure of centered  $2 \times 2$  [ $c(2 \times 2)$ ] S chemisorbed above magnetic Fe(001) (S/Fe), we found a number of important adsorption-induced changes in the Fe-like surface-state spectrum, which probably have bearing on the poisoning of iron's catalytic value in Fischer-Tropsch-type processes. The most prominent of these involves a striking level repulsion of minority surface states (SS's), all along a high symmetry ( $\Delta_2$ ) line of the  $c(2 \times 2)$  surface Brillouin zone (SBZ). This leads to an important decline in the density of states (DOS) at the Fermi level ( $E_F$ ), a narrowing of the widths associated with unoccupied minority states above  $E_F$ , and a reduction in the surface magnetism through the adsorption-induced occupation of highly localized, minority SS's.

Experimental verification of this level repulsion could provide an important test both of our results and of experimental probes of electronic structure. The effect involves a dramatic shift (by as much as  $\sim 1.2$  eV) in the energies of states near  $E_F$ . Thus, verification of this prediction involves measurements of energies and dispersions of Fe-like SS's both through spin-resolved angle-resolved ultraviolet photoemission spectrum (ARUPS) and spin-polarized  $k$ -resolved inverse-photoemission spectrum (KRIPES) experiments. However, the effect should be readily observable [especially near the  $\bar{X}$  point of the  $c(2 \times 2)$  SBZ]

since it occurs near and in a well-defined gap<sup>1</sup> in the (folded) projected bulk band structure associated with the SBZ of the  $c(2 \times 2)$  unit cell (see Fig. 1) and involves highly localized states (as discussed further below).

Experimental verification of the phenomenon also has direct bearing on theoretical questions related to the importance of magnetism in the interaction between S and Fe,<sup>1</sup> and by implication to its importance in the S-induced poisoning of iron's catalytic value.<sup>1</sup> In particular, we have inferred through a comparison between our results, which included the effects of magnetism, and those derived by Fernando and Wilkins<sup>2</sup> (FW), which neglected the effects of magnetism, that important interactions due to the large exchange splitting in iron play a critical role in this level repulsion. As a consequence, in the case of  $c(2 \times 2)$  S chemisorbed on paramagnetic Fe, a comparable level repulsion between Fe SS's near  $E_F$  does not take place, the adsorption induces minor changes in the DOS at and near  $E_F$ , and considerably greater transfer of charge to the S occurs. The impact of these differences in electronic structure, especially near  $E_F$ , between the spin-polarized and paramagnetic calculations not only results in considerably better agreement between our findings and experimentation for the value of the work function<sup>1,3</sup> and the positioning of the adsorbate-induced, sulfurlike bands,<sup>1,4</sup> but leads us to a very different hypothesis concerning the nature of the poisoning phenomenon.<sup>1,2</sup>

Though we identified this level repulsion and inferred that it was important in the S-Fe interaction earlier in Ref. 1 (henceforth I), we did not fully examine the origin of the effect and its relationship to the poisoning phenomenon. In the current paper, we will present some results which clarify these points. In addition, because of the complexity of the associated band structures, calculations, and the level of detail given in I, and because of the simplicity and amenability to experimental verification of

this particular effect, we have included additional information about the positions and dispersions of the associated SS's.

## RESULTS AND DISCUSSION

Because we have thoroughly discussed the details of our calculations and results in I, we will only briefly summarize our findings. We used the film full-potential linearized augmented-plane-wave (FLAPW) method due to Wimmer *et al.*<sup>5</sup> and Weinert *et al.*<sup>6</sup> to determine the equilibrium geometry and electronic and magnetic structures of  $c(2 \times 2)$  S/Fe. Our calculated geometry, work function, and the calculated positions and dispersions of surface states were in excellent agreement with the only available, experimentally derived structural<sup>3,7</sup> information and measurements related to electronic structure<sup>3,4</sup> associated with  $c(2 \times 2)$  S/Fe.

We emphasized the definite need for measurements that relate to magnetic structure (none have been performed) and for ARUPS and KRIPES experiments (spin resolved or spin averaged) in which the Fe-like portions of the spectrum are probed and the adsorption-induced modifications of *both* the occupied and unoccupied Fe-like SS's and surface resonance states (SR's) are identified. We specifically noted that identification of the Fe SS's and SR's is important because they play an important role in the differences between our findings and those derived through paramagnetic LAPW calculations by FW. Because these differences, which are largely responsible for the better agreement found in I with experiment, arise from the adsorption-induced occupation of minority Fe SS's, we emphasized especially that the spectrum near  $E_F$  should be measured.

Furthermore, we found that this adsorption-induced occupation of minority Fe SS's, which is intimately related to a *decline in the DOS at  $E_F$*  and the *reduction in surface magnetic moment*, is closely tied to the level repulsion between a pair of states near  $E_F$ , which are degenerate at  $\bar{X}$ . The occupation of these states (largely through this level repulsion), leads to a considerably smaller charge transfer away from the Fe (by a factor of  $\sim 2$ ) to the sulfur than in the paramagnetic case, where a comparable level repulsion is absent. Furthermore, because the induced charge transfer to the sulfur is reduced, our calculated increase in work function is considerably smaller and in better agreement with experiment. The repulsion also induces a narrowing of unoccupied minority states above  $E_F$ , which was not found by FW. As a consequence of these differences, we pointed out that magnetic effects play an important role through the large exchange splitting, which remains relatively constant as sulfur is adsorbed, in the S-Fe interaction and that the most profound changes in the electronic structure are due to modifications of the DOS near and above  $E_F$ . FW, on the other hand, emphasized that they found a relatively large electrostatic shift as a consequence of charge transfer to the S and that the DOS was not profoundly effected at energies above  $E_F - 4$  eV.

These distinctions led us to very different hypotheses concerning the origins of the poisoning: FW suggested the

phenomenon is driven electrostatically through the large adsorption-induced change in work function (an effect that is not observed experimentally<sup>3</sup>); we concluded that poisoning is tied in a critical manner to modifications of the DOS near and above  $E_F$ .

Thus, the level repulsion between minority states near  $E_F$  plays an important role in the very different mechanisms underlying the poisoning proposed in I and by FW. The energy bands associated with this effect are shown in Fig. 1, where we have plotted our calculated symmetry type two<sup>1</sup> (antisymmetric with respect to reflections through the plane normal to the surface containing the wave vector) SS's and SR's (Ref. 8) along the  $\bar{X}-\bar{\Gamma}$  line of the  $c(2 \times 2)$  SBZ before and after the adsorption. We initially identified the level repulsion by observing that after the adsorption, a large ( $> 1.4$  eV) separation is induced between the states immediately above and below  $E_F$  at  $\bar{X}$ . The comparable states in the clean Fe surface are located at 0.18 eV above  $E_F$  and are degenerate. [This degeneracy is due to the backfolding of bands from equivalent symmetry lines of the  $p(1 \times 1)$  SBZ]. Along most of the  $\bar{\Delta}$  ( $\bar{X}-\bar{\Gamma}$ ) line, the lowest S/Fe band and the two clean Fe bands are well-defined SS's since these states are all located in a gap of the projected bulk Fe band structure. At  $\sim 0.4d(\bar{X}-\bar{\Gamma})$ , the higher (unoccupied) band [which also is a well-defined SS between  $\bar{X}$  and  $\sim 0.4d(\bar{X}-\bar{\Gamma})$ ] leaves this gap of the bulk band structure and becomes a resonance, though it still maintains a large surface component along the remainder of the  $\bar{\Delta}$  line.

In Fig. 2 we present spatially resolved plots of the density in the plane of the Fe surface [Fe(S)] at  $\bar{X}$  of the two S/Fe SS's associated with the level repulsion. This plot shows a clear tendency for bonding by the occupied state and antibonding by the unoccupied state between Fe atoms within the Fe(S) plane. In particular, this figure shows that the unoccupied state is (1) considerably more

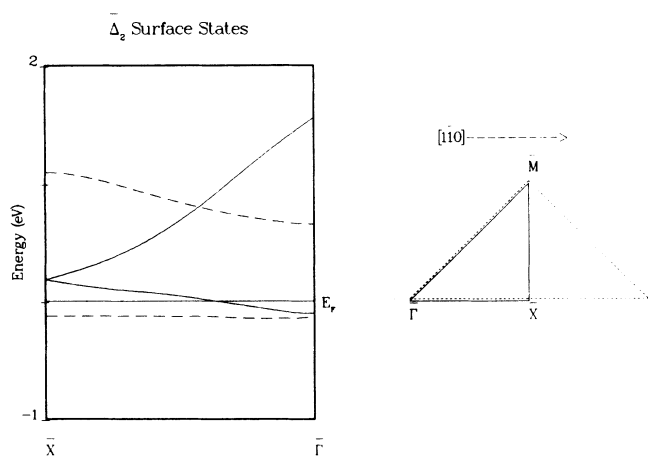


FIG. 1. Dependence on wave vector of the energy of the contamination sensitive, minority  $\bar{\Delta}_2$  SS's and SR's (left). Clean Fe SS's and SR's are plotted as solid lines. Dashed lines indicate states after the adsorption. Only those states which are odd with respect to  $z$  reflection are plotted (Ref. 8). Also shown (to the right) are the boundaries of the two-dimensional Brillouin zones associated with (1) the  $c(2 \times 2)$  unit cell (solid lines) and (2) the  $p(1 \times 1)$  unit cell of clean iron (dotted lines).

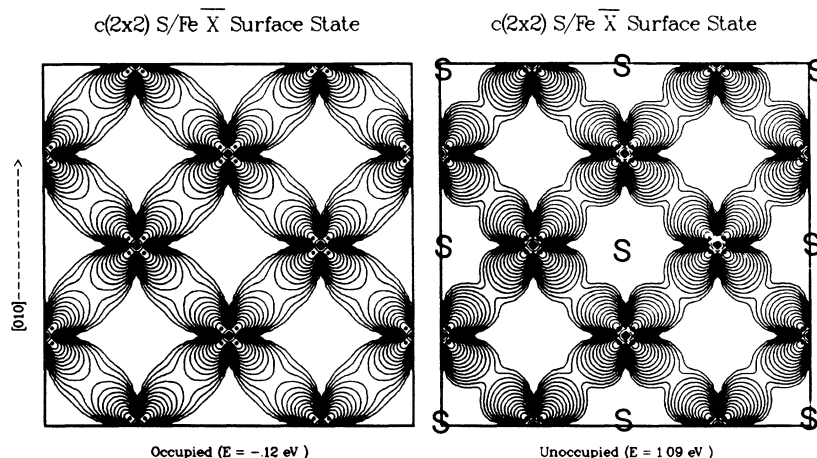


FIG. 2. Contour plots of the logarithm (base 10) of the densities (expressed in units of  $10^{-3} e/a.u.^3$ ) in the Fe(S) plane of the two contamination sensitive  $\bar{X}_2$  minority SS's associated with the level repulsion (as discussed in the text). Only the antisymmetric state with respect to  $z$  reflection is plotted. The position directly beneath each sulfur atom within this plane is marked by arrows. The lowest value of the density corresponds to  $10^{-3.1} e/a.u.^3$ . Contours are linearly spaced in increments of 0.2.

localized within the layer, (2) possesses a sharp, antibonding structure along the  $[110]$  and  $[\bar{1}\bar{1}0]$  directions (parallel to the diagonals of the plot) within the plane, and (3) the density along these two directions is more strongly lobed towards the nearest sulfur atom than in the direction away from it. The figure also shows that the regions of greatest density associated with the occupied state are contracted towards the Fe atoms within the surface plane relative to those associated with the unoccupied state, indicating that though this state exhibits greater bonding with the Fe(S) plane, the associated orbitals have strong out-of-plane character.

In Fig. 3 we present spatially resolved plots of the densi-

ty in the  $[1\bar{1}0]$  plane at  $\bar{X}$  of the clean Fe SS and the two S/Fe SS's associated with the level repulsion. The figure shows that (1) important bonding-antibonding hybridization involving  $S(p_x, p_y)$ -Fe( $d_{xz}, d_{yz}$ ) character is involved in the effect, (2) associated with the antibonding (unoccupied) state is a localization of density around the sulfur and a depletion of charge from the Fe surface [Fe(S)] layer, and (3) the bonding state is very similar to the (unoccupied) Fe SS; it does possess somewhat greater charge immediately below the surface and in the first subsurface [Fe(S-1)] layer. Perhaps even more significantly, it should be noted that although all of the  $[1\bar{1}0]$  planes passing through atoms in the clean substrate possess the same

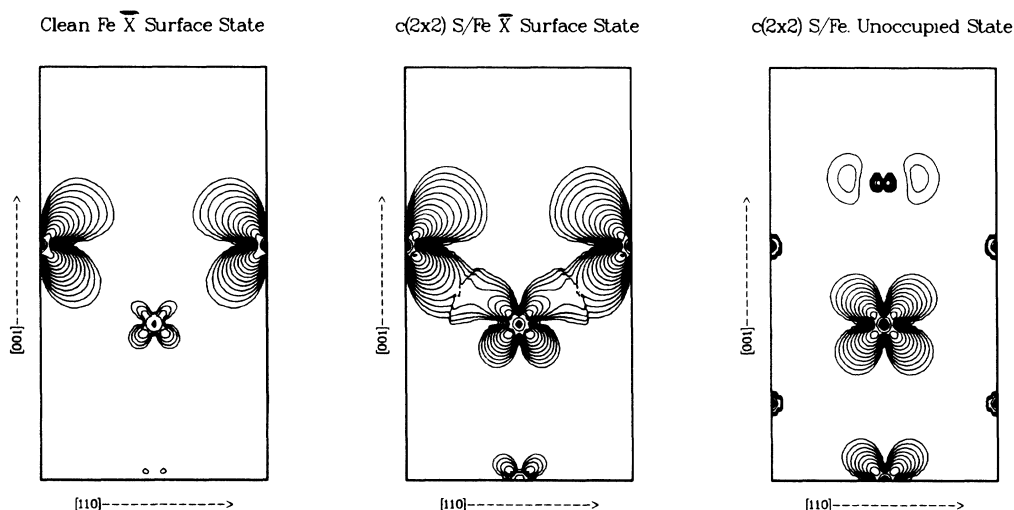


FIG. 3. Contour plots of the logarithm (base 10) of the densities in the  $[1\bar{1}0]$  plane of the clean Fe SS and the two S/Fe, minority,  $\bar{X}_2$  SS's associated with the level repulsion (as discussed in the text) between states near  $E_F$ . Contours are plotted as in Fig. 2, and as in Fig. 2, only the antisymmetric state with respect to  $z$  reflection is shown. Units of the density are as in Fig. 2, except that the density of each S/Fe SS is scaled upward by a factor of 2 to account for the difference in normalization between single-state densities associated with the clean Fe and  $c(2 \times 2)$  S/Fe unit cells.

density, after the adsorption, the  $[1\bar{1}0]$  planes which contain S atoms are distinct from those which do not, and that the S/Fe densities shown in the figure were taken from inequivalent  $[1\bar{1}0]$  planes because both the occupied and unoccupied states preferentially occupied a single  $[1\bar{1}0]$  plane. More specifically, the occupied state had negligible charge in the plane containing the sulfur, while the unoccupied state possessed appreciable charge in this plane and negligible charge in the other.

Furthermore, the density arising from the unoccupied state is negligible throughout most of the region of the Fe(S) layer in this plot of the  $[1\bar{1}0]$  plane. This indicates that the level repulsion acts to reduce the charge associated with the unoccupied state within the Fe(S) layer and induces the occupation of states in this layer preferentially with a tendency towards antibonding between S and Fe. Both of these features of the bonding can be related to the hypothesis put forth in I concerning the poisoning.

In particular, during a Fischer-Tropsch-type process, in which the desired catalytic effect of Fe is to reduce the strength of the C—O bond in CO, it is believed that this is accomplished by hybridization of low-lying CO states with the unoccupied Fe states and the formation of an occupied bonding orbital of primarily C-Fe character, accompanied by a transfer of charge from the highest occupied Fe states into antibonding states of predominantly O character. The presence of sulfur would poison this weakening of the bond by localizing the unoccupied Fe states in regions away from the iron surface, thereby reducing overlap between these states with low-lying states from a CO molecule. Also, although the adsorption-induced occupation of the lower  $\bar{\Delta}$  state results in an increase in the amount of Fe(S) minority charge, associated with this state are antibonding features between the Fe(S) and the

S. Thus, the charge from this state is unevenly distributed over the surface and involves an enhanced Fe(S—1) component. Furthermore, the occupation of the state is tied to a level repulsion and leads to an important reduction in the DOS at  $E_F$ . As a consequence, after the adsorption the highest occupied states are less likely to form antibonding states with the higher energy O-like states from the CO molecule because (1) the probability of overlap between these states with those from CO is reduced as a consequence of the changes in their spatial distribution, and (2) the presence of S acts to lower the energy of these Fe-like states.

As noted in the Introduction, as a consequence of the location (within a gap in the bulk band structure near  $E_F$ ) and magnitude of this level repulsion, experimental verification of this phenomenon is not difficult, but it requires the use of both spin-resolved ARUPS and KRIPES. The importance of the effect in our understanding of the poisoning phenomenon and to the significance of magnetic effects in the S-Fe interaction provide strong incentive for independent experimental verification. Because this adsorption-induced level repulsion of minority states is closely tied to the large exchange splitting in iron, we suspect that similar repulsion involving minority states near  $E_F$  should be present on other faces of Fe. In fact, our intuition about this has been confirmed for the Fe(110) surface where Schonhense has recently observed a similar sulfur-induced occupation of minority Fe states just below  $E_F$ .<sup>9</sup>

*Note added in proof.* Johnson *et al.*<sup>10</sup> have recently examined the magnetic splittings of the sulfurlike energy bands along the symmetry line  $\bar{\Sigma}$ , through spin-resolved ARUPS experiments, but have not performed comparable measurements along  $\bar{\Delta}$ .

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